Copper Complexes of some Potentially Binucleating Tetradentate Phthalazine-hydrazone Ligands. Spontaneous Reduction to form Copper(I) Derivatives

LAURENCE K. THOMPSON* and T. C. WOON

Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, A1B 3X7, Canada

Received April 19, 1985

Abstract

The tetradentate phthalazine-hydrazone ligands PHT and DMPH, formed by the reaction of 1,4-dihydrazinophthalazine (DHPH) and *p*-tolualdehyde and 2,5-dimethylbenzaldehyde respectively form predominantly copper(I) derivatives when reacted with copper(II) salts in solvents containing small amounts of water. The derivatives Cu(I)(PHT)X (X = NO_3^-, ClO_4^-) were produced by reaction of copper(II) salts with PHT in methanol, while in aqueous acetonitrile ligand hydrolysis occurred with no complex formation. In aqueous acetonitrile the hydrolysis occurs at one azomethine centre, generating initially a hydrazino derivative and *p*-tolualdehyde, followed by copper(II) reduction and nitrogen evolution and the formation of *p*-toluic acid and a cyanobenzene derivative (A) resulting from phthalazine ring cleavage. The copper(I) complexes of both PHT and DMPH can also be synthesized directly by reaction of copper(I) salts with the ligands in acetonitrile and copper(II) complexes of PHT can be synthesized with electronegative and coordinating anionic groups, e.g. Cl, Br.

Introduction

Substituted phthalazine ligands have been shown to generate binuclear copper(II) complexes which are of considerable interest from a magnetic and catalytic standpoint [1–11]. Hydroxy-bridged binuclear complexes were found to predominate and these were characterized by exhibiting antiferromagnetic exchange between the copper centres. In a series of pyridylaminophthalazine complexes involving six-membered chelate rings the dimensions of the binuclear centre could be tuned by varying the size of the non-hydroxy, anionic bridge [6, 7]. An increase of exchange integral from $-2J = 190$ to 532 cm^{-1} accompanying an increase in oxygen bridge angle from 100 to 115.5° was observed on replacing a chlorine bridge by a sulphate bridge [7]. The ligand

MIP (1,4-di(1'methyl-2'-imidazolyl)phthalazine) produces binuclear copper(II) complexes involving five-membered chelate rings and much larger oxygen bridge angles. For the complex Cu$_2$(MIP)(OH)Cl$_3$·2H$_2$O a Cu–O–Cu angle of 126.2° gives rise to an exchange integral of $-2J = 800$ cm^{-1} [8].

In the process of exploring other phthalazine ligands with the potential of producing strongly antiferromagnetically coupled complexes involving hydroxide bridges we focussed attention on 1,4-dihydrazinophthalazine (DHPH) and its derivatives. Copper(II) complexes of DHPH appear to be largely inaccessible because of the strongly reducing nature of this hydrazine derivative and so some sexadente hydrazone ligands derived from the condensation of DHPH with salicylaldehyde, pyridine-2-carboxaldehyde and N-methylimidazole-2-carboxaldehyde were investigated [9]. Hydroxy-bridged derivatives, with very low room temperature magnetic moments, were produced indicating strong antiferromagnetic exchange [9].

In the present study we have examined the reactivity of two potentially tetradentate phthalazine-hydrazone ligands derived from the condensation of DHPH with *p*-tolualdehyde (PHT) and 2,5-dimethylbenzaldehyde (DMPH) (Fig. 1). The lack of peripheral donor groups on these ligands appears to reduce the stability of their copper(II) derivatives, especially in aqueous media, with the result that the ligands become hydrolysed in most cases, on reaction with metal salts, leading to the formation of hydrazine or a hydrazino-phthalazine which act as reducing agents leading to the formation of copper(I) species with the release of nitrogen gas. Under controlled hydrolysis conditions in aqueous medium an estimate of the amount of nitrogen evolved has been established and two hydrolysis products have been identified.
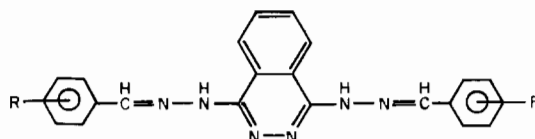

Fig. 1. R = 4-methyl (PHT); R = 2,5-dimethyl (DMPH).

