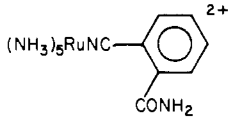
termediates in Schemes I and II as well as desolvation of the OH^- ion.

The rate enhancement for nitrile hydrolysis due to catalysis by the ortho carboxamide function has been quantified via rate comparisons with utilization of metal-coordinated nitrile groups. It is impossible to measure the rate of nitrile hydrolysis in uncoordinated *o*-cyanobenzamide since this molecule reacts with base to give the cyclic product 3-iminoisoindol-1-one.[13,14] However, Zanella and Ford have demonstrated that nitriles coordinated to the pentaammineruthenium(II) moiety exhibit little if any rate enhancement for the nitrile to amide hydrolysis reaction vis-â-vis the uncoordinated nitrile molecule[10] (Table III). This latter observation suggests a means of evaluating the effectiveness of the ortho-group participation in our system. When the complex



is reacted with base, the coordianted nitrile group is hydrolyzed to the carboxamido function as evidenced by the identification of Ru(II) and Ru(III) carboxamido complexes by analogy with the data of Zanella and Ford. Although side reactions are a complicating factor here, preliminary kinetic studies of this reaction yield second-order rate constants in the range 0.2–0.5 $M^{-1}\ s^{-1}$ at 25 °C. This corresponds to a rate enhancement of 5–6 orders of magnitude over the rate of hydrolysis of free and pentaammineruthenium(II)-coordinated benzonitrile where, of course, no ortho-group catalysis operates. Hence, for the pentaamminecobalt(III) complex of *o*-cyanobenzamide, the (2×10^6)-fold rate enhancement due to cobalt(III) coordination combined with the (10^5-10^6)-fold enhancement due to the neighboring amide function leads to an enormous rate enhancement of 11–12 orders of magnitude. It remains to be demonstrated in subsequent studies whether metal ion catalysis and neighboring-group assistance will operate cooperatively in other nitrile hydrolysis reactions.

Acknowledgment. We wish to thank the Natural Sciences and Engineering Research Council of Canada for support of this research.

Registry No. Pentaammine(1,2-benzenedicarbonitrile-*N*)cobalt(3+), 53739-00-7; pentaammine(2-cyanobenzamide-N^2)cobalt(3+), 69120-40-7; pentaammine(2,3-dihydro-3-imino-1*H*-isoindol-1-onato-N^2)cobalt(2+), 69120-38-3; pentaammine(2-cyanobenzamidato-N^1)cobalt(2+), 68893-64-1.

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Electrochemical Behavior of Metal Tricarbonyl Complexes of Several Tridentate Macrocycles Containing Soft (P, S) Ligating Sites[1]

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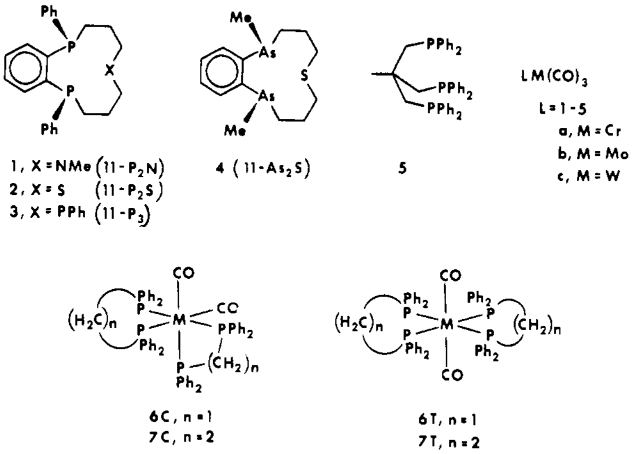
A series of *fac* group 6 metal tricarbonyl complexes of 11-membered tridentate macrocycles (ligating sites P_2N, P_2S, P_3, and As_2S) have been studied by cyclic voltammetry. These complexes undergo quasi-reversible single-electron oxidations with redox potentials dependent on the nature of X in the 11-P_2X series. The range of oxidation potentials is 0.42–0.47 V for a series X = N, S, P with a particular metal, with ease of oxidation decreasing as X is varied from N to S to P.

