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## Crystallographic Study of the Low-Spin Iron(II) and Iron(III) Bis Complexes of 1,4,7-Triazacyclononane

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An X-ray crystallographic study of  $[\text{Fe}([9]\text{aneN}_3)_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$  (I) and  $[\text{Fe}([9]\text{aneN}_3)_2]\text{Cl}_3 \cdot 5\text{H}_2\text{O}$  (II) is reported. I is orthorhombic, space group *Pbcn*, and the structure was refined to a conventional *R* factor of 0.0967, while II is trigonal *P3*, with *R* refined to 0.0824. II consists of alternating sheets, one containing the complex cation hydrogen bonded ( $\text{N} \cdots \text{Cl} = 3.18 \text{ \AA}$ ) to two chlorides, with the other sheet consisting of the remaining chloride hydrogen bonded to the water molecules in an ice-like structure. The cell constants for I are  $a = 10.342 \text{ \AA}$ ,  $b = 13.571 \text{ \AA}$ , and  $c = 15.088 \text{ \AA}$ , while for II were found  $a = b = 8.069 \text{ \AA}$  and  $c = 31.322 \text{ \AA}$ . The Fe-N bond lengths averaged 2.03 (1) and 1.99 (1)  $\text{\AA}$  for I and II, respectively. These lengths were compared with those for the Co(III) complexes, as well as with those for the 2,2'-bipyridyl and hexacyano complexes. It was concluded that low-spin Fe(II) and Fe(III) are, like Co(III), extremely small metal ions, where the observed bond lengths are actually stretched from the strain-free lengths, due to van der Waals repulsions between the ligands. The significance of this in relation to the spectral properties of complexes of macrocycles is discussed. The infrared spectra of the  $([9]\text{aneN}_3)_2$  complexes of several metal ions are reported, and the behavior of the metal-sensitive bands in the 800–200  $\text{cm}^{-1}$  region is used to support the idea that the order of bond strengths is  $\text{Fe(II)} > \text{Co(III)} > \text{Fe(III)} > \text{Cr(III)} \gg \text{Ni(II)} > \text{Cu(II)} > \text{Zn(II)}$ .

### Introduction

The nitrogen-donor macrocycles are of considerable interest in the high ligand field (LF) strength that they exert.<sup>1</sup> A recent<sup>2</sup> analysis of electronic spectra of complexes of the ligand  $[9]\text{aneN}_3$  (Figure 1) suggested that the ligand field strength exerted by two of these ligands in a bis complex was almost exactly the same as that exerted by 2,2'-bipyridyl (bpy) in its tris complexes. Low-spin iron(II) and iron(III) bis complexes of  $[9]\text{aneN}_3$  have recently been synthesized.<sup>3</sup> The low-spin state of the iron here is in accord with the idea<sup>2</sup> that  $[9]\text{aneN}_3$  exerts a ligand field as high as that of bpy, which also yields low-spin complexes of iron(II) and iron(III).

The above  $[9]\text{aneN}_3$  complexes are, apart from the fact that they are the first examples of low-spin iron complexes with all six donors as saturated nitrogens, of some interest. One point is the origin of the high LF strength exerted by  $[9]\text{aneN}_3$ , which is far higher<sup>4</sup> than that exerted by open-chain polyamines. It has been suggested<sup>5</sup> that the high LF strength calculated is only apparent. The high-energy position of the  $^3\text{A}_{2g} \rightarrow ^3\text{T}_{2g}$  transition is due to it being only one component of the transition, which is considered to be split by trigonal distortion of the complex. Another point of interest is the Fe-N bond lengths of Fe(II) and Fe(III) bound to saturated nitrogen donors. It has been found<sup>6</sup> that in the series of low-spin Fe(II) complexes of the series  $[\text{Fe}([13]\text{aneN}_4)(\text{CN})_2]$  through  $[\text{Fe}([15]\text{aneN}_4)(\text{CN})_2]$  the maximum in-plane LF strength occurs (Table I) in the  $[13]\text{aneN}_4$  complex. The ligand  $[13]\text{aneN}_4$  has a cavity size<sup>7</sup> such that metal ions with a M-N length of 1.92  $\text{\AA}$  fit best. It has been suggested<sup>6</sup> that the high in-plane LF in  $[\text{Fe}([13]\text{aneN}_4)(\text{CN})_2]$  is due to compression of the too large Fe(II) by the macrocycle. Alternatively, it has been suggested<sup>8,9</sup> that this represents the best-fit size for Fe(II) in a tetraaza macrocycle and that the high LF strength is due to the greater number of secondary nitrogens in a low-strain situation. Thus, the actual Fe-N lengths for iron(III), and particularly iron(II), are of considerable interest in order to settle this point and also gain an idea of the sizes of the low-spin iron(II) and iron(III) relative to other first-row ions, such as Ni(II) and Co(III).

We report here a crystallographic study of the complexes  $[\text{Fe}([9]\text{aneN}_3)_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$  and  $[\text{Fe}([9]\text{aneN}_3)_2]\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ , as well as the infrared spectra of the  $([9]\text{aneN}_3)_2$  complexes of Fe(II), Fe(III), Co(III), Cr(III), Ni(II), and Cu(II) in the region of metal-ligand vibrations, namely 800–200  $\text{cm}^{-1}$ .