---

*Author to whom correspondence should be addressed.

TABLE I. Analytical and Other Data

Compound		Colour	Found (%)				Calcd. (%)			
			C	H	N	Cu	C	H	N	Cu
I	Cu(PHT)(NO$_3$)·H$_2$O	Orange	53.36	4.40	18.09	11.82	53.57	4.46	18.23	11.81
II	Cu(PHT)(ClO$_4$)·0.5H$_2$O	Orange	50.97	4.15	15.33	11.23	50.85	4.06	14.84	11.68
III	Cu(PHT)Cl$_2$·H$_2$O	Green	52.91	4.07	15.34	11.40	52.69	4.39	15.37	11.61
IV	Cu(DMPH)(NO$_3$)·2H$_2$O	Brown	53.47	4.95	16.87	11.27	53.46	5.14	16.79	10.89
V	Cu(DMPH)(ClO$_4$)	Brown	52.87	4.61	14.73	10.86	53.33	4.44	14.36	10.97
A	C$_{16}$H$_{14}$N$_4$	White	73.67	4.95	21.55	–	73.28	5.34	21.37	–

Experimental

Electronic spectra were recorded with a Cary 17 spectrometer and infrared spectra with a Perkin-Elmer Model 283 spectrometer. Magnetic susceptibilities were obtained at room temperature by the Faraday method using a Cahn Model #7600 Faraday Magnetic Susceptibility system, coupled to a Cahn gram electrobalance. Nuclear magnetic resonance spectra were run as solutions in deuterochloroform and deuterodichloromethane using a Bruker WP80 spectrometer and mass spectra were run using a V.G. Micromass 7070 HS with the direct insertion probe. Microanalyses were carried out by Canadian Microanalytical Service, Vancouver (C, H, N). Metal analyses were determined by atomic absorption with a Varian Techtron AA-5, after digestion of the samples in concentrated HNO$_3$ or aqua regia.

Preparation of Ligands

PHT

1,4-dihydrazinophthalazine [9] (5.0 g, 26.3 mmol) and p-tolualdehyde (6.3 g, 52.6 mmol) were added to methanol (150 ml) and the mixture refluxed for 0.5 h, during which time the 1,4-dihydrazinophthalazine dissolved forming a red solution. The solution was cooled and reduced in volume to about 40 ml. On addition of a small amount of water a yellow crystalline product formed. The product was filtered, after standing in the refrigerator overnight, washed with water and dried in vacuo at 70 °C for 2 h. Yield 7.8 g, 75%; mp 179–183 °C. Anal. Calcd. for C$_{24}$H$_{22}$N$_6$·1.25H$_2$O: C, 69.2; H, 5.88; N, 20.2. Found: C, 69.2; H, 5.51; N, 19.6%. Mass spectrum major mass peaks (m/e (relative intensity)) 394(50) P, 303(53), 275(65), 259(40), 186(90), 171(20), 135-(100), 118(85), 91(90); ^{1}H NMR (CD$_2$Cl$_2$) data are given in Table III.

DMPH was prepared as described for PHT but using CHCl$_3$/MeOH (40/60) as the solvent. Yield 3.2 g, 48%; mp 203–206 °C. Anal. Calcd. for C$_{26}$H$_{26}$N$_6$: C, 73.9; H, 6.16; N, 19.9. Found: C, 73.7; H, 6.10; N, 19.6%. Mass spectrum, major mass peaks (m/e

(relative intensity)) 422(55) P, 317(100), 290(32), 288(42), 273(24), 261(7), 186(15). ^{1}H NMR (CD$_2$Cl$_2$) data are given in Table III.

