Table I. Important Bond Lengths and Angles in [Ni(TACNTA)][a]

	molecule 1	molecule 2	molecule 3
	Bond Lengths		
Ni-O_1	1.911 (7)	1.915 (7)	1.911 (7)
Ni-N	1.93 (1)	1.936 (8)	1.909 (8)
C_1-O_1	1.29 (1)	1.30 (1)	1.29 (1)
C_1-O_2	1.23 (1)	1.22 (1)	1.22 (1)
C_1-C_2	1.50 (2)	1.52 (2)	1.55 (2)
C_2-N	1.50 (1)	1.49 (1)	1.47 (1)
C_3-N	1.52 (2)	1.50 (1)	1.50 (1)
C_3-C_4	1.50 (2)	1.53 (2)	1.52 (2)
C_4-N	1.53 (2)	1.49 (2)	1.50 (2)
	Angles		
N-Ni-O_1	85.5 (4)	85.3 (3)	85.7 (3)
C_1-O_1-Ni	112.8 (6)	113.5 (7)	113.7 (6)
O_1-Ni-O_1′	91.2 (3)	91.6 (3)	91.2 (3)
C_2-N-Ni	105.4 (6)	104.7 (6)	105.0 (6)
C_3-N-Ni	108.5 (7)	105.3 (7)	106.1 (6)
C_3-N-C_2	113.5 (9)	112.9 (9)	112.3 (8)
N-Ni-N′	89.4 (4)	89.2 (4)	89.4 (4)
O_1-C_1-O_2	122.2 (10)	124.9 (11)	126.0 (10)
C_2-C_1-O_1	116.3 (9)	115.0 (10)	114.1 (9)
C_2-C_1-O_2	121.4 (9)	120.1 (10)	119.8 (10)

[a] Units are Å for bond lengths and deg for bond angles. For numbering scheme of atoms, see Figure 1. Numbers in parentheses are the standard deviations in the reported bond lengths and angles.

Table II. Metal to Ligand Bond Lengths and Twist Angles in TACNTA Complexes[a]

metal ion	M-N[b]	M-O[b]	twist angle[c]	ref
Ni(III)	1.93	1.91	6.9	this work
Ni(II)	2.04	2.08	12.0	*d*
Cr(III)	2.06	1.96	11.0	5
Cu(II)[e]	2.12	2.07	33.4	5
Fe(III)[e]	2.18	1.96	35.0	5[d]

[a] For definition of the twist angle, see text. [b] Units are Å. [c] Units are deg. [d] Unpublished work of the present authors. [e] Type II structure, as discussed in text.

lengths in TACNTA complexes plus the twist angle (ϕ) around the C_3 axis, which is the amount by which the upper three oxygen atoms are rotated in projection relative to the lower three nitrogen atoms, from the position expected for a regular octahedron. It is seen that the structure of the Fe(III) complex is more nearly trigonal prismatic than octahedral,[5] since ϕ would be 60° for trigonal-prismatic and 0° for octahedral coordination.

The base fragment 9-aneN_3 is chiral once coordinated to a metal ion, and so two possible conformers are obtainable, depending on whether the acetates attach themselves in a clockwise or anticlockwise fashion for one given arrangement of the base fragment. The structure shown for Ni(III) in the figure we designate as type I, and it is the structure found for Cr(III)[5] and Ni(II). We can visualize the type II structure from the figure if we detach all of the acetates, which are arranged in the figure in a clockwise fashion, and reconnect them in an anticlockwise fashion, with the conformation of the 9-aneN_3 base fragment remaining the same. The C_2 to O_1′ distance is considerably greater than C_2 to O_1, and so reconnection of the acetates to give the type II structure leads to the pulling of O_1′ toward N and the trigonal distortion of the Fe(III) complex with $\phi = 35°$. We have carried out an empirical force field (EFF) analysis of both the type I and II structures of the TACNTA complexes, using the EFF program described previously[7] and parameters for acetate groups reported by Snow.[8] The calculations carried out with parameters appropriate for Ni(II) showed the type I structure to be about 4 kcal·mol^{-1} more stable than the type II. The type II structure found for Fe(III)[5] only becomes more stable than the type I when the N-M-N, O-M-N, and O-M-O angle-bending force constants are lowered to 10% of their value for Ni(II), when type II structure is dictated by the ligand.

