Synthesis, Characterisation, and Electrochemical Studies of a Dioxo-bridged Molybdenum(V) Glycinate. Generation of an Oxo-bridged Mo^{V}–Mo^{VI} Species

Muktimoy Chaudhury
Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700032, India

The binuclear compound $[Mo_2O_4(glyO)_2(H_2O)_2]$ (glyO = $NH_2CH_2COO^-$), has been prepared and characterized. The aqueous solution of the compound is stable for at least 24 h when the pH of the solution is maintained above 5.5. Below pH 5.5, the compound in aqueous solution undergoes proton-assisted oxidation to a dimeric Mo^{V}–Mo^{VI} species giving a new electronic absorption band at 850 nm (ε 241 $dm^3 mol^{-1} cm^{-1}$) which is believed to be due to Mo^{V}–Mo^{VI} intervalence charge transfer. The kinetics of this oxidation have been studied in aqueous solution in the pH range 5.0—3.7. The oxidation step is preceded by the formation of a protonated species $[Mo_2O_4(glyO)_2(H_2O)_2H]^+$ and is first-order dependent on hydrogen ion concentration. The second-order rate constant is 2.52 $dm^3 mol^{-1} s^{-1}$ at 25 °C, I = 0.1 mol dm^{-3}. The Mo^{V}–Mo^{VI} compound could not be isolated in the solid state. Cyclic voltammetric and magnetic studies of the compounds are described.

It is now well established that molybdenum participates in a number of biochemical reactions associated with the functioning of at least six enzymes, which are distributed among bacteria, plants, mammals *etc.*[1-3] Although some molybdenum(v) has been detected by e.s.r.[4-8] in four of the enzymes in the presence of substrate, the oxidation state(s) of the molybdenum atom in the native enzymes is still not clearly understood. At present it is generally accepted that the valency of molybdenum in these enzymes alternates between Mo^{VI} and Mo^{IV} states during active electron transport. The redox potentials determined for xanthine oxidase[9,10] and nitrate reductase[11] confirm that the metal ion readily undergoes reversible one- or two-electron reduction, and at some stage of reduction the enzymes contain Mo^{V}. Several Mo^{V} compounds that mimic some of the properties of enzymes have been reported.[12,13]

In this paper we report the preparation and spectral characteristics of di-μ-oxo-bis[aqua(glycinato-*ON*)oxomolybdenum(v)], $[Mo_2O_4(glyO)_2(H_2O)_2]$ (glyO = $NH_2CH_2COO^-$), together with an investigation of its redox and electrochemical behaviour in aqueous acidic medium.

Experimental

All reactions and physical measurements were carried out in doubly distilled water. All chemicals were analytical grade and used without further purification.

Infrared spectra were recorded as KBr discs with a Beckman IR-20A spectrometer. Electronic spectra were recorded with a Pye Unicam model SP8-150 spectrophotometer. Proton n.m.r. spectra were obtained on a Varian model T-60 spectrometer. Magnetic susceptibility was measured on a Gouy balance with $Co[Hg(SCN)_4]$ as calibrant or by Evans method.[14] Cyclic voltammetric measurements were made with a PAR 174A polarographic analyser, PAR 175 universal programmer, and a PAR RE 0074 XY recorder. The three electrode measurements were carried out using a Metrohm E410 hanging mercury drop electrode as the working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode (s.c.e.). For coulometry a mercury pool electrode was used. All measurements were performed in solutions which were 0.1 mol dm^{-3} in NaCl at 298 K under a nitrogen atmosphere. The potentials reported in this paper were uncorrected for junction potentials.

