

# Intradimer and Interdimer Exchange Coupling in the Mixed Ligand Complex Bis- $\mu$ -chloro-bis[chloro(4-methylthiazole)dimethylformamidecopper(II)]: a Spin Ladder System

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## Abstract

The structure of the mixed ligand complex bis- $\mu$ -chloro-bis[chloro(4-methylthiazole)dimethylformamidecopper(II)] has been determined from three-dimensional X-ray counter data. The complex  $[\text{Cu}(\text{C}_4\text{H}_5\text{NS})(\text{DMF})\text{Cl}_2]_2$  crystallizes in the monoclinic space group  $P2_1/n$ , with two formula units in a cell of dimensions  $a = 7.349(7)$ ,  $b = 20.306(7)$ ,  $c = 8.909(3)$  Å and  $\beta = 112.53(6)^\circ$ . The final weighted  $R$  factor is 0.032 based on 1646 data. In this first example of a mixed ligand bis- $\mu$ -chloro-copper(II) complex, copper is five-coordinate, with the coordination geometry being distorted from an idealized tetragonal pyramidal. The  $\text{Cu}_2\text{Cl}_2$  bridging unit is constrained to be planar by the presence of a center of symmetry, and the Cu–Cl distances are 2.296(2) and 2.724(1) Å with a Cu–Cl $\cdots$ Cu' angle of 95.29(7) $^\circ$ . Magnetic susceptibility measurements reveal antiferromagnetic exchange coupling, and the best fit of the equation for an exchange coupled pair of  $S = 1/2$  ions yields  $J = -1.7 \text{ cm}^{-1}$  and  $g = 2.105$ . The exchange coupling constant lies in the range of values for a  $\phi/R_0$  value of 35 deg Å $^{-1}$ . The quality of the fit is markedly improved if interdimer exchange interactions are taken into account. The dimers pack in the solid state to form a ladder-like structure with copper(II)–sulfur contacts of 3.906(3) Å. Best fit exchange coupling constants for the spin ladder of  $-1.17$  and  $-1.0 \text{ cm}^{-1}$  were obtained from a calculation on a closed ring of 10 spins with nearest neighbor and next-nearest neighbor interactions.

## Introduction

Exchange coupling interactions can be transmitted over superexchange pathways in which there are some

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rather long internuclear separations, especially if there are heavy atoms such as sulfur in the superexchange pathway. For example, the out-of-plane copper–sulfur contact which forms the  $\text{Cu}_2\text{S}_2$  exchange coupled unit in the dimeric molecule  $[\text{Cu}(\text{H}^+\text{-TCH})\text{Cl}_2]_2$  ( $\text{H}^+\text{-TCH}$  is 1H-thiocarbonohydrazidium) is 3.310 Å [1], and the singlet–triplet splitting of  $24.8 \text{ cm}^{-1}$  is the largest yet reported in antiferromagnetically coupled sulfur-bridged copper(II) systems [2]. Also, the dimeric molecules  $[\text{Cu}(2,5\text{-DTH})\text{Cl}_2]_2$  and  $[\text{Cu}(4,7\text{-DTD})\text{Cl}_2]_2$  (2,4-DTH = dithiahexane, 4,7-DTD = dithiadecane) pack in the solid state with long copper–sulfur contacts ranging between 5 and 6 Å, and each compound exhibits alternating chain magnetism with exchange coupling constants and alternation parameters ( $J$ ,  $\alpha$ ) being ( $-20.6 \text{ cm}^{-1}$ , 0.35) and ( $-10.0 \text{ cm}^{-1}$ , 0.87), respectively [3].

We have found that there is significant interdimer exchange in the compound  $[\text{Cu}(\text{C}_4\text{H}_5\text{NS})(\text{DMF})\text{Cl}_2]_2$ , in which the dimers pack in the solid state to form a ladder-like structure. The structure and magnetic properties of  $[\text{Cu}(\text{C}_4\text{H}_5\text{NS})(\text{DMF})\text{Cl}_2]_2$  are presented in this article.

## Experimental

### Synthesis

The complex was synthesized as described in ref. 4. *Anal.* Calc. for  $\text{Cu}(\text{C}_4\text{H}_5\text{NS})(\text{DMF})\text{Cl}_2$ : C, 27.41; H, 3.94; N, 9.13. Found: C, 27.21; H, 3.75; N, 8.79%.

