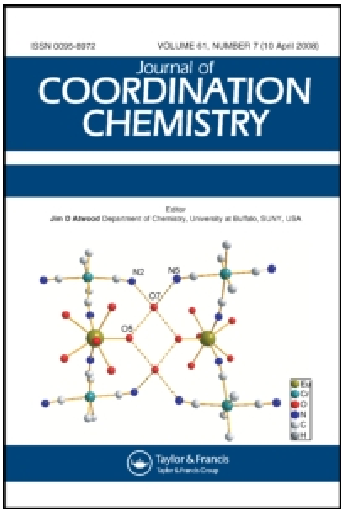

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# Synthesis, properties, and molecular structure of a novel polymeric complex : *catena*-poly[di-μ-(chloro)- *bis*(5-methyl-1,3-*bis*(pyrazol-1-ylmethyl)benzene)chlorocopper(ii)]

Wen-Kuen Chang[a]; Gene-Hsiang Lee[a]; Yu Wang[a]; Y. Oliver Su[a]; Tong-Ing Ho[a]; Yuan-Chuan Lin[a]
[a] Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China

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# SYNTHESIS, PROPERTIES, AND MOLECULAR STRUCTURE OF A NOVEL POLYMERIC COMPLEX : *CATENA*-POLY[DI-μ-(CHLORO)-*BIS*(5-METHYL-1,3-*BIS*(PYRAZOL-1-YLMETHYL)BENZENE)CHLOROCOPPER(II)]

WEN-KUEN CHANG, GENE-HSIANG LEE, YU WANG, Y. OLIVER SU[1]
TONG-ING HO, YUAN-CHUAN LIN

*Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China*

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The molecular structure of a binuclear copper(II) complex $[Cu_2L_2Cl_4]_n$ in which L, 5-methyl-1,3-*bis*(pyrazol-1-ylmethyl)benzene, has been reported. The complex is a polymeric compound and the molecular structure of the complex has been characterized by X-ray diffraction: monoclinic, space group $P2_1/c$, $Z = 2$, $a = 7.996(5)$, $b = 20.466(5)$, $c = 10.162(2)$ Å, $\beta = 99.51(4)$ °. The final $R$ and $Rw$ values are 0.035 and 0.033, respectively, for 2341 reflections with $I > 2\sigma(I)$. The copper(II) ion is five coordinated (N(1), N(4), Cl(1), Cl(1′) and Cl(2)) to form a distorted square-pyramidal geometry in which Cl(1′) is at the apical site. The mean value of the two Cu-N bonds is 2.006(3) Å and the three Cu-Cl bonds lie between 2.712(1) and 2.281(2) Å.

*Keywords:* copper; pyrazole; polymeric complex; X-ray structure

## INTRODUCTION

The reaction of copper(II) halides with nitrogen ligands is known to yield monomeric,[1–4] dimeric,[5–9] or polymeric[10–17] species, depending upon the precise nature of the ligand and the reaction condition. Some *bis*(μ-chloro) copper(II) dimers[6,8,18–22] have been prepared and their structural characterization vigorously pursued in many laboratories for several years. We were interested in studying the reaction or copper(II) halides with pyrazole ligands to form dimeric

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* Author for correspondence.

or polymeric *bis*(μ-halido) copper(II) complexes. In a previous paper, we reported a 1,3,5-*tris*(pyrazol-1-ylmethyl)benzene ligand, which reacted with Cu(II) to give polymeric *bis*(μ-chloro) copper(II) complexes.[11] The present paper concerns the ligand 5-methyl-1,3-bis(pyrazol-1-ylmethyl)benzene (L) and reports the synthesis, properties, and molecular structure of a polymeric *bis*(μ-chloro) copper(II) complex $[\{Cu_2L_2Cl_4\}_n]$.