### Experimental Section

**Materials.** The ligand  $[9]\text{aneN}_3$  was synthesized by standard methods.<sup>4</sup> These methods were used to synthesize the bis complexes of Fe(II)

and Fe(III) as described previously.<sup>3</sup> The  $([9]\text{aneN}_3)_2$  complexes of Cu(II), Ni(II), Co(III), and Cr(III) were obtained by standard literature procedures.<sup>3,4,10</sup>

**Structure Analysis.** For both compounds, diffraction quality crystals were selected by standard oscillation and Weissenberg techniques, using Cu K $\alpha$  radiation. The space group and approximate cell constants were determined at the same time. Intensity data and accurate cell dimensions were obtained at room temperature by using a Philips PW1100 diffractometer and Mo K $\alpha$  radiation. The crystal data and details of the crystallographic analysis are shown in Table II. For the Fe(III) complex, it was only slight differences in orientation of the complex cations that lowered the symmetry such that the space group was *P3* rather than *R3*. This understandably led to correlation problems, and the Fe-N, C-N, and C-C bond lengths had to be constrained to prevent distortions of the complex cations.

### Results and Discussion

**A. Description of the Structures.** (i)  $[\text{Fe}([9]\text{aneN}_3)_2]\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ . The complex cation is seen in Figure 2, showing the numbering scheme. It has the same conformation as has been found<sup>11</sup> for the analogous complex of Ni(II). What is of particular interest is the hydrogen-bonding arrangement in the crystal lattice. The structure consists essentially of alternating layers, as seen in Figure 3, where two unit cells are shown. In one layer, as seen in Figure 4, we have the complex cations, each accompanied by two chloride ions, all on special positions. The arrangement is such that each chloride ion is held by three hydrogen bonds to a complex cation, with an average N-Cl length of 3.18  $\text{\AA}$ , which appears<sup>12</sup> normal for a N-H $\cdots$ Cl hydrogen bond. Each of the complex cations in this layer has its N-H groups hydrogen bonded to the six chloride ions surrounding it. In the other layer (Figure 5) we have the remaining chloride ion and five water molecules. Here the chloride ion is surrounded by a ring of twelve water molecules, of which

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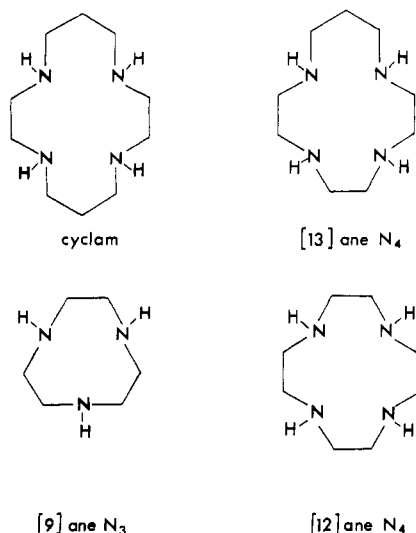
\* University of the Witwatersrand.

† Ruhr Universität.

**Table I.** In-Plane Ligand Field Strengths ( $Dq_{xy}$ ) for Complexes of Tetraaza Macrocycles

complex	best-fit M-N length in ligand <sup>b</sup>	$Dq_{xy}$ <sup>a</sup>			
		M = Fe(II), X = CN <sup>-c</sup>	M = Co(III), X = Cl <sup>-d</sup>	M = Ni(II), X = Cl <sup>-e</sup>	M = Cr(III), X = Cl <sup>-f</sup>
[M([13]aneN <sub>4</sub> )X <sub>2</sub> ]	1.92	2208	2750		
[M([14]aneN <sub>4</sub> )X <sub>2</sub> ]	2.05	2029	2562	1460	2450
[M([15]aneN <sub>4</sub> )X <sub>2</sub> ]	2.22	1842	2362	1240	2123
[M([16]aneN <sub>4</sub> )X <sub>2</sub> ]	2.38		2295	1100	
strain-free M-N length for metal <sup>g</sup>		1.96	1.925	2.10	2.05

<sup>a</sup>Units are cm<sup>-1</sup>. Italicized values are for the macrocycle into which the metal ion fits best. <sup>b</sup>From reference 7. Units are Å. <sup>c</sup>Reference 6. It has been found<sup>7</sup> that the nature of X has little effect on  $Dq_{xy}$ , so that X being CN<sup>-</sup> here should not affect the comparison. <sup>d</sup>Reference 7. <sup>e</sup>Reference 1. <sup>f</sup>Reference 23. <sup>g</sup>References 8 and 9. Fe(II), this work. Units are Å.

**Figure 1.** Ligands discussed in this paper.

three appear to be hydrogen bonded to it, with O-Cl distances of 2.91 Å. This appears to be rather short in comparison with other O-H-Cl hydrogen bond O-Cl distances, which are<sup>12</sup> in the region of 3.1 Å. There are three different environments for the water molecules in this layer. In one, the water molecule is in a general position, hydrogen bonded to the chloride ion (O-Cl = 2.91 Å) and two other water molecules at O-O distances of 2.92 and 2.73 Å. These latter two water molecules are on special positions, one being surrounded by three other water molecules at O-O distances of 2.73 Å, with O-O-O angles of 100.8°. The other water molecule is held by long O-O bonds of 2.92 Å, and by comparison with the previous type, is rather flattened, with O-O-O angle of 114.6°. We believe that the hydrogen-bonding