### Magnetic Measurements

Static magnetization data were collected on a powdered sample by using a Princeton Applied Research Model 155 vibrating sample magnetometer (VSM) equipped with a Janis Research Co. liquid helium dewar. The magnetometer was calibrated with  $\text{HgCo}(\text{NCS})_4$  [5]. The VSM magnet (Magnion H-96),

TABLE I. Positional Parameters for  $[\text{Cu}(4\text{-Metz})(\text{DMF})\text{-Cl}_2]_2$ 

	x	y	z
Cu	-0.00137(8)	0.08980(3)	0.04090(7)
Cl1	0.2275(2)	0.02054(5)	0.0078(1)
Cl2	-0.0710(2)	0.14007(6)	-0.1982(1)
S1	-0.5127(2)	0.18462(7)	0.1115(2)
O	0.1287(4)	0.0809(2)	0.2809(4)
N1	0.2589(6)	0.0232(2)	0.5129(5)
N3	-0.1987(5)	0.1460(2)	0.0868(4)
C2	-0.3792(7)	0.1290(2)	0.0561(6)
C4	-0.1580(7)	0.2076(2)	0.1583(6)
C5	-0.3137(8)	0.2343(3)	0.1791(7)
C6	0.0411(10)	0.2365(4)	0.2018(11)
C7	0.1691(7)	0.0281(3)	0.3556(6)
C8	0.2989(11)	-0.0408(4)	0.5936(9)
C9	0.3208(18)	0.0811(5)	0.6119(9)

power supply (Magnion HSR-1365) and associated field control unit (Magnion FFC-4 with a Rawson-Lush Model 920 MCM rotating coil gaussmeter) were calibrated against NMR resonances ( $^1\text{H}$  and  $^3\text{Li}$ ). A calibrated GaAs diode was used to monitor the sample temperature.

Magnetic susceptibility data were collected in the temperature range 1.8–70 K with a magnetic field of 10 kOe. The data were corrected to compensate for the diamagnetism of the constituent atoms and for the temperature independent paramagnetism of the Cu(II) ions ( $60 \times 10^{-6}$  cgsu) [6, 7].

#### X-ray Data Collection and Reduction

The data were collected at 20 °C and reduced in the manner we have described elsewhere [8]. Initial analysis of a green prismatic crystal suggested the monoclinic crystal system and investigation of the systematic absences identified the space group to be  $P2_1/n$  with  $0k0$ , ( $k = 2n + 1$ ) and  $h0l$ , ( $h + l = 2n + 1$ ). The cell constants were determined to be as follows:  $a = 7.349(7)$ ,  $b = 20.306(7)$ ,  $c = 8.909(3)$  Å, and  $\beta = 112.53(6)^\circ$ . The observed density of  $1.67(2)$  g cm $^{-3}$  agrees reasonably well with the calculated density of  $1.659$  g cm $^{-3}$  based upon two dimeric formula units per cell and a molecular weight of  $613.40$  g mol $^{-1}$ . The diffraction data that were collected had  $+h$ ,  $+k$ ,  $\pm l$ . A total of 2906 independent reflections was processed, but only the 1646 data with  $I \geq 3\sigma(I)$  were used in the refinement. The data were also corrected for Lorentz polarization effects.

#### Solution and Refinement of the Structure

The structure was solved by use of a three-dimensional Patterson function to locate the copper and chlorine atoms. Least-square refinement followed by a difference Fourier map yielded the positions

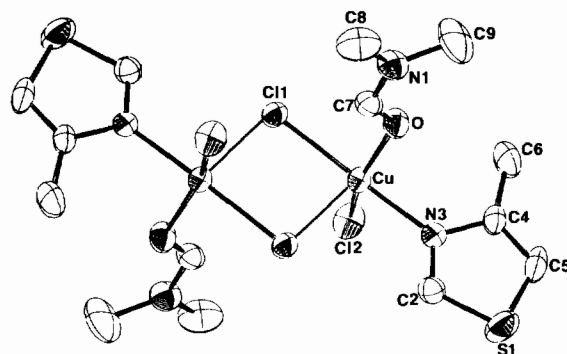


Fig. 1. View of the binuclear unit in  $[\text{Cu}(4\text{-Metz})(\text{DMF})\text{-Cl}_2]_2$ . Hydrogen atoms are omitted for clarity.

of all non-hydrogen atoms. Anisotropic refinement of these atoms gave values of  $R_1$  and  $R_2$  of 0.044 and 0.051, respectively, and a difference Fourier after this least-squares cycle provided the locations of the hydrogen atoms which were refined isotropically in the last cycles of least-squares. The final cycle of refinement gave values of  $R_1$  and  $R_2$  of 0.037 and 0.032, respectively. The positions of the atoms and their estimated standard deviations are listed in Table I, see also ‘Supplementary Material’.