## EXPERIMENTAL

### *Chemicals*

All reagents and solvents were purchased from commercial sources and used as received unless noted otherwise. 5-Methyl-1,3-*bis*(bromomethyl)benzene was prepared according to the literature.[23]

### *Physical Methods*

$H^1NMR$ spectra were recorded on Bruker AM 200WB instrument at 200 MHz using $CDCl_3$ as solvent and ESR spectra were recorded on a Bruker ESP 300 X-band instrument using diphenylpicrylhydrazyl (dpph) as standard. Magnetic susceptibilities were measured using the Faraday method on a Cahn 2000 instrument with $Hg[Co(SCN)_4]$ as standard and diamagnetic corrections were made using Pascal's constants. Mass spectra were recorded on a Finnigan MAT TSQ-46C instrument and infrared spectra on a Perkin Elmer 983G spectrophotometer using KBr as support. Elemental analyses were obtained using a Hitachi CHN-O-Rapid Analyer instrument. Electronic spectra was obtained with a Hewlett-Packard 8452A diode-array spectrometer using MeOH as solvent.

## SYNTHESES

### *5-Methyl-1,3-bis(pyrazol-1-ylmethyl)benzene (L)*

Pyrazole (1.36 g, 20 mmol) and sodium carbonate (2.12 g, 20 mmol) were dissolved in benzene (20 $cm^3$) then 5-methyl-1,3-*bis*(bromomethyl)benzene (2.78 g, 10 mmol) in benzene (20 $cm^3$) was added to the solution. After refluxing for 3h, the solvent was removed under reduced pressure and the residue washed with acetone. The product was purified by column chromatography (silica gel 60) using ethyl acetate-hexane (1:2) (Rf = 0.45) to give pale yellow oil, (yield, 1.3g, 40%). Found: C, 70.66; H, 6.33; N, 21.96% Calc. for $C_{15}H_{16}N_4$: C, 71.40; H, 6.39; N 22.20%. MS: *m/z* 252, 184. H[1] NMR ($CDCl_3$): $\delta$ = 2.25 (3H, s, aryl $CH_3$), 5.21 (4H, s, aryl $CH_2N$), 6.24 (2H, t, *J* 2.0 Hz, pyrazolyl $C^5$-H), 6.83 (1H, s, aryl H), 6.90 (2H, s aryl H), 7.34 (2H, d, *J* 1.0 Hz, pyrazolyl $C^5$-H), 7.50 (2H, d, *J* 1.0 Hz, pyrazolyl $C^3$-H). Infrared: $\nu_{max}$ = 3103m, 2925m, 1509m, 1430m, 1392s, 1285m, 1088m, 749s, 623m $cm^{-1}$.

### $[\{Cu_2L_2Cl_4\}_n]$

Copper(II) chloride dihydrate (170 mg, 1 mmol) and L (252 mg, 1 mmol) were dissolved in methanol (10 $cm^3$) at room temperature and filtered. Green crystals were obtained by slow diffusion of diethylether into the mixture. Found: C, 46.25; H,4.15; N,14.45%. Calc. for $C_{30}H_{32}Cl_4Cu_2N_8$: C,46.58; H,4.17; N,14.49%. Infrared: $\nu_{max}$= 3086m, 1606m, 1512m, 1455m, 1410m, 1284m, 1075s, 772s, 625m $cm^{-1}$.

### Structure Determination

Intensity data for a suitable crystal were collected at room temperature on a CAD-4 diffractometer using monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.71069 Å). The unit cell constants were derived from a least-squares refinement of 25 setting reflections. The $\omega$-2$\theta$ scan technique and a variable scan speed were used to obtain integrated intensities. Three reference reflections were monitored throughout the measurement; variation of intensities was less than 4%. Absorption corrections were applied according to the experimental psi rotation curve. Other crystal data are given in Table I

TABLE I Crystallographic data for the complex

| | |
|---|---|
| Formula | $[Cu_2L_2Cl_4]$ |
| *M* | 773.5 |
| Crystal size/mm | 0.40 × 0.43 × 0.44 |
| Crystal | Monoclinic |
| Space group | $P2_1/c$ |
| *a*/ Å | 7.996(5) |
| *b*/ Å | 20.466(5) |
| *c*/ Å | 10.162(2) |
| $\beta$/° | 99.51(4) |
| *V*/ $Å^3$ | 1640(11) |
| *Z* | 2 |
| *F*(000) | 720 |
| $D_c$/Mg $m^{-3}$ | 1.449 |
| $\mu$/$mm^{-1}$ | 1.66 |
| 2$\theta$ range/° | 2–50 |
| range of *h, k, l* | −9–9, 0–24, 0–12 |

