Stabilisation of Copper(I) by an Azoimine Ligand: Redox Properties and Reactions of Bis(phenylazoacetaldoximato)bis(phenylacetaldoxime)dicopper(I)

Samudranil Pal, Debkumar Bandyopadhyay, Dipankar Datta, and Animesh Chakravorty*
Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India

The high preference of phenylazoacetaldoxime, MeC(=NOH)N=NPh (HL), for copper(I) is rationalised in terms of electronic and steric factors. The complex $[Cu_2(HL)_2(L)_2]$ (**1**) undergoes a one-electron oxidation at ~0.8 V *vs.* saturated calomel electrode to an unstable $Cu^{II}Cu^{I}$ species. Tertiary phosphines displace HL from (**1**) affording $[CuL(PR_3)_2]$ [R = Ph (**2a**) or C_6H_4Me-*p* (**2b**)]. (**2a**) reacts with HCl to form $[\{Cu(PPh_3)Cl\}_4]$ and with $HClO_4$ to give the complex $[Cu(HL)(PPh_3)_2(ClO_4)]$. All complexes having the chelated CuL or Cu(HL) fragment are shown to have a characteristic low-energy metal-to-ligand charge-transfer transition (700—900 nm).

Known copper complexes with a CuN_4 co-ordination sphere are numerous. In the vast majority of cases the N_4 environment preferentially stabilises copper(II) relative to copper(I), resulting in low copper(II)–copper(I) formal potentials (E_{298}°). By utilising steric and/or electronic factors it has, however, been possible[1–4] to devise small groups of high potential [$E_{298}^{\circ} > 0.5$ V *vs.* saturated calomel electrode (s.c.e.)] CuN_4 complexes. Such species are of peripheral interest in modelling the function of copper oxidases.[5] In the present work we examine the dimeric copper(I) complexes of the azoimine ligand phenylazoacetaldoxime, MeC(=NOH)N=NPh (HL). The origin of the high preference of HL for the copper(I) state is scrutinised. The level of relative copper(I)–copper(II) stability is probed using cyclic voltammetry. The competition between HL and π-acid ligands such as carbon monoxide and teritary phosphines for copper(I) is also examined.

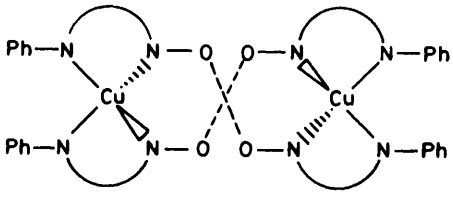
Results and Discussion

Preference for Copper(I).—On mixing copper(II) acetate with HL in methanolic solution spontaneous reduction of copper(II) to copper(I) occurs. The resulting complex,[6] $[Cu^{I}_2(HL)_2(L)_2]$, has structure (1) as determined[7] by *X*-ray crystallography. The stereochemistry of copper(I) is tetrahedral and the two Cu(HL)(L) units are linked by strong O···H···O hydrogen bonds [H atoms not shown in (1)].

Recent structural work[8–12] has shown that the azo-oxime function is a good π-acceptor and that in bis complexes there is a dominant steric interaction between the oxime oxygen of one ligand and the phenyl ring of the adjacent ligand favouring tetrahedral distortion. The π-acidity of HL (or L^-) stabilises[1] the copper(I) state *via* *d*(Cu)–π*(L) bonding. The steric factor which favours tetrahedral distortion in the bis(arylazo-oximates) also favours copper(I) since the natural geometry of the latter in four-co-ordination is tetrahedral. Hence the strong affinity of HL for copper(I).

Charge-transfer Spectra.—In systems where a good level of metal–ligand *d*–π* interaction exists in the ground state, one or more metal-to-ligand charge-transfer (m.l.c.t.) transition(s) is (are) also commonly observed in the visible region, particularly when the ligand is a conjugated chromophore. Among copper(I) bis-chelates, examples include the complexes of 2,2′-bipyridine-type ligands[13,14] and 2-(arylazo)pyridine.[1] Arylazo-oximates of a number of lower-valent (⩽2) metal ions are known[8,9,15–18] to display m.l.c.t. bands in the visible region.