*Preparation of Di-μ-oxo-bis[aqua(glycinato-*ON*)oxomolybdenum*(v)], $[Mo_2O_4(glyO)_2(H_2O)_2]$.—Glycine (1.5 g, 20 mmol) was dissolved in water (25 cm^3) to which was added sodium molybdate dihydrate (4.84 g, 20 mmol) dissolved in water (20 cm^3). The solution was cooled to 5 °C and the pH carefully brought to 6.0 (monitored by a pH meter) by the slow addition of a 4 mol dm^{-3} sodium hydroxide solution. To the stirred solution sodium dithionite (1.7 g) dissolved in water (15 cm^3) was added. The solution developed a deep orange colour which was then filtered. Isopropyl alcohol (40 cm^3) was added to the filtrate and on keeping the mixture in an ice chest for 3 h a deep orange layer separated at the bottom. After decantation of the supernatant the orange layer was dissolved in a minimum volume of water and was again treated with an equal volume of $Pr^{i}OH$. The orange layer obtained after cooling for 2 h, on trituration, gave a brown compound in microcrystalline form. The compound was recrystallised twice from water-$Pr^{i}OH$ (1 : 1 v/v) and dried in vacuum to achieve satisfactory analytical results (Found: C, 10.4; H, 2.85; Mo, 43.65; N, 6.20. $C_4H_{12}Mo_2N_2O_{10}$ requires C, 10.90; H, 2.75; Mo, 43.60; N, 6.35%). Yield, 0.6 g.

Kinetic Measurements.—Fresh solutions of $[Mo_2O_4(glyO)_2(H_2O)_2]$ (*ca.* 10^{-3} mol dm^{-3}) in doubly distilled water were prepared before kinetic runs were taken. The pH of the solutions were adjusted between 5.0 and 3.7 with 0.2 mol dm^{-3} sodium acetate–acetic acid buffer, and the ionic strength was maintained at 0.1 mol dm^{-3} with sodium perchlorate. The rate of increase in concentration of the mixed-valent Mo^{V}–Mo^{VI} species was followed at 850 nm, where it has a strong absorption band (ε 241 $dm^3 mol^{-1} cm^{-1}$). Kinetic runs were taken under pseudo-first-order conditions in a thermostatted cell controlled at 25 ± 0.1 °C.

Coulometric Reduction of $[Mo_2O_4(glyO)_2(H_2O)_2]$.—20 cm^3 of a solution of the molybdenum complex (1.25×10^{-3} mol dm^{-3}) adjusted to pH 5.6 by acetate buffer and containing 0.1 mol dm^{-3} of NaCl was electrolysed at a constant potential of −1.1 V *vs.* s.c.e. using a mercury pool working electrode to a constant coulomb count. The ratio of this count to the calculated count is equal to *n*, the total number of electrons transferred.

Results and Discussion

An attempt by Melby[15] to prepare $[Mo_2O_4(glyO)_2(H_2O)_2]$ from $MoCl_5$ resulted in a brown intractable sludge whose i.r. spectrum even lacked ligand absorptions. Our initial attempts to

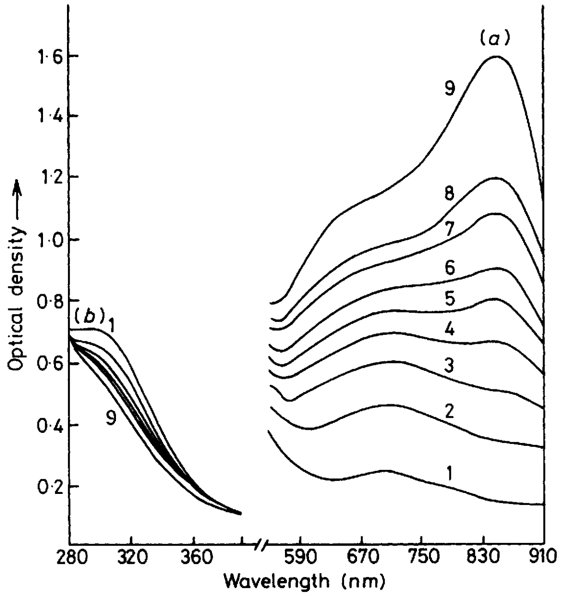
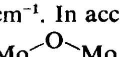