Cu(PHT)(NO$_3$)·H$_2$O (I)

Excess copper powder (4.5 g) was added to Cu(NO$_3$)$_2$·3H$_2$O (0.70 g, 2.9 mmol) dissolved in degassed acetonitrile (50 ml) and the mixture stirred under nitrogen until a colourless solution was obtained. This solution was filtered under nitrogen into a solution of PHT (1.0 g, 2.5 mmol) in degassed methanol (80 ml). The dark red solution which formed was warmed and stirred for 1 h in a nitrogen atmosphere and then solvent was removed under vacuum until an orange crystalline product began to form. After storage in the refrigerator for two days the product was filtered under nitrogen, washed with two 10 ml portions of degassed acetonitrile, dried under vacuum at room temperature and transferred to a dry box for storage. Compounds II, IV and V were prepared in a similar manner and stored in a dry box.

Cu(PHT)Cl$_2$·H$_2$O (III)

CuCl$_2$·2H$_2$O (3.5 g, 20.5 mmol) was dissolved in a minimal amount of hot methanol and the solution added to a solution of PHT (0.50 g, 1.3 mmol) in hot methanol (120 ml). The mixture was heated for 20 min on a steam bath and allowed to stand at room temperature. A small quantity of unidentified brown precipitate was filtered off, the filtrate warmed and allowed to stand at room temperature for several days. A green crystalline product formed which was filtered and air dried.

A green crystalline material was also obtained on reaction of PHT with excess cupric bromide in methanol. This compound appears to be a copper(II) derivative but could not be obtained in a pure enough form and so is not reported.

In reactions of both Cu(NO$_3$)$_2$ and Cu(ClO$_4$)$_2$ (approx 10:1) with PHT under reflux in methanol (undried) copper(II) species were not isolated but instead low yields of products I and II were obtained. Nitrogen gas was evolved during the reaction accom-

panied by a strong smell of *p*-tolualdehyde suggesting that some of the ligand had been hydrolysed. In order to examine the hydrolysis/redox process more closely the following reaction was carried out.

$Cu(NO_3)_3 \cdot 3H_2O$ (7.3 g, 0.03 mol) was dissolved in a mixture of 60 ml water and 130 ml acetonitrile and the solution refluxed. PHT (1.0 g, 0.0025 mol) was added quickly to the refluxing solution. Nitrogen gas evolution occurred almost immediately and the gas was collected by water displacement. Refluxing was continued until gas evolution ceased. Total gas evolution amounted to about 3 mmol (no attempt was made to thermostat the apparatus other than to stabilise the system under reflux before the addition of ligand). The green solution was cooled and reduced in volume until a white precipitate formed. After standing in the refrigerator the white crystalline material was filtered, washed with water, dried and recrystallized from chloroform (A, mp 193–196 °C). Subsequent reactions of this system revealed another product (mp. 180 °C) which was shown to be *p*-toluic acid.

In a similar reaction involving copper(II) perchlorate in CH_3CN/H_2O (70/30) and PHT rapid nitrogen evolution was observed on warming. On cooling the clear, colourless solution deposited a white crystalline material, which was identified as $[Cu(CH_3CN)_4]ClO_4$. The filtrate was extracted with chloroform, dried over anhydrous $CaSO_4$, and the chloroform removed under reduced pressure leaving an oil. The oil was sublimed giving the white solid (A) (recrystallized from chloroform; mp 194–196 °C) as an initial component followed by a second sublimate (mp 180–182 °C) which was shown by its infrared and NMR spectrum to be *p*-toluic acid. [Mass spectral data for A. M/e (rel. int.) 260 (100, P-2), 259(20), 132(56), 115(14), 88(16), 77(9), 64(14), 45(24)].

The ligand DMPH did not react cleanly with methanolic solutions of copper(II) salts, due largely to its lack of solubility in this and other solvents. However similar decomposition reactions were

observed involving nitrogen gas evolution. Both PHT and DMPH reacted readily with copper(I) chloride and bromide in degassed methanol/acetonitrile but the products were found to be extremely sensitive to traces of oxygen and were not fully characterized.

