Spectroscopic Evidence of Metal–Metal Interaction in Tetrakis(dithio-phenylacetato)dinickel(II)

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The crystal polarised spectrum of the title compound has been recorded. The spectrum contains more bands than those predicted for a mononuclear diamagnetic square planar Ni^{II} complex, a series of five bands with different polarisation characteristics being observed between 13 and 18 kK (1 kK = 1000 cm^{-1}). It is suggested that the spectra are indicative of substantial overlap of the d orbitals between the two nickel(II) atoms in the molecule, and an assignment of the spectrum in D_4 symmetry (for the dimeric $[Ni_2S_8]$ chromophore) put forward.

FEW dinuclear complexes having relatively short metal–metal distances are known, and most spectroscopic work so far has centred on copper(II) acetate monohydrate. The antiferromagnetism and e.s.r. spectra of copper(II) acetate monohydrate and related complexes [1] have been

interpreted in terms of both direct metal–metal bonding [2] and superexchange coupling *via* the carboxylate ligands.[3] Simple molecular orbital considerations suggested that interaction between the two halves of the molecule should give rise to ' doubling ' of the d orbitals of each

[1] M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, 1964, **64**, 99.

[2] B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 1956, 3837; R. W. Jotham and S. F. A. Kettle, *Chem. Comm.*, 1969, 258.

[3] D. M. L. Goodgame, N. J. Hill, D. F. Marsham, A. C. Skapski, M. L. Smart, and P. G. H. Troughton, *Chem. Comm.*, 1969, 629; G. F. Kokoszka, M. Linzer, and G. Gordon, *Inorg. Chem.*, 1968, **7**, 1730.

single metal ion [4] and this bonding model has recently been refined.[5]

Despite this interest, the electronic spectrum of copper(II) acetate monohydrate, both in solution and as a single crystal at low temperature, shows no features beyond those expected for a $C_{4v}[CuO_4 + O]$ chromophore.[6] The most recent assignment of the contentious band at 26 kK ascribed it to an $O(2p) \longrightarrow (d_{x^2-y^2})$ charge-transfer transition.[7] There is thus no convincing experimental evidence in the literature for the existence of δ-bonding (i.e., overlap between the $d_{x^2-y^2}$, and also the d_{xy}, orbitals of two metal ions in a dinuclear complex).

Recently the crystal structures of several Ni^{II} complexes in which sulphur-containing ligands bridge two
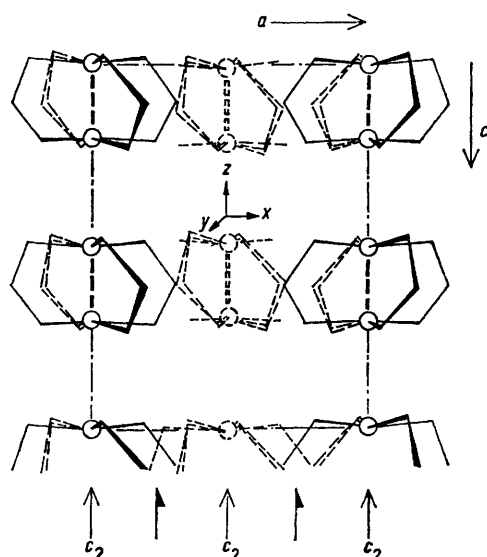

FIGURE 1   (010) projection of the molecules showing mutual alignment of Ni–Ni bonds; ○ = Ni

Ni^{II} ions to give dinuclear complexes have been solved. The crystal spectra of one of these, tetrakis(dithiophenylacetato)dinickel(II), $(C_6H_5CH_2CS_2)_4Ni_2$, [Ni$_2$(dtpa)$_4$], has been investigated to see whether there is evidence for the presence of δ-bonding. Since the structure determination showed that a short Ni–Ni bond is present and that there is an ' inward ' distortion of each NiS$_4$ half of the molecule,[8] this is already suggestive of metal–metal bonding.