On completing the Ni(II) structure, the short Ni-N bond lengths of 2.04 Å, compared with the strain-free length[7] of 2.10 Å, suggested that oxidation to Ni(III) was being driven by release of steric strain. However, our EFF analysis shows that the best fit size for metal ions in TACNTA complexes with both type I and II structures occurs with mean metal to ligand bond lengths of 2.0 Å, and so the Ni(III) structure, with Ni-N and Ni-O bond lengths here of 1.93 and 1.91 Å, is a bit small for the TACNTA system. It would still seem, however, that a large part of the stability of [Ni(TACNTA)] derives from the fact that this is still a better fit than is found in macrocycles such as cyclam, which require metal ions with M-N bond lengths of about 2.06 Å.[2,9] We are at present using the EFF program to determine the metal ion size preferences of other ligands that might conceivably stabilize Ni(III), with the hope of finding some with size preferences close to the 1.90-Å metal-ligand bond lengths in which the Ni(II) cannot escape compression by spin-pairing or ligand folding and so that the Ni(III) can be stabilized as much as possible.

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Registry No. Ni(TACNTA), 87306-48-7; H_3O[Ni(TACNTA)], 87306-49-8.

Supplementary Material Available: Listings of atomic coordinates, temperature factors, and observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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Electrochemical and Spectroelectrochemical Studies of Bis(peroxo)molybdenum(VI) Tetra-*m*-tolylporphyrin

Sir:

The detailed nature of the bonding of molecular oxygen to transition-metal complexes has been a subject of increasing interest because it represents a basic step in understanding the function of oxygen-carrying and -activating metalloproteins in biological systems.[1-3] The synthesis[4] and photolysis[5] of bis(peroxo)molybdenum(VI) tetra-*p*-tolylporphyrin, $(O_2)_2$Mo(TpTP), has recently been reported. UV irradiation

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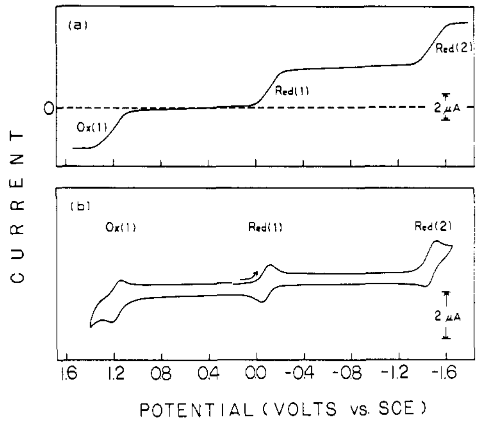

Figure 1. (a) Rotating-disk voltammogram at a Pt electrode of 1.0 mM $(O_2)_2Mo(TmTP)$ in CH_2Cl_2, 0.1 M TBAP (scan rate 5 mV/s, rotation speed 500 rpm). (b) Cyclic voltammogram of the same solution at a Pt electrode (scan rate 100 mV/s).

of $(O_2)_2Mo(TpTP)$ affords the related *cis*-dioxomolybdenum(VI) tetra-*p*-tolylporphyrin, $O_2Mo(TpTP)$. Unexpectedly, however, $(O_2)_2Mo(TpTP)$ was found to be thermally stable, and no traces of oxidation products from reaction with cyclohexene or triphenyl phosphine were detected.[5]

In this communication we present a mechanism for the electroreduction and electrooxidation of bis(peroxo)molybdenum(VI) tetra-*m*-tolylporphyrin, $(O_2)_2Mo(TmTP)$, at a platinum electrode in CH_2Cl_2 containing 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. Three well-defined redox couples are observed within the potential range of +1.6 to −1.7 V (vs. SCE). Voltammograms at a rotating-platinum-disk electrode (Figure 1a) indicate that the waves at −0.09 and −1.46 V are due to a reduction, while the wave at +1.18 V is due to an oxidation. Analysis of these reactions by cyclic voltammetry (Figure 1b) indicates that all three waves are diffusion controlled (as characterized by constant values of $i_p/v^{1/2}$ and $E_{1/2}$ with increase in potential scan rate). The difference in anodic and cathodic potential, $E_{pa} - E_{pc}$, was equal to 60 ± 5 mV for the single oxidation, suggesting the abstraction of one electron. This was confirmed by controlled-potential oxidation at +1.55 V, which yielded a value of 0.98 faraday in the oxidation step.