Figure 1. Time-interval spectra of $[Mo_2O_4(glyO)_2(H_2O)_2]$ in aqueous solution at pH 4.48. Concentrations of the solutions: (*a*) 6.6 × 10^{-3} mol dm^{-3}, (*b*) 1.32 × 10^{-4} mol dm^{-3}. Initial scan (1), 15 (2), 30 (3), 45 (4), 60 (5), 75 (6), 115 (7), 175 min (8), and 24 h (9)

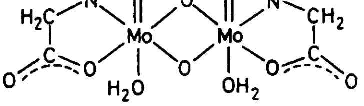
prepare this compound using $[NH_4]_2[MoOCl_5]$ were also unsuccessful. By the present method a reasonable yield (50%) of the crude product was obtained which however substantially depleted during two recrystallizations. The compound is hygroscopic and is stable for several months when kept in the absence of air. The aqueous solution of the compound when prepared in degassed doubly distilled water is stable for at least 24 h when the pH is maintained above 5.5. The compound is diamagnetic.

Infrared Spectra.—Of particular interest in the oxomolybdenum(V) species are two vibrations due to terminal Mo=O stretches in the region 900—1 000 cm^{-1}.[16-19] The complex $[Mo_2O_4(glyO)_2(H_2O)_2]$ shows two such bands at 980 and 920 cm^{-1}. In accordance with the vibrations reported [17,20,21] for a  $Mo\overset{O}{\underset{O}{\lessgtr}}Mo$ moiety, a weak band observed at 470 cm^{-1} and a strong one at 710 cm^{-1} are due to the symmetric and antisymmetric vibrational modes respectively. Two medium intensity bands appeared at 3 210 cm^{-1} [$\nu(NH_2)$] and 1 610 cm^{-1} [$\delta(NH_2)$] which are indicative of amino-group co-ordination. A broad band centred at 3 420 cm^{-1} is assigned to ν(OH). The carboxylic group here is of unidentate nature as the separation between $\nu_{asym}(CO_2^-)$ (1 625 cm^{-1}) and $\nu_{sym}(CO_2^-)$ (1 405 cm^{-1}) is 220 cm^{-1}, a value greater than that due to the free ligand (197 cm^{-1}).[22] The results clearly show that glycinate in this complex acts as a bidentate ligand co-ordinating through the amino-nitrogen and unidentate carboxylic group.

Electronic Absorption Spectra.—The electronic spectrum of $[Mo_2O_4(glyO)_2(H_2O)_2]$ in aqueous solution at pH 5.5 is characterized by two bands at 306 nm (ε 4 240 dm^3 mol^{-1} cm^{-1}) and 695 nm (ε 36 dm^3 mol^{-1} cm^{-1}). Similar bands at *ca.* 300 and *ca.* 700 nm with comparable molar extinctions are well documented in the literature [15,23] for Mo^{V} amino-acid complexes. No change in spectral characteristics of the solution at pH 5.5 is noted at least for 24 h. On longer standing in air the solution gradually becomes colourless due to oxidation to the Mo^{VI} state. The compound remains stable in the pH range 5.5—6.8. At a pH of less than 5.5, the original orange colour of the solution gradually changes to green. The rate of colour change is faster, the lower the pH of the solution. Figure 1 represents the interval scan spectra of the compound in aqueous solution at pH 4.48. It may be noted that the initial peak positions for the fresh solution (spectrum 1) are at 306 and 695 nm. However, with the passage of time the intensity of the band at 306 nm gradually decreases with concomitant increase in the intensity of the band at 695 nm together with the appearance of a new band at 850 nm. After *ca.* 24 h, the band at 306 nm has completely vanished, and that at 850 nm has developed into a strong band. This new band at 850 nm (ε 241 dm^3 mol^{-1} cm^{-1}) is of particular interest to us. We assume that this new low-energy band exhibited by the green solution at higher acidity is due to Mo^{V}–Mo^{VI} intervalence charge transfer which results as a sequel to partial aerial oxidation of the compound.

