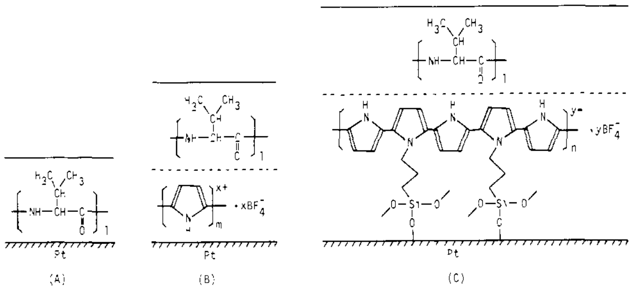
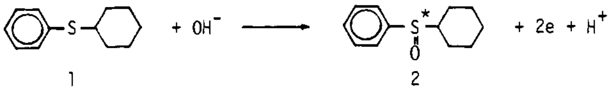


Figure 1. Poly(L-valine)-coated platinum electrodes.

dation of phenyl cyclohexyl sulfide (1) to phenyl cyclohexyl sulfoxide (2) (eq 1) was examined, and remarkably high optical



(1)

yields were obtained by using poly(L-valine)-coated platinum electrodes, as shown in Table I.

Three kinds of the poly(L-valine)-coated platinum electrodes (A, B, and C) shown in Figure 1 were used for the asymmetric oxidation. The coated electrode A was prepared by dipping a platinum plate (3 × 4 cm) into 0.5% (w/v) poly(L-valine) (M_w ca. 2000[5])/trifluoroacetic acid, similarly to preparation of a poly(L-valine)-coated graphite electrode in a previous work.[5] To prepare the coated electrode B, the platinum plate was first coated with polypyrrole by anodic polymerization at 1.5 V vs. Ag/AgCl for 2 min in 0.01 M pyrrole–0.1 M Bu_4NBF_4/acetonitrile and then with poly(L-valine) in layers by a dipping method similar to above. The coated electrode C was also prepared by double coating with polypyrrole and poly(L-valine). A polypyrrole film in this case was covalently bound by $Pt–OSi(CH_2)_3N$(pyrrole nucleus) bondings to the platinum surface. Coating of the polypyrrole film was carried out by a modified method of Simon et al.,[9] who developed the original method for the protection of n-type silicon photoanodes: The platinum plate was chemically modified with monomeric pyrrole by the reaction of its surface oxides with *N*-[3-(trimethoxysilyl)propyl]pyrrole in ethanol and then was anodically treated at 1.5 V vs. Ag/AgCl for 2 min in 0.01 M pyrrole–0.1 M Bu_4NBF_4/acetonitrile. The polypyrrole-coated platinum plate prepared thus was also coated with poly(L-valine) by the dipping method.

Phenyl cyclohexyl sulfide (1) (2 mmol) was oxidized by passing 386 C of charge at 1.75–1.85 V vs. Ag/AgCl at 0 °C in 70 mL of 0.1 M Bu_4NBF_4/acetonitrile (containing 1% water), using a potentiostat (Hokuto Denko Ltd., Model HA-201). After the electrolysis, phenyl cyclohexyl sulfoxide (2) was purely separated from the anodic solution by column chromatography (Kieselgel 60, chloroform–ethyl acetate, 9:1 v/v), and the optical rotation was measured in acetonitrile with a highly sensitive polarimeter (Union Co., automatic digital polarimeter Model PM-101). Because the optical rotating power of optically pure 2 has not been reported, the optical yield was calculated from NMR spectra of 2 measured in the presence of tris[3-[(trifluoromethyl)hydroxymethylene]-D-camphorato]europium(III) as an enantiomer-shift reagent.

The polypyrrole film is electronconductive, because it was doped with tetrafluoroborate ions.[10] The thickness of poly-L-valine films is estimated as ca. 10^{-4} cm by analogy with poly(L-valine)-coated graphite electrodes prepared in the previous work,[6] and the films are not electroconductive. Therefore, electron transfer between 1 and the electrode seems to occur on and/or in the polypyrrole film.