EXPERIMENTAL

Crystal Structure.—Ni$_2$(dtpa)$_4$ was prepared as in the literature,[9] and thin red-brown flakes were obtained from carbon disulphide solution. Crystals grow as flat plates

developed on (010) and elongated along c; they were so thin that reliable spectra parallel to b could not be obtained. The compound crystallises in space-group $Iba2$ with $a = 9·32$, $b = 29·42$, $c = 12·097$ Å, $Z = 4$ (dimer);[8] the structure is shown in Figure 1. The ligands bridge two nickel atoms, the nickel–nickel distance being 2·56 Å. The sulphur atoms from each $^-S_2C·CH_2Ph$ unit do not lie directly above one another, the dihedral angle between the two halves of the molecule being large, 26°. The Ni atoms are displaced from the plane of the four S atoms by 0·13 Å, so that each nickel atom can be considered to be formally five-co-ordinate. All the nickel atoms are in equivalent crystallographic sites of C_2 symmetry, but an approximate chromophore symmetry is D_4. The molecule appears to satisfy the conditions for optical activity, there being no centre of symmetry, no plane of symmetry between the two halves of the molecule, and no alternant axis, although both forms exist in the crystal. This is a singular case of a molecule with a C_4 principal axis being, theoretically, optically active. The nickel atoms are all aligned exactly along the c-axis.

Spectra.—Crystal polarised spectra were obtained as described previously,[10] several thicknesses of crystal being investigated so as not to ' lose ' bands, particularly critical in this case. Crystal thicknesses were in the range 2—10 μm, best results being obtained at ca. 2 μm. Estimates of band intensities were obtained by measuring crystal thicknesses by use of the microscope attachment of the spectrophotometer with the crystal viewed ' end on '. Since crystals had to be so thin, the intensity measurements of Table 1 give only orders of magnitude, although they are not too far

TABLE 1

Band energies with intensities (l mol^{-1} cm^{-1}) (estimates only, on dimer basis) in parentheses

| Energy/kK | Intensity | | Assignment |
	z	xy	
13·4	—	(85)	$a^1E \longleftarrow {}^1A_1$
14·3	(80)	—	$a^1A_1 \longleftarrow {}^1A_1$
15·3	—	(85)	$b^1E \longleftarrow {}^1A_1$
16·0	(75)	—	$b^1A_1 \longleftarrow {}^1A_1$
16·9	—	(130)	$c^1E \longleftarrow {}^1A_1$
(17·2)	(200)	?	—
18·95	(740)	(470)	See text
20·0sh	Masked	(340)	
21·2	(1500)	Masked	} c.t. Ni – – – Ni (?)
21·7	(1500)	(300)	}

removed from those in solution [11] (solution values of ε are slightly lower, presumably owing to some decomposition).

RESULTS

Assignment.—The spectra are shown in Figure 2. When $\vec{E}$ is parallel to a (molecular xy) a series of bands at 13·4, 15·3, and 16·9 kK is observed, followed by higher-intensity bands at 19·0, 20·0 (shoulder), and a shoulder at 21·7 kK. Rotation of the plane of polarised light so that $\vec{E}$ is parallel to c (molecular z) causes very clear changes in spectra. Bands appear at 14·3 and 16·0 followed by an indistinct

[4] M. L. Forster and C. J. Ballhausen, Acta Chem. Scand., 1962, 16, 1385.
[5] R. W. Jotham and S. F. A. Kettle, J. Chem. Soc. (A), 1969, 2816, 2821.
[6] L. Dubicki and R. L. Martin, Inorg. Chem., 1966, 5, 2203.
[7] L. Dubicki, Proc. XIIIth I.C.C.C., Kraków, Poland, 1970, 1, 129.

