

Structure and Magnetism in the Chloro-Bridged Copper(II) Complex Di- μ -chloro-bis[chlorobis(4-methyloxazole)copper(II)]

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The dimeric complex bis[dichlorobis(4-methyloxazole)copper(II)], $[\text{Cu}(4\text{-Meox})_2\text{Cl}_2]_2$ or $[\text{Cu}-\text{C}_4\text{H}_5\text{NO})_2\text{Cl}_2]_2$ has been synthesized and its structure has been determined from three-dimensional counter X-ray data. The complex crystallizes in the monoclinic space group $P2_1/n$ with two dimeric formula units in a cell of dimensions $a = 8.177(2)$, $b = 12.866(5)$, $c = 11.063(6)$ Å, $\beta = 98.31(3)^\circ$. The structure has been refined by least-squares techniques to a value of the conventional R-factor (on F) of 0.033 based on 2071 independent data. The geometry at each copper center is severely distorted tetragonal pyramidal, the basal ligands being two trans nitrogen atoms from the 4-Meox ligands and two trans chloride ligands while the apical site is occupied by an inversion-related chloride ion. Thus, the dimeric entity is of the axial-equatorial type in which the inversion-related bridging chloride ligands are each axial to one copper and equatorial to the other. The Cu–Cu separation in the dimer is 3.507(1) Å, and the bridging Cu–Cl–Cu' angle (ϕ) is 89.46(2)°. The magnetic susceptibility of the complex exhibits a maximum near 2 K, and the data have been fitted to the magnetization expression yielding $g = 2.118$ and a singlet–triplet separation of 2.6 cm^{-1} with the singlet as the ground state.

Introduction

The development of empirical relationships which relate the structural characteristics of binuclear and polynuclear transition metal complexes to their magnetic properties has been vigorously pursued in many laboratories for several years. Studies of this kind have provided significant results in a variety of complexes, including di- μ -hydroxocopper(II) [1–3] and chromium(III) [4–9] dimers, square planar di- μ -chlorocopper(II) [10] dimers, and polymeric di- μ -chlorocopper(II) [11–13] complexes. Experimental and theoretical work performed by several research groups has sought to relate the iso-

tropic exchange coupling constant, J, to specific structural quantities, which can then be related to the metal–ligand bonding and antibonding orbitals involved in the exchange pathway between the metal centers [2, 7–9, 14–22].

In an effort to extend the experimental investigations of exchange-coupled transition metal complexes and to further delineate the general applicability of empirical relationships between structural and magnetic properties we have recently undertaken the study of a series of parallel-planar copper(II) halogen bridged complexes. Particular emphasis has been focused on five-coordinate dimeric species of general stoichiometry CuA_2X_2 or CuLX_2 (where X represents Br^- or Cl^- , A is a monodentate ligand and L is a bidentate ligand). The structural and magnetic properties of several systems of this type have been investigated recently [23, 24]. Among these, a chloro-bridged dimer of type CuA_2X_2 , where A is 4-methylthiazole (4-Metz), displayed some very interesting and unexpected substitution and redox chemistry in solution, including the formation of a mixed-valence dimer of the type $\text{Cu(I)Cl}(4\text{-Metz})_2\text{—Cu(II)Cl}_2(4\text{-Metz})_2$. These observations encouraged us to investigate the oxygen analog of 4-Metz, 4-methyloxazole (4-MeOX), as a ligand in an analogous system in hopes of extending not only our magnetic correlations but also of further characterizing the redox chemistry associated with copper dimers of this type. We report herein the structural and magnetic properties of the title complex $\text{Cu}(4\text{-MeOX})_2\text{Cl}_2$ and compare these to the properties of the previously reported analog $\text{Cu}(4\text{-MeOX})_2\text{Br}_2$.