## Results and Discussion

#### Description of the Structure

The complex consists of a mixed ligand five-coordinate dimer having a planar  $\text{Cu}_2\text{Cl}_2$  bridging unit due to the presence of a crystallographic inversion center in the middle of the dimer. A view of the dimeric unit is given in Fig. 1. As shown in Fig. 1, the monodentate ligands are in a *cis* arrangement around the copper(II) centers so that this complex represents the first example of *cis* coordination in parallel planar di- $\mu$ -chlorocopper(II) compounds having monodentate ligands. The oxygen atom from the DMF group forms an angle about the copper with the terminal chloride Cl(2) of  $154.9(1)^\circ$  while the nitrogen, N(3), from the 4-methylthiazole ligand in conjunction with the short bridging chloride, Cl(1), makes an angle of  $175.2(1)^\circ$ . In a tetragonal pyramidal geometry, these four atoms about the copper would make up the base plane with the apical position being occupied by Cl(1') which is the chloride ion in the base plane of the neighboring copper(II) ion. From these angles and the other bond distances and angles given in Tables II and III, it is clear that there are distortions from idealized tetragonal pyramidal geometry. These distortions are readily observed by the deviations of the atoms from the least-squares plane through the four basal ligands. The atoms Cl(1), Cl(2), N(3) and O which make up the plane deviate

TABLE II. Internuclear Separations (Å) in [Cu(4-Metz)-(DMF)Cl<sub>2</sub>]<sub>2</sub>

Atoms	Distances
Cu-C11	2.296(2)
Cu-C12	2.238(2)
Cu-N3	2.006(4)
Cu-O	1.990(4)
Cu-C11'	2.724(1)
N3-C2	1.295(5)
C2-S1	1.688(5)
S1-C5	1.687(6)
C5-C4	1.341(6)
C4-N3	1.384(5)
C4-C6	1.485(7)
O-C7	1.237(6)
C7-N1	1.305(6)
N1-C8	1.460(7)
N1-C9	1.436(9)

TABLE III. Internuclear Angles (°) in [Cu(4-Metz)(DMF)-Cl<sub>2</sub>]<sub>2</sub>

Atoms	Angle	Atoms	Angle
C11-Cu-C12	94.02(6)	C2-N3-C4	111.2(4)
C11-Cu-N3	175.2(2)	N3-C2-S1	115.0(4)
C11-Cu-O	90.4(1)	C2-S1-C5	89.0(3)
C11-Cu-C11'	84.71(7)	S1-C5-C4	112.2(4)
C12-Cu-N3	90.8(1)	N3-C4-C5	112.6(4)
C12-Cu-O	155.0(1)	C5-C4-C6	127.7(5)
C12-Cu-C11'	108.63(7)	N3-C4-C6	119.7(4)
N3-Cu-O	85.5(1)	Cu-O-C7	125.1(3)
N3-Cu-C11'	93.2(1)	O-C7-N1	124.2(5)
O-Cu-C11'	96.3(1)	C7-N1-C8	121.4(5)
Cu-N3-C2	124.6(3)	C7-N1-C9	120.6(6)
Cu-N3-C4	124.3(3)	C8-N1-C9	118.0(6)

from it by 0.21, -0.21, 0.26 and -0.26 Å, respectively; the Cu atom sits out of this plane by 0.21 Å on the side of the apical atom, Cl(1').