Both reduction waves were also reversible on the cyclic voltammetry time scale, and $E_{pa} - E_{pc}$ was equal to 60 ± 5 and 70 ± 5 mV for the first and second steps, respectively, again indicating diffusion-controlled one-electron transfers. This was confirmed by controlled-potential coulometry for the first step, which gave 1.02 faradays, but not for the second reduction. Changing the potential from −0.6 to −1.70 V in controlled-potential electrolysis gave an additional 3 faradays, indicating that the product of the second reduction was unstable on longer time scales and that decomposition of $[(O_2)_2Mo(TmTP)]^{2-}$ had occurred. The difference between the single-electron transfer by cyclic voltammetry and the three electrons by controlled-potential electrolysis is due to a further reduction of the products of demetalation, which gave a final spectrum resembling reduced $TPPH_2$.[6]

Monitoring of the electronic absorption spectra during controlled-potential oxidation yielded the spectra shown in Figure 2a. A large decrease in molar absorptivity of the Soret band and a shift toward longer wavelengths was observed on going from $(O_2)_2Mo(TmTP)$ to the product of the first oxidation. This spectrum, with broad absorption peaks from 600 to 900 nm, is very characteristic of a cation radical.[7] This reaction was totally reversible, and the spectrum obtained after controlled-potential rereduction of the oxidized species was identical with that of the starting species.

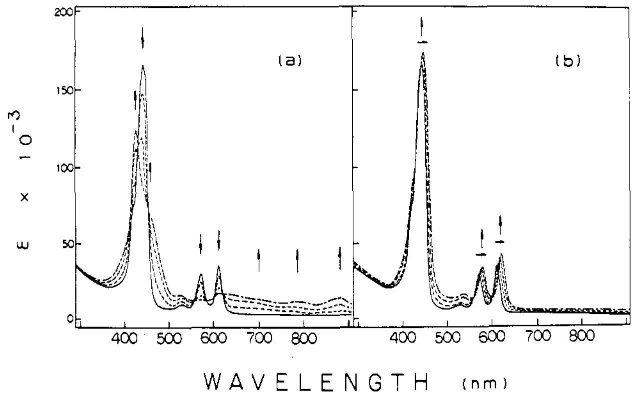

Figure 2. Time-resolved electronic absorption spectra obtained (a) during controlled-potential oxidation of $(O_2)_2Mo(TmTP)$ at +1.5 V and (b) during controlled-potential reduction at −0.6 V in CH_2Cl_2, 0.1 M TBAP.

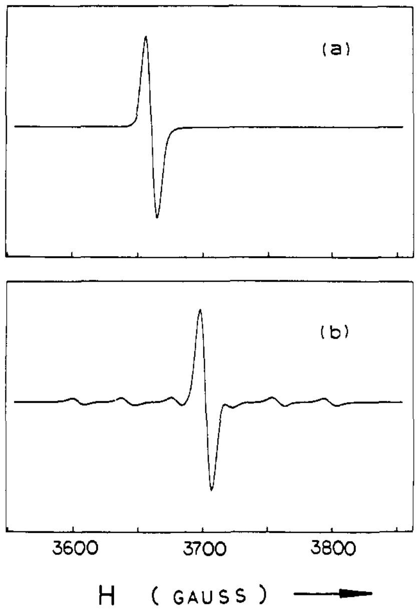

Figure 3. ESR spectra of electrogenerated (a) $[(O_2)_2Mo(TmTP)]^{+\cdot}$ and (b) $[(O_2)_2Mo(TmTP)]^-$ at 295 K.

Only small changes in the original spectrum were observed during controlled-potential reduction by one electron. This is shown in Figure 2b. The Soret band was shifted by 2 nm to longer wavelengths while 7- and 9-nm shifts were observed for the α and β bands, respectively. This type of shift and the lack of absorbances between 650 and 800 nm strongly suggest a metal-centered reaction.[8] In contrast to the second reduction, the first reduction was reversible on the macro electrolysis time scale.

The products of the first oxidation and the first reduction were investigated by ESR spectroscopy. Before electrolysis no ESR signal was observed. After electrolysis at +1.5 V the radical ESR signal shown in Figure 3a was obtained. In contrast, controlled-potential reduction at −0.6 V produced the Mo(V) ESR signal shown in Figure 3b. The spectrum at 295 K shows one intense line at the center and six weaker sym-

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(6) The final reduced product had absorbance maxima at 421, 514, 549, 589, and 645 nm, which were compared to those of the free base porphyrin, $[TPPH_2]^{2-}$, at 423, 513, 548, 589, and 644 nm, respectively.

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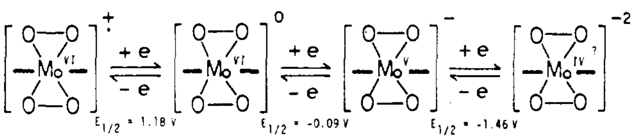
Scheme I



metrical bands. The intense absorption is attributed to the ^{96}Mo species, and the value of $g = 1.980$ closely approximates that for other complexes of OMo(TPP)X.[9,10] The expected hyperfine structure due to interactions with four nitrogen nuclei around the ^{96}Mo nucleus was not observed under our experimental conditions. The six weaker bands are assigned to the hyperfine structure caused by the interaction with ^{95}Mo and ^{97}Mo nuclei.