In benzene solution complex (1) shows several allowed bands (Figure 1 and Table 1). The band at 769 nm is readily assigned to a *d*→π* transition and to our knowledge represents the lowest energy reported so far for such a transition in a copper(I) complex. On addition of alkali to an acetonitrile solution of (1), the m.l.c.t. band shifts to even lower energy (860 nm) due to deprotonation. On the other hand in the protonated complex $[Cu(HL)_2]^+$, the band is blue shifted (680 nm). Such shifts apart, the low-energy m.l.c.t. band is a diagnostic feature of the $Cu^{I}L$ chelate ring (Table 1). A m.l.c.t. assignment to the more intense band of (1) at 580 nm is vitiated by its absence in $[CuL(PR_3)_2]$ and related species (see later) as well as in other[6] bis(arylazo-oximates) of copper.



(1)

Cyclic Voltammetry.—Cyclic voltammetry experiments were performed in order to ascertain the redox stability of (1) and to observe a possible copper(II) derivative. The best results were obtained in dichloromethane solvent with a glassy-carbon working electrode. All potentials are referenced to s.c.e.

An oxidative response is seen near 0.8 V, the anodic peak position (E_{pa}) shifting to higher potential on increasing the scan rate (Figure 2 and Table 2). The stoicheiometry of the electrode reaction could not be established by coulometry since attempted coulometry at potentials more positive than that of the anodic peak led to continuous coulomb counts. However the peak height of (1) was compared with that for the Ru^{II}→Ru^{III} oxidation in $[Ru(bipy)_2Cl_2]$ (bipy = 2,2′-bipyridine) under identical conditions. At each scan rate used the two heights agreed to within 10% showing that one electron is transferred per dimer and the electrode reaction can be written as (i). The dependence of the peak potential on scan rate

$$[Cu^{II}Cu^{I}(HL)_2(L)_2]^+ + e^- \longrightarrow [Cu^{I}_2(HL)_2(L)_2] \qquad (i)$$

suggests that the rate of electron transfer is slower than the Nernstian rate. On scan reversal a cathodic response is observed near 0.0 V. The peak height of this response is only half that of the anodic response near 0.8 V. It shifts to lower potential on increasing the scan rate. The process (i) is thus far removed from the reversible situation and the oxidised complex is unstable. We stress that the response at 0.0 V does not appear unless the 0.8 V region is scanned. On recycling, the same two responses

Table 1. Microanalytical and spectroscopic data for the copper(I) complexes

Compound	Analysis (%)[a] C	N	H	Cu	I.r.[b] ν(N–O)/ cm^{-1}	^1H N.m.r.[c] δ(Me)/ p.p.m.	Electronic spectra λ/nm ($\varepsilon^d/dm^3\ mol^{-1}\ cm^{-1}$)
(**1**) $[Cu_2(HL)_2(L)_2]$	49.4 (49.5)	21.4 (21.7)	4.4 (4.1)	16.1 (16.4)	*e*	2.21	769 (1 700), 580 (4 400), 447 (13 200)[f]
(**2a**) $[CuL(PPh_3)_2]$	70.0 (70.4)	5.8 (5.6)	5.0 (5.1)	8.7 (8.5)	1 225	2.25	780 (200), 470 (15 200)[g]
(**2b**) $[CuL\{P(C_6H_4Me\text{-}p)_3\}_2]$	71.3 (72.0)	5.1 (5.0)	6.1 (6.0)	7.8 (7.6)	1 225	2.28	760 (170), 440 (12 300), 280 (31 900)[h]
(**3**) $[CuL(Ph_2PCH_2CH_2PPh_2)]$	65.9 (65.4)	6.6 (6.7)	5.0 (5.2)	10.3 (10.2)	1 220	2.53	740 (230), 460 (20 100), 290 (15 850)[i]
(**5**) $[Cu(HL)(PPh_3)_2(ClO_4)]$	62.4 (62.1)	5.0 (4.9)	4.8 (4.6)	7.7 (7.5)	*j*	2.45	438 (5 800), 275 (24 900)[h]
(**6**) $[Cu(HL)_2]ClO_4{\cdot}2H_2O$	36.4 (36.6)	16.1 (16.0)	4.4 (4.2)	11.9 (12.1)	1 260	2.43	680 (2 000), 542 (5 800), 428 (10 750)[g]

