

# 13 Fe, Co, and Ni

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## 1 Introduction

Organometallic compounds are dealt with elsewhere in this volume and receive only a passing glance here. Similarly, coverage of complexes of macrocyclic ligands has been limited. Particular trends discernible this year include continued interest in binuclear iron oxo-species and in nickel complexes with sulfur ligands.

## 2 Simple Binary and Coordination Compounds of Oxygen, Nitrogen, and Halogen Donors

An important new book<sup>1</sup> covers the synthesis and structures of the various iron oxides, hydroxides, and basic iron salts.

The synthesis has been described of a  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/polymer nanocomposite as a magnetic material with appreciable transmission in the visible region of the spectrum.<sup>2</sup> Barium surface doped iron(III) oxide particles for high-density magnetic recording have been studied.<sup>3</sup> Photo-oxidation of matrix-isolated iron pentacarbonyl at 20 K leads to the identification of two binary iron oxides, one believed to be the peroxide Fe( $\eta^2$ -O<sub>2</sub>) and the other the planar (or nearly so) trioxide FeO<sub>3</sub>, rather than O=Fe=O as previously suggested.<sup>4</sup> The hydride CaMgNiH<sub>4</sub>, synthesized by sintering ternary metal alloy powders under dihydrogen, has tetrahedral [NiH<sub>4</sub>]<sup>4-</sup> anions present (Ni–D distances in the corresponding deuteride are 1.597–1.602 Å).<sup>5</sup>

The electron affinity of FeCl<sub>3</sub> has been reported<sup>6</sup> to be  $4.3 \pm 0.2$  eV.

**O-donors.**—A report<sup>7</sup> concerning higher oxidation states involves iron(vI) with the observation of sharp-line near-IR luminescence in FeO<sub>4</sub><sup>2-</sup>. A ferryl(v) intermediate has been invoked<sup>8</sup> in a study of DNA cleavage with a system involving an iron(II) complex and dioxygen or H<sub>2</sub>O<sub>2</sub>. [For some other iron(IV) complexes see pages 180 and 183.]

Among the aqua-complexes of metal halides, both *cis* and *trans*-stereochemistries

<sup>1</sup> U. Schwertmann and R. M. Cornell, 'Iron Oxides in the Laboratory. Preparation and Characterization'. VCH Weinheim, New York, 1991.

<sup>2</sup> R. F. Ziolo, E. P. Giannelis, B. A. Weinstein, M. P. O'Horo, B. N. Ganguly, V. Mehrotra, M. W. Russell, and D. R. Huffman, *Science*, 1992, **257**, 219.

<sup>3</sup> C. Sarda, C. Bonino, P. Mollard, and A. Rousset, *J. Magn. Magn. Mater.*, 1992, **109**, 127.

<sup>4</sup> M. Fanfarillo, A. J. Downs, T. M. Greene, and M. J. Almond, *Inorg. Chem.*, 1992, **31**, 2973.

<sup>5</sup> B. Huang, K. Yvon, and P. Fischer, *J. Alloys Compd.*, 1992, **178**, 173.

<sup>6</sup> M. M. Kborov, Y. V. Pervova, and L. N. Sidorov, *Mendeleev Commun.*, 1992, 41.

<sup>7</sup> M. Herren and H. U. Gudel, *Inorg. Chem.*, 1992, **31**, 3683.

<sup>8</sup> R. E. Shepherd, T. J. Lomis, and R. R. Koepsel, *J. Chem. Soc., Chem. Commun.*, 1992, 222.

are known for  $\text{MX}_2 \cdot 4\text{H}_2\text{O}$  units (Table 1 lists those whose structures have been determined). The structures of  $\text{FeBr}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{CoBr}_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$  all involve<sup>9</sup> octahedral coordination of the metal; the first two are *trans* but the nickel complex is *cis*. Steric repulsions between bromines may favour the adoption of the *trans*-isomer, though hydrogen-bonding and the effects of electron configuration may also be important.

**Table 1** Stereochemistry in  $\text{MX}_2 \cdot n\text{H}_2\text{O}$  ( $n = 2, 4, 6$ )

	Fe		Co		Ni	
<i>n</i>	Cl	Br	Cl	Br	Cl	Br
2	t	—	t	t	t	—
4	t	t	c	t	c	—
6	—	—	t	t	t	t

(c = *cis*; t = *trans*)

The two crystalline forms of  $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$  have been reinvestigated<sup>10</sup> and it is suggested that a previously reported structure of  $\text{FeF}_2 \cdot 4\text{H}_2\text{O}$  was in fact that of  $\alpha\text{-FeF}_3 \cdot 3\text{H}_2\text{O}$ .

Reports on halogenoferrates include the syntheses<sup>11</sup> from iron, bromine, and the appropriate bromide of several  $\text{AFeBr}_4$  (A = alkali metal,  $\text{NH}_4$ , Ag). Detailed magnetic studies have been made on two tetrachloroferrates.<sup>12,13</sup> The novel  $[\text{Fe}_2\text{Cl}_6]^{2-}$  ion, has a structure based on edge-sharing tetrahedra.<sup>14</sup>

Like the corresponding chloride,  $\text{FeBr}_3 \cdot 2\text{Ph}_3\text{PO}$  has been shown<sup>15</sup> to be *trans*- $[\text{FeBr}_2(\text{OPPh}_3)_4][\text{FeBr}_4]$ , and  $[\text{CoI}_2(\text{ONMe}_3)_2]$  is pseudotetrahedral, whilst  $[\text{CoCl}_2(\text{ONMe}_3)_2]$  is similar.<sup>16</sup>

$\text{FeCl}_3$  reacts with  $\text{ClOTeF}_5$  to form  $[\text{Fe}(\text{OTeF}_5)_3]$ , which readily reacts with bases and is believed to have a three-coordinate trigonal planar structure; it forms a distorted octahedral tris(adduct) with  $\text{SO}_2\text{ClF}$ .<sup>17</sup>

Iron(III) is well known to form complexes with polyols and sugars; magnetic susceptibility and ESR studies suggest that the iron exists in mononuclear (presumably aqua) species with normal magnetic moments at pH 1–2, polynuclear species with lowered moments at pH 3–10, and mononuclear complexes where the iron is probably coordinated to the alcoholic OH groups at higher pH.<sup>18</sup> Further investigations have been reported<sup>19,20</sup> in the complex area of iron(III)-nitrilotriacetate complexes; it is

<sup>9</sup> K. Waizumi, H. Masuda, and H. Ohtaki, *Inorg. Chim. Acta*, 1992, **192**, 173.

<sup>10</sup> D. G. Karraker and P. K. Smith, *Inorg. Chem.*, 1992, **31**, 1119.

<sup>11</sup> G. Thiele, D. Honert, and H. Rotter, *Z. Anorg. Allgem. Chem.*, 1992, **616**, 195.

<sup>12</sup> R. Shaviv, C. B. Lowe, J. A. Zors, C. B. Aakeroy, P. B. Hitchcock, K. R. Seddon, and R. L. Carlin, *Inorg. Chim. Acta*, 1992, **198–200**, 613.

<sup>13</sup> R. Shaviv, K. E. Merabet, D. P. Shum, C. B. Lowe, D. Gonzalez, R. Burriel, and R. L. Carlin, *Inorg. Chem.*, 1992, **31**, 1724.

<sup>14</sup> K. Ruhlandt-Senge and U. Muller, *Z. Naturforsch., Teil B*, 1992, **47**, 1075.

<sup>15</sup> E. Durcanska, T. Glowiak, E. Gyepes, I. Ondrejovicova, and G. Ondrejovic, *Acta Fac. Rerum Nat. Univ. Comenianae, Chim.*, 1991, **39**, 3 (*Chem. Abstr.*, 1992, **117**, 80 521).

<sup>16</sup> S. Jin, M. Nieuwenhuyzen, W. T. Robinson, and C. J. Wilkins, *Acta Crystallogr., Sect. C*, 1992, **48**, 274.

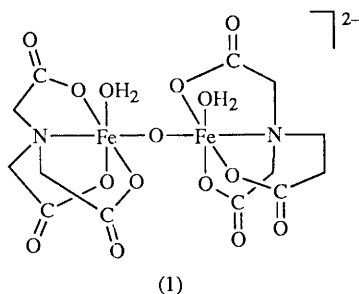
<sup>17</sup> T. Drews and K. Seppelt, *Z. Anorg. Allgem. Chem.*, 1991, **606**, 201.

<sup>18</sup> H. Yokoi, Y. Mori, T. Mitani, and S. Kawata, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 1898.

<sup>19</sup> S. L. Heath, A. K. Powell, H. L. Utting, and M. Helliwell, *J. Chem. Soc., Dalton Trans.*, 1992, 305.

<sup>20</sup> Y. Nishida, K. Yoshizawa, and T. Akamatsu, *Chem. Lett.*, 1991, 1521.

concluded that a mononuclear species is obtained at low pH which dimerizes to  $[\{\text{Fe}(\text{nta})(\text{H}_2\text{O})_2\}_2\text{O}]^{2-}$  at higher pH. The structure of the barium salt of the latter (1) has been reported.<sup>19</sup>



Octahedral six-coordinate iron has been confirmed for a bis(dipicolinato) ferrate iron(III) complex;<sup>21</sup> such iron(III) complexes catalyze the oxidation of saturated hydrocarbons by  $\text{H}_2\text{O}_2$  in pyridine–acetic acid, and the high-spin ion  $\text{cis-}[\text{FeCl}_2(\text{picolinate})_2]^-$  has been characterized as a model for one-iron non-haem enzymatic oxidations.<sup>22</sup> The reactive intermediates for this and a number of other intermediates for the metal-induced activation of  $\text{H}_2\text{O}_2$  have been investigated kinetically.<sup>23</sup>

Iron carboxylates investigated include<sup>24</sup>  $[\text{Fe}(\text{lactate})_2(\text{H}_2\text{O})_2]$  and the iron(III) oxydiacetate species  $[\text{Fe}\{\text{O}(\text{CH}_2\text{CO}_2)_2\}(\text{H}_2\text{O})_2\text{X}]$  ( $\text{X} = \text{Cl}, \text{Br}$ ) in which the carboxylate occupies meridional positions with the two water molecules *trans*.<sup>25</sup> Two different kinds of trinuclear carboxylates have attracted attention. Inelastic neutron scattering shows 11 transitions in the region between  $2\text{--}25\text{ cm}^{-1}$  in a ‘traditional’  $\mu_3$ -oxo-centred mixed-valence carboxylate,<sup>26</sup>  $[\text{Fe}_3\text{O}(\text{O}_2\text{CCD}_3)_6(\text{C}_5\text{D}_5\text{N})_3] \cdot (\text{C}_5\text{D}_5\text{N})$ . These transitions disappear on dilution in a host lattice, indicating that they originate in intermolecular electronic transitions. Iron(II) acetate reacts with a bidentate N-donor BPhMe [2,2′-bis(1-methylimidazolyl)phenylmethoxymethane] to give an unusual trinuclear complex  $[\text{Fe}_3(\text{OAc})_6(\text{BPhMe})_2]$  (2) in which the three irons have a linear, rather than triangular, arrangement featuring one monodentate and two bidentate bridging acetates. Magnetic susceptibility studies indicate ferromagnetic exchange coupling.<sup>27</sup>

Several iron carboxylate complexes featuring bridging ligands have been postulated as models for iron sites in proteins. These are discussed together with a number of  $\mu$ -oxo complexes in Section 7.

<sup>21</sup> A. Cousson, F. Nectoux, and E. N. Rizkalla, *Acta Crystallogr., Sect. C*, 1992, **48**, 1354.

<sup>22</sup> D. H. R. Barton, S. D. Beviere, W. Chavasiri, D. Doller, W.-D. Liu, and J. H. Reibenspies, *New J. Chem.*, 1992, **16**, 1019.

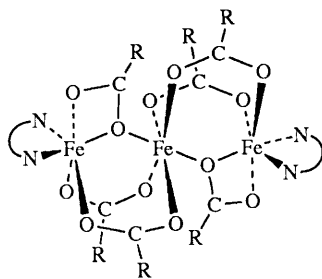
<sup>23</sup> H.-C. Tung, C. Kang, and D. T. Sawyer, *J. Am. Chem. Soc.*, 1992, **114**, 3445.

<sup>24</sup> P. Liu and M. Hong, *Jiegou Huaxue*, 1992, **11**, 44 (*Chem. Abstr.*, 1992, **117**, 101 459).

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<sup>26</sup> U. A. Jayasooriya, R. D. Cannon, C. E. Anson, S. K. arapKoske, R. P. White, and G. J. Kearley, *J. Chem. Soc., Chem. Commun.*, 1992, 379.

<sup>27</sup> R. L. Rardin, P. Poganiuch, A. Bino, D. P. Goldberg, W. B. Tolman, S. Liu, and S. J. Lippard, *J. Am. Chem. Soc.*, 1992, **114**, 5240.

