the spectra of both **2a** and **2b** eliminates the possibility that the equilibrium position is influenced by agostic C–H–M interactions. The absorptions due to **1b** disappear upon removal of the hydrogen atmosphere by vacuum followed by introduction of an argon atmosphere.

The infrared spectrum of a KBr pellet of **2c** under 1 atm of H_2 was seen to contain only the M–H absorptions of **2c** at 2334 and 2324 cm^{-1}, even upon prolonged standing. The infrared spectrum of a KBr pellet containing the material produced from a sample of **2c** which was dissolved in THF and recrystallized under 1 atm of H_2 was obtained under 1 atm of H_2. Similarly, the spectrum was seen to contain only the M–H absorptions of **2c**. Thus, we obtained no evidence for coordination of H_2 by **2c** in the solid state. As was the case with **2a** and **2b**, no absorptions assignable to agostic C–H stretches were observed, and we conclude that H_2 is excluded from the iridium center due to the steric shielding rather than competitive agostic interactions of the Bu^t groups.

Conclusion

Our solution NMR spectroscopic studies establish there is a threshold to the sensitivity of the kinetics and thermodynamics of the reversible loss of H_2 from our dihydrogen complexes to the steric environment at the iridium center. These studies indicate that the steric constraints are insignificant for the PPr^i_3 and PCy_3 (cone angles 152 and 170°, respectively) derivatives, **1a** and **1b**, but are dominant for the PBu^t (cone angle 182°) derivative, **1c**. The interaction of solvents with the unsaturated iridium species seems to have increased steric requirements, as both **2b** and **2c** appear to have much higher kinetic barriers to this process than **2a**. Reversible solvent coordination may stabilize **2a** in solution, thus accounting for the marked equilibrium shift toward **1a** in the solid state. Our results also demonstrate the pronounced destabilizing influence the chloride ligands have on the iridium–hydrogen interactions in saturated iridium polyhydride complexes.

The elimination of H_2 from our complexes is far more facile than has been generally observed for dihydrogen complexes and thus suggests a much weaker metal–dihydrogen bonding interaction. However, the rate of intramolecular exchange between the dihydrogen and hydride ligands in **1a** is similar to those that have been found for other iridium complexes containing dihydrogen and hydride ligands.[26,29] Thus our studies demonstrate that the strength of the iridium–dihydrogen interaction does not necessarily reflect the degree of activation of dihydrogen ligands in iridium polyhydride complexes.

Acknowledgment. The support of this research by the Solar Energy Research Institute is gratefully acknowledged.

Supplementary Material Available: A figure of variable-temperature ^1H NMR spectra for $IrClH_2(PCy_3)_2(H_2)$ and tables of crystal data, anisotropic thermal parameters, bond distances, bond angles, and hydrogen atom coordinates for $IrClH_2(PPr^i_3)_2(H_2)\cdot C_{10}H_8$ (7 pages); a listing of structure factors for $IrClH_2(PPr^i_3)_2(H_2)\cdot C_{10}H_8$ (26 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Biochemistry, Guelph-Waterloo Centre
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Kinetics and Mechanism of Metal Ion Substitution on a Cobalt(III) Complex Containing a Pendant Phenanthroline

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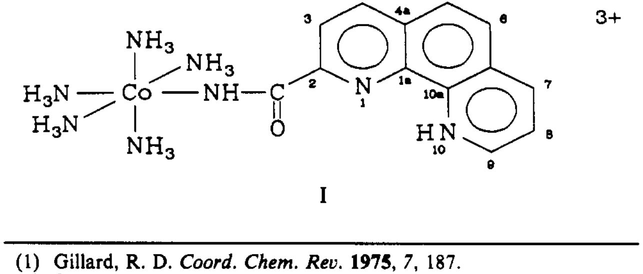
The kinetics for the substitution of the aqua ions of Fe(II), Co(II), and Ni(II) onto (phenanthroline-2-carboxamide)pentaamminecobalt(III) are reported in this study. For each metal studied, initial coordination occurs at *one* phenanthroline nitrogen and the adjacent carbonyl oxygen. For Co(II) and Ni(II), $k_{obsd} = k_1[M^{2+}] + k_{-1}$ where $k_1 = 980 \pm 70$ and 55 ± 4 $M^{-1}\,s^{-1}$ and $k_{-1} = 5.8 \pm 0.3$ and 0.23 ± 0.01 s^{-1}, respectively, at 25 °C and $I = 1.0$ M ($LiClO_4$). For Fe(II), $k_{obsd} = k_1[Fe^{2+}] + k_r[H^+]$ where $k_1 = 480 \pm 30$ $M^{-1}\,s^{-1}$ and $k_r = 525 \pm 40$ $M^{-1}\,s^{-1}$ at 25 °C and $I = 1.0$ M ($LiClO_4$). Possible mechanisms for these reactions are discussed.