Experimental

Synthesis

This complex was prepared by mixing a methanolic solution containing 0.01 mol of anhydrous CuCl_2 and a methanolic solution with slightly greater than 0.02 mol of the ligand 4-methyloxazole under

a nitrogen atmosphere. The methanol used in the reaction was freshly distilled over $\text{Mg}(\text{OMe})_2$. After mixing, the solution was stirred continuously for approximately five minutes during which a bright blue precipitate formed. The solution was filtered, sealed under N_2 , and placed in a freezing unit of a refrigerator for crystallization. The precipitate was washed with ether and then sealed in several small vials; some of the complex was analyzed whereupon acceptable C, H, and N percentages were obtained. *Anal.* Calcd. for $\text{Cu}(\text{C}_4\text{H}_5\text{NO})_2\text{Cl}_2$: C, 31.96; H, 3.35; N, 9.32. Found: C, 31.81; H, 2.82; N, 9.12.

Collection of the X-ray Data

A crystal of this compound mounted in a capillary was found to be in the monoclinic crystal system and upon observation of the systematic absences $0k0$, ($k = 2n + 1$) and $h0l$, ($h + l = 2n + 1$), the space group was assigned as $\text{P}2_1/n$ which was confirmed by the successful refinement of the structure. The cell constants were determined to be as follows: $a = 8.177(2)$ Å, $b = 12.866(5)$ Å, $c = 11.063(6)$ Å, and $\beta = 98.31(3)^\circ$. The calculated density based upon two dimeric formula units and a molecular weight of $601.26 \text{ g mol}^{-1}$ was calculated to be 1.734 g cm^{-3} . These results indicated the presence of a crystallographic inversion center in the middle of the dimer.

Diffraction data having ($\pm h$, $+k$, $+l$) were collected on an Enraf-Nonius CAD4 automated X-ray diffractometer using $\text{MoK}\alpha$ radiation and a graphite monochromator. Peaks were scanned in an ω - θ mode and the data, along with their estimated standard deviations, were corrected for Lorentz-polarization effects and absorption. The absorption coefficient for this complex using $\text{MoK}\alpha$ radiation was 24.1 cm^{-1} . A total of 2639 independent reflections was processed, of which 2071 had $I \geq 3\sigma(I)$; only these latter data were used in the refinement of the structure.

Solution and Refinement

The solution of the structure was effected by the use of a three-dimensional Patterson function to determine the position of the copper atom. Isotropic least-squares refinement of this position yielded values of the usual agreement factors $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ and $R_2 = [\sum \omega (|F_o| - |F_c|)^2 / \sum \omega (F_o)^2]^{1/2}$ of 0.504 and 0.561, respectively. All least-squares analyses in this work were carried out on F , the function minimized being $\sum \omega (|F_o| - |F_c|)^2$. The weights, ω , were initially given the value of unity, but were later replaced by a weighting scheme of the type $\omega = 4F_o^2 / \sigma^2(F_o^2)$, where $\sigma(F_o^2)$ is given by $\sigma(F_o^2) = [\sigma^2(I) + p^2 I^2]^{1/2}$ and p is assigned the value 0.01.

The positions of the chlorine atoms were located in a difference Fourier map and upon inclusion of these positions into the least-squares refinement, the