The coated-electrode B gave a higher optical yield than the coated-electrode A. The higher optical yield may be due to a tighter adhesion of the poly(L-valine) film to the polypyrrole-coated platinum surface of the coated-electrode B. The coated-electrode C gave a much higher optical yield of 54%. This may be also rationalized as due to the very strongly (covalently) bound adhesion of the polypyrrole film to the platinum surface of the coated-electrode C, comparing with that of the coated-electrode B.

In with the previous works[5,6] dealing with asymmetric reduction on poly(amino acid)-coated electrodes, this asymmetric oxidation using the platinum electrodes coated doubly with polypyrrole and poly(L-valine) clearly demonstrates the advantageous utilization of polymer-coated electrodes in electroorganic syntheses.

Acknowledgment. This study was performed as a preliminary investigation for a project supported financially by the Grant-in-Aids for Scientific Researches from the Japanese Ministry of Education, Science and Culture.

Registry No. Phenyl cyclohexyl sulfide, 7570-92-5; phenyl cyclohexyl sulfoxide, 3324-82-1; poly-L-valine, 25609-85-2; *N*-[3-(trimethoxysilyl)propyl]pyrrole, 80906-67-8; pyurrole, 109-97-7; tetrafluoroborate ion, 14874-70-5; polypyrole, 30604-81-0; (*S*)-poly[imino[1-(1-methylethyl)-2-oxo-1,2-ethanediyl]], 25667-19-0.

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[9] Simon A.; Ricco A. J.; Wrighton M. S. *J. Am. Chem. Soc.* **1982**, *104*, 2031.

[10] Prejze J.; Lundström I.; Skotheim T. *J. Electrochem. Soc.* **1982**, *129*, 1685.

Clay-Modified Electrodes

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We report here the modification of an electrode surface by coverage with a thin layer of a treated clay and describe the electrochemical behavior of several substances incorporated into this clay film. The modification of electrode surfaces, for example by covalent attachment or with polymer films, is currently an active area of research.[1] Clay and other inorganic layers on electrode surfaces have the advantage of high chemical stability and special structural features and, to our knowledge, have not previously been described.

Colloidal clays have recently attracted considerable attention because of their appreciable surface area and unusual intercalation properties. Clays are employed in many commercial processes[2] and are important as catalysts[3] or catalyst supports.[4] The immobilization of complex catalysts in clay structures is an area of growing interest, since apart from the obvious advantages of heterogeneous catalysis, clay colloids have been found to influence the specificity of catalysts as well.[5] Clay colloids have also been used in photocatalytic systems.[6]

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[1] See, for example: (a) Murray, R. W. In "Electroanalytical Chemistry"; Bard, A. J., Ed., Marcel Dekker: New York; Vol. 13, in press. (b) Merz, A.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 3229. (c) Rubinstein, I.; Bard, A. J. *Ibid.* **1981**, *103*, 5007. (d) Abruna, H. D.; Denisevich, P.; Umana, M.; Meyer, T. J.; Murray, R. W. *Ibid.* **1981**, *103*, 1. (e) Wrighton, M. S.; Palazzotto, M. C.; Bocarsly, A. B.; Bolts, J. M.; Fischer, A. B.; Nadjo, L. *Ibid.* **1978**, *100*, 7264. (f) Brown, A. P.; Anson, F. C. *Anal. Chem.* **1977**, *49*, 1589. (g) Ghosh, P. K.; Spiro, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 5543.

[2] (a) Bundy, W. M. *Chem. Eng. Prog.* **1967**, *63*, 57. (b) Larsen, D. H. *Clays Clay Miner.* **1955**, *1*, 269. (c) Ryland, L. B.; Tamele, M. W.; Wilson, J. N. In "Catalysis"; Emmett, P. H., Ed.; Reinhold: New York, 1960; Vol. 7, Chapter 1.