Similar low-energy bands have also been observed in the visible to near-i.r. region of the electronic spectra of a number of mixed-valence compounds, for example pyrazine-bridged diruthenium-type ions [24] and biferrocene molecules.[25] According to Hush [26] these bands are due to intervalence transfer transitions where light-induced electron transfer occurs between different valence state sites. In the context of molybdenum chemistry, to our knowledge there exist no examples of a Mo^{V}–Mo^{VI} species in the literature. However, two different groups of workers have investigated formal Mo^{I}–Mo^{0} compounds. For example Stone and co-workers [27] have isolated a series of η^7-cycloheptatrienylmolybdenum complexes, $[Mo_2(\mu\text{-}X)_3(\eta^7\text{-}C_7H_7)_2]$ (X = Cl, Br, or I). These compounds absorb strongly in the region 950—1 380 nm and photoelectron spectroscopic studies have established that these are Mo^{I}–Mo^{0} species with a localised trapped-valence ground state. A similar conclusion has been reached for $[(\eta^3\text{-}C_7H_7)(CO)_2Mo(OR)_3Mo(\eta^7\text{-}C_7H_7)]$ (R = alkyl) by Zeigler and co-workers [28] from e.s.r. studies. Since in our case the isolation of the Mo^{V}–Mo^{VI} species in the solid state was unsuccessful, the mixed valence in this compound is further examined in solution by cyclic voltammetry and n.m.r. studies (see later).

Thus on the basis of elemental analyses, i.r., electronic spectral features, and diamagnetic behaviour, (I) appears to be the structure of the compound.



(I)

Electrochemical Behaviour.—Figure 2 shows the cyclic voltammogram of $[Mo_2O_4(glyO)_2(H_2O)_2]$ (10^{-3} mol dm^{-3}) in water with 0.1 mol dm^{-3} NaCl as supporting electrolyte at pH 5.6. In the potential range 0 to −1.4 V at a scan rate of 50 mV s^{-1}, a large cathodic peak at −0.90 V* and a relatively weak anodic peak at −0.42 V have been observed. The cathodic wave at −0.90 V appears to involve transfer of two mol of electrons per mol of the molybdenum(V) dimer as evident from the large peak current and steep initial slope of the wave. This has been confirmed from coulometric reduction of $[Mo_2O_4(glyO)_2(H_2O)_2]$ at pH 5.6 at a potential of −1.1 V *vs.* s.c.e. which shows that the number of electrons transferred per mol is 1.8. This would mean that the Mo^{V}–Mo^{V} species undergoes two-electron reduction to a Mo^{IV} species which is

---

*All potentials were measured *vs.* s.c.e.

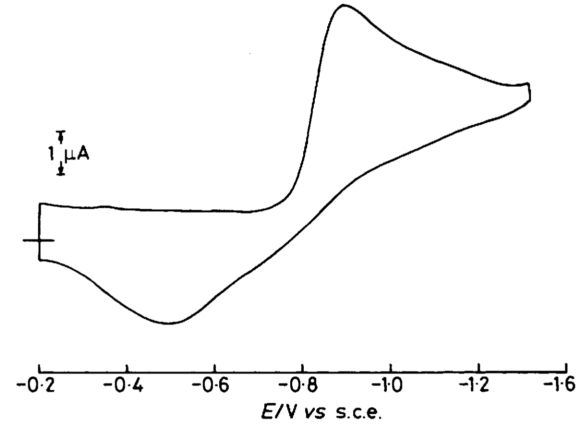
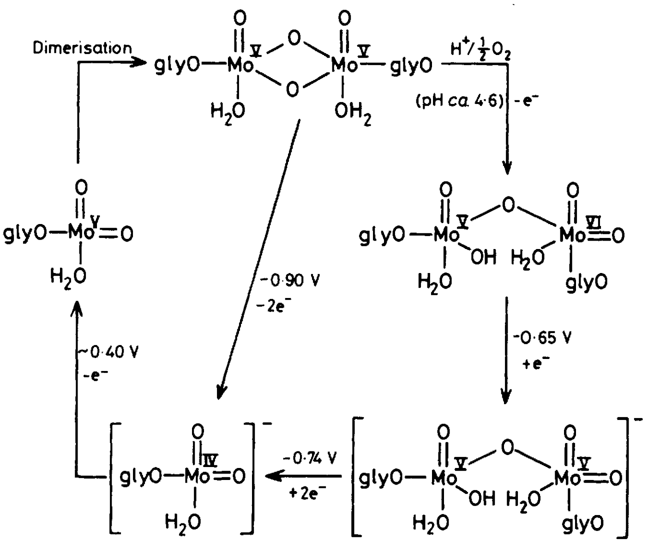