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

Atom	X	Y	Z
Cu	0.09826(5)	0.11910(3)	0.03836(3)
C11	0.09921(11)	0.29159(6)	0.08263(7)
C12	0.20284(9)	-0.04985(6)	0.00636(7)
O1A	0.0381(3)	0.1874(2)	-0.3301(2)
O1B	0.0273(4)	0.0607(2)	0.3915(2)
N3A	0.1063(3)	0.1532(2)	-0.1354(2)
N3B	0.1134(4)	0.0868(2)	0.2159(2)
C2A	-0.0120(4)	0.1617(3)	-0.2245(3)
C4A	0.2518(4)	0.1761(2)	-0.1840(3)
C5A	0.2067(4)	0.1964(3)	-0.3014(3)
C6A	0.4146(4)	0.1766(3)	-0.1069(3)
C2B	-0.0127(5)	0.0805(3)	0.2733(3)
C4B	0.2524(5)	0.0702(3)	0.3018(3)
C5B	0.1959(6)	0.0538(3)	0.4084(3)
C6B	0.4221(6)	0.0689(3)	0.2730(4)
HC2A	-0.126(4)	0.149(2)	-0.226(3)
HC5A	0.254(4)	0.216(2)	-0.361(3)
H1C6A	0.492(4)	0.189(3)	-0.152(3)
H2C6A	0.437(4)	0.110(3)	-0.068(3)
H3C6A	0.413(4)	0.231(3)	-0.041(3)
HC2B	-0.116(4)	0.096(2)	0.243(3)
HC5B	0.238(6)	0.026(4)	0.488(4)
H1C6B	0.433(5)	0.106(3)	0.213(4)
H2C6B	0.501(5)	0.076(3)	0.344(4)
H3C6B	0.453(5)	0.003(3)	0.255(4)

R-values decreased to 0.278 and 0.360, respectively. A subsequent difference Fourier map produced the locations of all non-hydrogen atoms and further isotropic least-squares cycles reduced R_1 to 0.098 and R_2 to 0.103; anisotropic refinement decreased these values to 0.053 and 0.064, respectively. After application of the absorption correction, the positions of the hydrogen atoms were determined from a difference Fourier map and in the final cycles of least-squares refinement, these atoms were included and refined with isotropic thermal parameters yielding values of R_1 and R_2 of 0.033 and 0.035, respectively. The final difference Fourier was featureless with no peak being greater than $0.14 \text{ e}\text{\AA}^{-3}$. The atomic positions and their estimated standard deviations are given in Table I and the atomic thermal parameters and observed and calculated structure amplitudes are available as supplementary material.

Collection of Magnetic Data

Magnetic susceptibility data were obtained on a Princeton Applied Research Model 155 vibrating-sample magnetometer (VSM) operating at a field strength of 10 kG. Temperatures at the sample were measured with a GaAs diode by observing the voltage on Fluke 8502 A 6.5-place digital multimeter; further details of the apparatus and temperature

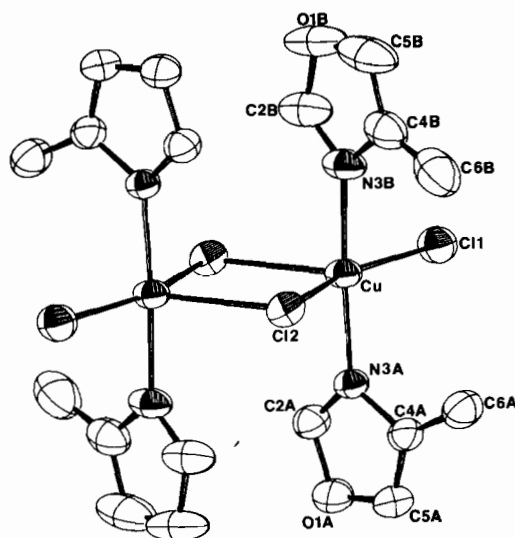


Fig. 1. View of the dimeric unit in $[\text{Cu}(4\text{-Meox})_2\text{Cl}_2]_2$. Thermal ellipsoids are drawn at the 40% probability level, and hydrogen atoms have been omitted for clarity.

measurement have been given elsewhere [25]. A finely ground polycrystalline sample of approximately 120 mg was packed in a precision milled Lucite sample holder. The data were corrected for the diamagnetism of the Lucite holder and for the underlying diamagnetism of the constituent atoms using Pascal's constants [26]. A value of 60×10^{-6} cgsu was assumed for the temperature independent paramagnetism (TIP) of copper [25].