[3] (a) Weiss, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 850. (b) Shimoyama, A.; Johns, W. D. *Nature (London), Phys. Sci.* **1971**, *232*, 140. (c) Durand, B.; Fripiat, J. J.; Pelet, R. *Clays Clay Miner.* **1972**, *20*, 21.

[4] (a) Van Olphen, H. "An Introduction to Clay Colloid Chemistry"; Wiley: New York, 1977. (b) Brindley, G. W.; Sempels, R. E. *Clay Miner.* **1977**, 12, 229.

[5] (a) Pinnavaia, T. J. *Science (Washington, D.C.)* **1983**, *220*, 365. (b) Thomas, J. M.; Adams, J. M.; Graham, S. H.; Tennakoon, D. T. B. *Adv. Chem. Ser.* **1977**, *163*, 298.

[6] (a) Nijs, H.; Fripiat, J. J.; Van Damme, H. *J. Phys. Chem.* **1983**, *87*, 1279. (b) Nijs, H.; Cruz, M. I.; Fripiat, J. J.; Van Damme, H. *J. Chem. Soc., Chem. Commun.* **1981**, 1026.

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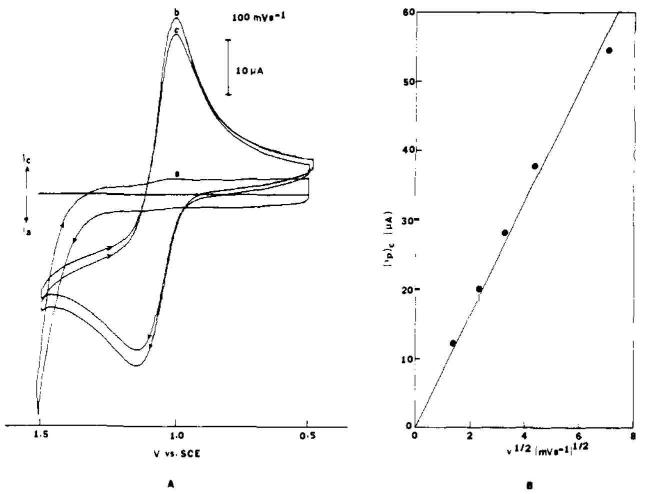

Figure 1. (A) Cyclic voltammograms for $Ru(bpy)_3^{2+}$ incorporated into clay (sodium) films on SnO_2 electrodes, in the absence (a) and in the presence (b, c) of colloidal Pt/PVA in the films; (b) initial scan, (c) 50th scan. Voltammograms were recorded in 0.1 M Na_2SO_4 (pH 7), and the electrode area was ~0.6 cm^2. (B) Plot of i_{pc} (cathodic peak current) vs. $v^{1/2}$ (v = scan rate) for the electroactive film.

The clay colloid used in our work was a sodium montmorillonite,[7] one of the members in the smectite group of clays. A clay-modified electrode could be formed by adding a few drops of a colloidal montmorillonite dispersion[8] to a tin oxide coated glass plate and subsequently evaporating the solvent to yield a film. Although such a film adhered very well to the electrode surface and strongly adsorbed $Ru(bpy)_3^{2+}$ (soaking the electrode in pure supporting electrolyte for several days failed to remove the strongly colored $Ru(bpy)_3^{2+}$ from the film), the film was found to be electroinactive (curve a in Figure 1A). The quality of the film was also very poor, and cracks in the film were obvious. When a small quantity of colloidal Pt[9] was added to the colloidal clay dispersion, the Pt–clay mixture[10] was considerably more viscous than either constituent alone (perhaps due to gelation), and films cast with this mixture appeared very uniform. Thickness measurements at several locations within the film[1c] confirmed that a smooth coating, about 2.9–3.2 μm thick, had been prepared. $Ru(bpy)_3^{2+}$ incorporated into these films by soaking them for 15 min in 5 mM $Ru(bpy)_3^{2+}$ was electroactive and cyclic voltammograms for the initial and 50th scan are shown as curves b and c in Figure 1A. The waves showed a diffusion-controlled shape (with peak currents (i_p) proportional to $v^{1/2}$, where v is the scan rate) even at v's as low as 2 mV/s (Figure 1B). The estimated apparent diffusion coefficient of $Ru(bpy)_3^{2+}$ in the film was $\sim 10^{-11}$ cm^2/s. Preliminary results also indicate that no more than 10% of the total incorporated $Ru(bpy)_3^{2+}$ was electroactive.