(2) R = CH<sub>3</sub>

The iron(III) complex of *N,N'*-bis(2-hydroxyphenyl)ethylenediamine-*N,N'*-diacetic acid<sup>28</sup> (H<sub>4</sub>edda) has a very high stability constant ( $\log K = 40.1$ ), though not as high as a new hexadentate ligand which has an affinity for iron exceeding that of enterobactin<sup>29</sup> at physiological pH. Iron catecholate complexes with cubane-like Fe<sub>4</sub>O<sub>4</sub> cores<sup>30</sup> (others are dimeric) have been synthesized, whilst monomeric bis(catecholate) complexes have likewise been characterized<sup>31</sup> and the redox properties of the iron(II)/(III) redox couples investigated. Metal complex ferrimagnets [NBu<sub>4</sub>][M<sup>II</sup>Fe<sup>III</sup>(ox)<sub>3</sub>] with three-dimensional network structures of alternating Fe<sup>III</sup> and M<sup>II</sup> ions have been prepared.<sup>32</sup>

Several papers have appeared concerning the effect of high pressure on kinetics. The reaction of the iron(III) aqua ion with azide has been studied by stopped-flow methods<sup>33</sup> and shown to involve predominantly the reactions of [Fe(H<sub>2</sub>O)<sub>5</sub>(OH)]<sup>2+</sup> with N<sub>3</sub><sup>-</sup> and HN<sub>3</sub>; the corresponding reaction with thiocyanate has been reinvestigated. The [Fe(CN)<sub>6</sub>]<sup>3-</sup>/[Fe(CN)<sub>6</sub>]<sup>4-</sup> self-exchange reaction involves a very high positive volume of activation.<sup>34</sup> The redox exchange of [Co(edta)]<sup>-</sup> and [Co(hedta)(H<sub>2</sub>O)]<sup>-</sup> has been described in terms of a non-adiabatic outer-sphere mechanism in which ring-closure and elimination of water precede electron transfer.<sup>35</sup> The pressure dependencies of the electrode potentials of [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>2+/3+</sup>, [Fe(phen)<sub>3</sub>]<sup>2+/3+</sup>, [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup>, and [Co(sepulchrate)]<sup>2+/3+</sup> have been reported.<sup>36</sup>

Several alkali metal tetra-alkoxo and aryloxo cobaltates of the general type M<sub>2</sub>[Co(OR)<sub>4</sub>] $\cdot$ *x*THF have been synthesized; from spectroscopic data, they seem generally to have tetrahedrally coordinated cobalt.<sup>37</sup>

Six-coordination is general for solvated species, including those of cobalt(II), in most O-donor solvents such as water, dmsO, and dmf, but an EXAFS study<sup>38</sup> of cobalt(II)

<sup>28</sup> J. F. Gibson and O. J. Vaughan, *J. Chem. Soc., Dalton Trans.*, 1992, 1375.

<sup>29</sup> R. J. Motekaitis, Y. Sun, and A. E. Martell, *Inorg. Chim. Acta*, 1992, **198–200**, 421.

<sup>30</sup> S. C. Shoner and P. P. Power, *Inorg. Chem.*, 1992, **31**, 1001.

<sup>31</sup> D. Zirong, S. Bhattacharaya, J. K. McCusker, P. M. Hagen, D. N. Hendrickson, and C. G. Pierpoint, *Inorg. Chem.*, 1992, **31**, 870.

<sup>32</sup> H. Tamaki, M. Mitsumi, K. Nakamura, N. Matsumoto, S. Kida, H. Okawa, and S. Iijima, *Chem. Lett.*, 1992, 1975.

<sup>33</sup> M. R. Grace and T. W. Swaddle, *Inorg. Chem.*, 1992, **31**, 4674.

<sup>34</sup> H. Takagi and T. W. Swaddle, *Inorg. Chem.*, 1992, **31**, 4669.

<sup>35</sup> W. H. Jolly, D. R. Stranks, and T. W. Swaddle, *Inorg. Chem.*, 1992, **31**, 507.

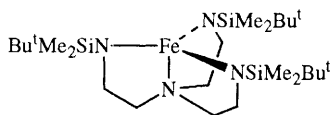
<sup>36</sup> H. Doine, T. W. Whitcombe, and T. W. Swaddle, *Can. J. Chem.*, 1992, **70**, 81.

<sup>37</sup> A. I. Ibrahim, W. Gaube, W. Kalies, and B. Witt, *J. Prakt. Chem.*, 1992, **333**, 397.

and its chloro complexes in hmpa indicates that four-coordination is general in species  $[\text{Co}(\text{hmpa})_{4-x}\text{Cl}_x]^{(2-x)+}$ . Co–O and Co–Cl bond lengths are shorter in the four-coordinate species than in corresponding ions like  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ . Among other complexes of simple O-donors, several cobalt complexes of pyridine *N*-oxide (PyO) and trimethylamine oxide have been studied<sup>39</sup> with structures determined for  $[\text{Co}(\text{OPy})_6][\text{CoCl}_4]$ ,  $[\text{Co}(\text{OPy})_6]\text{I}_2$ ,  $[\text{Co}(\text{ONMe}_3)_4]\text{I}_2$ , and  $[\text{Co}(\text{ONMe}_3)_2\text{X}_2]$  (X = Cl, I); as indicated by the formulae, six-coordination is general for pyridine *N*-oxide and tetrahedral four-coordination for trimethylamine oxide. Six-coordination also occurs<sup>40</sup> in  $[\text{Co}(\text{hfac})_2(\text{OPPh}_3)_2]$ .

A modified electrolytic process for the synthesis of cobalt(III) acetate has been described.<sup>41</sup>

**N-donors.**—Coordination numbers between 3 and 8 are known for iron(III) complexes. What appears to be a new geometry for four-coordination is the trigonal monopyramid, rather than the usual tetrahedron, for the brown high-spin pentane-soluble triamide complex (3), where the bulky trialkylsilyl groups inhibit access to the vacant axial position.<sup>42</sup>



(3)

The crystal structure of  $[\text{Fe}(\text{4-F-bipy})_3][\text{PF}_6]_2$  shows four of the eight possible isomers;<sup>43</sup> electronic spectra of iron(II) complexes of phen, bipy, terpy, and other ligands and their reduction products have been examined.<sup>44</sup>  $\text{FeN}_6$  coordination has been crystallographically characterized for an iron(II) tris(diimine) complex, and its dissociation in the presence of hydroxide examined in a number of different solvents;<sup>45</sup> the kinetics of reactions of diimine-cyanide complexes with various oxidizing agents have been analyzed.<sup>46</sup> A convenient synthesis<sup>47</sup> has been reported for the high-spin iron(III) poly(pyrazolyl)borate complex  $[\text{NEt}_4][\text{FeCl}_3\{\text{HB}(\text{pz})_3\}]$ .

The syntheses have been reported<sup>48,49</sup> of a large number of  $[\text{Co}(\text{N}_3)_3\text{L}_3]$  complexes (L = pyridine or substituted pyridines) as well as the structures of two examples (L = py, 4-Mepy); all appear to have *mer* geometry. Cobalt(III) amines are a hardy

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<sup>39</sup> (a) S. Jin, M. Nieuwenhuyzen, and C. J. Wilkins, *J. Chem. Soc., Dalton Trans.*, 1992, 2071; (b) S. Jin, M. Nieuwenhuyzen, W. T. Robinson, and C. J. Wilkins, *Acta Crystallogr. Sect. C*, 1992, **48**, 274.

<sup>40</sup> J. R. Polam and L. C. Porter, *Acta Crystallogr., Sect. C*, 1992, **48**, 1761.

<sup>41</sup> U. B. Ogutveren, R. E. Plimley, and I. Nieve, *J. Appl. Electrochem.*, 1992, **22**, 351.

<sup>42</sup> C. C. Cummins, J. Lee, R. R. Schrock, and W. D. Davis, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1501.

<sup>43</sup> C. K. Cho and A. S. Secco, *Acta Crystallogr., Sect. C*, 1992, **48**, 165.

<sup>44</sup> P. S. Brateman, J.-I. Song, and R. D. Peacock, *Inorg. Chem.*, 1992, **31**, 555.

<sup>45</sup> M. J. Blandamer, J. Burgess, J. Fawcett, P. Guardado, C. D. Hubbard, S. Nuttall, L. J. S. Prouse, S. Radulovic, and D. R. Russell, *Inorg. Chem.*, 1992, **31**, 1383.

<sup>46</sup> J. Burgess and B. Shraydeh, *Polyhedron*, 1992, **11**, 2015.

<sup>47</sup> S. Cho, D. Whang, K. Han, and K. Kim, *Inorg. Chem.*, 1992, **31**, 519.

<sup>48</sup> M. A. S. Goher, R. J. Wang, and T. C. W. Mak, *Polyhedron*, 1991, **11**, 829.

<sup>49</sup> F. A. Mautner, *Cryst. Res. Technol.*, 1991, **26**, 883.

perennial. The structure of  $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$  has been determined<sup>50</sup> above and below the transition temperature of 281 K. Thermal analyses have been carried out<sup>51–53</sup> on a number of hexaammine salts, with and without the presence of added potassium halides. A classic photoisomerization in  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)] \text{Cl}_2$  (nitro to nitrito) has been reinvestigated,<sup>54</sup> together with the reverse thermal isomerization, by single crystal diffraction. Kinetic studies have been carried out<sup>55</sup> on the spontaneous isomerization of  $[\text{Co}(\text{NH}_3)_5(\text{SCN})]^{2+}$ ; the synthesis and hydrolysis (showing first order dependence on  $\text{OH}^-$ ) of the  $[\text{Co}(\text{NH}_3)_5(\text{SMe}_2)]^{3+}$  ion has been reported.<sup>56</sup>  $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]\text{Cl}$  reacts in the solid state with  $\text{NH}_4\text{SCN}$  to give *trans*- $[\text{Co}(\text{NH}_3)_4(\text{NCS})_2]\text{Cl}$ , whilst in the analogous reaction with  $[\text{Co}(\text{en})_2(\text{CO}_3)]\text{Cl}$ , *cis*- $[\text{Co}(\text{en})_2(\text{NCS})_2]\text{Cl}$  is formed first, subsequently isomerizing into the *trans*-isomer.<sup>57</sup> The structure of  $[\text{Co}(\text{NH}_3)_4\{\text{(S)-alaninate}\}]\text{SO}_4$  has been reported.<sup>58</sup>

The structure of  $[\text{Co}(\text{CO}_3)(\text{phen})_2]$  shows<sup>59</sup> that Co–N bonds *trans* to O are slightly longer than the *cis*-Co–N bonds; *cis*- $[\text{Co}(\text{glycine})(\text{phen})_2] \text{Cl}_2$  has also been synthesized and crystallographically characterized.<sup>60</sup>

A series of papers<sup>61–63</sup> reports syntheses, structures, and configurations of  $[\text{CoX}(\text{dien})(\text{dapo})]^+$  (X = halide, pseudohalide,  $\text{NO}_2$ ,  $\text{ONO}$ ) complexes and their base hydrolysis. Other amine complexes reported include  $[\text{Co}(\text{medien})(\text{dien})]^{3+}$  (medien = 3-methyl-1,5-diamino-3-azapentane), where both the *fac* and *mer*-isomers have been isolated and subjected to molecular mechanics analysis,<sup>64</sup> and isomers<sup>65</sup> of  $[\text{Co}(\text{trien})(\text{salicylate})]^{2+}$ . Quinquepyridine ligands form mono-helical 1:1 and double-helical 2:2 cobalt(II) complexes;<sup>66,67</sup> the crystal structure (4) of the complex  $[\text{Co}(\text{cp}_2\text{qpy})(\text{MeOH})(\text{H}_2\text{O})][\text{PF}_6]_2$  [ $\text{cp}_2\text{qpy} = 4',4''\text{-bis(4-chlorophenyl)-2,2':6',2'':6'',2''':6''',2''''-quinquepyridine}$ ] shows pentagonal bipyramidal seven-coordination.

The structure of tetragonal  $[\text{NiCl}_2(\text{Py})_4]$  has been redetermined,<sup>68</sup> whilst the structures of planar *trans*- $[\text{NiCl}_2\text{L}_2]$  (L = 2,6-Me<sub>2</sub>Py, 2,3,6-Me<sub>3</sub>py) have also been

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<sup>53</sup> L. H. Khalil, N. A. Moussa, and S. Mikhail, *J. Mater. Sci.*, 1992, **27**, 557.

<sup>54</sup> M. Kubota and S. Ohba, *Acta Crystallogr. Sect. C*, 1992, **48**, 627.

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<sup>58</sup> B. Prelesnik, K. Andjelkovic, and N. Juraanic, *Acta Crystallogr. Sect. C*, 1992, **48**, 427.

<sup>59</sup> C. A. McAuliffe, R. G. Pritchard, M. R. Bermejo, A. Garcia-Vazquez, A. Macias, J. Sanmartin, J. Romero, and A. Sousa, *Acta Crystallogr., Sect. C*, 1992, **48**, 1841.

<sup>60</sup> B. Ye, T. Zheng, L. Ji, and H. Zhuang, *Chin. Chem. Lett.*, 1991, **2**, 529 (*Chem. Abstr.*, 1992, **116**, 206 613).

<sup>61</sup> P. Comba, D. A. House, W. G. Jackson, W. Marty, H. Stoeckli-Evans, and L. Zipper, *Helv. Chim. Acta*, 1992, **75**, 1130.

<sup>62</sup> P. Comba, W. G. Jackson, W. Marty, and L. Zipper, *Helv. Chim. Acta*, 1992, **75**, 1147.

<sup>63</sup> P. Comba, W. G. Jackson, W. Marty, and L. Zipper, *Helv. Chim. Acta*, 1992, **75**, 1172.

<sup>64</sup> I. M. Atkinson, F. R. Keene, J. M. Gulbis, G. H. Searle, and E. R. T. Tiekink, *J. Mol. Struct.*, 1992, **265**, 189.

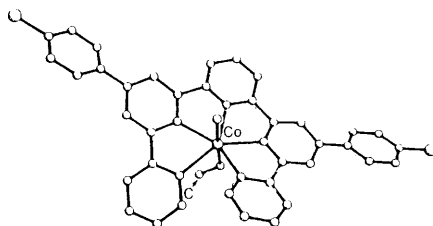
<sup>65</sup> Y. Yamamoto, E. Toyota, T. Kumon, and H. Sekizaki, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 283.

<sup>66</sup> E. C. Constable, J. V. Walker, D. A. Tocher, and M. A. M. Daniels, *J. Chem. Soc., Chem. Commun.*, 1992, 768.