Results and Discussion

Description of the Structure

Crystals of $[\text{Cu}(4\text{-Meox})_2\text{Cl}_2]_2$ are isomorphous with the bromide analogue, $[\text{Cu}(4\text{-Meox})_2\text{Br}_2]_2$, reported earlier [27] and thus display a dimeric structure similar to that observed in the bromide case. Again, the bridging unit lies on an inversion center requiring it to be planar as can be seen in Fig. 1. The geometry at each copper(II) center is a distorted tetragonal pyramid with the base plane made up of two *trans*-nitrogen atoms from the 4-Meox ligands and two *trans*-chloride ions; the apical site is occupied by a chloride ligand, $\text{Cl}(2)'$, which is basal to the other copper center in the dimer. The distortions from a tetragonal pyramidal geometry are considerable, but are less severe than those assuming a trigonal bipyramidal model. The distortions are readily observed by noting the *trans* $\text{Cl}(1)\text{-Cu-Cl}(2)$ angle and from the lack of planarity in the atoms of the basal plane. The *trans* angle formed by $\text{Cl}(1)$, $\text{Cl}(2)$, and Cu is $158.99(2)^\circ$

TABLE II. Internuclear Separations (\AA) in $[\text{Cu}(4\text{-Meox})_2\text{Cl}_2]_2$.

Atoms	Distances	Atoms	Distances
Cu—Cl1	2.272(1)	C4A—C5A	1.324(3)
Cu—Cl2	2.381(1)	C4A—C6A	1.474(3)
Cu—Cl2'	2.598(1)	O1A—C5A	1.375(3)
Cu—N3A	1.982(1)	O1B—C2B	1.325(3)
Cu—N3B	1.994(2)	C2B—N3B	1.289(3)
Cu—Cu'	3.507(1)	N3B—C4B	1.388(3)
O1A—C2A	1.334(2)	C4B—C5B	1.344(4)
C2A—N3A	1.282(3)	C4B—C6B	1.468(4)
N3A—C4A	1.405(2)	O1B—C5B	1.367(4)

TABLE III. Internuclear Angles (deg) in $[\text{Cu}(4\text{-Meox})_2\text{Cl}_2]_2$.

Atoms	Angles	Atoms	Angles
C11—Cu—Cl2	158.99(2)	N3A—C4A—C5A	106.6(2)
C11—Cu—Cl2'	110.46(2)	N3A—C4A—C6A	121.6(2)
C11—Cu—N3A	89.61(5)	C5A—C4A—C6A	131.9(2)
C11—Cu—N3B	89.62(5)	C4A—C5A—O1A	109.7(2)
C12—Cu—Cl2'	90.54(2)	C5A—O1A—C2A	104.1(2)
C12—Cu—N3A	89.72(5)	O1A—C2A—N3A	113.6(2)
C12—Cu—N3B	89.07(5)	Cu—N3B—C2B	123.9(2)
C12'—Cu—N3A	93.13(5)	Cu—N3B—C4B	129.4(2)
C12'—Cu—N3B	92.21(6)	C2B—N3B—C4B	106.7(2)
N3A—Cu—N3B	174.54(8)	N3B—C4B—C5B	105.9(3)
Cu—Cl2—Cu'	89.46(2)	N3B—C4B—C6B	124.0(2)
Cu—N3A—C2A	129.6(2)	C5B—C4B—C6B	130.1(3)
Cu—N3A—C4A	124.5(1)	C4B—C5B—O1B	109.7(3)
C2A—N3A—C4A	106.0(2)	C5B—O1B—C2B	104.4(2)
		O1B—C2B—N3B	113.4(3)

rather than the expected value of greater than 170° and the atoms $\text{Cl}(1)$, $\text{Cl}(2)$, N3A , N3B deviate from the best least-squares plane through them by -0.168 \AA , -0.161 \AA , 0.165 \AA , and 0.165 \AA , respectively. The copper atom sits out of this plane by 0.259 \AA on the side of the apical atom, $\text{Cl}(2)'$. This distorted geometry is very similar to that observed in $[\text{Cu}(4\text{-Meox})_2\text{Br}_2]_2$ but differs markedly from that seen in the 4-methylthiazole analogue, $[\text{Cu}(4\text{-Metz})_2\text{Br}_2]_2$, which has a geometry very close to that of an idealized tetragonal pyramid.