Introduction

During the last 25 years, 1,10-phenanthroline and its derivatives have played an important role in the understanding of both substitution and electron-transfer reactions of metal ion complexes.[1,2] One of the most important aspects of this ligand is the "inertness" it provides to otherwise labile metal ions, such as Cr(II) and Co(II), by binding strongly to these metals. This has allowed for a more complete study of their redox reactions.

Recently, this tendency to form strong complexes was exploited in a study of the Cr(II) reduction of complex I.[3] It was anticipated that the reductant would be strongly bound by the ligand and that the substitution and redox steps could be separated. Although saturation behavior was exhibited in this reaction, no hydrogen ion dependence was found as would be expected if Cr(II) were bound by *both* phenanthroline nitrogens before electron transfer. The authors were forced to conclude that the Cr(II) transferred its electron while bound to the carbonyl oxygen and one phenanthroline nitrogen. The subsequent Cr(III) complex then rearranged to give the final Cr(III) phenanthroline product with both nitrogens coordinated. This unexpected coordination behavior requires that protonation on the phenanthroline ligand be at the remote nitrogen as shown in I.



I

In order to explore the generality of this unusual binding step involving one phenanthroline nitrogen and the adjacent carbonyl oxygen, the substitution reactions of several redox-inert metals with complex I were studied. The results with the aqua ions of iron(II), cobalt(II), and nickel(II) are reported here.

Experimental Section

The cobalt(III) phenanthrolinecarboxamide complex[3] (I) and cobalt(III) pyridinecarboxamide,[4] $[(NH_3)_5CoNHCOpyH](ClO_4)_3$, com-

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(1) Gillard, R. D. *Coord. Chem. Rev.* **1975**, *7*, 187.

(2) Serpone, N.; Ponterini, G.; Jamieson, M.; Boletta, F.; Maestri, M. *Coord. Chem. Rev.* **1983**, *50*, 209.

(3) Alexander, C. Master's Thesis, University of Guelph, Guelph, Ontario, Canada, 1986.

0020-1669/92/1331-1832$03.00/0

plexes were prepared according to literature methods. *Caution*! Perchlorate salts are potentially explosive and should be handled with care. The purity of each complex was checked using ion-exchange chromatography prior to use.

Stock solutions of $Co(ClO_4)_2 \cdot 6H_2O$, $Fe(ClO_4)_2 \cdot 6H_2O$, and $Ni(ClO_4)_2 \cdot 6H_2O$ were prepared using analytical grade salts. These solutions were standardized by titrating the acid released by a cation-exchange resin from a known aliquot of metal ion solution with standardized sodium hydroxide.

Lithium perchlorate/perchloric acid mixtures were used to maintain constant ionic strength. These solutions were analyzed using conventional methods.[5] Perchlorates were purchased from the G. Frederick Smith Co. and used without further purification.

Kinetic measurements were performed using a Dionex D110 stopped-flow spectrophotometer interfaced with a DASAR digital storage unit. Observed rate constants were obtained from the DASAR by matching exponential traces with a calibrated curve generator. The rate constants obtained were typically good to at least 10%. During this study, the stopped-flow was interfaced to a computer and rate constants were determined using the OLIS Kinfit routines (On-Line Instrument Systems, Jefferson, GA). Rate constants determined by both methods were in good agreement. Spectrophotometric measurements were done on a Beckman Acta CIII spectrophotometer.