Results and Discussion

The condensation products of 1,4-dihydrazinophthalazine with a variety of aldehydes have been investigated as potential chemotherapeutic agents [12] but very few studies on the coordination chemistry of such systems have been carried out [9, 13]. From our investigations involving the reactivity of such potential ligands toward copper(II) salts it became apparent that sexadentate hydrazones involving periperal donors were capable of binding two copper centres forming binuclear copper(II) complexes [9]. However with ligands involving non-coordinating aromatic Schiff base residues the stability of the corresponding copper(II) complexes was found to be much lower.
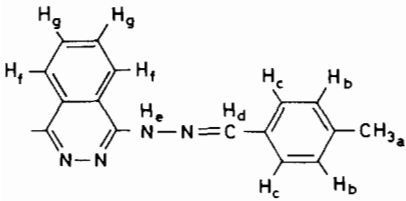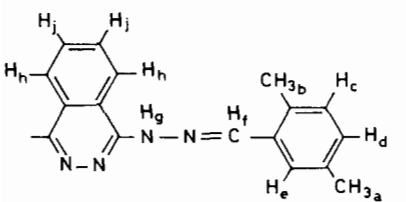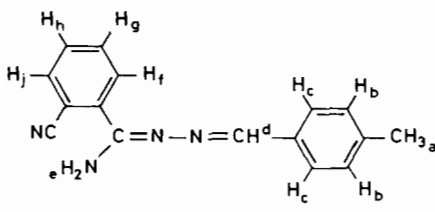
Reaction of copper(II) chloride and bromide with PHT (Fig. 1) in methanol produces copper(II) derivatives, although isolation of the bromide product in an analytically pure form was found to be very difficult. The green chloride complex **III** is considered to be a binuclear derivative, based on its low room temperature magnetic moment. A reasonable way to postulate the structure of this system would be as a binuclear dimer in which two copper(II) centres are sandwiched between two tetradentate ligands. Infrared data (Table II) indicate the presence of terminal copper-chlorine bonds, suggesting the possibility of five- or six-coordinate copper(II) centres. Also the involvement of an apical chlorine bridge between the two copper centres should be considered based on magnetic measurements. An X-ray structural study on crystals of this system has so far been unsuccessful.

TABLE II. Infrared, Electronic Spectral and Magnetic Data

Compound		Infrared (cm^{-1})	
		ν(CN)	Other
I	$Cu(PHT)(NO_3) \cdot H_2O$	1612, 1598, 1580	3410(H_2O), 3230(NH), 1750, 1758($\nu_1 + \nu_4$ NO_3^-)
II	$Cu(PHT)(ClO_4) \cdot 0.5H_2O$	1612, 1598, 1575	3540(H_2O), 3280(NH), 1110, 1052(ClO_4^-)
III	$Cu(PHT)Cl_2 \cdot H_2O$	1615, 1594	3460(H_2O), 335(Cu–Cl)
IV	$Cu(DMPH)(NO_3) \cdot 2H_2O$	1618, 1583, 1570	3390(H_2O), 1755, 1740($\nu_1 + \nu_4$ NO_3^-)
V	$Cu(DMPH)(ClO_4)$	1618, 1577, 1564	3270(NH), 1092, 1045(ClO_4^-)
A	$C_{16}H_{14}N_4$	2232(R–CN)	3230(NH)
		d–d (cm^{-1})^a	μ(BM)(RT)
III	$Cu(PHT)Cl_2 \cdot H_2O$	14800	1.58

^{a} Mull transmittance.