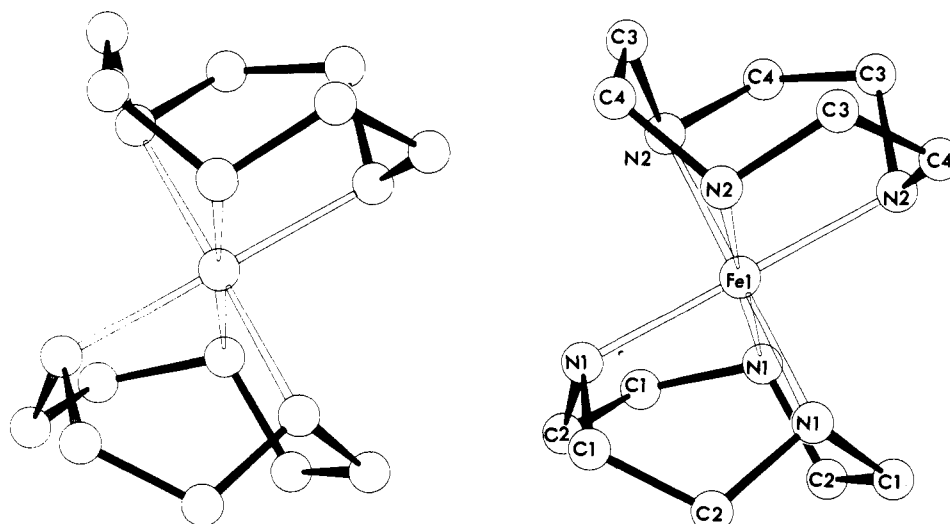
**Table II.** Crystal Data for [Fe([9]aneN<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub>·5H<sub>2</sub>O and [Fe([9]aneN<sub>3</sub>)<sub>2</sub>]Cl<sub>2</sub>·4H<sub>2</sub>O

formula	C <sub>12</sub> H <sub>40</sub> FeCl <sub>3</sub> N <sub>6</sub> O <sub>5</sub>	C <sub>12</sub> H <sub>38</sub> FeCl <sub>2</sub> N <sub>6</sub> O <sub>4</sub>
space group	P3	Pbcn
cell dimens		
<i>a</i> , Å	8.069 (8)	10.342 (9)
<i>b</i> , Å		13.571 (7)
<i>c</i> , Å	31.322 (9)	15.088 (9)
<i>V</i> , Å <sup>3</sup>	1766.12	2117.62
<i>Z</i>	3	4
radiation, Å	0.7107 (Mo Kα)	0.7107 (Mo Kα)
data collec	ω/2θ	ω/2θ
scan speed, deg·s <sup>-1</sup>	0.012	0.012
scan width	0.3	0.3
no. of unique data	975	1417
no. of data used	815	1257
final conventional <i>R</i> factor	0.0824	0.0967
<i>F</i> cutoff	<i>F</i> > σ( <i>F</i> )	<i>F</i> > σ( <i>F</i> )

arrangement around the chloride found here is novel and that this structure is of interest in relation to possible modes of solvation of the chloride ion in water.

(ii) [Fe([9]aneN<sub>3</sub>)<sub>2</sub>]Cl<sub>2</sub>·4H<sub>2</sub>O. The complex cation is seen in Figure 6, showing the numbering scheme. A stereoview of the crystal packing is seen in Figure 7, which shows that there are no alternating layers, as was found for the Fe(III) complex. Instead, we have pairs of water molecules with O-O distances of 2.74 Å. Each complex cation is hydrogen bonded to these water molecules, as well as chloride ions. The chloride ion is held by a hydrogen bond to the complex cation and also to the pairs of water molecules.

**B. Comparison with Other Structures.** What is of interest here is that the Fe(II)-N bond with a mean length of 2.03 (1) Å appears to be somewhat longer than the Fe(III)-N bond at 1.99 (1) Å. This is in contrast to the hexacyano complexes, where the Fe(III) Fe-C bond at 1.92 (1) Å is slightly longer than that for

**Figure 2.** Stereoview (ORTEP<sup>24</sup>) of the [Fe([9]aneN<sub>3</sub>)<sub>2</sub>]<sup>3+</sup> cation, showing the numbering scheme.

**Table III.** Fractional Atomic Coordinates and Thermal Parameters for  $[\text{Fe}(\text{[9]aneN}_3)_2]\text{Cl}_3 \cdot 5\text{H}_2\text{O}^a$ 