[8] M. Bonamico, G. Dessy, and V. Fares, Chem. Comm., 1969, 1106, and personal communication.
[9] C. Furlani and M. L. Luciani, Inorg. Chem., 1968, 7, 1586.
[10] A. A. G. Tomlinson, J. Chem. Soc. (A), 1971, 1409.
[11] A. Flamini, C. Furlani, O. Piovesana, and A. Sgamellotti, unpublished results.

shoulder at 17·2 kK (this is the only spectral feature which was not completely reproducible, and it may be caused merely by very slight misalignment of the crystals, and may represent some residual intensity from the oppositely polarised band at 16·9 kK). The band at *ca.* 19·0 kK is also
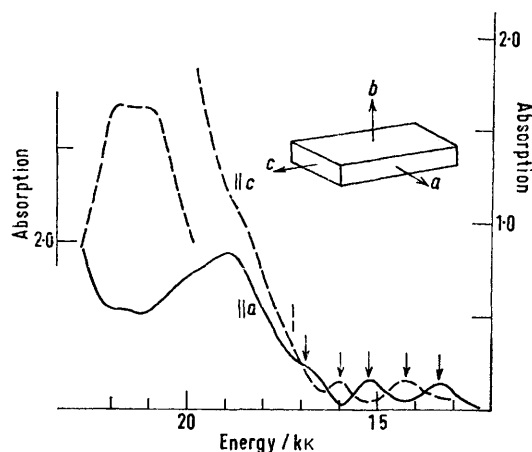

FIGURE 2 Crystal spectrum of face (010) of a crystal *ca.* 2·5 μm thick. The inset shows the crystal morphology

present parallel to *c*, as a distinct shoulder, and is followed by an intense peak at 21·5 kK, split by 0·5 kK. Reflectance spectra and spectra [11] in freshly prepared CS_2 solution gave no indication of any further bands being present below 13 kK. The sum of these bands in non-polarised spectra (single crystal, reflectance, and freshly prepared solution spectra although there may be some dissociation and more complicated species in the last [11]) is merely a slowly falling plateau, so that the bands could not have been identified without polarisation data.

The compound is diamagnetic, but the spectra are obviously not similar to those of quadratic diamagnetic complexes such as dithiocarbamates or phosphorodithioates, which give two, sometimes three, bands in the regions 14—16, 19—20, and 25—27 kK [12] depending on the Ni–S bond length,[13] all being assigned to *d–d* transitions, although two different assignments have been suggested.[13,14] Complexes with conjugating dithio-ligands (such as dithio-benzoato-ion), in those cases where association is not present,[11] show far fewer bands. Although the complex may be considered as five-co-ordinate the spectrum bears no resemblance to those of chromophore [NiS₄L] where L = nitrogen donor.[15] The further possibility, that the bands between 13 and 18 kK are merely due to singlet–triplet transitions of a separate [NiS₄] chromophore, is remote since there are too many, they are all grouped together (against any ligand-field description), and are too intense.

A reasonable interpretation is possible if it is assumed that there is, indeed, some interaction between the two halves of the molecule. From the co-ordinate system of Figure 1 and a molecular symmetry D_4 (due to the dihedral angle between the two halves of the molecule) the electronic states derived from a one-electron molecular orbital sequence usually assumed for a mononuclear [NiS₄] chromophore, such

as Figure 3 (i), are expected to be $\bar{v}_1 \longrightarrow 2A_1 + 2A_2$, $\bar{v}_2 \longrightarrow 4E$, and $\bar{v}_3 \longrightarrow 2B_1 + 2B_2$ for the split *d* orbitals only. The selection rules are then as shown in Table 2, and

TABLE 2

Electronic and vibronic selection rules for transitions in the dimer, in D_4 symmetry

			z	*xy*
$^1A_1$	$\longrightarrow$	$^1A_1$	a_2	e
	$\longrightarrow$	$^1A_2$	a_1 *	e
	$\longrightarrow$	$^1B_1$	b_2	e
	$\longrightarrow$	$^1B_2$	b_1	e
	$\longrightarrow$	^1E	e	* $a_1 + a_2 + b_1 + b_2$

* Signifies electronically allowed transition.

predict the presence of two bands when $\vec{E}$ is parallel to *z* and four when $\vec{E}$ is parallel to *xy*, representing $^1A_2 \longleftarrow {}^1A_1$ and $^1E \longleftarrow {}^1A_1$, respectively. From the spectrum, the bands at 14·3 and 16·0 kK may be assigned to $^1A_2 \longleftarrow {}^1A_1$ transitions while those at 13·4, 15·3, and 16·9 kK are assigned as three of the possible four $^1E \longleftarrow {}^1A_1$ transitions.