TABLE I (*Continued*).

| | |
|---|---|
| Scan parameters: | 1.4+0.7tanθ |
| Total number of reflections: | 2883(2341>2σ) |
| $R$, $R_w$ | 0.035,0.033 |
| $S$ | 3.70 |

The structure was solved by the heavy-atom method. Atomic parameters were obtained from subsequent Fourier syntheses and least-squares refinement. Final coordinates for the non-hydrogen are given in Table II. A weighting scheme of the form $1/[\sigma^2(F_o)]$ was used. All hydrogen atom parameters were calculated according to ideal geometry and were not refined. The structural analysis was carried out on a MicrovaxIII using NRCVAX programs.[24] Atomic scattering factors were taken from ref. 25. Full lists of anisotropic temperature factors, bond distances and angles, and calculated and observed structure factors are available on request from the authors.

TABLE II Final atomic positional parameters of non-hydrogen atoms for complex

| | $x/a$ | $y/b$ | $z/c$ | $B_{eq}$ |
|---|---|---|---|---|
| Cu | 0.01144(6) | 0.077031(24) | 0.09761(5) | 2.368(23) |
| Cl1 | 0.18331(13) | −0.03599 (5) | 0.07991(9) | 2.83 (5) |
| Cl2 | 0.19786(14) | 0.11876 (6) | 0.27144(10) | 3.37 (5) |
| N1 | 0.1296 (4) | 0.12644 (16) | −0.0310 (3) | 2.51 (15) |
| N2 | 0.1103 (5) | 0.18963 (17) | −0.0674 (3) | 2.98 (17) |
| N3 | −0.2952 (4) | 0.05871 (16) | 0.2347 (3) | 2.96 (16) |
| N4 | −0.1306 (4) | 0.04335 (16) | 0.2279 (3) | 2.53 (15) |
| C1 | 0.2556 (5) | 0.10412 (20) | −0.0883 (4) | 3.03 (19) |
| C2 | −0.3167 (6) | 0.15327 (24) | −0.1622 (4) | 3.61 (22) |
| C3 | 0.2207 (6) | 0.20620 (23) | −0.1474 (4) | 3.79 (22) |
| C4 | −0.0279 (6) | 0.23054 (21) | −0.0341 (4) | 3.61 (22) |
| C5 | −0.1584 (5) | 0.24460 (21) | −0.1560 (4) | 2.68 (19) |
| C6 | −0.2312 (6) | 0.19399 (21) | −0.2354 (4) | 3.56 (21) |
| C7 | −0.3503 (6) | 0.20417 (23) | −0.3481 (4) | 3.50 (22) |
| C8 | −0.4321 (7) | 0.1492 (3) | −0.4327 (5) | 5.5 (3) |
| C9 | −0.3991 (6) | 0.22955 (23) | 0.1179 (4) | 3.58 (22) |
| C10 | −0.3276 (5) | 0.17951 (20) | 0.1979 (4) | 2.62 (18) |
| C11 | −0.2029 (5) | 0.30855 (20) | −0.1871 (4) | 2.83 (19) |
| C12 | −0.3847 (5) | 0.11088 (23) | 0.1572 (4) | 3.31 (20) |
| C13 | −0.3496 (7) | 0.02355 (24) | 0.3311 (5) | 4.09 (24) |
| C14 | −0.2211 (7) | −0.01571 (25) | 0.3888 (4) | 4.4 (3) |
| C15 | −0.0863 (6) | −0.00162 (22) | 0.3213 (4) | 3.37 (21) |

$B_{eq}$ is the mean of the principal axes of the thermal ellipsoid

## RESULTS AND DISCUSSION

The complex is a polymeric compound containing a dimeric [$Cu_2L_2Cl_4$] unit Selected bond distances and angles are given in Table III. The repeating unit is shown in Figure 1.