The axial $\text{Cu-Cl}(2)'$ bond length of $2.598(1) \text{ \AA}$ is the second shortest distance observed in the parallel planar di- μ -chloro copper(II) complexes with only the guaninium complex [28], $[\text{Cu}(\text{GuaH})\text{Cl}_3]_2 \cdot 2\text{H}_2\text{O}$, having a smaller distance of $2.447(1) \text{ \AA}$. The basal Cu-Cl distances are $2.272(1) \text{ \AA}$ and $2.381(1) \text{ \AA}$ with the distance to the bridging atom $\text{Cl}(2)$ being appreciably longer than the distance to

TABLE IV. Structural and Magnetic Properties of Fully-Characterized Di- μ -chloro Copper(II) Dimers.^a

Complex	Cu–Cu' (Å)	Cu–Cl'(R) (Å)	Cu–Cl–Cu' (ϕ) (deg)	ϕ/R (deg/Å)	2J (cm ⁻¹)	References
1. [Cu(dmgH)Cl ₂] ₂	3.445	2.698	88.0	32.62	+6.3	29, 30, 31
2. [Cu(dmen)Cl ₂] ₂	3.458(3)	2.734(3)	86.13(8)	31.50	-2.1	32, 33
3. [Cu(4-Meox) ₂ Cl ₂] ₂	3.507(1)	2.598(1)	89.46(2)	34.43	-2.6	This work
4. [Cu(guaH)Cl ₃] ₂	3.575	2.447(1)	97.9	40.01	-82.6	28, 34
5. [Cu(Et ₃ en)Cl ₂] ₂	3.703(1)	2.728(1)	94.84(4)	34.75	+0.1	24
6. [Cu(4-Metz)(DMF)Cl ₂] ₂	3.721(1)	2.724(1)	95.29(7)	34.99	-3.4	23
7. [Co(en) ₃] ₂ [Cu ₂ Cl ₈]Cl ₂	3.722(5)	2.703(5)	95.2(1)	35.22	-14.6	35, 36
8. [Cu(tmso)Cl ₂] ₂	3.737(2)	3.020(2)	88.5(1)	29.30	-17.0	37
9. [Cu(tmen)Cl ₂] ₂	4.089(4)	3.147(4)	96.8(1)	30.76	-5.6	33, 38
10. [Cu(2-pic) ₂ Cl ₂] ₂	4.404(1)	3.364(1)	100.63(3)	29.91	-7.4	39, 40, 41

^aAbbreviations: dmgH = dimethylglyoxime; dmen = N,N-dimethylethylenediamine; 4-Meox = 4-methyloxazole; guaH = guaninium ion; Et₃en = N,N,N'-triethylethylenediamine; 4-Metz = 4-methylthiazole; DMF = N,N-dimethylformamide; en = ethylenediamine; tmso = tetramethylene sulfoxide; tmen = N,N,N',N'-tetramethylethylenediamine; 2pic = 2-methylpyridine.