Figure 2. Cyclic voltammogram of $[Mo_2O_4(glyO)_2(H_2O)_2]$ (10^{-3} mol dm^{-3}) in water containing 0.1 mol dm^{-3} NaCl at pH 5.6 at a scan rate of 50 mV s^{-1}

in turn oxidised to a Mo^V species in the anodic sweep at −0.42 V. Since the ratio of the cathodic to anodic current (I_{pc}/I_{pa}) is almost 2, we infer that the oxidation product is a monomeric Mo^V complex.[29]

The cyclic voltammogram of the proposed Mo^V–Mo^{VI} species is shown in Figure 3 {voltammogram is recorded after 2 h of dissolution of $[Mo_2O_4(glyO)_2(H_2O)_2]$ in water at pH 4.6 with 0.1 mol dm^{-3} NaCl as the supporting electrolyte}. The voltammogram consists of two cathodic peaks at −0.65 and −0.74 V and an anodic peak at −0.38 V. It appears that at the first stage of reduction, that is, at −0.65 V, the Mo^V–Mo^{VI} complex reduces to a Mo^V–Mo^V complex (different from the original Mo^V–Mo^V complex) which at −0.74 V undergoes further reduction to a Mo^{IV} species. This Mo^{IV} species appears to be identical to that obtained by reduction of $[Mo_2O_4(glyO)_2(H_2O)_2]$ at −0.90 V because in both the cases oxidation of the Mo^{IV} to Mo^V species takes place at −0.40 V (the slight difference in the potentials, −0.38 against −0.42 V, is most likely due to the difference in pH of the medium). The monomeric Mo^V species is dimerized to the more stable $[Mo_2O_4(glyO)_2(H_2O)_2]$. The redox processes are schematically shown below in Scheme 1.



Scheme 1.

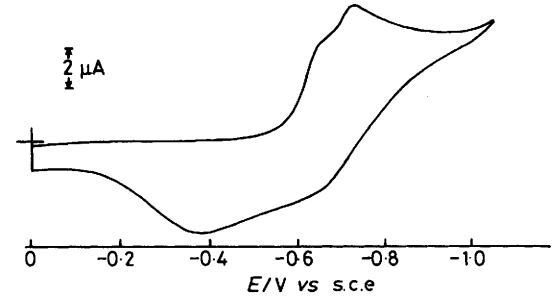
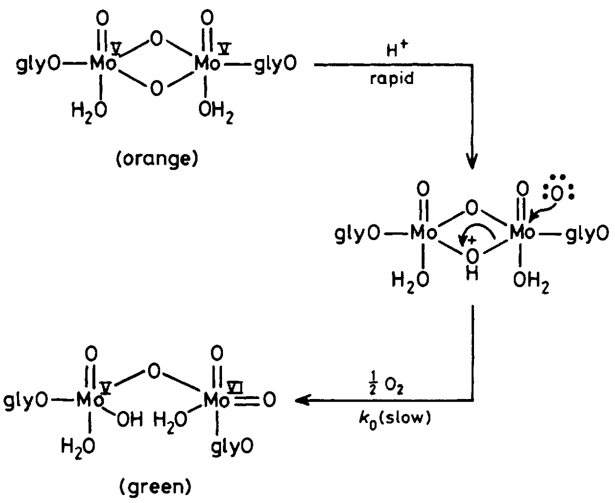


Figure 3. Cyclic voltammogram of $[Mo_2O_4(glyO)_2(H_2O)_2]$ (10^{-3} mol dm^{-3}) in water containing 0.1 mol dm^{-3} NaCl at pH 4.6. Voltammogram at a scan rate of 10 mV s^{-1} taken 2 h after dissolution of the compound