<sup>67</sup> E. C. Constable and J. V. Walker, *J. Chem. Soc., Chem. Commun.*, 1992, 884.

<sup>68</sup> R. E. Bachman, K. H. Whitmire, S. Mandal, and P. K. Bharadwaj, *Acta Crystallogr., Sect. C*, 1992, **48**, 1836.

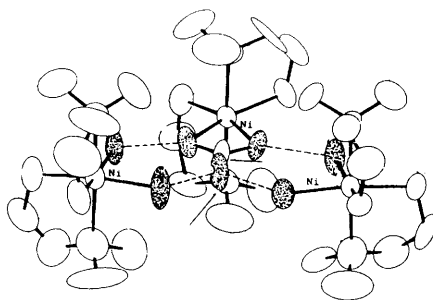
investigated.<sup>69</sup> Tetragonal pyramidal five-coordination occurs<sup>70</sup> in  $[\text{Ni}(\text{3,5-dimethyl-piperidine})_3(\text{NCS})_2]$  and the structures of five dimeric adducts of substituted pyridines with nickel(II) carboxylates likewise display five coordinate *sp* geometries with Ni–Ni distances of 2.708–2.765 Å.<sup>71</sup>



(4)

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The structure of *trans*- $[\text{Ni}(\text{en})_2(\text{NCS})_2]$  has been redetermined.<sup>72</sup> EXAFS has been used to provide comparative structural data on nickel(II) and (III) bis(diamine) complexes; both Ni–N and Ni–halogen distances shorten on increasing the oxidation state, the former proving, perhaps surprisingly, the more sensitive.<sup>73</sup> Ethanol solutions of the nickel(II) diamine complex  $[\text{Ni}(\text{N-Me}_2\text{en})_3][\text{ClO}_4]_2$  absorb and fix  $\text{CO}_2$  in air to give a trinuclear carbonato complex  $[\text{Ni}_3(\text{H}_2\text{O})_4(\text{CO}_3)(\text{Me}_2\text{en})_6][\text{ClO}_4]_4$  (5). The transformation can be reversed by passing  $\text{N}_2$  through the solution, whilst the presence of perchlorate seems to be important as only slight fixation is observed with other counter-ions (*e.g.*, halide, nitrate, sulfate).<sup>74</sup>



(5)

(Reproduced with permission from *Inorg. Chem.*, 1992, **31**, 1060)

<sup>69</sup> W. L. Darby, R. J. Butcher, and L. M. Vallarino, *Inorg. Chim. Acta*, 1992, **194**, 113.

<sup>70</sup> M. Koman, E. Jona, and E. Durcanska, *Acta Crystallogr., Sect. C*, 1992, **48**, 1652.

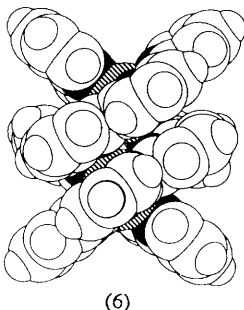
<sup>71</sup> M. Morooka, S. Ohba, M. Nakashima, T. Tokii, Y. Muto, M. Kato, and O. M. Steward, *Acta Crystallogr., Sect. C*, 1992, **48**, 1888.

<sup>72</sup> N. V. Podberezskaya, T. P. Shakhtshneider, A. V. Virovets, and P. A. Stabnikov, *Zh. Struct. Khim.*, 1991, **32**, 96 (*Chem. Abstr.*, 1992, **116**, 140 593).

<sup>73</sup> J. Evans, W. Levason, and R. J. Perry, *J. Chem. Soc., Dalton Trans.*, 1992, 1497.

<sup>74</sup> T. Tanase, S. Nitta, S. Yoshikawa, K. Kobayashi, T. Sakurai, and S. Yano, *Inorg. Chem.*, 1992, **31**, 1058.

A double helical complex  $[\text{Ni}_2(\text{spy})_2][\text{PF}_6]_4$  of the hexadentate ligand 2,2':6',2'':6'',2''':6''',2''''-sexipyridine (spy) has been synthesized<sup>75</sup> (6).



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Both tetrahedral monomeric and binuclear five-coordinate nickel(II) tris(pyrazolyl)borate complexes have been characterized.<sup>76</sup> Using a tripodal ligand, nickel(II) complexes with  $\text{NiN}_3\text{S}_2\text{O}$  and  $\text{NiN}_3\text{S}_3$  chromophores have been obtained;<sup>77</sup> for five-coordinate complexes with  $\text{NiN}_3\text{S}_2$  chromophores, related to hydrogenase, see Section 9.

### 3 Complexes of Tertiary Phosphines

Two groups have reported<sup>78,79</sup> *ab initio* calculations on  $\text{cis-}[\text{FeH}(\text{H}_2)(\text{PR}_3)_4]^+$ . The properties of  $[\text{FeXY}(\text{dmpp})_2]$  [ $\text{X}, \text{Y} = \text{H}, \text{Cl}$ ;  $\text{dmpp} = \text{Me}_2\text{P}(\text{CH}_2)_3\text{PMe}_2$ ] and the structure of the dichloro compound (*trans*-, unlike the others) have been reported,<sup>80</sup> as has that of *trans*- $[\text{FeBr}_2(\text{depe})_2]$ , which is a catalyst for the Kharasch reaction between  $\text{MgEtBr}$  and alkyl halides to give alkanes and alkenes. The two proposed mechanisms involve iron(I) and iron(III) species. The structure of *trans*- $[\text{FeBrH}(\text{depe})_2][\text{BPh}_4]$  has also been determined.<sup>81</sup> The preparation of the symmetrically bridged alkynide  $[\text{ClFe}(\text{dmpe})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C})(\text{dmpe})_2\text{FeCl}]$  and the redox properties of this and other dmpe complexes  $[\text{Fe}(\text{dmpe})_2(\text{X})(\text{Y})]$  ( $\text{X}, \text{Y} = \text{Cl}$  or  $\text{CCPh}$ ) have been reported.<sup>82</sup> The cation in  $[\text{Fe}(\text{NCMe})_2(\text{dppe})_2][\text{BF}_4]_2$  is *trans*.<sup>83</sup> Iron(II) complexes of a new bulky chelating phosphine, 1,2-bis(di-*n*-butylphosphino)ethane (dbpe), have been reported;  $[\text{FeCl}_2(\text{dbpe})_2]$ , a precursor for a series of alkyne complexes, is paramagnetic in solution but diamagnetic in the solid state.<sup>84</sup>

<sup>75</sup> E. C. Constable and R. Chotalia, *J. Chem. Soc., Chem. Commun.*, 1992, 64.

<sup>76</sup> S. Trofimenko, J. C. Calabrese, J. K. Kochi, S. Wolowicz, F. B. Hulsbergen, and J. Reedijk, *Inorg. Chem.*, 1992, **31**, 3943.

<sup>77</sup> K. G. Ragunathan and P. K. Bharadwaj, *J. Chem. Soc., Dalton Trans.*, 1992, 2417.

<sup>78</sup> J.-F. Riehl, M. Pelissier, and O. Eisenstein, *Inorg. Chem.*, 1992, **31**, 3344.

<sup>79</sup> F. Maseras, M. Duran, A. Lledos, and J. Bertran, *J. Am. Chem. Soc.*, 1992, **114**, 2922.

<sup>80</sup> N. Bampos, L. D. Field, and T. W. Hambley, *Polyhedron*, 1992, **11**, 1213.

<sup>81</sup> D. J. Evans, R. A. Henderson, A. Hills, D. L. Hughes, and K. E. Ogilvie, *J. Chem. Soc., Dalton Trans.*, 1992, 1259.

<sup>82</sup> L. D. Field, A. V. Goerge, F. Laschi, E. Y. Malouf, and P. Zanello, *J. Organomet. Chem.*, 1992, **435**, 347.

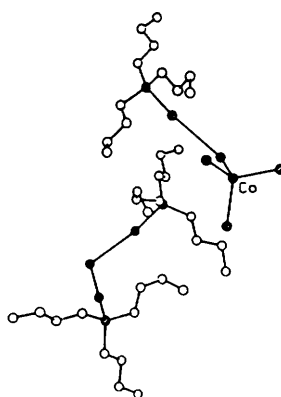
<sup>83</sup> A. J. Blake, A. J. Atkins, R. O. Gould, and M. Schroder, *Z. Kristallogr.*, 1992, **199**, 287.

<sup>84</sup> J. Lewis, M. S. Khan, A. K. Kakkar, P. R. Raithby, K. Fuhrmann, and R. H. Friend, *J. Organomet. Chem.*, 1992, **433**, 135.

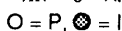
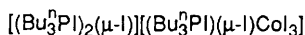


The non-classical hydride  $[\text{FeH}(\text{H}_2)(\text{pp}_3)]^+$  is<sup>85</sup> rigid in solution at low temperatures with the hydride and dihydrogen ligands *cis*. The related cation  $[\text{FeH}(\text{pp}_3)(\text{N}_2)]^+$  reacts with 4-pentynoic acid to give the octahedral pentynoate  $[\text{Fe}(\text{pp}_3)\{\text{O}_2\text{C}(\text{CH}_2)_2\text{C}\equiv\text{CH}\}]^+$  in which the carboxylate acts as a chelate.<sup>86</sup> Comparison of the analogous iron and ruthenium compounds indicates that the barrier to rotation of the dihydrogen ligand is higher in the former, indicating, rather surprisingly, that Fe is a better back-donor than Ru.<sup>87</sup>

An extension of earlier synthetic work on reactions between metal powders and halophosphoranes has led to the synthesis of *thp*  $[\text{CoI}_3(\text{PMe}_3)_2]$  from cobalt and  $\text{Me}_3\text{PI}_2$ . The corresponding reaction using  $\text{Bu}_3\text{PI}_2$  gives an unusual metal phosphane complex<sup>88</sup> (7).



(7)



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The solid cobalt(II) dinitrogen complex of the tripodal ligand  $\text{pp}_3$ ,  $[\text{Co}(\text{pp}_3)(\text{N}_2)]$   $[\text{BPh}_4]$  is transformed by gaseous  $\text{H}_2$  into a white dihydride (the addition can be reversed under a dinitrogen atmosphere) which has a classical dihydride structure. In contrast, if the reaction is carried out with the hexafluorophosphate salt of the  $\text{N}_2$  complex, the resulting red dihydrogen complex has a non-classical structure (Scheme 1).

The white tetraphenylborate salt dissolves in various solvents to give red solutions containing the  $\eta^2$ -complex; on adding ethanol the white classical dihydride precipitates. Similar ethanol precipitation with solutions of the hexafluorophosphate gives the

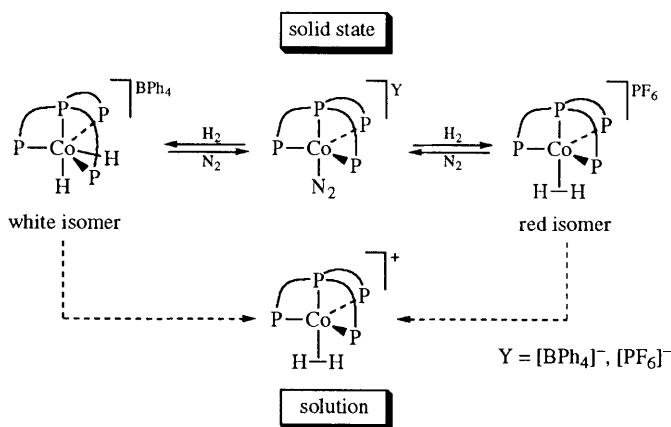
<sup>85</sup> C. Bianchini, M. Peruzzini, A. Pola, A. Vacca, and F. Zanobini, *Gazz. Chim. Ital.*, 1991, **121**, 543.

<sup>86</sup> K. Linn, D. Masi, C. Mealli, C. Bianchini, and M. Peruzzini, *Acta Crystallogr., Sect. C*, 1992, **48**, 2220.

<sup>87</sup> J. Eckert, A. Albinati, R. P. White, C. Bianchini, and M. Peruzzini, *Inorg. Chem.*, 1992, **31**, 4241.

<sup>88</sup> C. A. McAuliffe, S. M. Godfrey, A. G. Mackie, and R. G. Pritchard, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 919.

$\eta^2$ -dihydride. This is therefore an example of a solid-state/solution tautomerization, as well as a counter-ion influenced isomerization.<sup>89</sup>



Scheme 1

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Several new nickel(0) complexes of bulky diphosphines have been reported.<sup>90</sup>  $[\text{NiBr}_2(\text{PEtPh}_2)_2]$  has pseudotetrahedral coordination<sup>91</sup> whilst  $[\text{Ni}(\text{N}_3)_2(\text{PEt}_3)_2]$  has a *trans*-planar geometry.<sup>92</sup> Charge-transfer photolysis of the latter gives dimeric  $[\{\text{Ni}(\text{N}_3)_2(\text{PEt}_3)\}_2]$ . Several mono-, bi-, and tri-nuclear  $\text{Ni}(\text{PMePh}_2)$  fluoroalkyl complexes have been reported.<sup>93</sup> Square planar  $\text{NiCl}_2$  and  $\text{NiBr}_2$  complexes of 3,4-dimethyl-3',4'-bis(diphenylphosphino)tetrathiafulvalene have been synthesized and structurally characterized.<sup>94</sup> The results of force-constant calculations for  $[\text{Ni}(\text{PX}_3)_4]$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{Me}$ ) have been compared.<sup>95</sup> Elemental S reacts with  $[\text{NiX}_2(\text{PPh}_3)_2]$  ( $\text{X} = \text{halide}, \text{NO}_3, \text{NCS}$ ) to afford  $\text{NiX}_2$  and  $\text{Ph}_3\text{PS}$  whilst the corresponding reaction with  $[\text{NiX}(\text{S}_2\text{CNR}_2)(\text{PPh}_3)_2]$  gives  $\text{NiX}_2$  and  $[\text{Ni}(\text{S}_2\text{CNR}_2)_2]$  by disproportionation.<sup>96</sup> The new ylid complex  $[\text{Ni}(\text{CH}_2\text{PPh}_2\text{CH}_2\text{PPh}_2)_2]\text{Br}_2$  features square-planar coordination of nickel.<sup>97</sup> The influence of coligands on sulfur dioxide binding in  $\text{Ni}(\text{PR}_3)_3(\text{SO}_2)$  complexes has been investigated by MO calculations,<sup>98</sup> small phosphines which are strong donors are expected to favour the  $\eta^1$  pyramidal mode of bonding. Various nickel(o) diphosphine complexes bind  $\text{CO}_2$ .<sup>99</sup>

<sup>89</sup> C. Bianchini, C. Mealli, M. Peruzzini, and F. Zanobini, *J. Am. Chem. Soc.*, 1992, **114**, 5905.