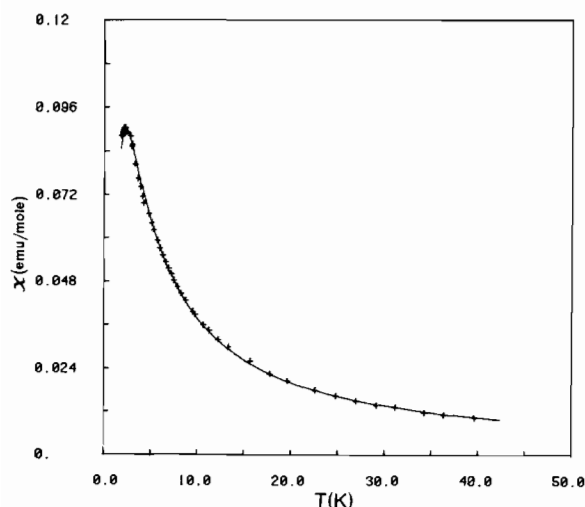


Fig. 2. Plot of the molar magnetic susceptibility, χ_m , of [Cu(4-Meox)₂Cl₂]₂ as a function of temperature. The solid line represents the best fit to the magnetization expression (see text) with $g = 2.118$ and $2J = -2.6 \text{ cm}^{-1}$.

the terminal chloride, Cl(1). These bond lengths are common for complexes of this type as are the Cu–N distances of 1.982(1) Å and 1.994(2) Å. The complex also has a bridging angle, Cu–Cl(2)–Cu' of 89.46(2)° and a Cu–Cu' distance of 3.507(1) Å which are within their respective ranges of 84.84(4)–100.63(3)° and 3.416–4.404 Å. Other bond distances and bond angles within this complex are given in Tables II and III, respectively. The metrical parameters within the bridging unit of [Cu(4-Meox)₂

Cl₂]₂ are compared to the corresponding values in related chloro-bridged dimers in Table IV; only those which have been characterized both structurally and magnetically are listed.

The two independent oxazole rings in the structure are planar, with no atom deviating from the five-atom least-squares plane by more than 0.003 Å in ring A and 0.003 Å in ring B. In both cases, the copper atom is displaced from the plane by approximately 0.04 Å while the methyl carbon atoms are about 0.03 Å out of the plane. The two oxazole planes are inclined at an angle of 9.7° to each other which is similar to the angle of 10.7° observed in the bromide complex. The bond lengths and angles within the oxazole ligands appear to be normal as can be seen in Tables II and III.

Magnetic Properties

The magnetic susceptibility of a powdered sample of [Cu(4-Meox)₂Cl₂]₂ as a function of temperature is shown in Fig. 2. As can be seen, the susceptibility data display a maximum at approximately 2 K indicating antiferromagnetic exchange coupling between the two copper(II) ions in the dimeric unit. The susceptibility data were analyzed using the magnetization expression [42] for exchange-coupled $S = \frac{1}{2}$ dimers

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

obtained from the exchange Hamiltonian

$$H_{\text{ex}} = -2J\hat{S}_1 \cdot \hat{S}_2 + g\mu_B H\hat{S} \quad (2)$$

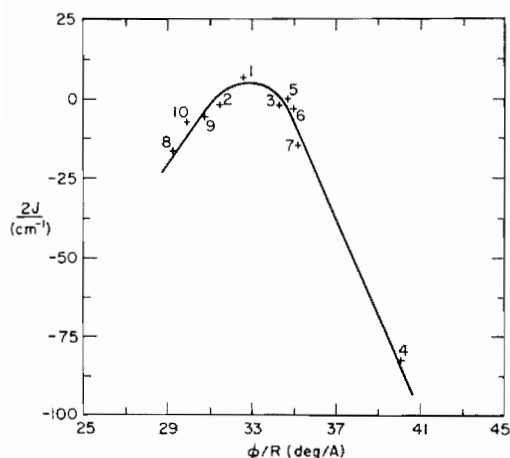


Fig. 3. Plot of the singlet-triplet splitting, $2J$, as a function of ϕ/R . The solid line is a guide for the eye. The data are numbered as in Table IV.

where \hat{S} is the total spin. The susceptibility data were fitted to the expression (1) using the relationship

$$\chi = M/H$$

where $H = 10,000$ G in all cases with g and J varied using a SIMPLEX fitting routine. The results of the best fit yielded values of g and $2J$ of 2.12 and -2.6 cm^{-1} , respectively, and is shown as the solid line in Fig. 2. Due to the excellent agreement, no adjustment to account for interdimer interactions seemed necessary and none was made. The value of $2J$ indicates that the triplet state lies about 2.6 cm^{-1} above the singlet state. While the type of interaction observed for this complex is the same as seen in $[\text{Cu}(4\text{-Meox})_2\text{Br}_2]_2$, the magnitude of the exchange interaction is quite different. In the bromide complex the $2J$ value was found to be -15.15 cm^{-1} .