Kinetics of the Proton-assisted Oxidation of $[Mo_2O_4(glyO)_2(H_2O)_2]$.—The rate of proton-assisted aerial oxidation of $[Mo_2O_4(glyO)_2(H_2O)_2]$ from orange to green below pH 5.5 increases with decrease in pH. However, at pH <3.6, the solution rapidly becomes blue and the spectrum lacks the band at 850 nm which is monitored for kinetic studies. We therefore restricted our kinetic measurements to the pH range 5.0—3.7. The first-order plots of log ($A_\infty - A_t$) against time (t) are linear over 80% of the course of reaction, where A_∞ and A_t are absorbances at 850 nm after 24 h and at a time t respectively. The first-order rate constant $k_{obs.}$ is dependent on $[H^+]$ in the pH range studied. The variation in glycinate concentration at constant pH is found to have an insignificant effect on the rate of oxidation.

From these observations it may be concluded that in the pH range 5.0—3.7 protonation of $[Mo_2O_4(glyO)_2(H_2O)_2]$ takes place. The protonated species is then attacked by the dissolved oxygen in water, giving the Mo^V–Mo^{VI} species as shown in Scheme 2 below. Considering the pseudo-first-order condition of the experiment, the observed rate constant can be expressed by $k_{obs.} = k_0[H^+]$. Thus a plot of $k_{obs.}$ *vs.* $[H^+]$ should yield a straight line from which k_0 can be evaluated. In the pH range 5.0—3.7, a plot of $k_{obs.}$ *vs.* $[H^+]$ gives a good linear fit of data passing through the origin. The second-order rate constant, k_0, evaluated from the slope is 2.52 dm^3 mol^{-1} s^{-1}.



Scheme 2.

The formation of intermediate Mo^{V}–Mo^{VI} species has also been proposed [30,31] in studying the kinetics of oxidation of $[Mo_2O_4(edta)]^{2-}$ (edta = ethylenediaminetetra-acetate) by $[IrCl_6]^{2-}$, $[Fe(phen)_3]^{3+}$ (phen = 1,10-phenanthroline), and $[(NH_3)_5Co(O_2^-)Co(NH_3)_5]^{5+}$. Although an intervalence charge-transfer band for the Mo^{V}–Mo^{VI} species is expected, no such band has ever been reported in the literature. To our knowledge we are the first to report this band at 850 nm for a molybdenum compound. In as much as a Mo^{V}–Mo^{VI} species is expected to have a paramagnetic Mo^{V} centre, further evidence for the formation of Mo^{V}–Mo^{VI} species has been obtained from the measurement of magnetic susceptibility of an aqueous solution of $[Mo_2O_4(glyO)_2(H_2O)_2]$ by the Evans method.[14] The n.m.r. spectrum is recorded 2 h after the dissolution of $[Mo_2O_4(glyO)_2(H_2O)_2]$ in water containing 2% t-butyl alcohol, the pH being maintained at 4.6. The value of $\mu_{eff.}$ thus obtained was *ca.* 0.6 B.M. (*ca.* 0.556×10^{-23} A m^2).

All our efforts to isolate the Mo^{V}–Mo^{VI} species in the solid state proved unsuccessful. It is generally believed that biological molybdenum is dimeric in the native enzymes, and if it remains dimeric in the presence of substrate, the Mo^{V} e.s.r. signals observed in four of the molybdenum enzymes in the presence of substrate must be due to a mixed oxidation state, possibly a Mo^{V}–Mo^{VI} dimer.[4,32] Formation of similar Mo^{V}–Mo^{VI} species has also been proposed by Howie and Sawyer [29] during the course of their electrochemical studies on some oxo- and sulphido-bridged binuclear Mo^{V} complexes. The present study offers a possible pathway for the generation of a dimeric Mo^{V}–Mo^{VI} species.

Acknowledgements

Thanks are due to Dr. K. Nag for helpful discussions and Dr. D. Datta for carrying out the electrochemical experiments. I am indebted to Professor A. Chakravorty for providing his Electrochemistry System.