The bond lengths between the copper atom and the atoms making up the coordination sphere are found to be normal when compared to similar bond distances in other compounds. The structure of the dimeric unit is also fundamentally similar to that of all other dimers of this general type [3, 9, 10]. As seen previously, the bond from the copper to the bridging chloride Cl(1) [2.296(1) Å] is slightly longer than that to the terminal ligand Cl(2) [2.238(1) Å]. The Cu-Cl(1') distance of 2.724(1) Å and Cu-Cl(1)-Cu' bridging angle of 95.29(7)° are also values which lie within the previously observed ranges [9]. The Cu-Cu' distance is 3.721(1) Å, which is in the middle of that appropriate range also.

The geometry of the 4-Metz ligand is unremarkable and the metrical parameters are consistent with

the anticipated values. The 4-methylthiazole group is planar with no atom deviating from the five-membered cyclic ring by more than 0.010 Å.

The isolation and identification of this complex is indicative of the abundant chemistry available with 4-methylthiazole complexes of copper(II). This structure adds several new aspects of interest within the study of di- $\mu$ -chloro bridged dimers. First, the complex [Cu(4-Metz)(DMF)Cl<sub>2</sub>]<sub>2</sub> represents the only system of this kind which displays a mixed ligand nature, and it is the only complex having monodentate ligands where these ligands have a *cis* arrangement. Also, owing to its relative ease of preparation, it may be possible to design and synthesize many other mixed ligand compounds that could be used in the analyses of structure-magnetism relationships.

An additional interesting feature is the facile isolation of a first row transition metal complex with DMF as a ligand. The isolation and characterization of a series of such complexes, including bi-, tri-, and tetranuclear complexes of copper(II), has recently been reported [11, 12], but in most cases the synthesis route involved the direct oxidation of the metal (copper or iron) in DMF-CCl<sub>4</sub> mixtures. It is noteworthy, however, that very recently the complex [Cu(DMF)<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub>, originally synthesized from copper metal [11], has been formed [12] by the simple recrystallization of anhydrous copper(II) chloride from DMF. This complex might be thought of as the final product of a sequence of substituents of the parent [Cu(4-Metz)<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub> dimer with DMF, but the only product which we isolate is the present mixed ligand species, [Cu(4-Metz)(DMF)Cl<sub>2</sub>]<sub>2</sub>. In all known DMF complexes the DMF is coordinated through the oxygen atom, the Cu-O distance of 1.990(4) Å in the present complex being longer than that of 1.950(6) Å in the trinuclear complex [12] [Cu<sub>3</sub>(DMF)<sub>2</sub>Cl<sub>6</sub>] and those of 1.924(11) to 1.969(10) Å in the tetranuclear cluster [Cu<sub>4</sub>OCl<sub>6</sub>(DMF)<sub>4</sub>], but intermediate between those of 1.953 and 2.014 Å in the related dimer [11] [Cu(DMF)<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub>. In six-coordinate iron(II) and nickel(II) complexes, distances in the range of 2.035 to 2.076 Å have been reported [11, 13]; a weakly coordinated DMF-copper(II) complex with a Cu-O separation of 2.537(10) Å has also been examined [14]. In all reported complexes the C-O separation in the bond DMF is longer than the value [15] of 1.211 Å in free DMF, which is suggestive of some weakening of this formal double bond upon coordination to the metal. In the present complex this bond length is 1.237(6) Å, which is among the shortest of the values of 1.229-1.369 Å reported for other complexes.

In the absence of the magnetic data (*vide infra*), this description of the present complex as an isolated dimer would appear to be justified. As is shown in Fig. 2, however, the sulfur atom of a 4-Metz ligand bound to an adjacent copper atom sits in the sixth