<sup>90</sup> P. Mastrolilli, G. Moro, C. F. Nobile, and M. Latronico, *Inorg. Chim. Acta*, 1992, **192**, 183.

<sup>91</sup> J. O. Malm, V. Alfredsson, G. Svensson, and J. Albertsson, *Acta Crystallogr., Sect. C*, 1992, **48**, 406.

<sup>92</sup> A. Becalska, R. J. Batchelor, F. W. B. Einstein, R. H. Hill, and B. J. Palmer, *Inorg. Chem.*, 1992, **31**, 3118.

<sup>93</sup> R. McDonald, K. C. Sturge, A. D. Hunter, and L. Shilliday, *Organometallics*, 1992, **11**, 893.

<sup>94</sup> M. Fourmigue and P. Batail, *Bull. Soc. Chim. Fr.*, 1992, **129**, 29.

<sup>95</sup> H. G. M. Edwards and V. Fawcett, *Inorg. Chim. Acta*, 1992, **197**, 89.

<sup>96</sup> J. Darkwa, W. A. A. Ddamba, and L. M. Koczon, *Bull. Chem. Soc. Ethiop.*, 1991, **5**, 73 (*Chem. Abstr.*, 1992, **116**, 222 285).

<sup>97</sup> J. K. Gong, T. B. Peters, P. E. Fanwick, and C. P. Kubiak, *Organometallics*, 1992, **11**, 1392.

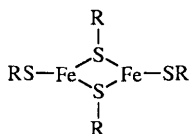
<sup>98</sup> J. Reinhold, M. Schuler, T. Hoffmann, and E. Wenschuh, *Inorg. Chem.*, 1992, **31**, 559.

<sup>99</sup> P. Mastrolilli, G. Moro, C. F. Nobile, and M. Latronico, *Inorg. Chim. Acta*, 1992, **192**, 189.

Some five-coordinate bis(triarsine) complexes of nickel show<sup>100</sup> an extensive nickel-centred redox chemistry with all oxidation states from 0 to +4 observed by cyclic voltammetry.

#### 4 Complexes with S and Se Donors

The bulky thiol 2,4,6-triphenylthiophenol (HSTriph) has been synthesized; its reaction with  $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_3]$  involves reduction to the iron(II) compound  $[\text{Fe}(\text{STriph})_2]$ , a dimer (8) like the analogous silylamide, with three-coordinate iron.<sup>101</sup>



(8) R = 2, 4, 6,  $\text{Ph}_3\text{-C}_6\text{H}_2$

Several investigations have concerned simple complexes of monomeric mercapto ligands. A general synthesis has been reported for stable  $[\text{Fe}^{\text{III}}(\text{SR})_4]^-$ , models for oxidized rubredoxin, with crystallographically characterized examples for R = Me, Et, and Ph.<sup>102</sup> The structure of  $[\text{NMe}_4]_2[\text{Fe}(\text{SePh})_4]$  has been determined;<sup>103</sup> the Fe–Se bond is reported to be more ionic than that between Fe and S. Several iron(II) thiolates are reversible CO carriers.<sup>104</sup> Syntheses have been reported for  $[\text{Fe}_2(\text{SMe})_2(\text{NO})_4]$ , a known tumorigenic promoter, and related systems.<sup>105</sup>

Electronic spectra and crystal-field calculations have been carried out for  $[\text{Ni}(\text{SR})_4]^{2-}$  and some solvolysis has been shown to occur;<sup>106</sup> mass spectra have been reported for several  $\text{Ni}_4$  and  $\text{Ni}_6$  thiolates along with the crystal structure of  $[\text{Ni}_6(\text{SPr})_{12}]$ .<sup>107</sup> Use of the bulky thiolate S-2,4,6- $\text{Pr}_3\text{C}_6\text{H}_2$  (SR) gives a binuclear species  $[\text{Ni}_2(\text{SR})_5]^-$  which is based on face-sharing bitetrahedra with three bridging thiolates.<sup>108</sup> Mixed-valence nickel thiolates  $[\text{Ni}_4(\text{SPr})_8\text{X}]$  (X = Br, I) have chain structures (related to those of  $[\text{Ni}_4(\text{SR})_8]$ ) with individual  $[\text{Ni}_4(\text{SR})_8\text{X}]$  molecules joined by halogen bridges. The halogen bridges are symmetrical in the iodide, but not in the bromide.<sup>109</sup>

Single-crystal ESR, electronic spectra, and magnetic susceptibility data have been reported<sup>110</sup> for  $[\text{PPh}_4]_2[\text{Co}(\text{SPh})_4]$  whilst  $[\text{Co}_2(\text{SPr})_5]^-$  is the first complex to have face-sharing  $\text{MS}_4$  tetrahedra.<sup>111</sup>

<sup>100</sup> J. Downard, L. R. Hanton, and R. L. Paul, *J. Chem. Soc., Chem. Commun.*, 1992, 235.

<sup>101</sup> K.-Ruhlandt-Senge and P. P. Power, *Bull. Soc. Chim. Fr.*, 1992, **129**, 594.

<sup>102</sup> L. E. Maelia, M. Millar, and S. A. Koch, *Inorg. Chem.*, 1992, **31**, 4594.

<sup>103</sup> N. Ueyama, H. Oku, W. Y. Sun, A. Nakamura, and K. Fukuyama, *Phosph., Sulph. Silicon Relat. Elem.*, 1992, **67**, 151.

<sup>104</sup> A. Szakacs, J. Kresz, L. Marko, Z. Nagy-Magos, and J. Takacs, *Inorg. Chim. Acta*, 1992, **198–200**, 401.

<sup>105</sup> A. R. Butler, C. Glidewell, and S. M. Glidewell, *J. Chem. Soc., Chem. Commun.*, 1992, 141; *Polyhedron*, 1992, **11**, 591.

<sup>106</sup> T. Yamamura and H. Arai, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 1799.

<sup>107</sup> H. Feld, A. Leute, D. Rading, A. Benninghoven, G. Henkel, T. Krueger, and B. Krebs, *Z. Naturforsch., Teil B*, 1992, **47**, 929.

<sup>108</sup> A. Silver and M. Millrear, *J. Chem. Soc., Chem. Commun.*, 1992, 948.

<sup>109</sup> T. Kruger, B. Krebs, and G. Henkel, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 54.

<sup>110</sup> K. Fukui, N. Kojima, H. Ohya-Nishiguchi, and N. Hirota, *Inorg. Chem.*, 1992, **31**, 1338.

The reaction of  $\text{NiCl}_2$ ,  $\text{PPh}_3$ , and  $\text{Na}_2(\text{edt})$  ( $\text{edt}$  = ethane-1,2-dithiolate) in methanol causes cleavage of a C-S bond and the isolation of square-planar  $[\text{Ni}(\text{PPh}_3)_2\{\text{S}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{S}\}]$ .<sup>112</sup> The octahedral anion  $[\text{Ni}(\text{thioxanthate})_3]^-$  is oxidized electrochemically to the  $\text{Ni}^{\text{III}}$  analogue; it does, however, decompose at room temperature to the dimer  $[\text{Ni}_2(\text{SET})_2(\text{CS}_3)_2]^{2-}$  which has thiolato bridges and one  $\text{CS}_3$  group chelated to each nickel.<sup>113</sup> Among dithiocarbamates,  $[\text{Fe}\{\text{S}_2\text{CN}(\text{CH}_2\text{CH}_2\text{OH})_2\}_3]$  and solvates have been reinvestigated<sup>114</sup> and previous studies re-evaluated. Tris(diallyldithiocarbamate)cobalt is isomorphous with the iron analogue with trigonally distorted octahedral coordination.<sup>115</sup>

## 5 Complexes of Porphyrins and other Macrocycles

**Porphyrins.**—There has again been intense activity in this field. Of interest are oxo-iron(IV) chlorin and porphyrin  $\pi$ -cation radical complexes, prepared by *m*-chloroperoxybenzoic acid oxidation of iron(III) species.<sup>116–119</sup> In contrast, NMR evidence has been adduced to support the assignment of  $\pi$ -anion radical character in two-electron reduced iron(III) meso( $\beta$ )-substituted porphyrins.<sup>120</sup> Resonance Raman and magnetic resonance<sup>121</sup> have been used to compare iron porphyrin complexes in the oxidation states (I) through (IV); electronic and Resonance Raman spectra have been used to characterize bis(imidazole) model complexes of iron(protoporphyrin).<sup>122</sup> Other applications of Resonance Raman spectroscopy to the study of iron porphyrins include<sup>123</sup> examination of Fe–OH bond strengths in high- and low-spin bis(hydroxides), of co-condensation products<sup>124</sup> of  $[\text{Fe}(\text{tpp})]$  with ethene and oxygen in matrices at 25 K, and of iron hydroporphyrins.<sup>125</sup>

A structurally characterized five-coordinate iron(III) 'picket-fence' porphyrin complex affords on reduction a five-coordinate iron(II) complex with unusually large quadrupole splitting in the Mössbauer spectra.<sup>126</sup> Other structures reported<sup>127</sup> include those of two salts of  $[\text{Fe}(\text{tpp})(\text{EtOH})_2]^+$ , of an iron(oep) cation radical,<sup>128</sup> and of a five-coordinate high-spin iron(III) oxophlorin complex.<sup>129</sup>

The structure of  $[\text{FeLCI}]$  ( $\text{L}$  = dioxobacteriochlorin), a model for heme  $\text{d}_1$ ,

<sup>111</sup> G. Henkel and S. Weissgraber, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1368.

<sup>112</sup> R. Cao, X. Lei, Z. Huang, M. Hong, and H. Liu, *J. Coord. Chem.*, 1992, **25**, 165.

<sup>113</sup> S. B. Choudhury and A. Chakravorty, *Inorg. Chem.*, 1992, **31**, 1055.

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<sup>115</sup> E. Kello, J. Lokaj, and V. Vrabel, *Coll. Czech. Chem. Commun.*, 1992, **57**, 332.

<sup>116</sup> A. L. Balch, C. R. Corman, L. Latos-Grazynski, and M. W. Renner, *J. Am. Chem. Soc.*, 1992, **114**, 2230.

<sup>117</sup> S. Ozawa, Y. Watanabe, and I. Morishima, *Inorg. Chem.*, 1992, **31**, 4042.

<sup>118</sup> H. Fujii and K. Ichikawa, *Inorg. Chem.*, 1992, **31**, 1110.

<sup>119</sup> K. Yamaguchi, Y. Watanabe, and I. Morishima, *Inorg. Chem.*, 1992, **31**, 156.

<sup>120</sup> K. Yamaguchi and I. Morishima, *Inorg. Chem.*, 1992, **31**, 3216.

<sup>121</sup> K. R. Rodgers, R. A. Reed, Y. O. Su, and T. G. Spiro, *Inorg. Chem.*, 1992, **31**, 2688.

<sup>122</sup> A. Desbois and M. Lutz, *Eur. Biophys. J.*, 1992, **20**, 321.

<sup>123</sup> K. H. Rogers, R. A. Reed, T. G. Spiro, and Y. O. Su, *New J. Chem.*, 1992, **16**, 533.

<sup>124</sup> A. Weselucha-Birczynska, I. R. Paeng, A. A. Shabana, and K. Nakamoto, *New J. Chem.*, 1992, **16**, 563.

<sup>125</sup> L. A. Andersson, M. Mylrajan, T. M. Loehr, E. P. Sullivan, and S. H. Strauss, *New J. Chem.*, 1992, **16**, 569.

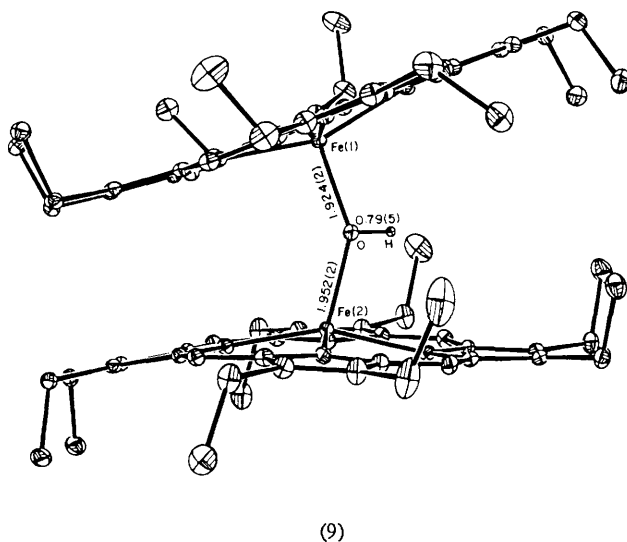
<sup>126</sup> E. L. Bominaar, X.-D. Ding, A. Gimelseed, E. Bill, H. Winkler, A. X. Trautwein, H. Nasri, J. Fischer, and R. Weiss, *Inorg. Chem.*, 1992, **31**, 1845.