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> , Å <sup>2</sup>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>
Fe1	0.0000	0.0000	0.0000		0.030 (7)	0.046 (6)	0.015 (3)
N1	0.112 (3)	0.115 (3)	-0.0394 (4)	0.037 (5)			
N2	0.116 (3)	-0.110 (3)	0.0394 (6)	0.049 (6)			
C1	-0.285 (4)	-0.052 (4)	-0.0602 (8)	0.046 (7)			
C2	0.038 (3)	0.236 (3)	-0.0729 (7)	0.039 (5)			
C3	0.234 (4)	0.035 (4)	0.0738 (8)	0.051 (8)			
C4	-0.053 (4)	-0.284 (4)	0.0601 (9)	0.048 (7)			
Fe2	0.6667	0.3333	0.3342 (3)		0.013 (3)	0.023 (7)	0.006 (1)
N3	0.554 (3)	0.112 (2)	0.2947 (6)	0.025 (5)			
N4	0.775 (2)	0.553 (3)	0.3747 (6)	0.027 (5)			
C5	0.717 (3)	0.101 (4)	0.2741 (8)	0.042 (6)			
C6	0.428 (4)	0.131 (4)	0.2622 (8)	0.037 (6)			
C7	0.630 (3)	0.537 (4)	0.4070 (8)	0.038 (6)			
C8	0.954 (3)	0.568 (3)	0.3930 (9)	0.033 (5)			
Fe3	0.3333	0.6667	0.6673 (4)		0.044 (5)	0.003 (3)	0.022 (2)
N5	0.552 (2)	0.775 (2)	0.6263 (5)	0.024 (4)			
N6	0.439 (2)	0.884 (3)	0.7081 (7)	0.038 (7)			
C9	0.567 (4)	0.951 (3)	0.6071 (8)	0.042 (6)			
C10	0.532 (4)	0.630 (6)	0.5947 (9)	0.044 (7)			
C11	0.297 (4)	0.867 (5)	0.7407 (8)	0.048 (7)			
C12	0.620 (4)	0.902 (4)	0.7247 (9)	0.046 (7)			
Cl1	0.3333	0.6667	0.0198 (5)		0.036 (5)	0.081 (9)	0.017 (2)
Cl2	0.6667	0.3333	0.9811 (7)		0.042 (6)	0.11 (1)	0.021 (3)
Cl3	0.6667	0.3333	0.6867 (5)		0.033 (5)	0.077 (9)	0.016 (3)
Cl4	0.3333	0.6667	0.3157 (5)		0.032 (5)	0.048 (8)	0.016 (2)
Cl5	0.0000	0.0000	0.3535 (5)		0.025 (4)	0.072 (9)	0.012 (2)
Cl6	0.0000	0.0000	0.6477 (5)		0.041 (5)	0.06 (1)	0.021 (3)
Cl7	0.6667	0.3333	0.5231 (9)		0.14 (1)	0.08 (1)	0.061 (5)
Cl8	0.3333	0.6667	0.8542 (9)		0.14 (1)	0.13 (2)	0.072 (7)
Cl9	0.0000	0.0000	0.1921 (7)		0.11 (1)	0.12 (2)	0.056 (5)
O1	0.6667	0.3333	0.872 (2)		0.12 (3)	0.16 (4)	0.06 (1)
O2	0.0000	0.0000	0.541 (1)		0.11 (2)	0.06 (2)	0.05 (1)
O3	0.3333	0.6667	0.206 (1)		0.1 (2)	0.06 (2)	0.05 (1)
O4	0.632 (4)	0.963 (5)	0.167 (1)	0.108 (9)			
O5	0.007 (5)	0.701 (4)	0.5003 (9)	0.097 (8)			
O6	0.571 (5)	0.340 (6)	0.833 (1)	0.111 (9)			
O7	0.6 (3)	0.4 (3)	0.14 (2)	0.03 (2)			
O8	0.23 (5)	0.59 (5)	0.482 (2)	0.12 (4)			
O9	0.0000	0.0000	0.812 (1)	0.05 (1)			

<sup>a</sup> Coordinates for non-hydrogen atoms only. Estimated standard deviations are given in parentheses.**Table IV.** Important Bond Lengths and Angles in  $[\text{Fe}(\text{[9]aneN}_3)_2]\text{Cl}_3 \cdot 5\text{H}_2\text{O}^a$ 

	cation 1	cation 2	cation 3
Lengths <sup>b</sup>			
Fe-N1	2.01 (2)	1.98 (2)	2.00 (1)
Fe-N2	2.00 (2)	1.99 (2)	1.99 (2)
N1-C1	1.52 (2)	1.50 (2)	1.48 (2)
N1-C2	1.53 (2)	1.50 (2)	1.48 (2)
N2-C3	1.53 (2)	1.50 (2)	1.48 (2)
N2-C4	1.52 (2)	1.50 (2)	1.48 (2)
C1-C2	1.48 (2)	1.49 (2)	1.49 (2)
C3-C4	1.49 (2)	1.51 (2)	1.51 (2)
Angles <sup>c</sup>			
N1-Fe-N1	86.2 (9)	85 (1)	83.1 (9)
N1-Fe-N2	178.9 (9)	178.8 (9)	180 (1)
N2-Fe-N2	86 (1)	84 (1)	83 (1)
C1-N1-Fe	106 (2)	108 (2)	108 (2)
C2-N1-Fe	109 (2)	108 (2)	108 (2)
C1-N1-C2	111 (2)	112 (2)	114 (2)
C3-N2-Fe	110 (2)	112 (2)	113 (2)
C4-N2-Fe	106 (2)	107 (1)	106 (2)
C3-N2-C4	110 (2)	115 (2)	116 (2)

<sup>a</sup> Estimated standard deviations in parentheses. <sup>b</sup> Lengths in Å. <sup>c</sup> Angles in deg.

Fe(II) at 1.90 (1) Å.<sup>13,14</sup> For the tris(1,10-phenanthroline) complexes for both Fe(II) and Fe(III), the Fe-N bond lengths are the same at 1.97 Å.<sup>15</sup> The longer Fe-N bond for Fe(II) here

**Table V.** Fractional Atomic Coordinates for  $[\text{Fe}(\text{[9]aneN}_3)_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}^a$ 

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Fe	0.0000	0.1913 (1)	0.2500
Cl1	0.8131 (3)	0.8866 (2)	0.1214 (2)
N1	0.4897 (8)	0.7905 (6)	0.3516 (5)
N2	0.6924 (8)	0.6922 (6)	0.2782 (6)
N3	0.4903 (9)	0.5909 (6)	0.3489 (6)
C1	0.469 (1)	0.742 (1)	0.438 (1)
C2	0.419 (1)	0.638 (1)	0.423 (1)
C3	0.6251 (8)	0.5597 (8)	0.3785 (9)
C4	0.724 (1)	0.592 (1)	0.310 (1)
C5	0.615 (1)	0.847 (1)	0.350 (1)
C6	0.724 (1)	0.592 (1)	0.310 (1)
O1	1.051 (1)	0.686 (1)	0.334 (1)
O2	1.090 (1)	0.527 (1)	0.442 (1)

<sup>a</sup> All atoms refined anisotropically. Thermal vibration parameters are available as supplementary material, as well as the coordinates and anisotropic thermal parameters for the hydrogen atoms. Estimated standard deviations are given in parentheses.

may reflect the effect of saturated nitrogen donors in the [9]aneN<sub>3</sub> ring, as opposed to the effect of unsaturated systems in cyanide and 1,10-phenanthroline ligands. This effect may also be reflected in the unusually low positive value of the Fe<sup>2+</sup>/Fe<sup>3+</sup> couple<sup>3</sup> for the ([9]aneN<sub>3</sub>)<sub>2</sub> system.