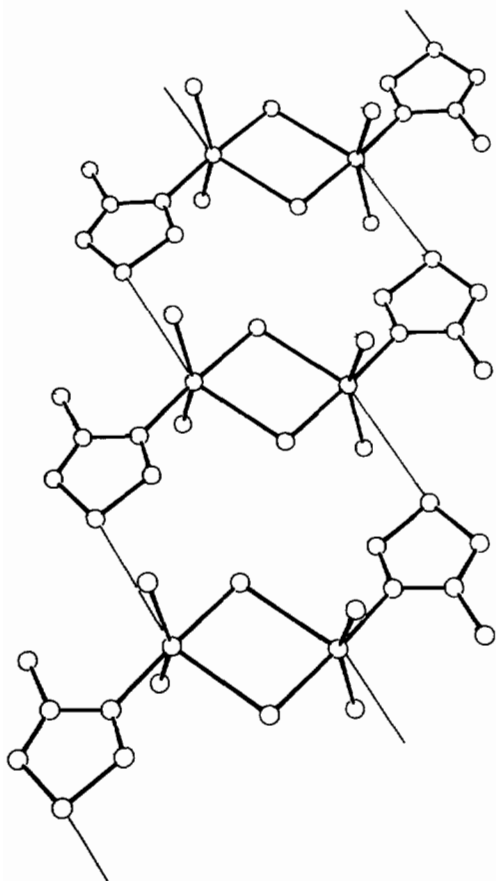


Fig. 2. The inner coordination geometry of  $[\text{Cu}(4\text{Metz})(\text{DMF})\text{Cl}_2]_2$ , showing the ladder-like interaction involving the sulfur atoms.

position of an approximate octahedron at copper, *i.e.* roughly *trans* to  $\text{Cl}(1')$ ; the  $\text{Cl}(1')\text{-Cu-S}$  angle is  $153.9(1)^\circ$ . The  $\text{Cu}\cdots\text{S}$  separation of  $3.906(3)$  Å is very long, but the magnetic properties of the complex (*v.i.*) clearly show that there is an interaction.

#### Magnetic Properties

The temperature-dependent magnetic susceptibility of a powdered sample of  $[\text{Cu}(\text{C}_4\text{H}_5\text{NS})(\text{DMF})\text{Cl}_2]_2$  is shown in Fig. 3. The maximum at about 3 K is indicative of an antiferromagnetic interaction between the  $S = 1/2$  ions. Assuming Heisenberg–Dirac–Van Vleck exchange coupling theory and the Hamiltonian

$$\mathcal{H} = \hat{S}_1 \cdot \hat{S}_2$$

the following expression results for the magnetization of an exchange-coupled pair of spins

$$M = \frac{Ng\beta \sinh(g\beta H/kT)}{\exp(-2J/kT) + 2\cosh(g\beta H/kT) + 1}$$

The expression was fit to the data using a Simplex non-linear least-squares fitting routine with the criterion of best fit being given by

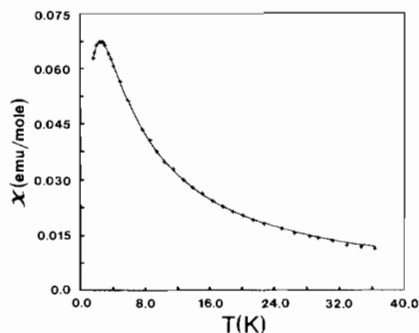


Fig. 3. The temperature dependence of the magnetic susceptibility of  $[\text{Cu}(4\text{-Metz})(\text{DMF})\text{Cl}_2]_2$ . The solid line represents the best fit to the spin ladder cluster model (see text).

$$F = \sum_i \frac{(X_i^{\text{obs}} - X_i^{\text{calc}})^2}{X_i^{\text{obs}}}$$

The best first parameters were  $J = -1.7$   $\text{cm}^{-1}$  and  $g = 2.10$ . This best least-squares fit fails to provide an accurate description of the data in the region of the maximum in the magnetic susceptibility. A molecular field correction was added to the magnetization expression yielding the equation

$$X_{\text{corr}} = \frac{X_{\text{iso}}}{1 - [2zJ'X_{\text{iso}}/Ng^2\beta^2]}$$

The resulting best fit yielded  $J = -1.45$   $\text{cm}^{-1}$ ,  $g = 2.20$ , and  $J' = -1.06$   $\text{cm}^{-1}$  with  $z$ , the number of nearest neighbors, being 2. Since  $J$  and  $J'$  were found to be of the same order of magnitude, an additional calculation was carried out using a cluster model [16].

As shown in Fig. 3, the data can be fit precisely with a ladder-like cluster model in which there are nearest neighbor (intradimer) and next-nearest neighbor (interdimer) exchange interactions. The cluster consisted of a closed ring of 10 spins, and the calculations were carried out using a computer program that has been described previously [16]. The best fit calculations yielded exchange coupling constants  $J_{\text{intra}}$  of  $-1.17$   $\text{cm}^{-1}$  and  $J_{\text{inter}}$  of  $-1.0$   $\text{cm}^{-1}$ .