[a] Calculated values are given in parentheses. [b] KBr disc. [c] $CDCl_3$ as solvent and $SiMe_4$ as internal standard. [d] Per Cu atom. [e] This complex gives only very broad and ill defined i.r. spectra. [f] In benzene. [g] In acetone. [h] In methanol. [i] In chloroform. [j] No band near 1 200 cm^{-1}.

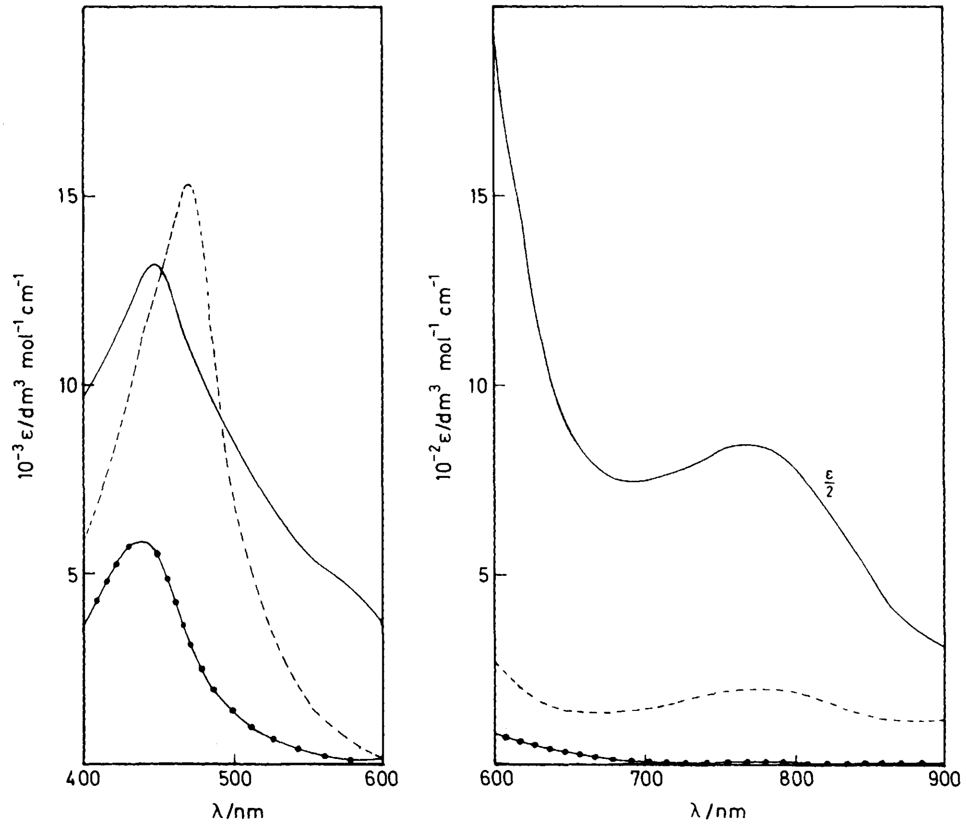


Figure 1. Electronic spectra of $[Cu_2(HL)_2(L)_2]$ (**1**) (——) (in benzene), $[CuL(PPh_3)_2]$ (**2a**) (– – – –) (in acetone), and $[Cu(HL)(PPh_3)_2(ClO_4)]$ (**5**) (– · – · –) (in methanol)

are repeatedly seen. The E_{pa} values (Table 2) of reaction (i) diagnose complex (**1**) as a high-potential CuN_4 species.

Reaction with Tertiary Phosphines (PR_3).—Experiments were performed to establish whether some or all of the ligands in (**1**) can be replaced by π-acids. Selected reactions are shown in the Scheme; all the arylazo-oximates shown have been isolated in pure form.