Since the geometry at the copper centers in the chloro and bromo 4-methyloxazole complexes is very similar, we can presumably ascribe the difference in their magnetic properties to the differences in the bridging angle ϕ [89.46° vs. 87.00°] and the axial separation R [2.598 Å vs. 2.710 Å]. At the present stage, no simple correlation between the exchange coupling constant and structural parameters has been identified in the bromide complexes but a correlation between $2J$ and ϕ/R has been suggested for the more numerous chloride bridged copper(II) dimers [23, 24]. The complex $[\text{Cu}(4\text{-Meox})_2\text{Cl}_2]_2$ has a distorted tetragonal pyramidal geometry and can therefore be compared to the other axial-equatorial copper(II) dimers [24]. As can be seen in Table IV and in Fig. 3, the present complex fits the suggested relationship between J and ϕ/R , its

J value falling very close to those of other complexes with similar ϕ/R ratios.

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References

- 1 D. J. Hodgson, *Prog. Inorg. Chem.*, **19**, 173 (1975).
- 2 W. E. Hatfield, *A.C.S. Symp. Ser. No. 5*, 108 (1974).
- 3 V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, **15**, 2107 (1976).
- 4 D. J. Hodgson, *A.C.S. Symp. Ser. No. 5*, 94 (1974).
- 5 K. Michelsen and E. Pedersen, *Acta Chem. Scand., Ser. A*, **32**, 847 (1978).
- 6 W. E. Hatfield, J. J. MacDougall and R. E. Shepherd, *Inorg. Chem.*, **20**, 4216 (1981).
- 7 S. J. Cline, D. J. Hodgson, S. Kallesøe, S. Larsen and E. Pedersen, *Inorg. Chem.*, in press.
- 8 R. P. Scaringe, *Ph.D. Dissertation*, The University of North Carolina, Chapel Hill, N.C., 1976; R. P. Scaringe, D. J. Hodgson and W. E. Hatfield, *Transition Met. Chem.*, **6**, 340 (1981).
- 9 J. Glerup, D. J. Hodgson and E. Pedersen, *Acta Chem. Scand.*, in press.
- 10 S. G. N. Roundhill, D. M. Roundhill, D. R. Bloomquist, C. Landee, R. D. Willett, D. M. Dooley and H. B. Gray, *Inorg. Chem.*, **18**, 831 (1979).
- 11 J. A. C. van Ooijen and J. Reedijk, *Inorg. Chim. Acta*, **25**, 131 (1977).
- 12 W. E. Hatfield, R. R. Weller and J. W. Hall, *Inorg. Chem.*, **19**, 3825 (1980).
- 13 P. D. W. Boyd, S. Mitra, C. L. Raston, G. L. Rowbottom and A. H. White, *J. Chem. Soc., Dalton Trans.*, **13** (1981).
- 14 P. J. Hay, J. C. Thibeault and R. Hoffmann, *J. Am. Chem. Soc.*, **97**, 4884 (1975).
- 15 O. Kahn and B. Briat, *J. Chem. Soc., Faraday Trans. II*, **72**, 268 (1976); **72**, 1441 (1976).
- 16 M. F. Charlot, S. Jeannin, Y. Jeannin, O. Kahn, J. Lucrece-Abaul and J. Martin-Frere, *Inorg. Chem.*, **18**, 1675 (1979).
- 17 O. Kahn, P. Tola, J. Galy and H. Coudanne, *J. Am. Chem. Soc.*, **100**, 3931 (1978).
- 18 G. von Kalkeren, W. W. Schmidt and R. Block, *Physica*, **97B**, 315 (1979).
- 19 W. E. Hatfield, *Comments Inorg. Chem.*, **1**, 105 (1981).
- 20 J. Glerup, *Acta Chem. Scand.*, **26**, 3775 (1972).
- 21 A. Bencini and D. Gatteschi, *Inorg. Chim. Acta*, **31**, 11 (1978).
- 22 J. A. Bertrand and C. E. Kirkwood, *Inorg. Chim. Acta*, **6**, 248 (1972).
- 23 W. E. Marsh, *Ph.D. Dissertation*, University of North Carolina, Chapel Hill, N.C., 1982.
- 24 W. E. Marsh, K. C. Patel, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, in press and references therein.
- 25 W. E. Hatfield, R. R. Weller and J. W. Hall, *Inorg. Chem.*, **19**, 3825 (1980).