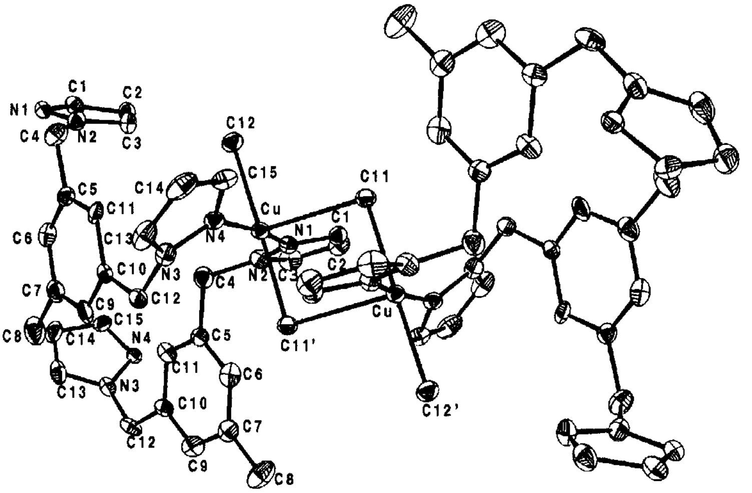

FIGURE 1 The asymmetric unit of the complex, showing the numbering scheme.

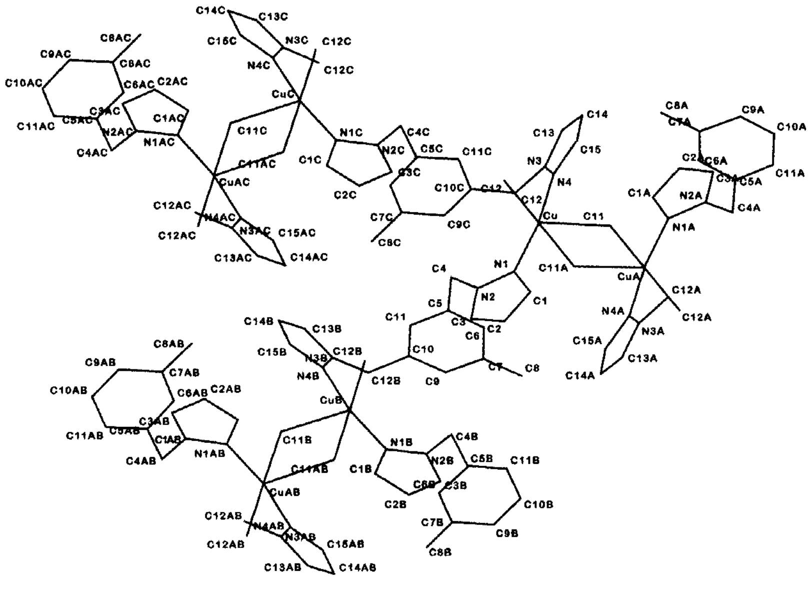

FIGURE 2 Unit cell contents of the complex.

TABLE III Selected bond distances (Å) angles (°) for the complex

| | | | |
|---|---|---|---|
| Cu...Cu′ | 3.714(1) | Cu—Cl(1) | 2.712(1) |
| Cu—Cl(1′) | 2.336(2) | Cu—N(1) | 2.008(3) |
| Cu—N(4) | 2.004(3) | Cu—Cl(2) | 2.281(2) |
| Cl(1) —Cu—Cl(1′) | 85.55(5) | Cu—Cl(1) —Cu′ | 94.45(5) |
| Cl(1) —Cu—N(1) | 95.07(10) | Cl(1) —Cu—N(1) | 95.69(10) |
| Cl′(1) —Cu—N(1) | 90.22(9) | Cl(1′)—Cu—N(4) | 90.47(10) |
| Cl(1′)—Cu—Cl(2) | 178.84(5) | Cl(1) —Cu—Cl(2) | 95.58(5) |
| N(1) —Cu—N(4) | 169.24(14) | N(1) —Cu—Cl(2) | 89.88(10) |
| N(4) —Cu—Cl(2) | 89.22(10) | | |

In the dimeric unit, each copper(II) centre is surrounded by five donors: two bridging nitrogen atoms (N(1), N(4)) from the pyrazolyl ring of the ligand (L), two bridging chloride ions (Cl(1), Cl(1′)) and a non-bridging chloride ion (Cl(2)) that occupies the fifth coordination site. The geometry at each copper(II) centre is best described as distorted square pyramidal. The basal plane involves N(1), N(4), Cl(1′) and Cl(2), and Cl(1) occupies the apical position. Cu-N(1) is 2.008(3) and Cu-N(4) is 2.004(3) Å, as normal. The N(1)-Cu-N(4) angle, 169.24(14), and Cl(1′)-Cu-Cl(2), 178.84(5)°, show distortion from the ideal value of 180°.