Carbon monoxide is unreactive towards (**1**) in acetone even with boiling. Tertiary phosphines however react readily affording the mixed complexes $[CuL(PR_3)_2]$ [R = Ph (**2a**) or C_6H_4Me-*p* (**2b**)] and (**3**). In palladium(II) complexes tertiary phosphines are known[16] to cleave selectively the Pd–NPh bond of chelated arylazo-oximes. In the case of copper(I), the strong metal–PR_3 affinity drives the reaction further and HL is eliminated. Complexes (**2**) and (**3**) have optimum levels of stability and are unaffected by excess phosphine. They are not electroactive even up to 1.40 V. The proposed chelation of L in (**2**) and (**3**) is supported by the appearance of the m.l.c.t. band near 750 nm (Figure 1 and Table 1) together with the strong and characteristic[16–19] ν(N–O) band (Table 1). The relatively low intensity of the m.l.c.t band in (**2**) and (**3**) [compared to that of (**1**)] is understandable on two counts: (*a*) in (**2**) and (**3**) there is only one CuL chelate ring as opposed to two such rings (per

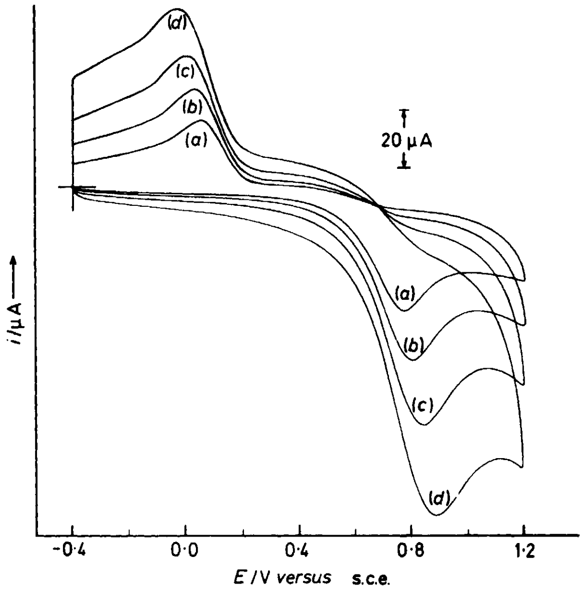
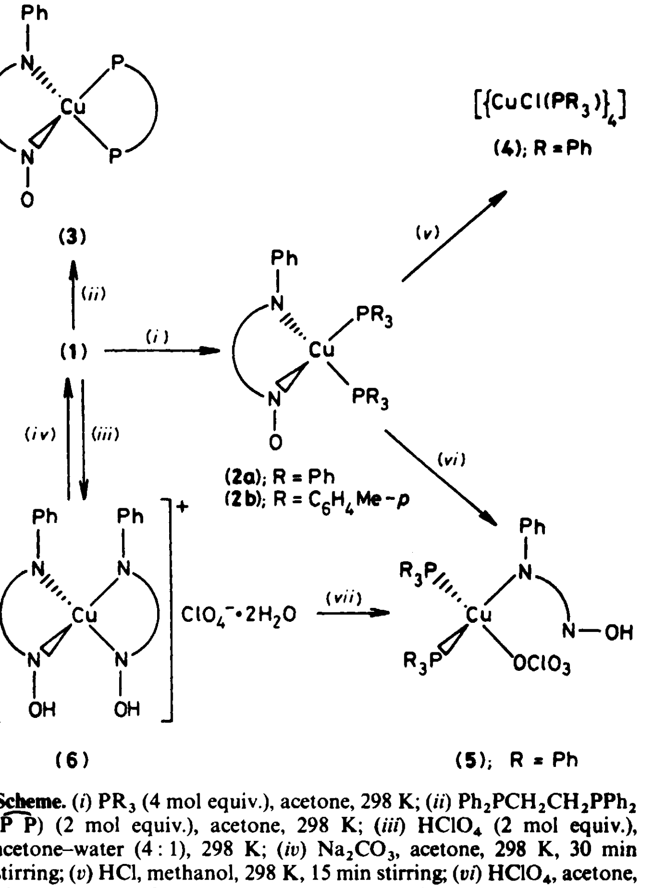