If we examine other d<sup>6</sup> systems, we find that the Co-N bond length in its bis complex with Me[9]aneN<sub>3</sub><sup>16</sup> (2-methyl-1,4,7-triazacyclononane) is 1.97 Å, so that the Co-N bond lengths are

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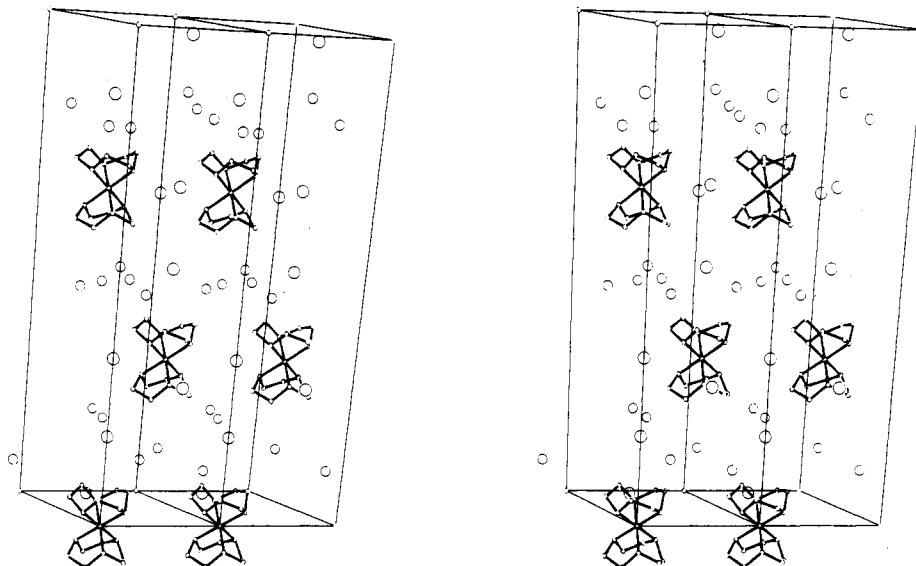


Figure 3. Stereoview (ORTEP<sup>24</sup>) of two unit cells of  $[\text{Fe}([9]\text{aneN}_3)_2]\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ . The complex cations are the molecule ions with filled bonds, as seen in Figure 2. The larger open circles are chloride ions, while the smaller open circles are the oxygens of water molecules.

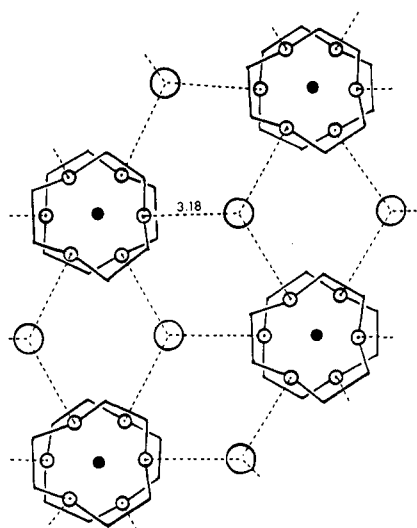


Figure 4. View down the 3-fold axis of the layer in the  $[\text{Fe}([9]\text{aneN}_3)_2]\text{Cl}_3 \cdot 5\text{H}_2\text{O}$  structure, which contains the complex cations. Each chloride ion (large open circles) is surrounded by three complex cations, to which it is held by a hydrogen bond to the nitrogen (small open circles) of each complex cation. Six chlorides surround each complex cation, which is represented by a filled circle (the iron atom), with the carbon atoms represented as bends in the lines joining the nitrogen atoms together.

Table VI. Important Bond Lengths and Angles in  $[\text{Fe}([9]\text{aneN}_3)_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}^a$

Lengths			
Fe-N1	2.04 (1)	N2-C6	1.49 (1)
Fe-N2	2.03 (1)	N3-C2	1.49 (1)
Fe-N3	2.02 (1)	N3-C3	1.52 (1)
N1-C1	1.48 (1)	C1-C2	1.51 (2)
N1-C5	1.50 (1)	C3-C4	1.52 (2)
N2-C4	1.48 (1)	C5-C6	1.53 (2)
Angles			
N1-Fe-N2	84.0 (9)	N1-C1-C2	109.5 (9)
N2-Fe-N3	84.9 (9)	C1-C2-N3	110.0 (9)
N3-Fe-N1	83.7 (8)	N3-C3-C4	109.7 (9)
C1-N1-C5	111.6 (9)	N2-C4-C3	109.4 (9)
C4-N2-C6	113.7 (8)	N2-C6-C5	111.3 (9)
C2-N3-C3	110.7 (9)	N1-C5-C6	107.2 (8)

<sup>a</sup> Bond lengths in Å and angles in deg. Estimated standard deviations are given in parentheses.