References

1 R. C. Bray and J. C. Swann, *Struct. Bonding (Berlin)*, 1972, **11**, 107.
2 E. I. Stiefel, *Prog. Inorg. Chem.*, 1977, **22**, 1.
3 E. I. Stiefel, W. E. Newton, G. D. Watt, K. L. Hadfield, and W. A. Bulen, *Adv. Chem. Ser.*, 1977, **162**, 355.
4 H. Beinert and W. H. Orme-Johnson in ' Magnetic Resonance in Biological Systems,' eds. A. Ehrenberg, B. G. Mahlstrom, and T. Vanngard, Pergamon Press, Oxford, 1967, p. 221.
5 A. Nason, ' The Enzymes,' eds. P. D. Boyer, H. Lardy, and K. Myrback, Academic Press, New York, 1963, vol. 7, p. 587.
6 G. Palmer and V. Massey, *J. Biol. Chem.*, 1969, **244**, 2614.
7 C. H. Fewson and D. J. D. Nicholas, *Biochim. Biophys. Acta*, 1961, **44**, 335.
8 D. J. D. Nicholas, P. W. Wilson, W. Heinen, G. Palmer, and H. Beinert, *Nature*, 1962, **196**, 433.
9 J. S. Olson, D. P. Ballou, G. Palmer, and V. Massey, *J. Biol. Chem.*, 1974, **249**, 4363.
10 R. Cammack, M. J. Barber, and R. C. Bray, *Biochem. J.*, 1976, **15**, 469.
11 S. P. Vincent, *Biochem. J.*, 1979, **177**, 757.
12 G. D. Lawrence and J. T. Spence, *Biochemistry*, 1975, **14**, 3626.
13 A. Kay and P. C. H. Mitchell, *Nature*, 1968, **219**, 267; *J. Chem. Soc. A*, 1970, 2421.
14 D. F. Evans, *J. Chem. Soc.*, 1959, 2003.
15 L. R. Melby, *Inorg. Chem.*, 1969, **8**, 349.
16 P. C. H. Mitchell, *Quart. Rev.*, 1966, **20**, 103.
17 F. W. Moore and M. L. Larson, *Inorg. Chem.*, 1967, **6**, 998.
18 C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1959, 3552.
19 M. D. Joesten, *Inorg. Chem.*, 1967, **6**, 1598.
20 W. D. Griffith, *J. Chem. Soc. A*, 1969, 211.
21 R. M. Wing and K. P. Kallahan, *Inorg. Chem.*, 1969, **2**, 871.
22 K. Nakamoto, ' Infrared Spectra of Inorganic and Coordination Compounds,' Wiley, London, 1963, p. 205.
23 A. Kay and P. C. H. Mitchell, *J. Chem. Soc. A*, 1970, 2421.
24 M. J. Powers, R. W. Callahan, D. J. Salmon, and T. J. Meyer, *Inorg. Chem.*, 1976, **15**, 894 and refs. therein.
25 D. O. Cowan, C. LeVanda, J. Park, and F. Kaufman, *Acc. Chem. Res.*, 1973, **6**, 1 and refs. therein.
26 N. S. Hush, *Prog. Inorg. Chem.*, 1967, **8**, 391; *Electrochim. Acta*, 1968, **13**, 1005.
27 G. C. Allen, M. Green, B. J. Lee, H. P. Kirsch, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1976, 794.
28 B. Kanellakopulos, D. Nöthe, K. Weidenhammer, H. Wienand, and M. L. Ziegler, *Angew. Chem. Int. Ed. Engl.*, 1977, **16**, 261.
29 J. K. Howie and D. T. Sawyer, *Inorg. Chem.*, 1976, **15**, 1892.
30 K. Wharton, J. F. Ozo, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1975, 1526.
31 Y. Sasaki, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1939.
32 K. V. Rajagopalan, P. Handler, G. Palmer, and H. Beinert, *J. Biol. Chem.*, 1968, **243**, 3784.

Received 27*th May* 1982; *Paper* 2/883