Figure 2. Cyclic voltammograms of $[Cu_2(HL)_2(L)_2]$ (**1**) in dichloromethane at a glassy-carbon electrode at scan rates v = (*a*) 0.050, (*b*) 0.100, (*c*) 0.200, and (*d*) 0.400 V s^{-1}



Scheme. (*i*) PR_3 (4 mol equiv.), acetone, 298 K; (*ii*) $Ph_2PCH_2CH_2PPh_2$ ($\widehat{\text{P P}}$) (2 mol equiv.), acetone, 298 K; (*iii*) $HClO_4$ (2 mol equiv.), acetone–water (4 : 1), 298 K; (*iv*) Na_2CO_3, acetone, 298 K, 30 min stirring; (*v*) HCl, methanol, 298 K, 15 min stirring; (*vi*) $HClO_4$, acetone, 298 K; (*vii*) PR_3 (2 mol equiv.), acetone–ethanol (5 : 1), 298 K

copper) in (**1**), and (*b*) in (**2**) and (**3**) the tertiary phosphine can partially weaken the charge-transfer interaction between L and copper(I) through competitive demand on electrons.[14]

The chelate ring in (**2**) can be cleaved and eliminated by HCl resulting in the formation of the chloride-bridged tetramer[20] (**4**). This can be rationalised as follows: (*a*) protonation of the oximato-function, (*b*) cleavage of the Cu–NOH bond by Cl^-, and (*c*) subsequent cleavage of Cu–NPh to accommodate chloride bridging. The first two steps have good analogies[16] in the chemistry of palladium(II) arylazo-oximates. More direct evidence is the reaction (**2**)→(**5**) brought about by $HClO_4$. In this case step (*c*) is unavailable. As expected, complex (**5**) with unidentate HL shows neither the low-energy m.l.c.t. band (Figure 1) nor the high-energy (~ 1 200 cm^{-1}) N–O stretch. On the other hand, the ν_3 band of ClO_4^- is clearly split into a relatively sharp and intense doublet (1 115 and 1 035 cm^{-1}) and ν_1 appears with considerable intensity (920 cm^{-1}). Thus the bound ClO_4^- ion in (**5**) has the required C_{3v} symmetry. In methanol solution (**5**) acts as a 1 : 1 electrolyte (Λ_M = 84 Ω^{-1} cm^2 mol^{-1}) evidently due to solvolysis. Complex (**5**) can also be obtained by the alternative route (**2**)→(**6**)→(**5**). The 1 : 1 electrolytic (Λ_M = 132 Ω^{-1} cm^2 mol^{-1} in acetonitrile) complex (**6**) has a broad ClO_4^- ν_3 band around 1 100 cm^{-1} and ν_1 is not observed suggesting lack of any major co-ordination by ClO_4^-.

Table 2. Cyclic voltammetric data for $[Cu_2(HL)_2(L)_2]$ (**1**) in CH_2Cl_2 at a glassy-carbon electrode with NEt_4ClO_4 as supporting electrolyte

v/V s^{-1}	0.050	0.100	0.200	0.400
E_{pa}/V	0.770	0.810	0.850	0.890
E_{pc}/V	0.060	0.030	0.010	−0.030

Concluding Remarks.—The arylazo-oximates of copper are members of the small class of high-potential CuN_4 species. A comparison with bis complexes of other unsaturated *NN′*-ligands (α-di-imine or azo-imine) such as 2,2′-bipyridine (bipy) and 2-(phenylazo)pyridine (pap) is in order. From bond distance and redox potential data it has been suggested[21] that the π-acidity towards ruthenium(II) followed the order bipy < pap < HL. This order should also apply to copper(I). Both copper(II) and copper(I) form bis complexes with bipy and pap, however $[Cu(pap)_2]^{2+}$ is more readily reduced[1] than $[Cu(bipy)_2]^{2+}$. On the other hand HL stabilises only copper(I). The behaviour of the three ligands towards copper qualitatively correlates with π-acidity considerations alone. Steric factors must also be important but unfortunately the relative steric requirements of the three ligands are not readily assessed.