TABLE III. Nuclear Magnetic Resonance Data (ppm in CDCl$_3$)

Compound	δH_a	δH_b	δH_c	δH_d	δH_e	δH_f	δH_g
PHT[a]	2.37s	7.16d 7.26d	7.65d 7.77d	8.46s	10.08 8.23	7.5–8.0m (unsymmetric)	
I Cu(PHT)(NO$_3$)·H$_2$O	1.93s	6.23d 6.33d	6.95d 7.05d	8.23s	11.60s	8.20m	7.77m
II Cu(PHT)(ClO$_4$)·0.5H$_2$O	1.96s	6.23d 6.33d	6.95d 7.05d	8.34s	10.41s	8.15m	7.82m

Compound	δH_a	δH_b	$\delta H_{c,d}$	δH_e	δH_f	δH_g	δH_h	δH_j
DMPH[a]	2.33d 2.36d	2.44d 2.50d	7.10	7.62 7.69	8.22 8.77	10.08 (8.52)	7.8–8.2m (unsymmetric)	
IV Cu(DMPH)(NO$_3$)	1.25s	1.83s	6.51s	7.18s	8.52s		8.00m	7.65m
V Cu(DMPH)(ClO$_4$)	1.20s	1.86s	6.61s	7.29s	8.55s	10.58	8.10m	7.77m

Compound	δH_a	δH_b	δH_c	δH_d	δH_e	$\delta H_{f,g,h,j}$
A C$_{16}$H$_{14}$N$_4$	2.37s	7.15d 7.27d	7.75d 7.85d	8.17d 8.27d	11.53s	7.3–7.7

[a]CD$_2$Cl$_2$ solvent.

Reaction of copper(II) nitrate and perchlorate led to a very different situation. No copper(II) derivatives were isolated on reaction with PHT in methanol and instead low yields of the copper(I) complexes I and II were obtained. In addition nitrogen gas evolution was observed during the reactions. Identical products were obtained by reaction of the appropriate copper-(I) salt with PHT in degassed methanol/acetonitrile mixture in a nitrogen atmosphere. Analogous copper-(I) complexes involving the ligand DMPH were also prepared in a similar manner. Although DMPH reacted smoothly with copper(I) salts its general lack of solubility prevented a satisfactory investigation of its reactivity towards copper(II) salts.

The NMR spectrum of PHT itself (Table III) is characterized by having two resonances associated

with NH protons and a complex and very asymmetric region associated with the fused benzene ring protons. These features suggest that the ligand exists in a tautomeric form in which one proton resides on a phthalazine nitrogen. The NMR spectra of **I** and **II** in chloroform (Table III) indicate significant shifts of all proton resonances with respect to the free ligand. One striking feature of the spectra is the very symmetric nature of all the aromatic proton resonances. Well defined, symmetric pairs of doublets are observed for protons H_b, H_c, shifted upfield from the free ligand values, and symmetric AA'BB' splitting patterns are observed for the fused benzene ring (phthalazine) protons (in contrast to the free ligand). The chemical shifts of the carbon proton resonances for both **I** and **II** are approximately the same but the NH proton resonance is shifted 1.2 ppm further downfield in the case of the nitrate complex.

The symmetric nature of the NMR spectra suggests that in solution the copper(I) complexes are indeed binuclear and that the two metal centres are sandwiched between adjacent pairs of ligands in a symmetric arrangement. The most likely donor atoms are the phthalazine and azomethine nitrogens which would generate four donor sites per metal in such an arrangement (the involvement of only one of these nitrogen donors per metal should not be ruled out). The downfield shift of the NH proton resonance in the nitrate complex indicates a likely difference in the copper coordination sphere in **I** and **II** which can be attributed to possible coordination of the nitrate group, a situation which seems likely in the solid state also. The NMR spectra of the DMPH complexes **IV** and **V** were very similar but again with significant shifts of proton resonances when compared with the free ligand. The NMR spectrum of the free ligand (Table III) is once again characterized by molecular asymmetry indicating the preference of a tautomeric form in which a proton resides on a phthalazine nitrogen. The phthalazine proton resonances in **IV** and **V** however appear as a very symmetric AA'BB' pattern and the methyl resonances appear as two singlets, indicating the symmetric nature of the ligand in these complexes in solution.