<sup>127</sup> W. R. Scheidt, D. K. Geiger, Y. J. Lee, P. Gans, and J. C. Marchon, *Inorg. Chem.*, 1992, **31**, 2660.

<sup>128</sup> W. R. Scheidt, H. Song, K. J. Haller, M. K. Safo, R. D. Orosz, C. A. Reed, P. G. Debrunnerand, and C. E. Schulz, *Inorg. Chem.*, 1992, **31**, 939.

<sup>129</sup> A. L. Balch, L. Latos-Grazynski, B. C. Noll, M. M. Olmstead, and E. P. Zovinka, *Inorg. Chem.*, 1992, **31**, 2248.

shows<sup>130</sup> significantly longer Fe–N bonds to the saturated pyrroline rings (2.11 Å) compared with those to the unsaturated pyrrole rings (2.04 Å); binuclear [ $\{\text{Fe}(\text{tpp})\}_2\text{O}$ ] has been suggested as a model for cytochrome P-450 monooxygenase.<sup>131</sup> [ $\{\text{Fe}(\text{oep})\}_2\text{O}$ ] can be protonated to give a  $\mu$ -hydroxo complex ion [ $\{\text{Fe}(\text{oep})\}_2\text{OH}\]^+$  whose crystal structure (9) shows a large Fe–O–Fe angle (146.2°) owing to ring–ring interactions.<sup>132</sup>



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A modified picket fence iron(III) porphyrin has been suggested as a model for haemoglobin mutants.<sup>133</sup> Reaction of the picket-fence species [ $\text{Fe}(\text{NO}_2)_2(\text{TpivPP})\text{]}^-$  ( $\text{H}_2\text{TpivPP} = \alpha, \alpha, \alpha, \alpha$ -*meso*-tetrakis-*o*-pivalamidophenyl)porphyrin) with mercaptans gives iron(II) NO complexes, but on reaction with KSR, anionic iron(III) complexes [ $\text{Fe}(\text{NO}_2)(\text{SR})(\text{TpivPP})\text{]}^-$  are obtained; structures are reported for both types.<sup>134</sup> Several low-spin bis-ligated (porphinato)iron(III) complexes of the type [ $\text{Fe}(\text{tmp})\text{L}_2\text{]}^+$  (tmp = tetramesitylporphinato; L = 2-MeHim, substituted pyridine) have been synthesized. Structures of several examples have been determined<sup>135</sup>; the axial ligands are perpendicularly aligned, leading to the ‘large  $g$  max’ type of ESR spectra characteristic of cytochromes b. The effect of substituent size on free rotation of the axial bases of cytochrome b models has been studied,<sup>136</sup> and  $^1\text{H}$  COSY has been used to determine

<sup>130</sup> K. M. Barkigia, C. K. Chang, J. Fager, and M. W. Renner, *J. Am. Chem. Soc.*, 1992, **114**, 1701.

<sup>131</sup> C. Guo, S. Zhu, and M. Gui, *Huaxue Xuebao*, 1992, **50**, 129 (*Chem. Abstr.*, **116**, 206 669).

<sup>132</sup> W. R. Scheidt, B. Cheng, M. K. Safo, F. Cukiernik, J.-C. Marchon, and P. G. Debrunner, *J. Am. Chem. Soc.*, 1992, **114**, 4420.

<sup>133</sup> H. Imai, S. Nakagawa, and E. Kyuno, *Inorg. Chim. Acta*, 1992, **193**, 105.

<sup>134</sup> H. Nasri, K. J. Haller, Y. Wang, B. H. Huynh, and W. R. Scheidt, *Inorg. Chem.*, 1992, **31**, 3459.

<sup>135</sup> M. K. Safo, G. P. Gupta, C. T. Watson, U. Simonis, F. A. Walker, and W. R. Scheidt, *J. Am. Chem. Soc.*, 1992, **114**, 7066.

<sup>136</sup> F. A. Walker, U. Simonis, H. Zhang, J. M. Walker, T. McDonald Ruscitti, C. Kipp, M. S. A. Ampuch, B. V. Castilio, S. H. Cody, D. L. Wilson, R. E. Graul, G. J. Yong, K. Tobin, J. T. West, and B. A.

spin densities at the pyrrole  $\beta$ -positions of unsubstituted low-spin iron(III) tpp complexes.<sup>137</sup>

EXAFS studies on iron(II) and (III) 'basket-handle' porphyrins include<sup>138</sup> the assignment of an  $\text{Fe}^{\text{II}}(\text{O}_2)$  rather than an  $\text{Fe}^{\text{III}}(\text{O}_2^-)$  formulation to a dioxygen adduct; <sup>17</sup>O NMR and FTIR studies of oxygenated 'hybrid' haemoprotein models with axial hindered bases indicate considerable polarizability of the  $\text{Fe}-\text{O}_2$  moiety; there is, however, no hydrogen bonding between the dioxygen and the NH groups of the picket fence, in contrast to the results with unhindered bases.<sup>139</sup>

Syntheses have been reported<sup>140</sup> for several octaethyltetraazaporphyrin complexes of iron; the ligand is a stronger  $\sigma$ -donor and  $\pi$ -acceptor than porphyrins and therefore stabilizes the unusual 'intermediate' spin state of 3/2 for iron(III) in  $\text{Fe}(\text{LCl})$ . Pyrolysis<sup>141</sup> of  $[\text{Fe}(\text{tpp})\text{Cl}]$  has been studied by FTIR and Mössbauer spectroscopy;  $\text{Fe}(\text{tpp})$  complexes have been investigated as surface-polymer coupling reagents and as corrosion inhibitors.<sup>142</sup>

Iodine oxidation of (tetrabenzoporphyrinato)cobalt(II),  $\text{Co}(\text{tbp})$ , affords  $\text{Co}(\text{tbp})\text{I}$ , a macrocycle-oxidized molecular conductor.<sup>143</sup> One-electron reduction of methylcobalamin adds an electron to an antibonding orbital, considerably weakening the  $\text{Co}-\text{C}$  bond, resulting in a  $> 10^{15}$  enhancement of bond homolysis.<sup>144</sup> The structure of a dicobalt cofacial porphyrin<sup>145</sup> and the characterization of a  $\mu$ -superoxo complex have been reported whilst the ground states of  $[\text{Co}(\text{tpp})]$  and  $[\text{Co}(\text{oep})]$  cation radicals have been probed by ESR.<sup>146</sup> A simple synthesis of aquacobalamin has been described,<sup>147</sup> as has a new  $\text{B}_{12}$  model system using a ligand with a pendant pyridyl group.<sup>148</sup>

The structures of several nickel(II)  $\beta$ -halogenated pyrrole porphyrins have been determined,<sup>149</sup> as well as a nickel chlorin,<sup>150</sup> whilst the first chlorophin has been obtained from oxidative ring-opening of an (octadehydrocorrinato)nickel(II) salt.<sup>151</sup> The nickel(I) octaethylisobacteriochlorin anion is being investigated as an F 430 model.<sup>152</sup>

**Other Macrocycles.**—This area is reviewed elsewhere in this volume; a selection of

Barichivich, *New J. Chem.*, 1992, **16**, 609.

<sup>137</sup> Q. Lin, U. Simonis, A. R. Tipton, C. J. Norvell, and F. A. Walker, *Inorg. Chem.*, 1992, **31**, 4216.

<sup>138</sup> C. Cartier, M. Momenteau, E. Dartyge, A. Fontaine, G. Tourillon, A. Michalowicz, and M. Verdaguer, *J. Chem. Soc., Dalton Trans.*, 1992, 609.

<sup>139</sup> I. P. Gerpothanassis, B. Looock, and M. Momenteau, *J. Chem. Soc., Chem. Commun.*, 1992, 598.

<sup>140</sup> J. P. Fitzgerald, B. S. Hafferty, A. L. Rheingold, L. May, and G. A. Brewer, *Inorg. Chem.*, 1992, **31**, 2006.

<sup>141</sup> (a) T. Sheng, B. Rebenstorf, A. Widoloev, and R. Larsson, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 477; (b) J. Blomquist, H. Laang, R. Larsson, and A. Widoloev, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 2007.

<sup>142</sup> B. Meyer-Roscher, T. Siemens, and H. Brockmann, *Adv. Mater.*, 1992, **4**, 496.

<sup>143</sup> K. Liou, T. P. Newcomb, M. D. Heagy, J. A. Thompson, W. B. Heuer, R. L. Musselman, C. S. Jacobsen, B. M. Hoffmann, and J. A. Ibers, *Inorg. Chem.*, 1992, **31**, 4517.

<sup>144</sup> B. D. Martin and R. G. Finke, *J. Am. Chem. Soc.*, 1992, **114**, 585.

<sup>145</sup> J. P. Collman, J. E. Hutchison, M. A. Lopez, A. Tabard, R. Guillard, W. K. Seok, J. A. Ibers, and M. L'Her, *J. Am. Chem. Soc.*, 1992, **114**, 9869.

<sup>146</sup> M. Satoh, Y. Ohba, S. Yamaguchi, and M. Iwaizumi, *Inorg. Chem.*, 1992, **31**, 298.

<sup>147</sup> R. Bieganski and G. Klar, *J. Chem. Res.*, (S), 1992, 116.

<sup>148</sup> A. Gerli, M. Sabat, and L. G. Marzilli, *J. Am. Chem. Soc.*, 1992, **114**, 6711.

<sup>149</sup> D. Mandon, P. Ochenbein, J. Fischer, R. Weiss, K. Jayaraj, R. N. Austin, A. Gold, P. S. White, O. Brigaud, P. Battioni, and D. Mansuy, *Inorg. Chem.*, 1992, **31**, 2044.

<sup>150</sup> K. M. Barkigia, M. A. Thompson, J. Fajer, R. K. Pandey, K. M. Smith, and M. G. H. Vicente, *New J. Chem.*, 1992, **16**, 599.

<sup>151</sup> C. K. Chang, W. Wu, S. Chern, and S. Peng, *Angew. Chem., Int. Edn. Engl.*, 1992, **31**, 70.

<sup>152</sup> G. K. Lahiri, L. J. Schussel, and A. M. Stoltzenberg, *Inorg. Chem.*, 1992, **31**, 4991.

papers is discussed here where the interest lies principally in the metal centre.

A macrocyclic tetraanionic ligand has been used to stabilize iron(IV) as a six-coordinate bis(butylisocyanide) adduct (10).<sup>153</sup>

The five-coordinate(*SP*) iron(III) complex of a tetraimidazole ligand, [FeLCl], loses the chloride in methanol solution to become a six-coordinate bis(MeOH) solvate whose properties model the lipoxxygenase binding site.<sup>154</sup>

Non-octahedral cobalt(III) complexes are still relatively rare, as are paramagnetic cobalt(III) compounds; several five-coordinate tropocoronands (11) with both square pyramidal and the more unusual trigonal bipyramidal geometries have been synthesized, with the larger macrocycle ring favouring the latter geometry.<sup>155</sup>

Complexation of CoCl<sub>2</sub> with the pentadentate crown ether 15-crown-5 has led to the isolation<sup>156,157</sup> of several complexes which are generally pentagonal bipyramidal, [Co(15-crown-5)L<sub>2</sub>]<sup>2+</sup> (L = MeCN, H<sub>2</sub>O). Polymer-supported cobalt(II) complexes of tetraazamacrocycles form dioxygen adducts with considerably greater lifetimes than the same complexes in solution.<sup>158</sup> The effect of ring size upon ligand field strength and redox potential has been studied for cobalt(III) complexes of some N<sub>4</sub> macrocycles.<sup>159</sup> The crystal structure and electron density distribution are reported<sup>160</sup> for trigonally compressed *meso*-[Co(hexaen)]Cl<sub>3</sub> at 106 K (hexaen = 1,4,7,10,13,16-hexaazacyclooctadecane). The effects of the donor atoms and their position and spacing, and of the ring size have been examined for a number of cobalt and nickel(II) complexes of mixed-donor macrocycles.<sup>161</sup>

Nickel(I) and (III) complexes continue to attract interest. The N<sub>6</sub> donor hexaen (1,4,7,10,13,16-hexaazacyclooctadecane) forms<sup>162</sup> stable [Ni(hexaen)][AsF<sub>6</sub>] on reduction of the Ni<sup>II</sup> analogue. The structure of the tetragonal nickel(III) complex [Ni([13]aneN<sub>4</sub>)Br<sub>2</sub>]Br ([13]aneN<sub>4</sub> = 1,4,7,10-tetraazacyclotridecane) has been determined.<sup>163</sup> Oxidation of [Ni{(9)aneS<sub>3</sub>}<sub>2</sub>]<sup>2+</sup> affords the isolable Ni<sup>III</sup> analogue, which has significantly shorter Ni–S distances than the Ni<sup>II</sup> compound.<sup>164</sup> Complexes of cyclam-type ligands continue to be popular. Kinetic studies show<sup>165</sup> that the formation of such complexes consists of a fast second-order reaction [first order in both nickel(II) and ligand] followed by a slower first-order rearrangement of the intermediate. Studies of nickel(II) complexes of sterically congested substituted cyclams indicate the substituents affect the magnetic behaviour, with less congested complexes more

<sup>153</sup> T. J. Collins, B. G. Fox, Z. G. Hu, K. L. Kostka, E. Munck, C. E. F. Rickard, and L. J. Wright, *J. Am. Chem. Soc.*, 1992, **114**, 8725.

<sup>154</sup> E. Mulliez, G. Guillot-Edelheit, P. Leduc, J. C. Chottard, C. Bois, A. Bousseksou, and W. Nitschke, *New J. Chem.*, 1992, **16**, 435.

<sup>155</sup> B. S. Jaynes, T. Ren, S. Liu, and S. J. Lippard, *J. Am. Chem. Soc.*, 1992, **114**, 9670.