The ^{13}C spectra were obtained in d_6-DMSO or D_2O solutions on Bruker AC 300 and AM 500 spectrometers operating at 75.47 and 135.72 MHz, respectively. Chemical shifts were referenced internally to the solvent (d_6-DMSO = 39.5 ppm relative to TMS) or externally to $CDCl_3$ (77.0 ppm relative to TMS). Spectra were recorded using a pulse delay of 5 s with a digital resolution of 1 Hz/point corresponding to a data length of 32 K. The flip angle and acquisition time were 60° and 1 s, respectively.

Standard *J*-modulated spin-sort experiments on the ^{13}C spectra were performed to distinguish between CH and quaternary carbons. Delay times of D1 = 5 s and VD = 0.0074 s were employed.

A majority of ^{13}C assignments were made through use of a $^{13}C-^{1}H$ shift correlated experiment.[6] One hundred and twenty-eight scans were accumulated per t_1 value with a recycle delay of D1 = 2 s. The initial data matrix was 1 K by 256t_1 values. Before Fourier transformation, zero-filling was used in the F_1 dimension. Delay times (D2 and D3) were both set to 0.0035 s. Remaining ^{13}C resonances were assigned by performing selective decoupling experiments.

Results and Discussion

Site of Protonation. Complex I exists in both a protonated and a deprotonated form in acidic solution:

$$(NH_3)_5Co(NHCOphenH)^{3+} \rightleftharpoons (NH_3)_5Co(NHCOphen)^{2+} + H^+$$

The pK_a as defined above was found to be 3.61 at 25 °C by potentiometric titration with sodium hydroxide.[3] There are four possible protonation sites on the complex: N-1 and N-10 on phenanthroline and the carboxamido N and O. The latter sites are not likely, since no change in the visible spectrum is observed over the pH range 7–0. For other carboxamido complexes which are known to protonate at N or O, appreciable spectral changes occur in the visible region of the spectrum upon protonation. Furthermore, for complex I, changes were observed in the UV spectrum when the pH was changed from 7 to 0. Similar changes in the UV spectrum were also observed for the uncomplexed ligand. Thus, it appears likely that protonation occurs at one of the phenanthroline nitrogens. The ^{1}H NMR data obtained previously[3] suggest that N-10 is the site of protonation. This conclusion is based on the large downfield shift of protons 7 and 8 when the complex is protonated. Protons 3 and 4, on the other hand, do not shift appreciably. Since the site of protonation is crucial to the mechanistic interpretation of the substitution reactions, a detailed ^{13}C NMR study was undertaken in an attempt to assign the protonation site unambiguously. The ^{13}C chemical shift data are given in Table I. On the basis of possible resonance forms, protonation at N-1 should mainly affect C-2, C-1a, and C4 whereas protonation at N-10 would have the largest effect on C-9, C-10a, and C-7. The data in Table I clearly show that C-9 and C-7 experience large chemical shifts whereas C-2 and C-4 remain essentially the same. Unfortunately, both C-1a and C-10a experience a substantial chemical shift when only C-10a is expected to shift for protonation at N-10.

Table I. ^{13}C Chemical Shift Data for $(NH_3)_5Co(2\text{-}NHCOphen)^{2+}$ and $(NH_3)_5Co(2\text{-}NHCOphenH)^{3+}$ in D_2O

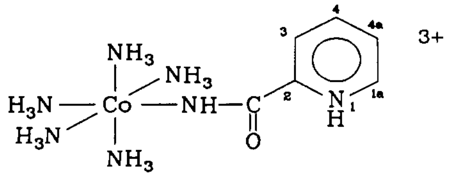
^{13}C assgnt	unprotonated complex	protonated complex
C=O	176.8	175.8
C-2	150.2	151.2
C-9	149.5	143.3
C-1a,10a	144.0, 143.2	138.0, 137.6
C-4	138.5	139.2
C-7	137.8	146.2
C-4a,6a	129.4, 129.0	130.6, 130.3
C-5,6	127.6, 126.2	129.4, 126.4
C-8	124.1	124.8
C-3	119.5	122.1

Table II. ^{13}C Chemical Shift Data for $(NH_3)_5Co(2\text{-}NHCOpy)^{2+}$ and $(NH_3)_5Co(2\text{-}NHCOpyH)^{3+}$ in D_2O