Several other redox couples incorporated into montmorillonite films were also electroactive; representative voltammograms with diffusion-controlled waves are shown in Figure 2. The half-wave potentials for all couples examined were near those obtained for these solution species at a bare electrode. Except for the $Fe(bpy)_3^{3+/2+}$ couple, which was ejected more readily from the clay film, voltammograms for the other couples were stable for successive scans, although some attenuation of the peak heights occurred during prolonged scanning over the redox waves. From the voltammograms, there were at least 50–100 equivalent layers of electroactive material in these films, and thus charge transport within the film either by a hopping mechanism or by actual diffusion of redox species to the electrode surface is the rate-limiting process for these modified electrodes.

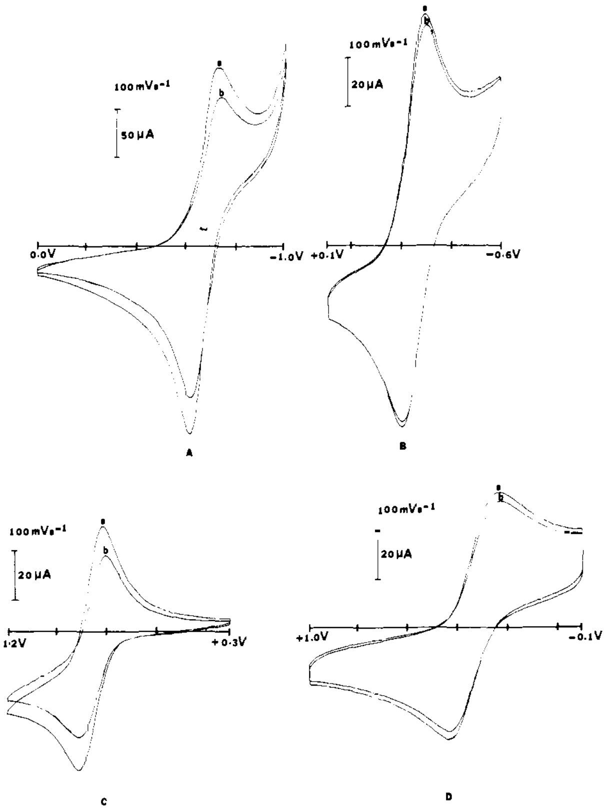

Figure 2. Cyclic voltammograms for electroactive compounds incorporated into sodium montmorillonite films containing colloidal Pt: (A) methyl viologen (MV^{2+}) (a) initial scan, (b) 100th scan; (B) $Ru(NH_3)_6^{3+}$ (a) initial scan, (b) 105th scan; (C) $Fe(bpy)_3^{2+}$ (a) initial scan, (b) 40th scan; (D) TMA $Fe(Cp)_2^{+}$ (TMA = trimethylammonium) (a) initial scan, (b) 40th scan. Voltammograms were recorded in 0.1 M Na_2SO_4 (pH 7).

The mechanism operative in generating film electroactivity is still unclear. Although the films become electroactive as a result of incorporation of Pt into the coating, in control experiments where only PVA was added to the clay dispersion (note that the solutions of colloidal Pt contained PVA) electroactivity was also found. Thus, Pt must not play any major role in promoting electroactivity of the films. However, films formed in the absence of Pt were mechanically less sturdy and more prone to cracking. While the role of PVA remains unclear, appropriate film morphology is important in expediting the charge-transfer process. Perhaps gelation of the clay colloid[12] by addition of PVA or colloidal Pt causes a high degree of particle association, which results in better communication among the redox species incorporated into these particles.