<sup>156</sup> O. K. Kireeva, B. M. Bulychev, N. R. Streltsova, V. K. Belsky, and A. G. Duniun, *Polyhedron*, 1992, **14**, 1801.

<sup>157</sup> B. M. Bulychev, O. K. Kireeva, V. K. Belsky, and N. R. Streltsova, *Polyhedron*, 1992, **11**, 1809.

<sup>158</sup> J. H. Cameron and S. Graham, *J. Chem. Soc., Dalton Trans.*, 1992, 385.

<sup>159</sup> M. Tsuchimoto and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 191.

<sup>160</sup> M. Morooka, S. Ohba, and K. Toriumi, *Acta Crystallogr., Sect. B*, 1992, **48**, 459.

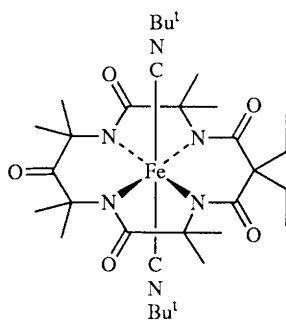
<sup>161</sup> K. R. Adam, M. Antolovich, D. S. Baldwin, L. G. Brigden, P. A. Duckworth, L. F. Lindoy, A. Bashall, M. McPartlin, and P. A. Tasker, *J. Chem. Soc., Dalton Trans.*, 1992, 1869.

<sup>162</sup> G. Gencheva, M. Miteva, E. Zhecheva, and P. R. Bonchev, *Teor. Eksp. Khim.*, 1991, **27**, 339 (*Chem. Abstr.*, **116**, 50 267).

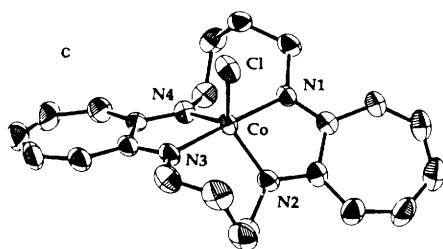
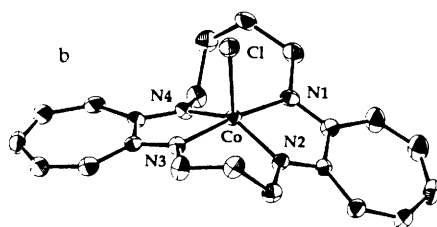
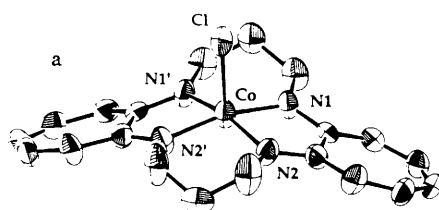
<sup>163</sup> H. Miyamae, K. Yamauchi, and M. Yamashita, *J. Chem. Soc., Dalton Trans.*, 1992, 2921.

<sup>164</sup> A. J. Blake, R. O. Gould, M. A. Halcrow, A. J. Holder, T. I. Hyde, and M. Schroder, *J. Chem. Soc., Dalton Trans.*, 1992, 3427.

<sup>165</sup> J. R. Roeper and H. Elias, *Inorg. Chem.*, 1992, **31**, 1202.



(10)



(11)

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likely to be high-spin.<sup>166</sup> *cis*-[Ni(isocyclam)(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O (isocyclam = 1,4,7,11-tetraazacyclotetradecane) has six-coordinate geometry with *cis*-water molecules, more distorted than that in the corresponding cyclam complex. On heating, it undergoes deaquation-anation to give *cis*-[NiCl<sub>2</sub>(isocyclam)] and on further heating isomerizes irreversibly to the *trans*-isomer, with concomitant configurational change in the ligand. In contrast, *cis*-[Ni(cyclam)(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O does not isomerize on heating.<sup>167</sup>

Some new asymmetric tetraaza macrocyclic complexes of nickel have been prepared<sup>168</sup> and their binding to synthetic polymer supports examined. The study of nickel complexes of ligands with pendant arms added to the cyclic 1,5-diazacyclooctane has shown that metal–ligand bonding can influence the adoption of the unfavourable chair/chair configuration of the fused metallacycle rings.<sup>169</sup>

## 6 Schiff Base and Related Complexes

Trends in the UV/visible and EPR spectra and in the redox potentials of mononuclear iron(III) complexes of Schiff bases derived from salicylaldehyde have been examined, resulting in a correlation between the frequency of a ligand–metal CT band and the Fe<sup>III/II</sup> redox potential.<sup>170</sup>

The  $\mu$ -oxo complex [ $\{\text{Fe}(\text{salophen})\}_2\text{O}\}$  forms a dmsO adduct that has a square-pyramidal structure linked by a bent Fe–O–Fe bridge,<sup>171</sup> whilst octahedrally coordinated iron is found in low-spin K[Fe(acacen)(CN)<sub>2</sub>]·2H<sub>2</sub>O. Structures have also been reported<sup>172</sup> for [Fe(acacen)X] (X = Cl, NO<sub>3</sub>) and [ $\{\text{Fe}(\text{acacen})\}_2\text{O}\}$ . [acacen = *N,N'*-ethylenebis(acetylacetonylideneimine)]. Another binuclear complex features a terephthalate bridge.<sup>173</sup>

Electrochemical oxidation of the oxygen carrier [Co(salen)] has been studied<sup>174</sup> in a range of solvents. Solid-state <sup>15</sup>N NMR studies on NO adducts of cobalt *N*-substituted salicylideneimine complexes suggest that the shift tensor may be used as a criterion of bond angle; the structure of the bent [Co(NO)(esal)<sub>2</sub>](Co–N–O 129°) (esal = *o*-OC<sub>6</sub>H<sub>4</sub>CH=NEt) was determined.<sup>175</sup>

In the field of reduced Schiff base complexes, acetone solutions of the nickel tetrahydrosalen complex (12a) add O<sub>2</sub> at low temperatures, changing in colour from cherry-red to yellow-orange with dehydrogenation only as far as a dihydrosalen complex (12b); the reaction has been shown in one case to be first order in both O<sub>2</sub> and the nickel complex. [No such dehydrogenation reaction is observed with corresponding Fe<sup>III</sup> and Cu<sup>II</sup> complexes]. The reaction is inhibited by adduct formation (*e.g.* with

<sup>166</sup> K. Kaobiro, A. Nakyama, T. Hiro, and Y. Tobe, *Inorg. Chem.*, 1992, **31**, 676.

<sup>167</sup> Y. Satake, Y. Ihara, H. Senda, M. Suzuki, and A. Uehara, *Inorg. Chem.*, 1992, **31**, 3248.

<sup>168</sup> J. H. Cameron, H. B. Harvey, and I. Soutar, *Inorg. Chim. Acta*, 1992, **192**, 253; *J. Chem. Soc., Dalton Trans.*, 1992, 597.

<sup>169</sup> M. Y. Darensbourg, I. Font, D. K. Mills, M. Pala, and J. H. Reibenspies, *Inorg. Chem.*, 1992, **31**, 4965.

<sup>170</sup> K. Ramesh and R. Mukherjee, *J. Chem. Soc., Dalton Trans.*, 1992, 83.

<sup>171</sup> F. M. Ashmawy, A. R. Ujaimi, C. A. McAuliffe, R. V. Parish, and R. G. Pritchard, *Inorg. Chim. Acta*, 1991, **187**, 155.

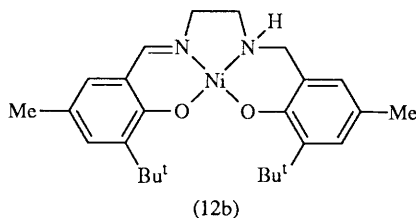
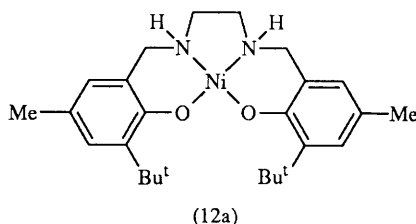
<sup>172</sup> X. Wang, W. T. Pennington, D. L. Ankers, and J. C. Fanning, *Polyhedron*, 1992, **11**, 2253.

<sup>173</sup> M. Dusek, V. Petricek, J. Kamenicek, and Z. Sindelar, *Acta Crystallogr., Sect. C*, 1992, **48**, 1579.

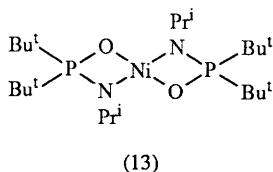
<sup>174</sup> E. Eichhorn, A. Rieker, and B. Speiser, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1214.

<sup>175</sup> C. J. Groombridge, L. F. Larkworthy, A. Marecaux, D. C. Povey, G. W. Smith, and J. Mason, *J. Chem. Soc., Dalton Trans.*, 1992, 3125.

py); nickel complexes of either the corresponding salen or dihydrosalen ligands do not form such adducts.<sup>176</sup>



Schiff base complexes of  $\text{Ni}^{\text{II}}$  are of course noted for their interesting magnetic properties. It is generally assumed that diamagnetic tetracoordinate complexes are square planar and paramagnetic complexes are tetrahedral; equilibria between the two are often observed in solution depending upon solvent and temperature. Some complexes with  $\text{NiN}_2\text{S}_2$  chromophores exhibit similar behaviour. The characterization of a square-planar paramagnetic complex (13) of a related ligand, but with  $\text{N}_2\text{O}_2$



coordination of nickel, rather shatters this comfortable illusion.<sup>178</sup> Nickel complexes of unsymmetrical quadridentate Schiff bases with a pendant *N*-acetyl or trifluoroacetyl substituent have been synthesized; the crystal structure of one of the latter shows<sup>179</sup> that a 'non-bonding' Ni–F interaction may be responsible for inhibited enantiomer interconversion. Crystal structures have been reported for two nickel complexes.<sup>180</sup>  $[\text{Fe}(\text{acac})_2(\text{NO}_3)]$  has been synthesized from  $[\text{Fe}(\text{acac})_3]$  and used to make the binuclear heterometallic  $[\text{Cu}(\text{salen})\text{Fe}(\text{acac})_2(\text{NO}_3)]$ .<sup>177</sup>

<sup>176</sup> A. Bottcher, H. Elias, L. Muller, and H. Paulus, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 623.

<sup>177</sup> D. Laroque, I. Morgenstern-Badarau, H. Winkler, E. Bill, A. X. Trautwein, and M. Julve, *Inorg. Chim. Acta*, 1992, **192**, 107.

<sup>178</sup> T. Frommel, W. Peters, H. Wunderlich, and W. Kuchern, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 612.

<sup>179</sup> M. Kwiatkowski and G. Bandoli, *J. Chem. Soc., Dalton Trans.*, 1992, 379.

<sup>180</sup> Y. Elerman, H. Paulus, I. Svoboda, and H. Fuess, *Z. Krist.*, 1992, **198**, (a)129; (b) 132.

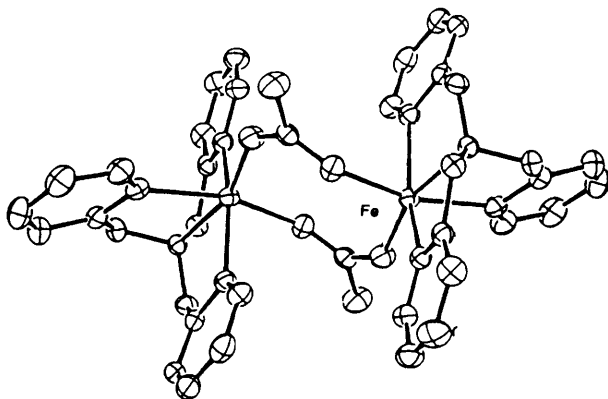
## 7 Oxo-bridged Species and Models for Oxygen-containing Proteins

There have been two reviews relevant to this area, which includes such important iron-containing biological systems as haemerythrin and ferritin. One<sup>181</sup> discusses synthetic models for iron-oxygen aggregation and biomineralization, the other<sup>182</sup> binuclear iron centres in proteins.

Dicobalt substitution of iron in haemerythrin has been carried out; EXAFS measurements indicate a dicobalt site (Co–Co 3.54 Å) with histidine ligation.<sup>183</sup>

*Ab initio* Hartree–Fock calculations reported<sup>184</sup> on the well-known binuclear ion  $[\text{Fe}_2\text{OCl}_6]^{2-}$  indicate the coupling between the irons to be sensitive to the Fe–O distance, but less so to the Fe–O–Fe angle; the bromide analogue  $[\text{Fe}_2\text{OBr}_6]^{2-}$  has a similar structure.<sup>185</sup>

Many structurally characterized iron complexes have been reported. A di-iron(II) complex,  $[\text{Fe}_2(\mu_2\text{-OAc})_2(\text{tpa})_2][\text{BPh}_4]_2$  [tpa = tris(2-pyridylmethyl)amine] has been suggested as a model for the core of ribonucleotide reductase. The iron atoms are some 4.29 Å apart, consonant with the very weak observed antiferromagnetic interaction. On oxidation, it converts to a  $\mu$ -oxo species  $[\text{Fe}_2(\mu\text{-O})(\text{OAc})_2(\text{tpa})_2][\text{BPh}_4]_2$  (14) with



(14)

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the advent of the  $\mu$ -oxo bridge accompanied by a switch to monodentate terminal behaviour by the acetates.<sup>186</sup> Diferrous complexes with two OH bridges  $[\text{Fe}_2\text{L}_2(\text{OH})_2]$  [L = HB(3,5-Pr<sup>i</sup>)<sub>2</sub>]<sub>3</sub>] or alternatively with one OH and one carboxylate bridge.

<sup>181</sup> K. S. Hagen, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1010.