^{13}C assgnt	unprotonated complex	protonated complex	^{13}C assgnt	unprotonated complex	protonated complex
C=O	177.8	170.3	C-4	138.7	146.2
C-2	151.5	145.0	C-4a	126.2	128.2
C-1a	148.7	142.5	C-3	121.0	124.3

For unsubstituted 1,10-phenanthroline, the proton is shared equally between the two nitrogens due to the symmetry of the molecule. As expected, protonation causes a large upfield shift of both C-2,9 and C-1a,10a.[7] For comparative purposes, the formamide-substituted phenanthroline ligand, 2-H_2NCOphen, was also investigated. The shifts obtained upon protonation were virtually identical to those obtained for complex I: C-9, 149.3 to 144.4 ppm; C-7, 137.8 to 146.6 ppm; C-1a,10a, 143.9, 142.0 to 137.3, 136.6 ppm, respectively. As for the complex, all the data indicate protonation at N-10 except for the shift of C-1a. This "anomalous" shift could be explained by a weak H-bonding interaction between the proton on N-10 and N-1, either by direct means or via a water molecule.[8] Overall, however, protonation at N-10 predominates.

To substantiate this assignment, further ^{13}C spectra were obtained for complex II and the data are collected in Table II. This complex serves as a model for protonation on N-1, since it is known to protonate at the pyridine nitrogen with a pK_a of 2.31 at 25 °C (potentiometric determination). The same numbering scheme as in complex I is used to facilitate comparison. The shifts of the ring carbons are in accord with those observed for pyridine itself upon protonation[9] with C-2 and C-1a, giving large upfield shifts due to protonation. More importantly, the shift of the carbonyl carbon is particularly large and indicates that the proton which is primarily bound by N-1 is also hydrogen-bonded to the carbonyl oxygen. In complex I, no such shift in the carbonyl carbon resonance is observed upon protonation of the complex. Thus, the evidence strongly supports N-10 in complex I as the predominant protonation site.



II

Nickel(II) Complexation. For nickel(II) in excess over the cobalt(III) phenanthroline complex, the reaction was monitored

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(4) (a) Balahura, R. *Can. J. Chem.* **1974**, *52*, 1762. (b) Balahura, R. *Inorg. Chem.* **1974**, *13*, 1350.

(5) Balahura, R.; Jordan, R. *J. Am. Chem. Soc.* **1970**, *92*, 1533.

(6) Bax, A.; Morris, G. *J. Magn. Reson.* **1981**, *42*, 501.

(7) Rosenberger, H.; Pettig, M.; Madeja, K.; Pehk, T.; Lippmaa, E. *Org. Magn. Reson.* **1970**, *2*, 329.

(8) We thank a reviewer for this suggestion.

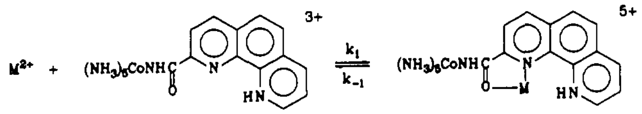
(9) Levy, G.; Lichter, R.; Nelson, G. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; John Wiley: New York, 1980; p 122.

Table III. Rate Constants[a] for Substitution Reactions of $[(NH_3)_5Co(2\text{-}NHCOphenH)]^{3+}$ [b]

metal	k_1, $M^{-1}\ s^{-1}$	k_{-1}, s^{-1}
Ni^{2+}	55 ± 4	0.23 ± 0.01
Co^{2+}	980 ± 70	5.8 ± 0.3
Fe^{2+}	480 ± 30	525 ± 40[c]

[a] Observed rate constants are given in the supplementary material. [b] $I = 1.0$ M ($LiClO_4$); $\lambda = 360$ nm for Ni^{2+}, 330 nm for Co^{2+}, and 480 nm for Fe^{2+}. [c] This is the value of k'_{-1}/K_aK_c and has units of $M^{-1}\ s^{-1}$ (see text).