The bands at higher energy are not easily ascribed; that at *ca.* 19·0 kK does not appear to be due to a $^1E \longleftarrow {}^1A_1$ transition because it is also present, with roughly the same intensity, parallel to *xy*. It is possible that the band is due to a charge-transfer transition, since several complexes having chromophore [NiS₄] with conjugating ligands also contain a band in this region (at 19—20 kK [11]). However, in this case it might have been expected to be strongly
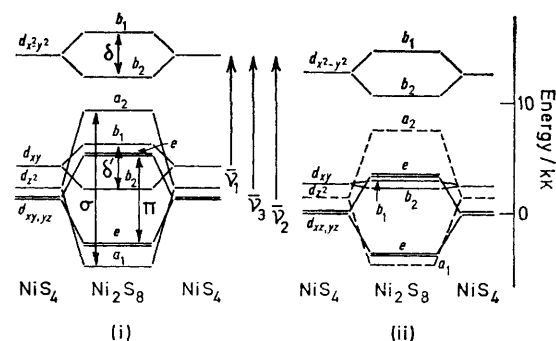

FIGURE 3 (i) A possible energy level sequence (for one-electron orbitals) for D_4 symmetry; symbols refer to splittings caused by Ni–Ni bonding only; (ii) experimental energy sequence obtained after applying interelectron repulsion parameters described in the text. The splitting of the d_{z^2} orbitals is arbitrary (broken lines)

polarised in the ligand plane. The assignment in which there are both a charge-transfer transition and also a further $^1E \longleftarrow {}^1A_1$ transition, polarised in the opposite sense, seems unconvincing. The shoulder at 20 kK is also problematic, and could be the ' missing ' $^1E \longleftarrow {}^1A_1$ transition, but it is impossible to observe its polarisation properties in *z*.

The intense band at 21·5 kK is very strongly polarised, being absent when $\vec{E}$ is parallel to *xy*, and does not also appear to be present in square planar complexes with con-

[12] C. K. Jørgensen, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1571.
[13] A. A. G. Tomlinson and C. Furlani, *Inorg. Chim. Acta*, 1969, **3**, 487.

[14] R. Dingle, *Inorg. Chem.*, 1971, **10**, 1141.
[15] A. A. G. Tomlinson, unpublished results.

jugating ligands [e.g., monomeric bis(dithiobenzoato)nickel-(II) has bands at 23·4, 29·2, and 34·1 kK [11]]. The band has polarisation properties expected for a metal–metal charge-transfer transition.

Application of interelectronic repulsion parameters (1) and (2) [16] with $F_2 = 10F_4 = ca.$ 950 cm^{-1} gives the partial

$$E(d_{xy} \longrightarrow d_{x^2-y^2}) = \bar{\nu}_1 - 4F_2 - 15F_4 \qquad (1)$$

$$E(d_{xz,yz} \longrightarrow d_{x^2-y^2}) = \bar{\nu}_3 - 3F_2 - 20F_4 \qquad (2)$$

one-electron energy level sequence shown in Figure 3 (ii) for [Ni$_2$S$_8$]. The energies of the split d_{z^2} orbitals cannot be found experimentally (transitions derived from $\bar{\nu}_3$ are electronically forbidden).

The alternative description, with splitting of d_{z^2} being so large as to push a_2 (from d_{z^2}) higher in energy than the levels derived from δ-bonding between $d_{x^2-y^2}$ orbitals, gives selection rules which do not fit the spectrum so well. This sequence would, further, give a value for $e_{\sigma(Ni-Ni)}$ of $ca.$ 35 kK, which is rather large.