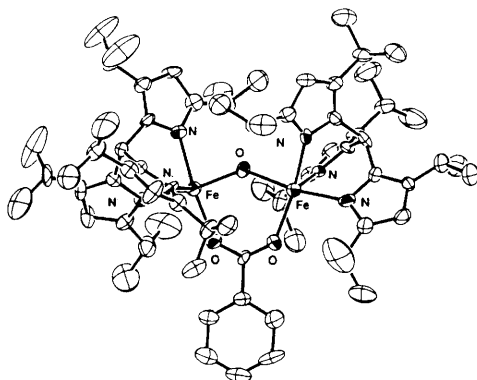
<sup>182</sup> R. G. Wilkins, *Chem. Soc. Rev.*, 1992, **21**, 171.

<sup>183</sup> J. Zhang, D. M. Kurtz, M. J. Maroney, and J. P. Whitehead, *Inorg. Chem.*, 1992, **31**, 1359.

<sup>184</sup> J. R. Hart, A. K. Rappe, S. M. Gorun, and T. H. Upton, *Inorg. Chem.*, 1992, **31**, 5254.

<sup>185</sup> P. J. M. Evans, B. W. Fitzsimmons, W. G. Marshall, A. J. Golder, L. F. Larkworthy, D. C. Povey, and G. W. Smith, *J. Chem. Soc., Dalton Trans.*, 1992, 1065.

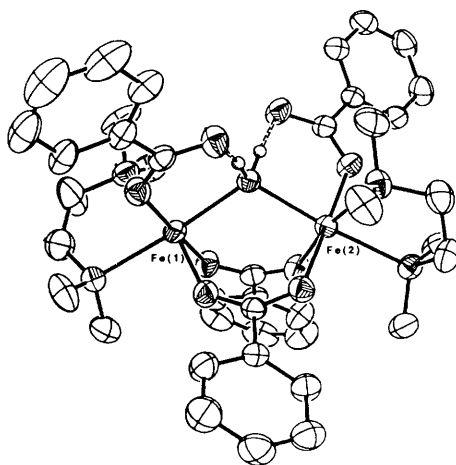
<sup>186</sup> S. Menage, Y. Zang, M. P. Hendrich, and L. Que, *J. Am. Chem. Soc.*, 1992, **114**, 7786.



(15)

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$[\text{Fe}_2\text{L}_2(\text{OH})(\text{O}_2\text{CPh})]$  (15) have been characterized and suggested as haemerythrin models.<sup>187</sup> A different type of bridging system in a di-iron(II) complex (16) is provided<sup>188</sup> by two benzoates and a water molecule in  $[\text{Fe}_2(\text{H}_2\text{O})(\text{O}_2\text{CPh})_4(\text{tmen})_2]$ . Bridging by two carboxylates and a  $\mu$ -oxo group has been reported this year, in models for the di-iron oxo centres in haemerythrin and the B2 subunit of ribonucleotide



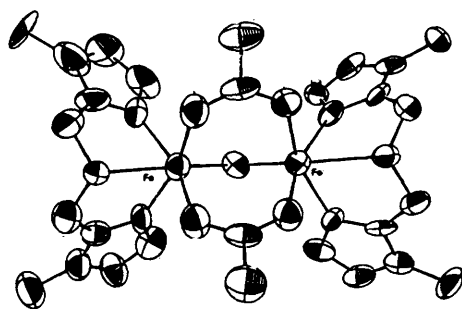
(16)

(Reproduced with permission from *J. Am. Chem. Soc.*, 1992, **114**, 8741)

<sup>187</sup> N. Kitajima, N. Tamura, M. Tanaka, and Y. Moro-oka, *Inorg. Chem.*, 1992, **31**, 3342.

<sup>188</sup> K. S. Hagen and R. Lachicotte, *J. Am. Chem. Soc.*, 1992, **114**, 8741.

reductase (RRB2). For  $[\text{Fe}_2\text{O}(\text{bmima})_2(\text{O}_2\text{CR})_2]^{2+}$  [bmima = bis{(1-methylimidazole-2-yl)methyl}amine; R = Me, Ph] (17) magnetic data are fitted with temperature-dependent  $J$  values and interpreted in terms of a weakening of the hydrogen bond between a solvate water molecule and the oxo bridge.<sup>189</sup> Complexes such as  $[\text{Fe}_2\text{O}(\text{H}_2\text{O})_2(\text{O}_2\text{CCH}_2\text{Cl})_2(\text{bipy})_2][\text{NO}_3]_2$  have been made by a new route from the parent iron carboxylate, ferric nitrate, and bipy.<sup>190</sup> Mixed-metal  $\mu$ -oxobis(acetato) dimers, where one metal may be iron, have been the subject of detailed magnetic study.<sup>191</sup>



(17)

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Among spectroscopic measurements, the first detailed 2D NMR study of paramagnetic di-iron complexes, both ferrous and mixed valence, has been made.<sup>192</sup> Electron transfer in  $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$  complexes with both phenoxo and carboxylate bridges and high-spin  $\text{FeN}_3\text{O}_3$  chromophores has been studied by NMR and ESR.<sup>193</sup> The first iron(III) complex exhibiting<sup>194</sup> a nematic mesophase, believed to involve an oxo-bridge, is reported (18).

A hexanuclear cluster  $[\text{Fe}_6(\mu_4\text{-O})_2(\mu_2\text{-OMe})_8(\text{OMe})_4(\text{tren})_2]^{2+}$  has been suggested<sup>195</sup> as a soluble model for the core of ferritin.

Possibly the most interesting report of the year concerns the trapping of quite large iron hydroxide units containing hydroxo(oxo) iron clusters with 17 and 19 iron atoms.

<sup>189</sup> K. J. Oberhausen, J. F. Richardson, R. J. O'Brien, R. M. Buchanan, J. K. McCusker, R. J. Webb, and D. N. Hendrickson, *Inorg. Chem.*, 1992, **31**, 1123.

<sup>190</sup> K. L. Taft, A. Masschelein, S. Liu, S. J. Lippard, D. Garfinkel-Shweky, and A. Bino, *Inorg. Chim. Acta*, 1992, **198–200**, 627.

<sup>191</sup> R. Hotzelmann, K. Wiegardt, J. Ensling, H. Romstedt, P. Gutlich, E. Bill, U. Florke, and H.-J. Haupt, *J. Am. Chem. Soc.*, 1992, **114**, 9470.

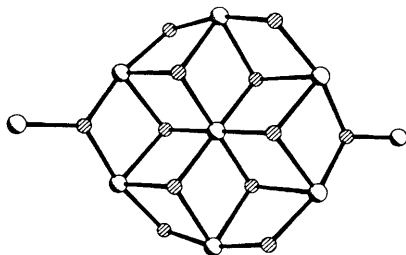
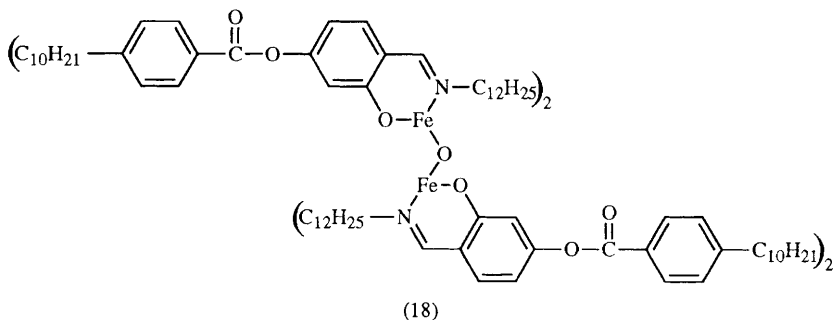
<sup>192</sup> L.-J. Ming, H. G. Jang, and L. Que, *Inorg. Chem.*, 1992, **31**, 359.

<sup>193</sup> M. S. Mashuta, R. J. Webb, J. K. McCusker, E. A. Schmitt, K. J. Oberhausen, J. F. Richardson, R. M. Buchanan, and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1992, **114**, 3815.

<sup>194</sup> Y. Galyametdinov, G. Ivanova, K. Griesar, A. Prosvirin, I. Ovchinnikov, and W. Haase, *Adv. Mater.*, 1992, **4**, 739.

<sup>195</sup> V. S. Nair and K. S. Hagen, *Inorg. Chem.*, 1992, **31**, 4048.

Their structures have a common core (19), confirmed by *X*-ray diffraction, and have important implications for biomineralization processes.<sup>196</sup>



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## 8 Cluster Complexes Including Iron-Sulfur Proteins

An extensive volume<sup>197</sup> containing 10 reviews devoted to iron-sulfur proteins has appeared. Articles discuss trinuclear cuboidal and heterometallic cubane-type clusters;<sup>198a</sup> the replacement of S by Se,<sup>198b</sup> the EPR spectra,<sup>198c</sup> and the structural and functional diversity<sup>198d</sup> of iron-sulfur proteins; and Fe-S clusters in enzymes.<sup>198e</sup>

An iron(II) complex with a tetradentate peptide has been proposed<sup>199</sup> as a model for the reduced form of rubredoxin. Iron-sulfur dimers have been synthesized as models for Rieske-type proteins; the ESR spectra of the reduced forms indicate oxygen coordination.<sup>200</sup>

<sup>196</sup> S. L. Heath and A. K. Powell, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 191.

<sup>197</sup> 'Adv. Inorg. Chem.', Vol. 38, ed. R. Cammack, Academic Press, 1991.

<sup>198</sup> (a) R. H. Holm in ref. 197, p. 1; (b) J. Meyer, J.-M. Moulis, J. Gaillard, and M. Lutz, in ref. 197, p. 74; (c) W. R. Hagen, in ref. 197, p. 165; (d) H. Matsubara and K. Saeki, in ref. 197, p. 223; (e) R. Cammack, in ref. 197, p. 281.

<sup>199</sup> W. Sun, A. Kajiwar, N. Ueyama, and A. Nakamura, *J. Chem. Soc., Dalton Trans.*, 1992, 3255.

<sup>200</sup> P. Beardwood and J. F. Gibson, *J. Chem. Soc., Dalton Trans.*, 1992, 2457.

FAB MS has been applied to four-iron clusters.<sup>201</sup> Crystal structures reported include  $[\text{AsPh}_4]_2[\text{Fe}_4\text{S}_4(\text{SAd})_4]$  (SAd = 1-adamantanethiolate),<sup>202</sup> and  $\text{Fe}_4\text{S}_4$  clusters where both thiolates and thiourea are the terminal ligands.<sup>203</sup> An oxidative conversion<sup>204</sup> of an  $\text{Fe}_4\text{S}_4$  core into an  $\text{Fe}_3\text{S}_4$  centre has been reported whilst clusters  $[\text{MFe}_3\text{S}_4]$  (M = Mo, W) that are structurally and electronically analogous to the reduced three-iron centres in ferredoxins have been characterized,<sup>205</sup> as have cubane clusters with  $\text{NiFe}_3\text{E}_4$  (E = S, Se) cores.<sup>206</sup> The characterization of high nuclearity clusters  $[\beta\text{-Na}_2\text{Fe}_{18}\text{S}_{30}]^{8-}$  and  $[\text{Na}_9\text{Fe}_{20}\text{Se}_{38}]^{9-}$  has been reported.<sup>207</sup>

Notable selenium and tellurium-containing clusters are  $[\text{Fe}_4\text{Te}_4(\text{PEt}_3)_4][\text{PF}_6]$  (cubane),  $[\text{Fe}_6\text{Se}_8(\text{PEt}_6)][\text{PF}_6]$  (stellated octahedron)<sup>208</sup> and  $[\text{Fe}_4\text{Te}_4(\text{PEt}_3)_4]$  (cubane).<sup>209</sup> Single-crystal ESR spectra<sup>210</sup> have been obtained at 4.2 K of  $[\text{Co}_6(\mu_3\text{-S})_8(\text{PEt}_3)_6][\text{BPh}_4]$  whilst  $\text{CoBr}_2$ ,  $\text{Na}_2\text{S}$  and dppm give a cluster<sup>211</sup> with a distorted  $\text{Co}_6$  core,  $[\text{Co}_6(\mu_3\text{-S})_8\{\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2\}_6]$ . On the other hand,  $[\text{CoCl}(\text{PPh}_3)_3]$  reacts with excess  $\text{Li}_2\text{S}$  to give  $[\text{Co}_7(\mu_4\text{-S})_3(\mu_3\text{-S})_3(\text{PPh}_3)_4\text{Br}_{1.5}\text{Cl}_{1.5}]$  which has a capped prismatic core.<sup>212</sup>

A range of clusters with between 4 and 21 nickels results from the reactions of  $\text{Se}(\text{SiMe}_3)_2$  with  $[\text{NiCl}_2\text{L}_2]$  (L =  $\text{R}_3\text{P}$ ), e.g.  $[\text{Ni}_7\text{Se}_5(\text{PPRi}_3)_6]$ .<sup>213</sup>

## 9 Other Metalloproteins

Reviews have appeared on the electronic structures of the active sites in non-haem iron enzymes,<sup>214</sup> and of multiple weak forces in ion-binding molecules such as enterobactins.<sup>215</sup> Two families of synthetic chiral enterobactin analogues have been made, one catechoylamide being the most efficient iron(III) binder yet synthesized, with a stability constant for the  $\text{Fe}^{3+}$  complex within three orders of magnitude of enterobactin itself;<sup>216</sup> two structures have been determined of simple iron(III) complexes that relate to that of enterobactin.<sup>217</sup>

A comparison of the X-ray absorption spectra of nickel complexes with  $\text{NiN}_3\text{S}_2$  chromophores, e.g.  $[\text{Ni}(\text{terpy})(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{S})_2]$ , with those of a  $[\text{FeNi}]$  hydrogenase indicate the latter to have a distorted *tbp* nickel centre with a mixed N/O and S donor environment.<sup>218</sup> ESR spectroscopy has been used to probe the redox behaviour of

<sup>201</sup> W. L. Lee, D. A. Gage, Z. H. Huang, C. K. Chang, M. G. Kanatzidis, and J. Allison, *J. Am. Chem. Soc.*, 1992, **114**, 7132.