Each copper(II) ion is bridged by two chloride ions (Cl(1), Cl(1′)) to form a $Cu_2Cl_2$ unit comprising a centrosymmetric, planar, four-membered ring. The Cu-Cl-Cu′ bridging angle of 94.45(5)°, the Cl-Cu-Cl′ angle of 85.55(5)°, and the Cu···Cu′ distance of 3.714(1) Å are all within previously observed ranges for *bis*(μ-chloro)copper(II) complexes as recorded by Hodgson *et al.*[6, 8, 19] The basal Cu-Cl(2) distance is 2.281(2) Å, the Cu-Cl (1′) distance is 2.336(2) Å and the axial Cu-Cl(1) distance is 2.712(1) Å, similar to other (μ-chloro) copper(II) complexes.[19-22]

As shown in Figure 2, the ligand possesses two donor sites ((N(1) and N(4B)) and both are coordinated to metal(II) ions, N(1) to Cu and N(4B) to Cu(B). Cu and Cu(B) are coordinated by N(4) and N(1B) [N(4) and N(1B) are from different ligands], respectively. The complex is a dinuclear network and it possesses a infinite three dimensional structure, which is different from the normal, linear, chain-type structure.[10,13,14,16]

The IR spectrum of the complex reveals a C=N peak at 1512 cm$^{-1}$. The electronic spectrum recorded in methanol reveals two absorption at 226 nm for the pyrazolyl group and 268 nm for the benzenyl group. *X*-band powder ESR spectra and magnetic moments were measured at room temperature. The spectra indicate that the complex is rhombic ($g_1 = 2.058$, $g_2 = 2.126$, $g_3 = 2.190$) and is consistent with a $d_x{}^2 - {}_y{}^2$ ground state, *i.e.*, square-pyramidal coordination sphere for the copper(II) ion.[27] The magnetic moment is 1.82BM per copper, significantly near the spin-only value of 1.73 for the free copper(II) ion.[28]

Hatfield and Hodgson[6] show the exchange coupling constant, $J$, relation with the quantity $\phi$/R, where $\phi$ is the Cu-Cl-Cu′ bridging angle and R is the (longer) Cu–Cl distance. The complex has a $\phi$/R value of 34.83 and compares with related complexes. For $[Cu(dmgH)Cl_2]_2$ [dmgH = dimethylglyoxime][29], $\phi/R = 32.62, 2J = 6.3$; $[Cu(dmen)Cl_2]_2$ [dmen = *N*, *N*-dimethylethylenediamine][30], $\phi/R = 31.50$, $2J = -2.1$; $[Cu(4\text{-Metz})(DMF)Cl_2]_2$ [4-Metz = 4-methylthiazole][6], $\phi/R = 34.99$, $2J = -3.6$; $[Cu(Et_3en)Cl_2]_2$ [$Et_3en$ = *N,N,N′*-triethylethylenediamine][6], $\phi/R = 34.75$, $2J = 0.1 cm^{-1}$; the $J$ values are very small when $\phi$/R values are in the range 31–35. These results indicate that the $J$ value of the $Cu_2Cl_2$ unit in the present complex should be small and suggests a very weak magnetic interaction between the two copper(II) ions.