Scheme I



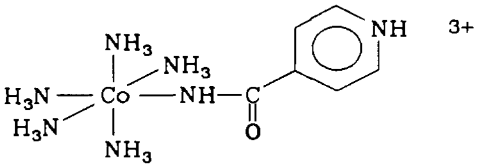
by following absorbance changes at 360 nm. The kinetics showed a linear dependence on the nickel(II) concentration and a positive *y*-intercept. Absorbance changes increased with increasing nickel concentrations. These observations are consistent with an equilibrium reaction. The experimental rate law is given by eq 1, where

$$-d[Co(III)]/dt = k_{obsd}[Co(III)] \quad (1)$$

$k_{obsd} = k_1[Ni^{2+}] + k_{-1}$. The observed rate constant was independent of the hydrogen ion concentration over the range 0.05–0.30 M. Values for k_1 and k_{-1} were calculated from a plot of k_{obsd} versus $[Ni^{2+}]$ where the slope and intercept are equal to k_1 and k_{-1}, respectively (Table III).

The absence of a hydrogen ion dependence for the forward and reverse rate constants precluded the involvement of *both* nitrogens of the phenanthroline ring in binding the nickel ion, since in the acid range employed at least one phenanthroline nitrogen is protonated. In this case, monodentate bonding of the nickel ion to the carbonyl oxygen or one phenanthroline nitrogen does not seem likely (vide infra). Thus, it is postulated that bidentate coordination occurs via N-1 and the adjacent carbonyl oxygen as shown in Scheme I.

The reasonableness of this mechanism was tested by studying the reaction of nickel with (pyridine-2-carboxamide)pentaamminecobalt(III) (complex II) and (pyridine-4-carboxamide)pentaamminecobalt(III) (complex III). For the 4-substituted pyridine complex no reaction with nickel(II) was observed spectrally over wide concentration ranges of nickel and hydrogen ion. In the case of the 2-substituted pyridine, however, a reaction was observed at 330 nm with rate law given in (2). Values for k_f and k_{-1} are 0.30 s^{-1} and 0.05 s^{-1}, respectively. The rate constant k_f is actually a composite of K_ak_1, since deprotonation of the pyridine nitrogen is necessary before coordination can occur. Using the value of 0.0011 M for K_a as previously determined,[4b] k_1 equals 282 $M^{-1}\ s^{-1}$.

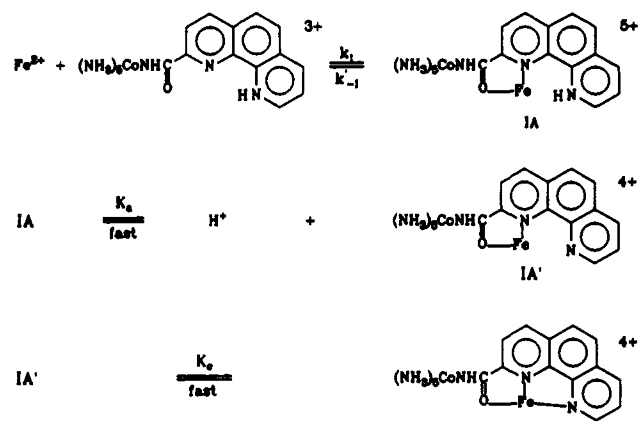


III

$$-d[Co(III)]/dt = (k_f[Ni^{2+}][H^+]^{-1} + k_{-1})[Co(III)] \quad (2)$$

These results support two important points in Scheme I. The first is that coordination at the carbonyl oxygen alone probably does not occur. If the substitution proceeded at this oxygen, then a reaction with the 4-substituted pyridine complex could have been expected. Since no reaction was observed, substitution either does not occur or k_f is much less than 1 and no spectral evidence is obtainable. Since no reaction was observed upon changing $[H^+]$, substitution at the pyridine nitrogen is also unlikely (vide infra). These experiments thus discount monodentate binding of the nickel(II) ion as a major reaction pathway under these conditions.

Scheme II



In the case of the 2-substituted complex, a reaction was observed because of the potential for a chelated product. The inverse dependence on the hydrogen ion concentration for the forward reaction is a strong indication that the binding involves the pyridine nitrogen. Although the additional involvement of the carbonyl oxygen has not been unambiguously established, it is reasonable to assume a chelated product on the basis of increased stability of chelates. Thus, it appears that both the pyridine nitrogen and the adjacent carbonyl oxygen are necessary for binding of nickel(II). In the case of complex I, N-1 is not protonated (but could be weakly H-bonded to the proton on N-10) and thus the reaction is independent of $[H^+]$. Therefore the mechanism of Scheme I seems reasonable.