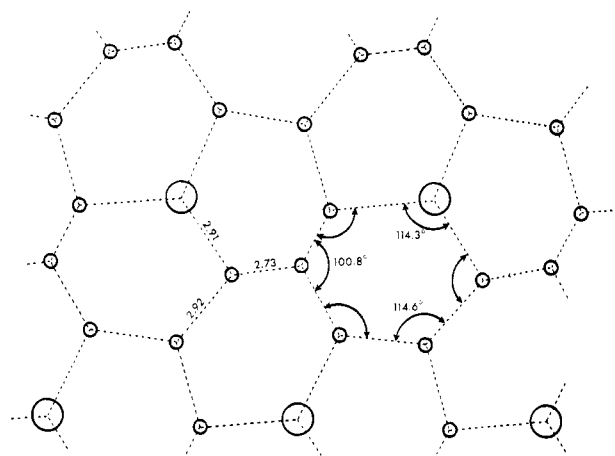


Figure 5. The water layer in  $[\text{Fe}([9]\text{aneN}_3)_2]\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ . The large open circles are chloride ions, which are surrounded by a ring of 12 water molecules (small open circles are the oxygen atoms thereof). The chlorides are hydrogen bonded to three of these. Hydrogen-bonded lengths are indicated in Å.

somewhat shorter than Fe-N for Fe(II) and Fe(III). Again, the Co-C bond length in the  $[\text{Co}(\text{CN})_6]^{3-}$  ion is<sup>17</sup> 1.89 Å, slightly shorter than that for the Fe(II) and Fe(III) analogues. We have shown<sup>18</sup> that the strain-free Co-N bond length, i.e. the Co-N length that would be realized in the absence of any steric strain, is 1.925 Å. This result is based on molecular mechanics (MM) calculations, which show that van der Waals repulsions between, for example, the hydrogen atoms on the 9[aneN<sub>3</sub>] rings in  $[\text{Co}([9]\text{aneN}_3)_2]^{3+}$  are responsible for stretching the Co-N bond out from 1.925 to 1.97 Å. This is somewhat like the familiar idea of radius ratios in ionic solids, where anions ("ligands") above a certain size are unable to approach a small metal ion sufficiently closely. In the same way as is seen for Co(III), the observed Fe-N bonds in the  $([9]\text{aneN}_3)_2$  complexes of Fe(II) and Fe(III) will be much longer than the strain-free Fe-N lengths. By the use of similar calculations, the strain-free Fe-N lengths would be expected to be 1.94 Å for Fe(III) and 1.96 Å for Fe(II).

We thus see that the low-spin Fe(II) and Fe(III) ions are very small. Very few other metal ions fall into this category at all, i.e. where the observed bond lengths are almost invariably longer

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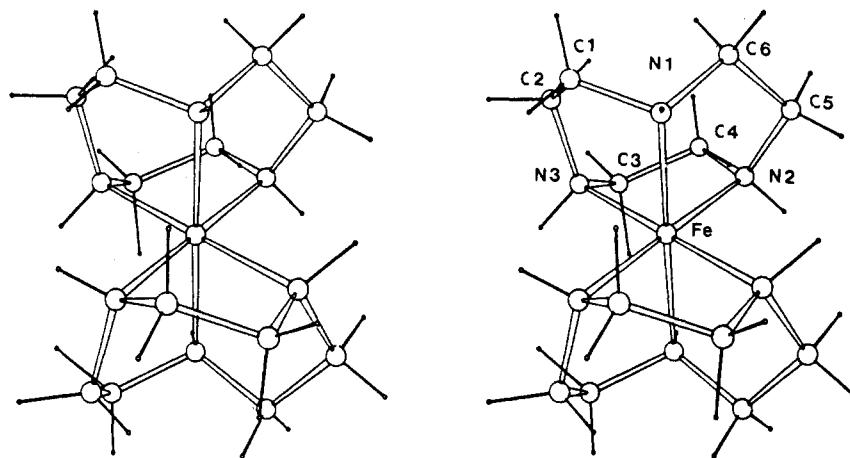


Figure 6. ORTEP<sup>24</sup> stereoview of the  $[\text{Fe}([9]\text{aneN}_3)_2]^{2+}$  cation, showing the numbering scheme.

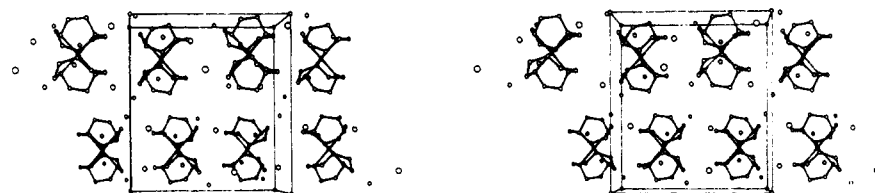


Figure 7. Stereoview (ORTEP<sup>24</sup>) of the unit cell of  $[\text{Fe}([9]\text{aneN}_3)_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ .

than the strain-free lengths. Other examples of such metal ions are low-spin Ni(III) ( $\text{Ni}-\text{N} = 1.93 \text{ \AA}$ ),<sup>19</sup> low-spin Ni(II) ( $\text{Ni}-\text{N} = 1.89 \text{ \AA}$ ),<sup>20</sup> Ni(IV), and Co(III) itself. This small size has rather special consequences for the structural chemistry of the metal ion. Very few ligands can approach the metal ion sufficiently closely for the strain-free bond length to be realized. An important example where this should be realizable is in tetraaza macrocycles, specifically  $[13]\text{aneN}_4$  (1,4,7,11-tetraazacyclotridecane), which has a cavity such that metal ions with a  $\text{M}-\text{N}$  bond length of  $1.92 \text{ \AA}$  fit best.<sup>21</sup> We find, in accord with this, that maximum in-plane ligand field strengths are realized with the *trans*- $[\text{M}([13]\text{aneN}_4)\text{X}_2]^{n+}$  complexes, where X may be  $\text{Cl}^-$ ,  $\text{CN}^-$ ,  $\text{SCN}^-$ , and so on. This is seen in the selected examples in Table I. For larger metal ions such as high-spin Ni(II) or Cr(III), the maximum in-plane ligand field strength is realized in the  $[14]\text{aneN}_4$  complex. The small size of low-spin Fe(II) means that the maximum in-plane LF strength occurs in the  $[13]\text{aneN}_4$  complex (Table I), which one would also predict to be the case for low-spin Fe(III).