On the basis of coulometric, voltammetric, and spectroscopic data Scheme I may be assigned for $(O_2)_2$Mo(TmTP) oxidation–reduction in CH_2Cl_2 on the cyclic voltammetry time scale.

Attempts to spectrally identify the site of the second reduction (i.e., metal or ring based) were unsuccessful due to decomposition of $[(O_2)_2Mo(TmTP)]^{2-}$ at larger time scales of electrolysis. In all cases only $[TmTPH_2]^{2-}$ and some form of Mo^{IV} were obtained. Evidence for the latter oxidation state of Mo comes from cyclic voltammetry after bulk electrolysis that yielded a wave at 0.0 V, which is characteristic for a Mo^{IV}/Mo^{V} redox couple.

The interesting and significant aspect of the above mechanism is that reduction of $(O_2)_2$Mo(TmTP) appears to be at the central metal and not at the porphyrin ring. The alternate explanation of π-radical formation can be ruled out on the basis of the potential for Red(1) and the large separation between Red(1) and Red(2),[11] as well as by the nonradical spectrum illustrated in Figure 3b. This provides the first example where a peroxo-bound metalloporphyrin can be reduced at the central metal without affecting the nature of the metal–oxygen bond.

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Registry No. $(O_2)_2$Mo(TmTP), 87371-95-7; $[(O_2)_2Mo(TmTP)]^+$, 87371-96-8; $[(O_2)_2Mo(TmTP)]^-$, 87371-97-9.

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(11) All known tetraphenylporphyrin derivatives show ring reductions between −1.0 and −1.8 V vs. SCE, and the majority exhibit potential differences of 300–470 mV between $E_{1/2}$ values for formation of the anion radical and dianion.[8]

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Articles

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Synthesis of Chelating Bidentate and Tridentate Cyano Ligands and Their Complexes with Group 7 Metal Carbonyls

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Two new bidentate cyano ligands, DiCN-3 (**2**) and DiCN-4 (**3**) (α,ω-bis(2-cyanophenoxy)propane and -butane, respectively), have been prepared. These ligands and the ethane analogue DiCN-2 (**1**) react with $Mn(CO)_5Br$ to afford complexes of the composition $Mn(CO)_3$(DiCN-*n*)Br (*n* = 2, **9**; *n* = 3, **10**; *n* = 4, **11**). Complexes **9** and **10** appear to be mononuclear and contain 13- and 14-membered chelate rings, respectively. Ligand **3** in **11** might be either chelated or bridged. IR studies of the reaction between **1**–**3** and $Mn_2(CO)_6(CH_3CN)_2(\mu\text{-}Br)_2$ show that, under identical conditions, more nitrile groups of **1** than of **2** and **3** are bound to the $Mn(CO)_3Br$ unit; this results suggests that DiCN-2 is a better chelating ligand than DiCN-3 or DiCN-4. A novel tricyano ligand, TriCN (1,3,5-tris(2-cyanophenyl)benzene (**8**)) has been synthesized from 2-methylacetophenone. TriCN functions either as a bidentate ligand, as in $M(CO)_3$(TriCN)Br (M = Mn, **12**; M = Re, **14**), or as a tridentate ligand, as in $[M(CO)_3(TriCN)]PF_6$ (M = Mn, **13**; M = Re, **15**). Complexes **13** and **15** of TriCN are the first examples in which a tridentate cyano ligand chelates to a single metal center through its nitrogen lone pairs.

Introduction

Recently, we described the synthesis of bidentate cyano (DiCN) and isocyano (DiNC and *t*-BuDiNC) ligands, which were shown to form chelate complexes with a variety of low-valent transition metals.[1,2] The DiCN ligand of those studies is the first example of a dicyanide capable of chelation to a single metal through its nitrogen lone pairs. We report here the synthesis and reactions of two new bidentate cyano ligands, DiCN-3 and DiCN-4. These ligands are structurally similar to the previously reported DiCN ligand (hereafter referred to as DiCN-2 (**1**)). The three ligands vary only in *n*, the number of methylene units connecting the phenoxy oxygens, and should be capable of forming chelate rings containing 13 (DiCN-2) to 15 (DiCN-4) members. Also reported here is the synthesis of a novel tricyano ligand, TriCN (**8**), and several of its metal

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