DISCUSSION

The assignment, depending on the assumptions of some interaction between the two halves of the molecule, a dimer symmetry of D_4 (which is reasonable since projections onto the xy plane of all SNiS angles within each half are exactly 90°) and electronic selection rules, appears to fit the spectrum reasonably well, both so far as concerns polarisations and intensities of bands, between 13 and 18 kK. It is not easy to find an alternative explanation for the many bands in this region.

It is uncommon that the intensities of all the bands between 12·5 and 18 kK are the same. First, it is usual to assume that electronically allowed transitions have associated with them some vibronic character as well, which is allowed from vibrations having different ' enabling ' powers. Secondly, vibrations of symmetry e are not active, otherwise a broad ' plateau ' would have been obtained between 13 and 17 kK in xy polarisation, all transitions, apart from $^1E \longleftarrow {}^1A_1$, being allowed vibronically in xy by these vibrations. Since a similar argument applies to other e and a vibrations the present assignment requires that the bands are almost purely electronically allowed in origin.

Since the interpretation given shows that there is splitting of antibonding and bonding molecular orbitals, the angular overlap model might appear attractive to fit the spectrum. With the axis notation of Figure 1, and allowance for all the displacements from the planes of S atoms, and also the dihedral angles between the two

halves of the molecule, we obtain the bonding parameters (3)—(6) with the notation of Schaeffer and

$$E(d_{z^2}) = 0·96e_\sigma S + 0·08e_\pi S \pm e_{\sigma(Ni-Ni)} \qquad (3)$$

$$E(d_{xz,yz}) = 0·04e_\sigma S + 1·96e_\pi S \pm e_{\pi(Ni-Ni)} \qquad (4)$$

$$E(d_{x^2-y^2}) = 2·95e_\sigma S + 0·03e_\pi S \pm 0·4e_{\delta(Ni-Ni)} \qquad (5)$$

$$E(d_{xy}) = 3·97e_\pi S \pm 0·6e_{\delta(Ni-Ni)} \qquad (6)$$

Jørgensen.[17] The part relative to the unperturbed [NiS$_4$] entity would then give experimental parameters $e_\sigma S = ca.$ 5 kK and $e_\pi S = ca.$ 1·2 kK which compare well with those in the literature.[18] However, this model is a second-order perturbation treatment which depends upon the approximation (7). This is true only if the

$$E_{(mol.\ orbital)} \approx ne_\sigma \approx \frac{H_L^2 S_{ML}^2}{(H_M - H_L)} \approx S_{ML}^2 \qquad (7)$$

diagonal element of one-electron energy, H_L, of the σ orbitals is much more negative than that, H_M, of the l orbitals considered.[17] For the Ni–Ni interaction (treated above as a $D_{\infty h}$ perturbation) this does not hold (in this case, M = Ni$_1$ and L = Ni$_2$), instead we have the approximation (8) where β $\approx S_{Ni-Ni}$. We conclude

$$E_{(mol.\ orbital)} \approx E_{(atomic\ orbitals\ Ni)} \mp \beta \qquad (8)$$

that the angular overlap model is applicable to metal–metal interactions only if e_λ is given the significance of a covalent bonding or antibonding effect independently of second-order perturbation arguments.[18]

It is notable that δ and δ' are very different, while simple m.o. considerations would predict that they be equal.[4,5] This suggests that the radial parts of the d orbital wavefunctions for these two orbitals are no longer identical.

Conclusions.—Present data obviously do not allow a full quantitative description of δ-bonding in this complex, and besides there may be some different explanation of the many bands appearing in the spectrum. However, the assignment suggested accounts reasonably for the spectrum, and we feel the evidence for the presence of δ-bonding to be convincing. From the points discussed above we conclude that only a complete molecular orbital treatment would be capable of interpreting the spectral results fully.

[16] H. B. Gray, ' Transition Metal Chemistry,' Dekker, New York, 1964, vol. 1, p. 243.

[17] C. E. Schaeffer and C. K. Jørgensen, *Mol. Phys.,* 1965, **9**, 401.

[18] H. H. Schmidtke, *Theor. Chim. Acta,* 1971, **20**, 92.