Cobalt(II) Complexation. In order to determine the generality of Scheme I, the substitution of complex I with cobalt(II) was also examined. With cobalt(II) in excess, a linear dependence on the cobalt(II) concentration and a positive *y*-intercept were found. As in the nickel(II) system, absorbance changes increased with increasing cobalt(II) concentrations, thereby indicating an equilibrium situation. The experimental rate law is given by eq 3. No variation in rate was observed between 0.05 and 0.30 M acid concentration. Determination of k_1 and k_{-1} was accomplished as in the nickel(II) system, and the values are also given in Table III.

$$-d[Co(III)]/dt = (k_1[Co^{2+}] + k_{-1})[Co(III)] \quad (3)$$

Again, the data are consistent with a substitution process at the carbonyl oxygen and one phenanthroline nitrogen (Scheme I).

Iron(II) Complexation. The addition of iron(II) to complex I results in the formation of an orange solution. The complex formed has an absorption maximum at 477 nm with an extinction coefficient equal to 677 $M^{-1}\ cm^{-1}$. The binding site appears to be at the phenanthroline ring, since its spectral characteristics are similar to those of $[Fe(OH_2)_4(phen)]^{2+}$ (λ_{max} 450 nm, $\epsilon \sim 500$ $M^{-1}\ cm^{-1}$).[10] The orange complex decomposes upon addition of acid. No redox reaction was observed even though iron(II) is a potential reductant in this system. This is probably due to the stabilizing effect of phenanthroline on the iron(II) oxidation state.

With iron(II) in excess, a linear dependence on the iron(II) concentration is observed. The presence of a positive *y*-intercept is indicative of an equilibrium situation. In this case

$$k_{obsd} = k_1[Fe^{2+}] + k_r[H^+] \quad (4)$$

The rate constants k_1 and k_r were obtained from the slope and intercept of a plot of k_{obsd} versus $[Fe^{2+}]$. Between 0.05 and 0.30 M acid, no change in the slope was observed. The intercept of this plot, k_r, however, was found to increase linearly with increasing acid concentrations. An independent evaluation of k_r was obtained by plunging the preequilibrated complex of iron(II) into a solution of known acid concentration and an iron concentration equal to

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(10) Bell, R. S.; Sutin, N. *Inorg. Chem.* **1962**, *1*, 359.

that in the complex solution. A plot of k_{obsd} versus $[H^+]$ gave a straight line with a zero *y*-intercept. The values for these rate constants are given in Table III.

A mechanism consistent with these observations is shown in Scheme II. The two equilibria represented by K_a and K_c are rapid and are not seen as distinct steps in the complexation reactions. The formation of the chelated phenanthroline complex is consistent with the orange color of the complex and the first-order $[H^+]$ dependence on the reverse reaction. Similar results have been obtained for the Ti^{3+} and V^{2+} reactions with complex I prior to electron transfer.[11]

For the mechanism in Scheme II, the experimentally determined value of k_r can be written as follows:

$$k_r = k'_{-1}/K_aK_c \qquad (5)$$

Unfortunately, no determinations of K_a or K_c are available; thus evaluation of k'_{-1} is not possible.

The kinetic equilibrium constants for formation of the Ni^{2+} and Co^{2+} complexes with I are 239 and 169 M^{-1}, respectively. These values are not strictly comparable to those for the free ligand, since we are dealing with complexation of a 2+ ion with a 3+ complex. However, the values for this process are expected to be much smaller than those for uncomplexed ligand. No values are available for the phenanthroline-2-carboxamide ligand, but for 2-substituted pyridines containing a carboxyl group, the formation constants are in the range 10^6–10^{10} M^{-1} [12] for complexation with Ni^{2+} whereas, for the complexation of $(NH_3)_5Co(2\text{-}NHCOpy)^{2+}$ with Ni^{2+}, the kinetically determined equilibrium constant is only 5.6×10^3 M^{-1}. Presumably, in the case of the phenanthroline-carboxamide ligand, steric effects and the increased electrostatic repulsion will decrease the formation constants of the pentaammine complex substantially.