Introduction

The importance of macrocyclic coordinating ligands in controlling the electronic properties of a coordinated metal ion has long been recognized.[2] Because of their similarity with the biologically important heme proteins, tetraaza macrocyclic complexes have been investigated extensively.[3] It is also clear that metal–macrocycle coordination and aggregation profoundly influence the facility of photoinduced redox reactions in the primary photoprocesses of both green-plant and bacterial photosynthesis.[4]

In order to more clearly delineate the effect of other strongly coordinating macrocyclic ligands on the electronic and redox properties of complexed metals, we have undertaken an electrochemical study of a series of *fac*-$(CO)_3M$(macrocycle) complexes, where M is a group 6 metal (Chart I). We describe herein the effect of *fac*-tridentate metal coordination by the macrocycles **1–4** on the redox properties (specifically, oxidation potential and stability of the complex) and the

Chart I



1, X = NMe (11-P_2N)
2, X = S (11-P_2S)
3, X = PPh (11-P_3)
4 (11-As_2S)
5
6C, n = 1
7C, n = 2
6T, n = 1
7T, n = 2

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Table I. Peak Potentials[a] and Absorption Maxima for Oxidation of Some Macrocycle-Metal Complexes

		electrode process						
		$M^0 \rightarrow M^I$			$M^I \rightarrow M^{II}$		M → ligand oxidn	
compd	λ_{max}[b]	E_{p_a}, V[c]	E_{p_c}, V[c]	W,[d] mV	E_{p_a}, V[c]	W,[d] mV	E_{p_a}, V[c]	W,[d] mV
1a (11-P_2NCr)	430	−0.22	−0.46	50	+0.70	100	+1.10	180
1b (11-P_2NMo)	392	+0.11	−0.15	70	+0.80	205		
1c (11-P_2NW)	389	−0.09	~0.3 (br)	70	+0.49	150	+0.92	220
2a (11-P_2SCr)[e]	404	+0.05	−0.02	70	+1.08	80	+1.15	180
2b (11-P_2SMo)[e]	378	+0.18	~0.09 (br)	75				
2c (11-P_2SW)[e]	377	+0.19	+0.08	70	+0.81	110	+1.15	155
3a (11-P_3Cr)		+0.21	−0.05	70	+0.49	150	+1.15	200
3b (11-P_3Mo)		+0.58	+0.48	80	+1.23	140		
3c (11-P_3W)	356 (s)	+0.33	+0.24	90	+0.96	140	+1.15	180
4b (11-As_2SMo)	367	−0.08		120	+0.55	200	+1.25	150
5b (triphosMo)		+0.34	+0.27	70	~2.0	110		

[a] Potentials were measured by cyclic voltammetry in anhydrous CH_2Cl_2 containing 0.1 M tetrabutylammonium perchlorate at −78 °C; scan rates 100–1000 mV/s. Potentials were initially measured against a silver wire quasi-reference electrode, but the reported potentials are corrected, by addition of an internal standard, to the standard calomel electrode reference. [b] Complex concentration ~10^{-3} M in anhydrous CH_2Cl_2. [c] ±0.1 V vs. SCE. [d] W = width of oxidative wave; $2(E_p - E_{p/2}) \pm 5$ mV. [e] Cyclic voltammograms for **2a–2c** were obtained at 0 °C because of solubility limitations.

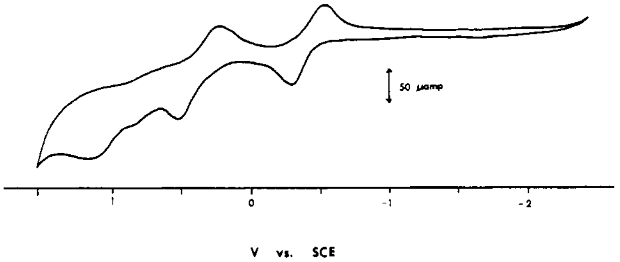

Figure 1. Cyclic voltammogram of **3a** (5 × 10^{-3} M) in anhydrous CH_2Cl_2 containing 0.14 M tetrabutylammonium perchlorate at 0 °C and scan rate 500 mV/s.

electronic spectra of these complexes.

Results

A detailed description of the preparation and spectroscopic properties of series **1a**–**c** has appeared,[5] and the other metal complexes were prepared similarly and will be described elsewhere. The 11-membered ligands **1**–**4** can tricoordinate an octahedral metal only in a *fac* manner as indicated by the study of Dreiding molecular models, and as confirmed in two cases by a single-crystal X-ray determination (**1b** and **3c**).[6] All the complexes exhibited two strong IR absorptions in the regions 1950 and 1850 (often split) cm^{-1}, characteristic of *fac*-tricarbonyl species.[5,7] The preparations of macrocycles **1**–**3**[8] and **4**[9] have been described. We will refer to the macrocyclic ligands using the abbreviations shown in Chart I.[10]

A cyclic voltammogram for the oxidation of **2a** in CH_2Cl_2 is shown in Figure 1. As is typical for the entire series of complexes studied, a quasi-reversible oxidation of the central metal (e.g., Cr(0) → Cr(I)) is observed at +0.2 ± 0.4 V. The reversibility of this oxidation was measured by searching for temperature dependence in the wave shape, by measuring the peak half-width, and by examining the dependence of the peak potential on the sweep rate.[11] A second oxidative wave could be seen also at potentials 0.5–1 V more positive than the first. This wave, like the first, was associated with central-metal oxidation. A complex series of broad, irreversible oxidative waves at more positive potentials was associated with metal-coordinated ligand oxidations. No reduction waves for the neutral complexes were observable at potentials less negative than −2 V.