The copper(I) complexes **I**, **II**, **IV**, **V** are all diamagnetic and devoid of any visible absorption associated with d–d transitions. The nitrate derivatives exhibit combination ($\nu_1 + \nu_4$) modes indicative of terminally bound nitrate groups [14] while the slight splitting of the ν_3 perchlorate vibrations suggests possible weak coordination or lattice asymmetry involving this group as an ion. Structurally the coordination number and stereochemistry in these systems is difficult to document. General spectral similarities within the series suggest the same basic solid state structure but the establishment of the ligands as tetradentate or bidentate is difficult. In keeping with NMR data it seems likely that in the solid state

binuclear structures exist with two ligands encompassing two metal centres in a symmetric arrangement. Well formed octahedral shaped crystals of **I** and **II** were obtained from reactions of PHT with copper(II) salts in methanol but unfortunately they were not suitable for X-ray structural investigation.

The spontaneous reduction of copper(II) salts by PHT in methanol was of particular interest and distinguishes this type of ligand from the sexadentate hydrazones reported previously [9] where this activity was not observed. The formation of copper(I) derivatives of PHT itself, and not of some oxidation product, is perhaps surprising but parallels similar reactions observed with a series of substituted hydrazones [15] in which the presence of water was indicated to be the controlling factor.

In order to indentify the decomposition products in this reaction the ligand was reacted with twelve equivalents of copper(II) nitrate in aqueous acetonitrile (Experimental). Approximately one equivalent of nitrogen gas was released followed by the formation of compound A and *p*-toluic acid. A similar situation resulted when copper(II) perchlorate was used, except in this case $[Cu(CH_3CN)_4]ClO_4$ precipitated out during the reaction. No copper(I)/PHT complexes were obtained and all the ligand decomposed. The formation of copper(I) acetonitrile complexes is seen here as a driving force in the decomposition reaction which appears to be initiated by the hydrolysis of PHT.

The formation of nitrogen gas appears to be the result of the hydrazine reduction of copper(II). The hydrazine is released by the metal ion mediated hydrolysis of PHT, which occurs with the formation of A and toluic acid. The formation of about one equivalent of nitrogen suggests that hydrolysis occurs at one hydrazone function only. The formation of copper(II) chloride and bromide derivatives with PHT in methanol indicates the enhanced stability of the copper(II) state in the presence of electronegative, coordinated anions. That copper(I) derivatives involving nitrate and perchlorate are produced in methanol is seen as a reflection on the stability of the copper(I)/PHT system in comparison with any copper(I) derivative of A,*p*-tolualdehyde or *p*-toluic acid. Thus, as in the case of other hydrazone systems [15], the reduction, at least in methanol, appears to proceed only until enough copper(I) has been produced to combine with the remaining unhydrolysed ligand. However in aqueous acetonitrile the presence of excess acetonitrile results in the formation of the more stable species $[Cu(CH_3CN)_4]^+$ which prevents the formation of any Cu(I)/PHT species, thus favouring the complete hydrolysis of the ligand.

Despite the large excess of copper(II) salt used in these reactions the hydrolysis appears to involve just one hydrazone site suggesting that the initial coordination of copper(II) occurs on one side of the

molecule only. Also, instead of the formation of a simple monosubstituted phthalazine derivative, rupture of the phthalazine N–N bond occurs with the apparent formation of a substituted cyanobenzene. The identification of **A** (Table III) is based upon CHN analysis (Table I), mass spectral data (Experimental), infrared data (Table II) and NMR data (Table III).

The instability of hydrazone groups towards hydrolysis in the presence of Cu^{2+} ions has been demonstrated with two classes of hydrazine derivatives [15] and appears in part to be the result of the ready reduction of copper(II) by the hydrazine function itself. However hydrolysis reactions involving the azomethine centre in typical Schiff base complexes of copper(II) have been reported previously in a number of cases, indicating the general hydrolytic instability of this functional group in the presence of transition metal centres [16–20]. Presumably coordination of the azomethine nitrogen atom leads to an increase in the electrophilic nature of the azomethine carbon thus facilitating hydrolysis.