Conclusions

The complexation reactions of I, which possesses a pendant phenanthroline with a carbonyl group in the 2-position, occur via the carbonyl oxygen and the adjacent nitrogen on the phenanthroline ring. Subsequent rearrangement reactions may occur which result in a tridentate complex involving the carbonyl oxygen and *both* phenanthroline nitrogens. The latter behavior has been observed for Fe(II), Ti(III), and V(II). Further work on the substitution and electron-transfer reactions of complex I are in progress.

Acknowledgment. We thank Dr. M. Mlekuz and L. Randall for acquiring the ^{13}C NMR spectra. We also thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Supplementary Material Available: Tables of rate constants for metal ion complexation reactions (3 pages). Ordering information is given on any current masthead page.

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[11] Johnson, M.; Balahura, R. Unpublished data.

[12] *Stability Constants of Metal-Ion Complexes*; Special Publication No. 17; Chemical Society: London, 1964; Section II, Organic Ligands.

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Bimetallic Reactivity. Synthesis, Structure, and Reactivity of Homo- and Heterobimetallic Complexes of a Binucleating Macrocyclic Ligand Containing 6- and 4-Coordination Sites

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A binucleating macrocyclic ligand which embodies 6- and 4-coordinate sites has been prepared. Both homobimetallic and site-specific heterobimetallic complexes of Zn(II), Co(II), and Mn(II) have been isolated and characterized. The dimanganese(II) species reacts with dioxygen to give a mixed-valence compound containing both Mn(II) and Mn(III). All of the manganese-containing complexes are effective catalysts for the oxygenation of styrene using iodosobenzene. Crystal structures of these bimetallic complexes confirm the overall structures but also reveal that the 6-coordinate site has an unsymmetrical arrangement of ligands possibly due to macrocyclic strain. The results from these studies suggest modifications which may result in metal cooperativity in dioxygen uptake and for catalytic epoxidation.

1. Introduction

Numerous multimetallic coordination compounds derived from multinucleating ligands have been prepared.[1] For the most part, the objectives of these investigations were to determine the structure and physical properties and to reproduce the coordination of multimetallic sites of metalloproteins.[2] Few of these studies were directed at the potentially unique reactivities that these systems might provide. The notable exception is that of dioxygen binding where the redox cooperativity of bimetallic complexes has been demonstrated.[3] In all of these cases, however, both metals are involved in binding to the dioxygen molecule. We are aware of only one structurally established synthetic example where the dioxygen molecule binds to a single metal of a bimetallic system and where both metals appear to be involved in the reduction of O_2.[4] Similarly, in the case of oxo transfer, the oxo moiety is believed to bind to both metals when bimetallic systems are used.[5]

Table I. Magnetic Moments in μ_B at 25 °C for Complexes Derived from the Ligands $(pyral)H_2$ and $(cyclim)H_2$

complex	magn moment, μ_B solid	magn moment, μ_B solution[a]
[Co(pyral)]	4.5	4.5
$[Zn(cyclim)CoCl]PF_6$	4.9	4.7
$[Co(cyclim)CoCl]PF_6$	6.2	6.7 (6.93)[b]
$[Co(cyclim)Co](PF_6)_2$	6.3	6.2 (6.93)
[Mn(pyral)]	5.7	5.8
$[Mn(cyclim)ZnCl]PF_6$	5.6	5.8
$[Zn(cyclim)MnCl]PF_6$	6.0	6.1
$[Mn(cyclim)MnCl]PF_6$	7.7	8.0 (10.95)
$[Mn(cyclim)(\mu\text{-}Cl)MnCl]PF_6$	7.5	7.8 (9.95)

[a] [M(pyral)] complexes were measured in methylene chloride; the bimetallics were measured in acetonitrile.[6] The magnetic moment values given in parentheses are the spin-only values expected for spin-interacting dimers. For bimetallic complexes all of the magnetic moments are calculated for the dimer.

This paper is the first in a series directed at developing binucleating ligands which fully encapsulate one metal but which allow

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