The value of  $J_{\text{intra}}$  is in the range expected for a bis- $\mu$ -chloro-bridged copper(II) compound with a  $\phi/R_0$  value of  $35$   $\text{deg} \text{ \AA}^{-1}$  ( $\phi$  is the  $\text{Cu-Cl}\cdots\text{Cu}'$  angle and  $R_0$  is the long  $\text{Cu-Cl}$  bond distance in the  $\text{Cu}_2\text{Cl}_2$  exchange-coupled unit) [17, 18].  $J_{\text{inter}}$  describes the exchange coupling between copper(II) ions which are bridged by 4-methylthiazole. The superexchange pathway is  $\text{Cu-N-C-S}\cdots\text{Cu}'$ , and the sulfur–copper contact is  $3.906$  Å. The existence of this exchange interaction arises from delocalization of the unpaired electron onto the ligand and

overlap of the orbital on sulfur containing the unpaired electron density with the magnetic orbital on copper in the adjacent dimer. There are no other close contacts between the dimers, and there is no alternative superexchange pathway.

Exchange coupling in this spin-ladder system arises as a result of the large radial extension of sulfur orbitals. In related work, we have found that long interdimer contacts in  $[\text{Cu}(4\text{-methylthiazole})_2\text{Cl}_2\cdot\text{MeOH}]_2$  also give rise to significant interdimer exchange [10]. In  $[\text{Cu}(4\text{-methylthiazole})_2\text{Cl}_2\cdot\text{MeOH}]_2$ , the most likely superexchange pathway involves a  $\text{S}(1)\text{A}\cdots\text{Cl}(2)$  interdimer separation of 3.507 Å, where Cl(2) is the terminal Cl. The Cu–Cl(2) distance is 2.303 Å, and the Cu–Cl(2) $\cdots$ S(1)A angle is 128.5°; thus, the Cu $\cdots$ S separation is 5.259 Å. Also, S(1)A is 4.454 Å from Cu(A).

Exchange coupling over long superexchange pathways has been observed in other systems. For example, (adeninium) $_2$ CuCl $_4$  and (adeninium) $_2$ CuBr $_4$  exhibit linear chain behavior with exchange coupling constants of  $-7.6$  and  $-36.5$  cm $^{-1}$ , respectively [19]. In these compounds the chains are formed by non-bonded halide–halide contacts yielding nearly linear Cu–X $\cdots$ X–Cu superexchange pathways. The exchange coupling constants in these chains are comparable to or larger than those exhibited by bis- $\mu$ -halo-bridged copper compounds such as  $[\text{Cup}_2\text{Cl}_2]_n$  ( $J = 9.2$  cm $^{-1}$ ) [20, 21] and  $[\text{Cu}(3,5\text{-dimethylpyridine})_2\text{Br}_2]_n$  ( $J = -21$  cm $^{-1}$ ) [22]. The exchange coupling is a result of substantial unpaired electron density of the ligands.

Sulfur atoms are particularly effective in transmitting superexchange interactions through non-bonded contacts. The sulfur–sulfur contact between molecular units in  $[(\text{C}_2\text{H}_5)_4\text{N}][\text{Ni}(\text{DDDT})_2]$  (DDDT is 5,6-dihydro-1,4-dithiin-2,3-dithiolate) is 3.98 Å, yet these molecules are exchange-coupled into two-dimensional layers with  $J = -8.5$  cm $^{-1}$ . Furthermore, these two-dimensional layers undergo long-range order near 15 K, even though the nickel–nickel interlayer separation is 8.152 Å [23]. There is EPR evidence that there is substantial delocalization of electron density onto the ligand in  $[(\text{C}_2\text{H}_5)_4\text{N}][\text{Ni}(\text{DDDT})_2]$ , and this delocalization leads to the intermolecular exchange interactions and ultimately to long-range order.

It appears that some long-held views concerning magnitudes of exchange coupling constants may have to be reevaluated. It has been appreciated for some time that significant exchange coupling could be transmitted over long superexchange pathways [24–27], especially those involving conjugated networks; now relatively large exchange coupling constants are being found in systems with long non-bonded contacts. These findings were unexpected and provide the stimulation for additional synthetic, structural, and magnetic studies.

## Supplementary Material

Tables of hydrogen atom parameters, anisotropic thermal parameters, and observed and calculated structure amplitudes are available from the authors on request.