Clay films were also cast on glassy carbon and platinum electrodes, and experiments with $Fe(bpy)_3^{2+}$ indicate that the voltammetric behavior at all three electrodes is comparable. Experiments are currently underway to help gain a better understanding of the properties of these montmorillonite films and of the charge and mass transport processes within them. Con-

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(7) Montmorillonite has a layer lattice structure and has strong sorptive properties due to the expandability of the internal layers. The unit cell formula for this clay in the sodium form can be written as $Na_{0.67}[(Si)_8(Al_{3.3}Mg_{0.67})O_{20}(OH)_4]$.

(8) Ten grams of sodium montmorillonite (Crook County, Wy) was dispersed in 100 mL of triply distilled water and then diluted to 300 mL. The above solution was then centrifuged at 5000 rpm for 1 hr and the colloidal clay content of the supernatant was found to be 12g/L.

(9) This was prepared according to literature procedure (Hirai, H.; Nakao, Y.; Toshima, H. *J. Macromol. Sci., Chem.* **1979**, *A13* (6), 727) and contained 0.84 mmol of Pt and 3 g of PVA (polyvinyl alcohol) in 1000 mL of 1:1 $EtOH/H_2O$.

(10) The mixture comprised 0.112 g/L Pt, 4 g/L clay, and 2 g/L PVA in 2:3 $EtOH/H_2O$.

(11) The $E_{1/2}$ value of 1.08 V vs. SCE is very similar to the $E_{1/2}$ value obtained for the solution couple. Recent reports of $Ru(bpy)_3^{2+}$ in clay indicate considerable shifts in the MLCT absorption spectrum (Della Guardia, R. A.; Thomas, J. K. *J. Phys. Chem.*, **1983**, *87*, 990) and in the Ru $3d_{5/2}$ binding energy (Abdo, S.; Canesson, P.; Cruz, M.; Fripiat, J. J.; Van Damme, H. *Ibid.* **1981**, *85*, 797).

(12) The gelation phenomenon is believed to result from layer edge-to-face interactions that generate a "house-of-cards" structure.[4a]

siderable improvements in behavior should be possible with this system, since no attempts were made to optimize parameters such as film thickness and clay/PVA ratio in the present work. Experiments with different clay types and incorporated substances are also in progress. Finally the strategy employed here should be applicable to other types of materials of interest, such as zeolites[13] and silicas.[14]

Acknowledgment. We thank Dr. M. Krishnan for many helpful suggestions and for carrying out the film-thickness measurements; the support of the National Science Foundation (CH7903729) is gratefully acknowledged.

Registry No. $Fe(bpy)_3^{2+}$, 15025-74-8; $TMAFe(Cp)_2^+$, 86527-05-1; $Ru(NH_3)_6^{3+}$, 18943-33-4; $Ru(bpy)_3^{2+}$, 15158-62-0; SnO_2, 18282-10-5; Pt, 7440-06-4; C, 7440-44-0; PVA, 9002-89-5; MV^{2+}, 4685-14-7; montmorillonite, 1318-93-0.

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[13] Faulkner, L. R.; Suib, S. L.; Reuschler, C. L.; Green, M. J.; Bross, P. R. In "Chemistry in Energy Production"; Southwest-Southeast Regional Meeting, ACS, New Orleans, Dec. 10, 1980; Publ. ORNL; CONF-801226, Mar. 1982.

[14] Willner, I.; Yand, J. M.; Laane, C.; Otvos, J. W.; Calvin, M. *J. Phys. Chem.* **1981**, *85*, 3277.