Experimental

Starting Materials.—Complex $[Cu_2(HL)_2(L)_2]$ (**1**) was prepared as described previously.[6] Dichloromethane and tetraethylammonium perchlorate used in the electrochemical work were prepared by standard methods.[22] Dinitrogen was purified by bubbling through an alkaline dithionite solution.

Physical Measurements.—Electronic spectra were recorded with a Pye-Unicam SP8-150 or a Cary 17D spectrophotometer and i.r. spectra (KBr disc, 4 000—400 cm^{-1}) with a Beckman IR-20A spectrophotometer. N.m.r. spectra were recorded with a Varian T-60A spectrometer (60 MHz). Cyclic voltammetric measurements were carried out using a PAR model 174A polarographic analyser, model 175 universal progammer, model RE0074 *X-Y* recorder, and a model 377A cell system. The experiments were carried out at 298 K under a dinitrogen atmosphere in a three-electrode configuration with a PAR G0021 glassy-carbon working electrode. The potentials reported are uncorrected for the junction contribution.

Synthesis of Complexes and their Reactions.—(Phenylazo-acetaldoximato)bis(triarylphosphine)copper(I): *reaction* (**1**)→(**2**).

Triarylphosphine (2 mmol) was added pinchwise to [$Cu_2(HL)_2(L)_2$] (**1**) (0.5 mmol) in acetone (50 cm^3) with constant stirring. The wine red solution was allowed to evaporate at room temperature to give a dark red crystalline complex which was filtered off and recrystallised from acetone–ethanol (3:1). Yield, 60—70%.

[1,2-*Bis(diphenylphosphino)ethane*](*phenylazoacetaldoximato*)*copper*(I): *reaction* (**1**)→(**3**). The red crystalline complex (**3**) was prepared in the above manner using 1 mmol of $Ph_2PCH_2CH_2PPh_2$ and 0.5 mmol of (**1**). Yield, 60%.

Bis(phenylazoacetaldoxime)copper(I) *perchlorate dihydrate*, (**6**). A cold methanolic solution (20 cm^3) of $Cu(ClO_4)_2{\cdot}6H_2O$ (2 mmol) was added to a cold methanolic solution (25 cm^3) of HL (5 mmol) with constant stirring. The violet mixture was filtered and the filtrate kept in the refrigerator for several days. The gummy mass so obtained was dissolved in acetone–water (4:1) and when left in air the solution deposited a black crystalline compound which was washed thoroughly with benzene and water and then dried in vacuum over P_4O_{10}. Yield, 60%.

Reaction (**1**)→(**6**). Perchloric acid (8 cm^3; 0.5 mol dm^{-3}) was added to [$Cu_2(HL)_2(L)_2$] (**1**) (1 mmol) in acetone–water (4:1, 50 cm^3). The violet mixture was left for aerial evaporation. The dark crystalline solid that separated out was filtered off and washed thoroughly with benzene and water. Yield, 80%.

Reaction (**6**)→(**1**). [$Cu(HL)_2$]$ClO_4{\cdot}2H_2O$ (**6**) (100 mg) was dissolved in acetone (10 cm^3) and sodium carbonate (50 mg) was added pinchwise with constant stirring. After 30 min the crystalline precipitate of [$Cu_2(HL)_2(L)_2$] (**1**) was filtered off and washed thoroughly with water and dried in vacuum over P_4O_{10}. Yield, 50 mg.

Reaction (**2a**)→(**4**). Concentrated hydrochloric acid (0.01 cm^3) was diluted in methanol (10 cm^3). To this solution, [$CuL(PPh_3)_2$] (0.1 mmol) was added pinchwise with constant stirring. White crystalline [$\{CuCl(PPh_3)\}_4$] (**4**) immediately started to precipitate. It was filtered off, washed with methanol, and dried in vacuum over P_4O_{10}. Yield, 80%.