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## *References*

[1] W.E. Marsh, W.E. Hatfield and D.J. Hodgson, *Inorg. Chem.*, **21**, 2679 (1982).
[2] R.B. Wilson, J.R. Wasson, W.E. Hatfield and D.J. Hodgson, *Inorg. Chem.*, **17**, 641 (1978).
[3] H. Yamaguchi, M. Nagase, Y. Yukawa, Y. Inomata and T. Takeuchi, *Bull. Chem. Soc. Jpn.*, **61**, 2763 (1988).
[4] H. Yamaguchi, Y. Inomata and T. Takeuchi, *Inorg. Chim. Acta*, **181**, 31 (1991).
[5] W.E. Marsh, T.L. Bowman, C.S. Harris, W.E. Hatfield and D.J. Hodgson, *Inorg. Chem.*, **20**, 3864 (1981).
[6] W.E. Marsh, K.C. Patel, W.E. Hatfield and D.J. Hodgson, *Inorg. Chem.*, **22**, 511 (1983).
[7] W.E. Marsh, T.L. Bowman, W.E. Hatfield and D.J. Hodgson, *Inorg. Chim. Acta*, **59**, 19 (1982).
[8] W.E. Marsh, D.S. Eggleston, W.E. Hatfiel, and D.J. Hodgson, *Inorg. Chim. Acta*, **70**, 137 (1983).
[9] W.C. Velthuizen, J.G. Haasnoot, A.J. Kinneging, F.J. Rietmeijer and J. Reedijk, *J. Chem. Soc., Chem. Commun.*, 1366 (1983).
[10] W.E. Marsh, E.J. Valente and D.J. Hodgson, *Inorg. Chim. Acta*, **51**, 49 (1981).
[11] W.-K. Chang, S.-C. Sheu, G.-H. Lee, Y. Wang, T.-I. Ho and Y.-C. Lin, *J. Chem. Soc., Dalton Trans.*, in press.
[12] D.D. Swank and R.D. Willett, *Inorg. Chem.*, **19**, 2321 (1980).
[13] F.S. Keij, R.A.G. de Graaff, J.G. Haasnoot, A.J. Oosterling, E. Pedersen and J. Reedijk, *J. Chem. Soc., Chem. Commun.*, 423 (1988).
[14] F.S. Keij, R.A.G. de Graaff, J.G. Haasnoot, J. Reedijk and E. Pederson, *Inorg. Chim. Acta*, **156**, 65 (1989).
[15] J.A.C. van Ooijen and J. Reedijk, *Inorg. Chim. Acta*, **25**, 131 (1977).
[16] W.E. Hatfield, R.R. Weller and J.W. Hall, *Inorg. Chem.*, **19**, 3825 (1980).
[17] P.D.W. Boyd, S. Mitra, C.L. Raston, G.L. Rowbottom and A.H. White, *J. Chem. Soc., Dalton Trans.*, 13 (1981).
[18] 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).
[19] W.E. Marsh, W.E. Hatfield and D.J. Hodgson, *Inorg. Chem.*, **27**, 1819 (1988).

[20] F.S. Keij, J.G. Haasnoot, A.J. Oosterling, J. Reedijk, C.J. O'Connor, J.H. Zhang and A.L. Spek, *Inorg. Chim. Acta*, **181**, 185 (1991).

[21] M. Kwiatkowski, E. Kwiatkowski, A. Olechnowicz and G. Bandoli, *Inorg. Chim. Acta*, **182**, 117 (1991).

[22] P. Baran, M. Koman, D. Valigura and J. Mrozinski, *J. Chem. Soc., Dalton Trans.*, 1385 (1991).

[23] R.R. Hree, T. Enkoji and J.P. Dailey, *J. Am. Chem. Soc.*, **79**, 4230 (1957).

[24] E.J. Gabe, Y. Le Page, P.S. White and F.L. Lee, *Acta Crystallogr.*, **A43**, S294 (1987).

[25] *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, Vol. 4. (1974).

[26] H. Oshio, K. Toriumi and Y. Hayashi, *J. Chem. Soc., Dalton Trans.*, 293 (1990).

[27] B.J. Hathaway and D.E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).

[28] B.J. Hathaway, 'Comprehensive Coordination Chemistry. The Synthesis, Reacations, Properties & Applications of Coordination Compounds, ' eds. G. Wilkinson, R.D. Gillard and J.A. McCleverty, Vol. 5, pp. 53, 533–774 (Pergamon, Oxford, 1987).

[29] N.T. Watkins, E.E. Dixon, V.H. Grawford, K.T. McGregor and W.E. Hatfield,, *J. Chem. Soc., Chem. Commun.*, 133 (1973).

[30] D.W. Phelps, W.H. Goodman and D.J. Hodgson, *Inorg. Chem.*, **15**, 2266 (1976).