<sup>202</sup> H. Kambayashi, M. Nakamoto, S. M. Peng, H. Nagao, and K. Tanaka, *Chem. Lett.*, 1992, 919.

<sup>203</sup> U. Bierbach, W. Saak, D. Haase, and S. Pohl, *Z. Naturforsch., Teil B.*, 1991, **46**, 1629.

<sup>204</sup> E. K. H. Roth and J. Jordanov, *Inorg. Chem.*, 1992, **31**, 240.

<sup>205</sup> D. Coucouvanis, S. A. Al-Ahmad, A. Salifoglou, V. Papaefthymiou, A. Kostikas, and A. Simopoulos, *J. Am. Chem. Soc.*, 1992, **114**, 2472.

<sup>206</sup> S. Ciurli, P. K. Ross, M. J. Scott, B.-B. Yu, and R. H. Holm, *J. Am. Chem. Soc.*, 1992, **114**, 5415.

<sup>207</sup> J. F. You, G. C. Papaefthymiou, and R. H. Holm, *J. Am. Chem. Soc.*, 1992, **114**, 2697.

<sup>208</sup> F. Cecconi, C. A. Ghilardi, S. Midollini, and A. Orlandini, *J. Chem. Soc., Chem. Commun.*, 1992, 910.

<sup>209</sup> M. L. Steigerwald, T. Siegrist, S. M. Stuczynski, and Y. U. Kwon, *J. Am. Chem. Soc.*, 1992, **114**, 3155.

<sup>210</sup> A. Bencini, S. Midollini, and C. Zanchini, *Inorg. Chem.*, 1992, **31**, 2132.

<sup>211</sup> M. Hong, Z. Huang, X. Lei, B. Kang, F. Jiang, and H. Liu, *Chin. J. Chem.*, 1992, **9**, 425.

<sup>212</sup> F. Jiang, L. Huang, X. Lei, H. Liu, B. Kang, Z. Huang, and M. Hong, *Polyhedron*, 1992, **11**, 361.

<sup>213</sup> D. Fenske, H. Krautscheid, and M. Mueller, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 321.

<sup>214</sup> E. I. Solomon and Y. Zhang, *Acc. Chem. Res.*, 1992, **25**, 343.

<sup>215</sup> A. Shanzler, J. Libman, and S. Lifson, *Pure Appl. Chem.*, 1992, **64**, 1421.

<sup>216</sup> Y. Tor, J. Libman, A. Shanzler, C. Felder, and S. Lifson, *J. Am. Chem. Soc.*, 1992, **114**, 6661.

<sup>217</sup> T. D. P. Stack, T. B. Karpishin, and K. N. Raymond, *J. Am. Chem. Soc.*, 1992, **114**, 1512.

<sup>218</sup> M. M. Olmstead, J. P. Whitehead, C. Bagyinka, M. J. Maroney, and P. K. Mascharak, *Inorg. Chem.*, 1992, **31**, 3612.

related species, with both  $\text{Ni}^{\text{I}}$  and  $\text{Ni}^{\text{III}}$  compounds identifiable.<sup>219</sup> Compounds with  $[\text{NiN}_x\text{Se}_y]$  chromophores have also been explored.<sup>220</sup> A nickel macrocyclic complex catalyses the reduction of protons to  $\text{H}_2$  under electrochemical conditions.<sup>221</sup> The electronic and NMR spectra of nickel(II)-substituted carboxypeptidase have been measured and its reactivity with D- and L-phenylalanine investigated.<sup>222</sup>

## 10 Complexes with Unusual Magnetic Properties, including Spin-equilibrium Compounds

Reviews in this area have covered intersystem crossing in iron(II) complexes,<sup>223</sup> spin-frustration<sup>224</sup> in iron(III) complexes, and electronic spin crossovers in cobalt(II) complexes.<sup>225</sup>

Among iron(II) complexes, the effect of substituents on the spin state of iron(II) tris-complexes of substituted bipyridyls has been examined.<sup>226</sup> Magnetism of the crossover compound<sup>227</sup>  $[\text{Fe}(\text{NCS})_2(5,6\text{-dmp})_2]$  (dmp = dimethylphenanthroline) has been examined, including LIESST studies below 70 K. The crystal structure of the 'non-spin-crossover' 2,9-dmp analogue has been determined; comparison with the parent  $[\text{Fe}(\text{NCS})_2(\text{phen})_2]$  suggests that steric hindrance is responsible for high-spin behaviour down to 6 K. Specific heat anomalies in spin-transition systems  $[\text{Fe}(\text{NCS})_2(\text{bts})_2]$  and  $[\text{Fe}(2\text{-pic})_3]\text{Cl}_2$  [bts = 2,2'-bis(4,5-dihydro-5-methyl-1,3-thiazole); 2-pic = 2-picolyamine] have been studied by microcalorimetry and thermal conductivity.<sup>228</sup>

A structural comparison of the spin-crossover compounds  $[\text{Fe}(\text{NCS})_2\text{L}_2]$  (L = 2,2'-4,5-dihydrothiazine or phen) which exhibit rather different crossover behaviour has been made, the former showing a gradual singlet–quintet transition, the latter an abrupt transition. Whilst the overall molecular changes are broadly similar in terms of bond-shortening and a trend towards a more regular  $\text{FeN}_6$  octahedron, the rapidity of changes in the lattice parameters differs, mirroring the susceptibility changes, while there are also differences in structural anisotropy.<sup>229</sup> The first two-step spin crossover (at 164 and 197 K) to be observed in a polynuclear complex has been detected in dinuclear  $[\{\text{Fe}(\text{bt})(\text{NCS})_2\}_2\text{bipym}]$  (bt = 2,2'-bithiazoline) by magnetic susceptibility and Mössbauer measurements.<sup>230</sup> Sub-picosecond  $\Delta S = 2$  intersystem crossing has been observed in the low-spin state of a spin-crossover compound.<sup>231</sup>

A kinetic study of the high-spin  $\rightarrow$  low-spin relaxation in  $[\text{Fe}(\text{ptz})_6][\text{BF}_4]_2$

<sup>219</sup> N. Baidya, M. M. Olmstead, and P. K. Mascharak, *J. Am. Chem. Soc.*, 1992, **114**, 9666.

<sup>220</sup> N. Baidya, B. C. Noll, M. M. Olmstead, and P. K. Mascharak, *Inorg. Chem.*, 1992, **31**, 2999.

<sup>221</sup> L. L. Eftros, H. H. Thorp, G. W. Brudvig, and R. H. Crabtree, *Inorg. Chem.*, 1992, **31**, 1722.

<sup>222</sup> I. Bertini, A. Donaire, R. Monnanni, J.-M. Moratal, and J. Salgado, *J. Chem. Soc., Dalton Trans.*, 1992, 1443.

<sup>223</sup> A. Hauser, *Coord. Chem. Rev.*, 1992, **111**, 275.

<sup>224</sup> J. K. McCusker, E. A. Schmitt, and D. N. Hendrickson, *NATO ASI Ser., Ser. E*, 1991, **198**, 297 (*Chem. Abstr.*, 1992, **116**, 226 404).

<sup>225</sup> J. A. Zarembowitch, *New. J. Chem.*, 1992, **16**, 255.

<sup>226</sup> D. Onngo and H. A. Goodwin, *Aust. J. Chem.*, 1991, **44**, 1539.

<sup>227</sup> D. C. Figg, R. H. Herber, and J. A. Potenza, *Inorg. Chem.*, 1992, **31**, 2111.

<sup>228</sup> R. Jakobi, H. Romstedt, H. Spiering, and P. Gutlich, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 178.

<sup>229</sup> J.-A. Real, B. Gallois, T. Granier, F. Suez-Panama, and J. Zarembowitch, *Inorg. Chem.*, 1992, **31**, 4972.

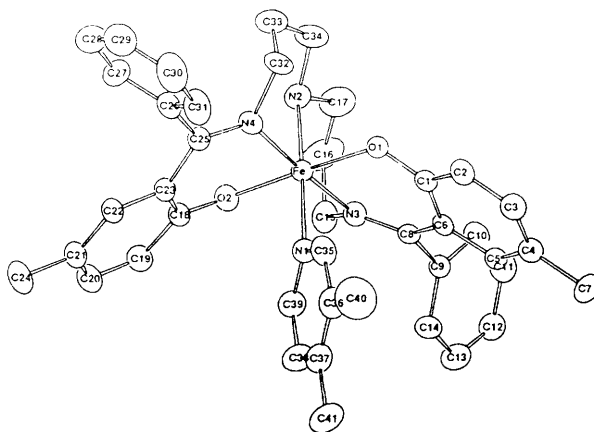
<sup>230</sup> J.-A. Real, H. Bolvin, A. Bousseksou, A. Dworkin, O. Kahn, F. Varret, and J. Zarembowitch, *J. Am. Chem. Soc.*, 1992, **114**, 4650.

<sup>231</sup> J. K. McCusker, K. N. Walda, R. C. Dunn, J. D. Simon, D. Magde, and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1992, **114**, 6919.



**Iron(III) complexes.**—The ability of the octaethyltetraazaporphyrin ligand to stabilize the  $S = 3/2$  state for iron(III) has already been mentioned (p. 182).

The complex  $[\text{Fe}(\text{sal}_2\text{trien})][\text{BPh}_4]$  (sal<sub>2</sub>trien is a hexadentate ligand derived from salicylaldehyde and triethylenetetraamine) has been isolated in two crystalline forms; the monoclinic form is a spin-crossover system whilst twin crystals are high-spin.<sup>233</sup> The crystal structure of the monoclinic form at 290 K reveals bond lengths intermediate between those expected for pure high and low-spin systems. Another Schiff-base type complex with a pentadentate ligand (mbpN) forms a six-coordinate lutidine adduct  $[\text{Fe}(\text{mbpN})(\text{lut})][\text{BPh}_4]$  (20) that undergoes spin-state interconversion faster than the lifetime of the  $^{57}\text{Fe}$  excited state.<sup>234</sup>



(20)

Two studies examining equilibria between 3/2 and 1/2 states may be noted. One paper<sup>235</sup> examined nitrosyl-iron complexes of a Jager-type ligand whilst the complex  $[\text{Fe}(\text{bipy})_2\{\text{ONC}(\text{CN})_2\}_2][\text{ONC}(\text{CN})_2]$  has magnetic moments of  $3.63 \mu_{\text{B}}$  at 378 K and  $2.56 \mu_{\text{B}}$  at 80 K.<sup>236</sup>

Several paramagnetic cobalt(III) tropocoronands have already been mentioned in Section 5. The complex  $[\text{Co}(\text{tripyam})_2][\text{ClO}_4]_2$  (tripyam = tri-2-pyridylamine) when freshly prepared contains some low-spin isomer with the  $^2\text{E}$  ground state frozen into the solid; this reverts to the high-spin  $^4\text{T}$  form over some months. On ion-exchange

<sup>2,3,3</sup> Y. Maeda, H. Oshio, Y. Tanigawa, T. Oniki, and Y. Takashima, *Hyperfine Interact.*, 1991, **68**, 157.

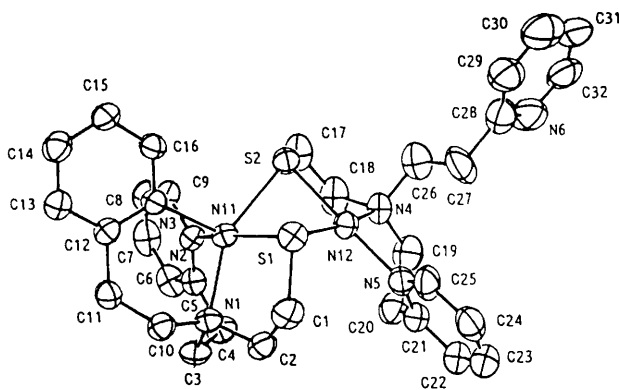
<sup>235</sup> E. König, G. Ritter, J. Dengler, and L. F. Larkworthy, *Inorg. Chem.*, 1992, **31**, 1196.

<sup>236</sup> N. N. Gerasimchuk, N. Laslo, and V. V. Skopenko, *Dokl. Akad. Nauk. Ukr. SSR*, 19

*Abstr.*, 1992, 116, 142-644).

onto laponite, it is absorbed as a pink aqua complex  $[\text{Co}(\text{tripyam})_2(\text{H}_2\text{O})_2]^{2+}$  with bidentate ligands, but if microwave-accelerated, the orange  $[\text{Co}(\text{tripyam})_2]^{2+}$  species is absorbed. Iron(II) complexes of this ligand have likewise been studied.<sup>237</sup>

The first paramagnetic planar  $\text{Ni}^{\text{II}}$  complex to be characterized has already been mentioned in Section 6, and the effect of ring substituents on nickel cyclam complexes in section 5. Some binuclear nickel(II) complexes with thiolate bridges (21) have been synthesized and studied; these are unusual in that one nickel site has square planar  $\text{N}_2\text{S}_2$  coordination of low-spin  $\text{Ni}^{\text{II}}$  and the other has a square pyramidal  $\text{N}_3\text{S}_2$  donor set yielding high-spin nickel(II).<sup>238</sup>



(21)

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<sup>237</sup> S. P. Bond, C. E. Hall, C. J. McNerlin, W. R. McWhinnie, and D. J. Walton, *J. Mater. Chem.*, 1992, **2**, 37.

<sup>238</sup> M. Mikuriya, M. Handa, S. Shigematsu, S. Funaki, F. Adachi, and H. Okawa, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 512.