Reaction (**2a**)→(**5**). To [$CuL(PPh_3)_2$] (75 mg) in acetone (25 cm^3) was added acetone (5 cm^3) containing $HClO_4$ (10 mg) slowly with constant stirring. Absolute ethanol (5 cm^3) was then added and the mixture left for aerial evaporation. The dark red crystals so obtained were filtered off, washed thoroughly with benzene and water, and dried in vacuum. Yield, 60 mg.

Reaction (**6**)→(**5**). To [$Cu(HL)_2$]$ClO_4{\cdot}2H_2O$ (0.1 mmol) dissolved in acetone (25 cm^3), triphenylphosphine (0.2 mmol) was added pinchwise with stirring. Absolute ethanol (5 cm^3) was then added and the mixture left in air for evaporation. The dark red crystals so obtained were washed thoroughly first with benzene to remove [$Cu_2(HL)_2(L)_2$] and free HL formed in the reaction and then with water. The compound was dried in vacuum over P_4O_{10}. Yield, 75%.

Acknowledgements

We thank the Department of Science and Technology (New Delhi) and the Council of Scientific and Industrial Research (New Delhi) for financial assistance.

References

1 D. Datta and A. Chakravorty, *Inorg. Chem.*, 1983, **22**, 1085.
2 P. J. Burke, K. Henrich, and D. R. McMillin, *Inorg. Chem.*, 1982, **21**, 1881.
3 T. N. Sorell and D. L. Jameson, *Inorg. Chem.*, 1981, **20**, 1014.
4 B. R. James and R. J. P. Williams, *J. Chem. Soc.*, 1961, 2007.
5 B. G. Malmstrom in 'New Trends in Bioinorganic Chemistry,' eds. R. J. P. Williams and J. R. R. F. Da Silva, Academic Press, New York, 1978, p. 59.
6 S. Gupta, K. C. Kalia, and A. Chakravorty, *Inorg. Chem.*, 1971, **10**, 1534.
7 M. H. Dickman and R. J. Doedens, *Inorg. Chem.*, 1980, **19**, 3112.
8 D. Bandyopadhyay, P. Bandyopadhyay, A. Chakravorty, F. A. Cotton, and L. R. Falvello, *Inorg. Chem.*, 1983, **22**, 1315.
9 A. R. Chakravarty, A. Chakravorty, F. A. Cotton, L. R. Falvello, B. K. Ghosh, and M. Tomas, *Inorg. Chem.*, 1983, **22**, 1892.
10 D. Bandyopadhyay, P. Bandyopadhyay, A. Chakravorty, F. A. Cotton, and L. R. Falvello, *Inorg. Chem.*, 1984, **23**, 1785.
11 D. Bandyopadhyay, P. Bandyopadhyay, A. Chakravorty, F. A. Cotton, L. R. Falvello, and S. Han, *J. Am. Chem. Soc.*, 1983, **105**, 6327.
12 T. Roy and S. P. Sengupta, *Cryst. Struct. Commun.*, 1980, **9**, 965.
13 J. R. Kirchhoff, R. E. Camache, jun., M. W. Blaski, A. A. Del Paggio, R. K. Lengel, and D. R. McMillin, *Inorg. Chem.*, 1983, **22**, 2380.
14 S. Kitagawa and M. Munakata, *Inorg. Chem.*, 1981, **20**, 2261.
15 A. R. Chakravarty and A. Chakravorty, *Inorg. Chem.*, 1981, **20**, 3138; *Inorg. Nucl. Chem. Lett.*, 1979, **15**, 307.
16 P. K. Mascharak and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1980, 1698.
17 P. Bandyopadhyay, P. K. Mascharak, and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1981, 623.
18 P. Bandyopadhyay, P. K. Mascharak, and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1982, 675.
19 K. C. Kalia and A. Chakravorty, *Inorg. Chem.*, 1968, **7**, 2016.
20 K. L. Kalra and M. R. Churchill, *Inorg Chem.*, 1974, **13**, 1899.
21 S. Goswami, R. N. Mukherjee, and A. Chakravorty, *Inorg. Chem.*, 1983, **22**, 2825.
22 D. Datta, P. K. Mascharak, and A. Chakravorty, *Inorg. Chem.*, 1981, **20**, 1673.

Received 6*th March* 1984; *Paper* 4/379