Attempts to prepare copper(II) derivatives of 1,4-dihydrazinophthalazine have proved unsuccessful because of the strong reducing tendency of the hydrazine, $-NHNH_2$ functional group. The synthesis of copper(II) hydrazones is possible with sexadentate Schiff base adducts of DHPH in which the peripheral groups are donors and in fact no ligand hydrolysis is observed [9]. However copper(II) complexes of tetradentate hydrazones of 1,4-dihydrazinophthalazine, involving non-coordinating Schiff base residues, are hydrolytically unstable and rapid evolution of nitrogen gas signals imine hydrolysis followed by copper(II) reduction. Since *p*-toluic acid is produced during metal ion mediated hydrolysis of PHT in aqueous acetonitrile the *p*-tolualdehyde, which is produced initially, must act, as expected, as a reducing agent in the presence of excess Cu^{2+} ions. In a separate experiment *p*-tolualdehyde was stirred at room temperature with excess copper(II) nitrate–diethylenetriamine (1:1) in a water/acetonitrile mixture (50/50). After several days a white crystalline product formed in almost quantitative yield, which was shown (mp, NMR) to be *p*-toluic acid. That *p*-toluic acid is not produced to any significant extent in the reactions between PHT

and copper nitrate and perchlorate in methanol probably reflects the absence of acetonitrile, a good ligand for the stabilization of copper(I), and the much smaller concentration of water present in the system.

Acknowledgement

References

1 L. K. Thompson, V. T. Chacko, J. A. Elvidge, A. B. P. Lever and R. V. Parish, *Can. J. Chem., 47*, 4141 (1969).
2 J. C. Dewan and L. K. Thompson, *Can. J. Chem., 58*, 221 (1980).
3 J. C. Dewan and L. K. Thompson, *Can. J. Chem., 60*, 121 (1982).
4 D. V. Bautista, J. C. Dewan and L. K. Thompson, *Can. J. Chem., 60*, 2583 (1982).
5 G. Bullock, F. W. Hartstock and L. K. Thompson, *Can. J. Chem., 61*, 57 (1983).
6 L. K. Thompson, *Can. J. Chem., 61*, 579 (1983).
7 L. K. Thompson, A. W. Hanson and B. S. Ramaswamy, *Inorg. Chem., 23*, 2459 (1984).
8 L. K. Thompson, F. W. Hartstock, P. Robichaud and A. W. Hanson, *Can. J. Chem., 62*, 2755 (1984).
9 P. Robichaud and L. K. Thompson, *Inorg. Chim. Acta, 85*, 137 (1984).
10 A. B. P. Lever, B. S. Ramaswamy and S. R. Pickens, *Inorg. Chim. Acta, 49*, L59 (1980).
11 G. Marongiu and E. C. Lingafelter, *Acta Crystallogr., Sect. B:, 38*, 620 (1982).
12 B. Prescott, G. Lones and G. Caldes, *Antimicrob. Agents Chemother.,* 262 (1968).
13 D. A. Sullivan and G. J. Palenik, *Inorg. Chem., 16*, 1127 (1977).
14 A. B. P. Lever, E. Mantovani and B. S. Ramaswamy, *Can. J. Chem., 49*, 1957 (1971).
15 T. C. Woon, L. K. Thompson and P. Robichaud, *Inorg. Chim. Acta, 90*, 201 (1984).
16 L. Casella and S. Ghelli, *Inorg. Chem., 22*, 2458 (1983).
17 L. Casella and J. A. Ibers, *Inorg. Chem., 20*, 2438 (1981).
18 L. F. Lindoy, *Q. Rev., 25*, 379 (1971).
19 C. J. Hipp and D. H. Busch, in A. E. Martell (ed.), 'Coordination Chemistry', Adv. Chem. Ser. No. 174, American Chemical Society, Washington, D.C., 1978, Chap. 2.
20 A. C. Braithwaite, C. E. F. Rickard and T. N. Waters, *J. Chem. Soc., Dalton Trans.,* 2149 (1975).