Peak potentials for the oxidative waves for the series of complexes are listed in Table I. Upon warming of the complexes (to 0 °C or to ambient temperature) only small positive shifts were observed (0–0.1 eV), although the integrated area under the reduction wave observed on scan reversal often decreased somewhat. Table I also lists breadths of oxidative waves at half-height ($E_p - E_{p/2}$). For a reversible charge-transfer step, a wave breadth of 59 mV[12,13] is anticipated.

If inert electrolyte (TBAP) is replaced by an electrolyte containing active nucleophilic anions (e.g., tetrabutylammonium bromide (TBAB)), the reversbility of the cyclic voltammetric oxidation disappears.

Electronic absorption spectral data for complexes **1**–**4** are also listed in Table I. Finally, cyclic voltammetric studies on the free ligands established that the oxidative processes observed in this study were due to metal-based electrons.

Discussion

The most obvious effects of complexation by our macrocycles on the redox behavior of group 6 metals are the pronounced cathodic shifts (1.2–2.0 V) in observed redox potentials and, particularly with molybdenum and tungsten, enhanced stability of the oxidized complex. With regard to the latter observation, we observe irreversible oxidations at 1.75 V for $Mo(CO)_6$ and 1.78 V for $W(CO)_6$ in dichloromethane solution and quasi-reversible oxidation of $Cr(CO)_6$ at 1.80 V. In contrast, the one-electron redox process has been reported to be completely reversible at −20 °C for $Cr(CO)_6$ and both $Mo(CO)_6$ and $W(CO)_6$ were oxidized irreversibly, all at 1.53 V, in acetonitrile solution.[14] We observe near-Nernstian peak shapes with little temperature dependence for the M(0) ↔ M(I) process similar to the reports of Bond and co-workers for *trans*-dicarbonylbis(diphenylphosphino)ethane (**6T**)[15a] and -methane (**7T**)[15b] group 6 complexes.

Because of the constraints on the placement of the ligating sites enforced by incorporation into an 11-membered ring, only the *fac*-tricarbonyl isomers can be formed and therefore one of the complications that Bond and co-workers[15] faced, that of cis–trans isomerization (*fac–mer* in our case), is absent in our systems. In the presence of a good nucleophile (Br^-) in

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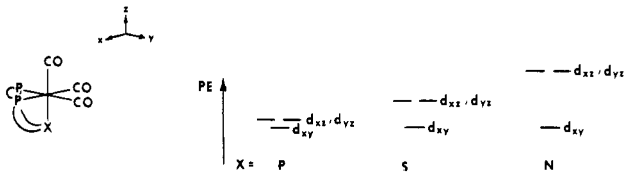

Figure 2. Schematic representation of the effect of variation of X in the macrocyclic ligand on the t_{2g}* set of orbitals in the macrocycle–metal carbonyl complexes.

the supporting electrolyte, decomposition of the one-electron oxidized intermediate is rapid and all reversibility is lost in the cyclic voltammogram.

Several trends are discernible in the data contained in Table I. The ligand 11-P_2N gives the most easily oxidizable complexes, 11-P_2S intermediately oxidizable complexes, and 11-P_3 the least easily oxidizable complexes with all three metals. The oxidation potentials of 6C and 7C[15] fall between those of **1a–c** and **3a–c** and in fact are fairly close to those of **2a–c**.[16] The second anodic process, presumably M(I) ↔ M(II), is reasonably similar for **6**, **7**, **2a–c**, and **3a–c**, but is significantly more facile for **1a–c**. The variation of X in **1–3** causes differences in first oxidation potential in the range 0.42–0.47 V. The ease of oxidation as a function of the metal is Cr > W > Mo, in contrast to the observations of Bond's results (Cr > Mo ≃ W).[15] The nature of the P_3 ligand can cause a substantial difference in oxidation potential (compare **3b** and **5b**). Finally, the diars-containing ligand (**4**) very much facilitates oxidation but produces a less stable oxidized complex. Replacement of $(PhP)_2$ sites with $(MeAs)_2$ sites with X = S causes a −0.33 V shift in oxidation potential of the bound $Mo(CO)_3$ moiety. Indeed, the second anodic process of **4b** occurs at lower potential than that of the first anodic process of **3b**.