- 26 R. R. Weller and W. E. Hatfield, *J. Chem. Educ.*, *56*, 652 (1979).
- 27 W. E. Marsh, T. L. Bowman, W. E. Hatfield and D. J. Hodgson, *Inorg. Chim. Acta*, *59*, 19 (1982).
- 28 J. A. Carrabine and M. Sundaralingam, *J. Am. Chem. Soc.*, *92*, 369 (1970);
J. P. Declercq, M. Debboudt and M. van Meersche, *Bull. Soc. Chim. Belges*, *80*, 527 (1971);
M. Sundaralingam and J. A. Carrabine, *J. Mol. Biol.*, *61*, 287 (1971).
- 29 D. H. Svedung, *Acta Chem. Scand.*, *23*, 2865 (1969).
- 30 N. T. Watkins, E. E. Dixon, V. H. Crawford, K. T. McGregor and W. E. Hatfield, *J. Chem. Soc., Chem. Commun.*, 133 (1973). It should be noted that a value of $2J = +0.62 \text{ cm}^{-1}$ has been reported [31].
- 31 M. Megnamisi-Belombe and M. A. Novotny, *Inorg. Chem.*, *19*, 2470 (1980).
- 32 D. W. Phelps, W. H. Goodman and D. J. Hodgson, *Inorg. Chem.*, *15*, 2266 (1976).
- 33 W. E. Estes, *Ph.D. Dissertation*, The University of North Carolina, Chapel Hill, N.C., 1977.
- 34 R. F. Drake, V. H. Crawford, N. W. Laney and W. E. Hatfield, *Inorg. Chem.*, *13*, 1246 (1974);
J. F. Villa, *Inorg. Chem.*, *12*, 2054 (1973).
- 35 D. J. Hodgson, P. K. Hale and W. E. Hatfield, *Inorg. Chem.*, *10*, 1061 (1971).
- 36 J. A. Barnes, W. E. Hatfield and D. J. Hodgson, *Chem. Phys. Letters*, *7*, 374 (1970);
K. T. McGregor, D. B. Losee, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, *13*, 756 (1974).
- 37 D. D. Swank, G. F. Needham and R. D. Willett, *Inorg. Chem.*, *18*, 761 (1979).
- 38 E. D. Estes, W. E. Estes, W. E. Hatfield and D. J. Hodgson *Inorg. Chem.*, *14*, 106 (1975).
- 39 V. F. Duckworth and N. C. Stephenson, *Acta Crystallogr., Sect. B*, *B25*, 1795 (1969).
- 40 D. Y. Jeter, D. J. Hodgson and W. E. Hatfield, *Inorg. Chim. Acta*, *5*, 257 (1971).
- 41 W. E. Marsh, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, *21*, 2679 (1982).
- 42 B. E. Meyers, L. Berger and S. A. Friedberg, *J. Appl. Phys.*, *40*, 1149 (1969).