Dicopper Complexes of a Macrocyclic Ligand as Models for Type 3 Copper Proteins

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Recent chemical and physical studies on hemocyanin[1] and tyrosinase[2] derivatives allow the identification of certain basic requirements in synthetic models for these and probably other type 3 copper proteins. These include (i) a binucleating capability on the part of the synthetic ligand that permits a relatively close approach (3–4 Å) of the copper ions, (ii) accessibility of both Cu(I) and Cu(II) oxidation states, (iii) coordinative unsaturation of the metal ions in the reduced state, and (iv) a coordination polyhedron for each metal ion that includes two (or three) nitrogen donors. The provision of a bridging group that mediates antiferromagnetic coupling between the Cu(II) ions may also be important. Recently, several synthetic dicopper complexes that incorporate some or all of these features have been described[3] including some that exhibit (partially) reversible O_2-binding activity[3a,3b] (cf. hemocyanin) and monooxygenase[3f] or oxidase activity[3c,i,k,l] (cf. tyrosinase, laccase, etc.). We here report on the structures and properties of some dicopper(I) and dicopper(II) complexes of a macrocyclic ligand that also satisfy the requirements noted above and that, additionally, function as catalysts for the oxidation of several organic substrates, including catechols, in the presence of oxygen.

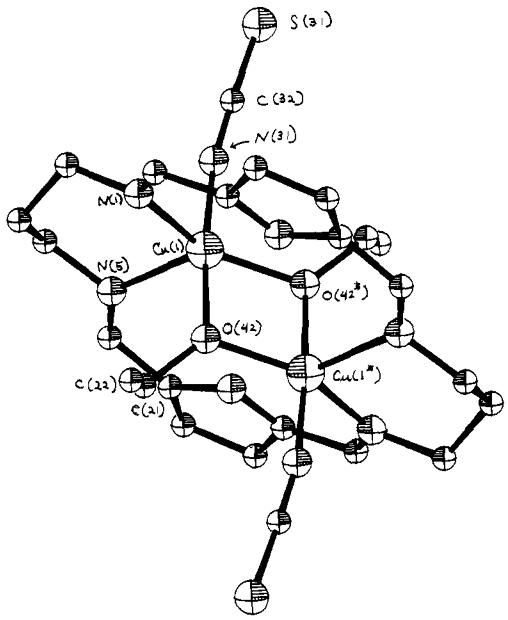
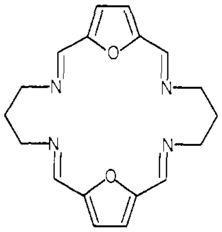


Figure 1. Structure of $[Cu_2L(OEt)_2(NCS)_2]$. Selected bond distances (Å): Cu(1)–N(1) = 2.108 (18); Cu(1)–N(5) = 2.282 (19); Cu(1)–O(42) = 1.943 (14); Cu(1)–N(31) = 1.919 (23).

The macrocycle L (**1**) was synthesized as the complex BaL$(ClO_4)_2$·EtOH from 2,5-diformylfuran and 1,3-diaminopropane by use of Ba^{2+} ion as a template.[4] Replacement of Ba^{2+} by Cu^{2+} led to a series of diCu(II) complexes including $Cu_2L(OH)_2(ClO_4)_2·H_2O$ (**2**), $[Cu_2L(OR)_2(MeCN)_2][BPh_4]_2$ (**3**), and $[Cu_2L(OR)_2(NCS)_2]$ (**4**) (R = Me, Et, *n*-Pr). The structure[5] of $[Cu_2L(OEt)_2(NCS)_2]$ (**4**) is shown in Figure 1. Each Cu(II) ion is bonded to two imino nitrogens of the macrocycle, the nitrogen of one (terminally bound) thiocyanate ion, and to two bridging ethoxide groups in an approximate trigonal-bipyramidal geometry. The two metal ions are displaced by 0.57 Å on opposite sides of the roughly planar macrocycle so that each bridging ethoxide occupies an axial site in the coordination sphere of one metal ion and an equatorial site of the other. The Cu···Cu separation is 3.003 (4) Å. The furan oxygens are not coordinated (Cu···O > 2.95 Å).