The data can be rationalized by considering the effect of facial ligation by the 11-P_2X species on the highest occupied orbitals in the complex, the metal-based t_{2g}* set. The energy levels of the d_{xy}, d_{xz}, and d_{yz} orbitals in the coordinate system shown in Figure 2 will vary as a function of the π-accepting ability of X, but those of the other five ligands will be essentially invariant in the 11-P_2X series. The π acidity of X has been established to be P > S > N,[17] and the carbonyl stretching frequencies we observe for our complexes are completely in agreement with this ordering.[18] Thus, with the assumption of analogous products and entropy effects in the series, the energies of d_{xz} and d_{yz} will increase as the X is changed from P to S to N, which leads to increasing ease of oxidation in this series.[19]

We conclude that oxidation potential as measured by cyclic voltammetry of group 6 metal tricarbonyls can be modified over a substantial range as a function of the ligating sites within the attached macrocyclic ligand.

Experimental Section

Reagents. The metal complexes were prepared as described elsewhere[5] and were analytically pure. Chromium, molybdenum, and tungsten hexacarbonyls were purchased from Alfa-Ventron and resublimed before use. Reagent grade methylene chloride was purified by standard techniques[20] and was stored under a purified nitrogen atmosphere. Tetrabutylammonium perchlorate (TBAP, Southwestern Analytical Chemicals) and bromide (TBAB, Alfa-Ventron) were recrystallized and dried overnight under vacuum.

Cyclic Voltammetry. A standard three-compartment electrochemical cell was used, a silver wire quasi-reference electrode having been isolated from the test solution by a fine-porosity frit. The potential of the reference was determined following each series of experiments by adding anthracene, a compound whose redox behavior is known.[21] To the cell was attached an adapter, which permitted the addition of solids to degassed solvent–electrolyte mixtures. A platinum-disk (0.05 cm^2) working electrode and platinum-coil counterelectrode completed the cell. The electrochemical experiments were conducted with a Princeton Applied Research (PAR) Model 173 potentiostat equipped with a Model 175 universal programmer. A Model 179 digital coulometer equipped with positive feedback for *IR* compensation was used for preparative electrolyses, and an X-Y recorder (Houston Instruments) was used to record current–potential curves.

The electrochemical measurements were carried out in purified methylene chloride (7 mL) made 0.14 M in TBAP at −78 °C, and ambient temperature. This mixture was degassed by a three-cycle freeze–pump–thaw sequence until no trace of oxygen was detectible by cyclic voltammetry. After addition of the solid complex, the mixture was cooled to the appropriate temperature with a dry or wet ice bath and cyclic voltammograms (scan rates 100, 200, 500, and 1000 mV/s) were successively recorded.

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Registry No. **1a**, 79297-09-9; **1a**$^+$, 79172-76-2; **1a**$^{2+}$, 79172-77-3; **1b**, 79297-10-2; **1b**$^+$, 79172-78-4; **1b**$^{2+}$, 79172-79-5; **1c**, 79297-07-7; **1c**$^+$, 79172-80-8; **1c**$^{2+}$, 79172-48-8; **2a**, 79172-49-9; **2a**$^+$, 79172-50-2; **2a**$^{2+}$, 79172-51-3; **2b**, 79172-52-4; **2b**$^+$, 79172-53-5; **2c**. 79172-54-6; **2c**$^+$, 79172-55-7; **2c**$^{2+}$, 79172-56-8; **3a**, 65219-53-6; **3a**$^+$, 79190-81-1; **3a**$^{2+}$, 79190-82-2; **3b**, 65219-52-5; **3b**$^+$, 79190-83-3; **3b**$^{2+}$, 79190-84-4; **3c**, 79190-85-5; **3c**$^+$, 79190-86-6; **3c**$^{2+}$, 79190-87-7; **4b**, 75361-71-6; **4b**$^+$, 79190-88-8; **4b**$^{2+}$, 79190-89-9; **5b**, 79190-90-2; **5b**$^+$, 79190-91-3; **5b**$^{2+}$, 79190-92-4.

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(19) We note that there is a rough correlation between the first oxidation potentials and the UV absorption maxima (d–d transition) for these complexes. The latter process involves a transition between the X-affected t_{2g}* occupied orbitals and the LUMO (e_g*), whose energy is affected by the σ-donating ability of X. Apparently the way in which the e_g (and hence e_g*) and t_{2g}* sets of orbitals are related is sufficiently regular to lead to these rough correlations.

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