Trigonal twist distortion ( $\phi$ ) is the amount by which the nitrogens in the upper  $[9]\text{aneN}_3$  ligand are twisted in projection relative to those in the lower ligand, away from the value expected in a regular octahedron. For a regular octahedron,  $\phi$  will have a value of  $0^\circ$ , while in the extreme case, where a trigonal-prismatic coordination geometry is found,  $\phi$  will be  $60^\circ$ . In  $[\text{Ni}([9]\text{aneN}_3)_2]^{2+}$  the value of  $\phi$  is  $3.4^\circ$ ,<sup>11</sup> while here it has a value of  $1.0^\circ$  (Fe(II)) and  $2.0^\circ$  (Fe(III)). The polar angle,  $\omega$ , is the angle between the  $\text{M}-\text{N}$  bond and the 3-fold axis passing through the metal ion, which in a regular octahedron has a value of  $54.8^\circ$ . In Ni(II),  $\omega$  has a value of  $49.6^\circ$ , while in Fe(II) and Fe(III) it has values of  $50.5^\circ$  and  $52.3^\circ$ , respectively. These small distortions away from the values expected for a regular octahedron hardly seem sufficient to account for the shifting of the bands in the spectrum of  $[\text{Ni}([9]\text{aneN}_3)_2]^{2+}$ , if we consider that in  $[\text{Ni}(\text{en})_3]^{2+}$ , which has a normal LF strength for saturated nitrogen donors,  $\phi$  has a value<sup>22</sup> of  $9.8^\circ$  and  $\omega$  a value of  $52.4^\circ$ .

Table VII. Bands in the  $850\text{--}200\text{-cm}^{-1}$  Region of Infrared Spectra of  $([9]\text{aneN}_3)_2$  Complexes<sup>a</sup>

	N(II)	Cu(II)	Zn(II)	Fe(II)	Fe(III)	Cr(III)	Co(III)
	817	805	802	841	829	817	831
	794	763	780	820	809	796	808
	576	560	560	625	613	594	615
	565	535		595	578	573	585
		495					
	475	455	470	525	533	506	532
$\nu_{\text{M}-\text{N}}^b$	406	403	390	483	477	456	479
		390					
				415			412

<sup>a</sup> Units are  $\text{cm}^{-1}$ . Spectra recorded as KBr pellets. Ni(II), Cu(II), and Zn(II) were the nitrate salts, otherwise spectra are of the chloride salts. <sup>b</sup> Tentative assignment only, based on comparison with hexammine assignments in ref 21.

We have suggested<sup>6</sup> that the high LF strength observed in  $[\text{Ni}([9]\text{aneN}_3)_2]^{2+}$  is real and is due to the greater donor power of the secondary nitrogen donor atoms, here in a situation of low steric strain. In accord with this, it is found that the Fe(II) and Fe(III)  $([9]\text{aneN}_3)_2$  complexes are low spin.<sup>3</sup> The infrared spectra indicate exactly the same kind of increase in  $\text{M}-\text{N}$  bond strength as is found<sup>21</sup> in the  $(\text{bpy})_3$  complexes. We have not assigned the bands in the  $\text{M}-\text{N}$  region of the infrared spectra of the  $[\text{M}([9]\text{aneN}_3)_2]^{2+}$  complexes, but this is not important for our discussion here. We see in Table VII that all the bands below  $800 \text{ cm}^{-1}$  in the IR spectrum move in parallel as the metal ion is changed and that the bands for the Fe(II) and Fe(III) complexes indicate  $\text{M}-\text{N}$  bonding of the same strength as found in the Co(III) complex, higher than that in the Cr(III) complex, and very much higher than that in the Cu(II) and Ni(II) complexes. For high-spin Fe(II), the  $\text{M}-\text{N}$  stretching frequencies, e.g. in the hexammine complexes,<sup>21</sup> are lower than those for other first-row divalent metal ions such as Co(II), Ni(II), or Zn(II). It is only on spin pairing, as is found in the tris(bipyridyl) complexes,<sup>21</sup> that the Fe-N stretching frequencies increase so as to be close to those in Co(III). What is perhaps a little surprising is that the position of the bands for Fe(II) suggests a higher bond strength than that in Co(III). The order of bond strengths is otherwise in good

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agreement with the results of crystallographic studies,<sup>11,16</sup> the infrared bands indicating the order Fe(II) > Co(III) > Fe(III) > Cr(III) >> Ni(II) > Cu(II) > Zn(II).

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**Registry No.** I, 97134-61-7; II, 97134-62-8; [Ni([9]aneN<sub>3</sub>)<sub>2</sub>], 59034-12-7; [Cu([9]aneN<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>, 59034-09-2; [Zn([9]aneN<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>, 97102-39-1; [Cr([9]aneN<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub>, 97134-63-9; [Co([9]aneN<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub>, 75592-25-5.

**Supplementary Material Available:** Listings of observed and calculated structure factors, temperature factors, and coordinates for hydrogen atoms (12 pages). Ordering information is given on any current masthead page.