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## References

- 1 A. M. Landredi, A. Tiripicchio and M. T. Camellini, *J. Chem. Soc., Dalton Trans.*, 2168 (1975).
- 2 W. E. Hatfield, H. W. Richardson and J. R. Wasson, *Inorg. Nucl. Chem. Lett.*, 13, 137 (1977).
- 3 W. E. Hatfield, L. W. ter Haar, M. M. Olmstead and W. K. Musker, *Inorg. Chem.*, 25, 558 (1986).
- 4 W. E. Marsh, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, 22, 2899 (1983).
- 5 D. B. Brown, V. H. Crawford, J. W. Hall and W. E. Hatfield, *J. Phys. Chem.*, 81 1303 (1977).
- 6 B. N. Figgis and J. Lewis, in J. Lewis and R. G. Williams (eds.), 'Modern Coordination Chemistry', Interscience, New York, 1960, Chap. 6, p. 403ff.
- 7 R. R. Weller and W. E. Hatfield, *J. Chem. Educ.*, 56, 652 (1979).
- 8 B. J. Graves and D. J. Hodgson, *Acta Crystallogr., Sect. B*, 38, 135 (1982).
- 9 D. J. Hodgson, *J. Mol. Catal.*, 23, 219 (1984), and refs. therein.
- 10 W. E. Marsh, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, 27, 1819 (1988).
- 11 I. P. Lavrentiev, L. G. Korableva, E. A. Lavrentieva, G. A. Nifontova, M. L. Khidekel, I. G. Gusakovskaya, T. I. Larkina, L. D. Arutyunian, O. S. Filipenko, V. I. Ponomarev and L. O. Atovmyan, *Transition Met. Chem.*, 5, 193 (1980).
- 12 G. A. Nifontova, I. P. Lavrentiev, V. I. Ponomarev, O. S. Filipenko, O. N. Krasochka, L. O. Atovmyan and M. L. Khidekel, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1691 (1982).
- 13 R. J. Butcher, C. J. O'Connor and E. Sinn, *Inorg. Chem.*, 20, 3486 (1981).
- 14 K. Henrick, P. M. Judd, M. McPartlin, P. A. Tasker and R. W. Turner, *Inorg. Chim. Acta*, 53, L265 (1981).
- 15 R. E. Cobbleddick and R. W. H. Small, *Acta Crystallogr., Sect. B*, 29, 1659 (1973).
- 16 A. K. Gregson, R. R. Weller and W. E. Hatfield, *Inorg. Chem.*, 19, 3446 (1980).
- 17 W. E. Hatfield, *Comments Inorg. Chem.*, 1, 105 (1981).
- 18 W. E. Marsh, D. S. Eggleston, W. E. Hatfield and D. J. Hodgson, *Inorg. Chim. Acta*, 137 (1983).
- 19 D. B. Brown, J. W. Hall, H. M. Helis, E. G. Walton, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, 16, 2675 (1977).
- 20 D. Y. Jeter and W. E. Hatfield, *J. Inorg. Nucl. Chem.*, 11, 1826 (1972).
- 21 W. Duffy, J. Venneman, D. Strandberg and P. M. Richards, *Phys. Rev. Sect. B*, 9, 2220 (1974).
- 22 J. A. C. van Ooijen, J. Reedijk, E. J. Sonneveld and J. W. Visser, *Transition Met. Chem.*, 4, 305 (1979).

- 23 C. T. Vance, R. D. Bereman, J. Bordner, W. E. Hatfield and J. H. Helms, *Inorg. Chem.*, **25**, 558 (1985).
- 24 D. B. Losee, H. W. Richardson and W. E. Hatfield, *J. Chem. Phys.*, **59**, 3601 (1973).
- 25 H. W. Richardson and W. E. Hatfield, *J. Am. Chem. Soc.*, **98**, 835 (1976).
- 26 H. W. Richardson, J. R. Wason, W. E. Hatfield, E. V. Brown and A. C. Plaszczyk, *Inorg. Chem.*, **15**, 2916 (1976).
- 27 D. N. Hendrickson in R. D. Willett, D. Gatteschi and O. Kahn (eds.), 'Magneto-Structural Correlations in Exchange Coupled Systems', Reidel, Dordrecht, 1985, p. 523ff.