(**1**)

The complexes (**3**) have nearly identical ligand field spectra with those of **4** (λ_{max} 715, 1070 nm) and therefore undoubtedly have closely similar structures. The spectrum of **2** is different

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[1] (a) Freedman, T. B.; Loehr, J. S.; Loehr, T. M. *J. Am. Chem. Soc.* **1976**, *98*, 2809. (b) Larrabee, J. A.; Spiro, T. C. *Ibid.* **1980**, *102*, 4217. (c) Dooley, D. M.; Scott, R. A.; Ellinghaus, J.; Solomon, E. I.; Gray, H. B. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 2094. (d) Himmelwright, R. S.; Eickman, N.; LuBien, C. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 5378. (e) Co, M. S.; Hodgson, K. O.; Eccles, T. K.; Lontie, R. *Ibid.* **1981**, *103*, 984, 3210. (f) Brown, J. M.; Powers, L.; Kincaid, B.; Larrabee, J. A.; Spiro, T. G. *Ibid.* **1980**, *102*, 4210.

[2] Eickman, N. C.; Solomon, E. I.; Larrabee, J. A.; Spiro, T. G.; Lerch, K. *J. Am. Chem. Soc.* **1978**, *100*, 6529. Himmelwright, R. S.; Eickman, N. C.; Lubien, C. D.; Lerch, K.; Solomon, E. I. *Ibid.* **1980**, *102*, 7339. Winkler, M. E.; Lerch, K.; Solomon, E. I. *Ibid.* **1981**, *103*, 7001.

[3] (a) Bulkowski, J. E.; Burk, P. L.; Ludman, M.-F.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1977**, 498. (b) Simmons, M. G.; Merrill, C. L.; Wilson, L. J.; Bottomley, L. A.; Kadish, K. M. *J. Chem. Soc., Dalton Trans.* **1980**, 1827. (c) Burnett, M. G.; McKee, V.; Nelson, S. M. *J. Chem. Soc., Chem. Commun.* **1980**, 829. (d) Burk, P. L.; Osborn, J. A.; Youinou, M.-T.; Agnus, Y.; Louis, R.; Weiss, R. *J. Am. Chem. Soc.* **1977**, *99*, 4111. (e) Gagne, R. R.; Allison, J. L.; Gall, R. S.; Koval, C. A. *Ibid.* **1977**, *99*, 7170. (f) Karlin, K. D.; Dahlstrom, P. L.; Cozette, S. N.; Scensny, P. M.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1981**, 881. (g) Sorrell, T. N.; Malachowski, M. R.; Jameson, D. L. *Inorg. Chem.* **1982**, *21*, 3252. (h) McKee, V.; Dagdigian, J. V.; Bau, R.; Reed, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 7000. (i) Nishida, Y.; Oishi, N.; Kuramoto, H.; Kida, S. *Inorg. Chim. Acta* **1982**, *57*, 253. (j) Hendriks, H. M. J.; Birker, P. J. M. W. L.; van Rijn, J.; Verschoor, G. C.; Reedijk, J. *J. Am. Chem. Soc.* **1982**, *104*, 3607. (k) Lever, A. B. P.; Ramaswany, B. S.; Pickens, S. R. *Inorg. Chim. Acta.* **1980**, *46*, L59. (l) Moore, K.; Vigee, G. S. *Ibid.* **1982**, *66*, 125.

[4] Drew, M. G. B.; Esho, F.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.*, in press.

[5] All complexes gave satisfactory C, H, and N analyses for the formulae indicated: data supplied to referees.

[6] Crystal data: monoclinic, a = 15.356 (9) Å, b = 10.239 (11) Å, c = 18.662 (10) Å; β = 102.5 (1)°; Z = 4; space group $I2/c$; Mo Kα radiation; 1023 independent reflections above background refined to R 0.073.

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