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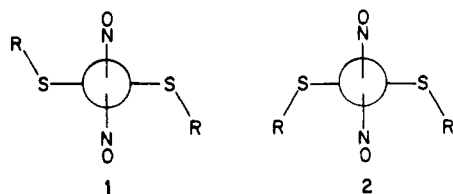
## Nitrogen-15 and Carbon-13 NMR Study of Roussin Salts and Esters and of Pentacyanoferrate Complexes

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High-frequency <sup>15</sup>N NMR spectroscopy, using 99% isotopic enrichment for <sup>15</sup>N, shows that the Roussin esters Fe<sub>2</sub>(SR)<sub>2</sub>(NO)<sub>4</sub> (R = Me, *i*-Pr) exist as an equimolar mixture of two conformers having C<sub>2v</sub> and C<sub>2h</sub> symmetries respectively. Similar <sup>15</sup>N spectroscopy of [Fe<sub>4</sub>X<sub>3</sub>(NO)<sub>7</sub>]<sup>-</sup> (X = S, Se) shows that the solid-state structure for X = S persists in aqueous solution and demonstrates that the anion having X = Se is isostructural in solution; this is confirmed by natural-abundance <sup>77</sup>Se NMR. The cubane type Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>4</sub> retains its structure in solution, and Fe<sub>4</sub>Se<sub>4</sub>(NO)<sub>4</sub> is isostructural. A combination of <sup>13</sup>C and <sup>15</sup>N NMR spectra obtained at high frequency with 90% <sup>13</sup>C and 99% <sup>15</sup>N enrichment reveals two mechanisms for the conversion of [Fe(CN)<sub>5</sub>NO]<sup>2-</sup> to [Fe(CN)<sub>5</sub>NO<sub>2</sub>]<sup>4-</sup>, one involving nucleophilic attack by hydroxide and the other attack by nitrite. The spectral data allow ready identification of pentacyanoferrate complexes arising from the reactions of nitroprusside with nucleophiles.

The X-ray structural analysis of the ethyl ester of Roussin's red salt, Fe<sub>2</sub>(SEt)<sub>2</sub>(NO)<sub>4</sub>, showed<sup>1</sup> the molecule to be centrosymmetric, of approximately C<sub>2h</sub> (2/m) molecular symmetry. In contrast to this solid-state structure, a series of esters Fe<sub>2</sub>(SR)<sub>2</sub>(NO)<sub>4</sub> (R = Me, Et, *n*-Pr, *i*-Pr, CH<sub>2</sub>Ph,<sup>2</sup> and Ph<sup>3</sup>) have been shown by <sup>1</sup>H NMR to exist in solution as an equimolar mixture of two components that were presumed to be conformers of C<sub>2h</sub> and C<sub>2v</sub> symmetry, 1 and 2, respectively. Although activation



barriers for the equilibration of the two forms were measured<sup>2</sup> for R = Me, Et, *n*-Pr, *i*-Pr, and CH<sub>2</sub>Ph, the structures of these two forms in solution have not been rigorously established.

Roussin's black anion, [Fe<sub>4</sub>S<sub>3</sub>(NO)<sub>7</sub>]<sup>-</sup>, has been shown to have C<sub>3v</sub> symmetry in the solid state<sup>4,5</sup> and to react with elemental sulfur<sup>2</sup> to yield the cubane-like complex<sup>6</sup> Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>4</sub>. The selenium analogue [Fe<sub>4</sub>Se<sub>3</sub>(NO)<sub>7</sub>]<sup>-</sup> has been prepared<sup>2</sup> and characterized by analysis as its tetraphenylarsonium salt. This anion reacted with elemental selenium<sup>7</sup> to yield a complex whose infrared spectrum was very similar to that of Fe<sub>4</sub>S<sub>4</sub>(NO)<sub>4</sub>, and the constitution Fe<sub>4</sub>Se<sub>4</sub>(NO)<sub>4</sub> was tentatively assigned. The structures

of both [Fe<sub>4</sub>Se<sub>3</sub>(NO)<sub>7</sub>]<sup>-</sup> and Fe<sub>4</sub>Se<sub>4</sub>(NO)<sub>4</sub> in solution have not been established directly, but assumed by comparison with their sulfur analogues.

In this paper we present <sup>15</sup>N NMR evidence which both establishes the identities of the two forms of Fe<sub>2</sub>(SR)<sub>2</sub>(NO)<sub>4</sub> in solution and provides definite proof of structure for both [Fe<sub>4</sub>Se<sub>3</sub>(NO)<sub>7</sub>]<sup>-</sup> and Fe<sub>4</sub>Se<sub>4</sub>(NO)<sub>4</sub> in solution.

The nitroprusside ion, [Fe(CN)<sub>5</sub>NO]<sup>2-</sup>, although stoichiometrically and structurally quite different from Roussin's salts and esters, is in fact readily interconvertible<sup>8,9</sup> with the black Roussin anion, [Fe<sub>4</sub>S<sub>3</sub>(NO)<sub>7</sub>]<sup>-</sup>. Since we have found<sup>10</sup> that there is very ready isotopic exchange of nitrosyl groups with labeled nitrite in the paramagnetic mononuclear complexes of types [Fe(NO)<sub>2</sub>(SR)<sub>2</sub>]<sup>-</sup> and Fe(NO)(S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub>, which are readily formed from Fe<sub>2</sub>(SR)<sub>2</sub>(NO)<sub>4</sub> and [Fe<sub>4</sub>S<sub>3</sub>(NO)<sub>7</sub>]<sup>-</sup>, it was of interest to determine whether the mononuclear nitroprusside ion would also react with isotopically labeled nitrite: we report here <sup>13</sup>C and <sup>15</sup>N NMR evidence that exchange is rapid and complete in the presence of excess [<sup>15</sup>NO<sub>2</sub>]<sup>-</sup>.

Nitrogen-15 NMR studies of metal nitrosyls have been few in number,<sup>11-14</sup> but the <sup>15</sup>N chemical shift has been established<sup>12-14</sup> as a simple criterion of structure, readily distinguishing between linear and bent M-N-O fragments. Earlier <sup>14</sup>N studies have been summarized in a comprehensive review of <sup>14</sup>N and <sup>15</sup>N NMR spectroscopy.<sup>15</sup>

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