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First-Row Transition-Metal Complexes of Bis(2-pyridyl)phenylcarbinol

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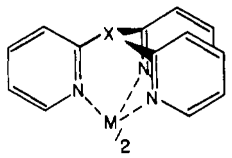
A series of complexes containing the ligand bis(2-pyridyl)phenylcarbinol ((py)$_2$PhCOH) with first-row transition-metal ions has been prepared and characterized. The ligand functions in a tridentate mode (N,N,O) whether the carbinol group remains protonated or not. Complexes of the formulas Ni((py)$_2$PhCOH)$_2$(ClO$_4$)$_2$, M((py)$_2$PhCOH)((py)$_2$PhCO)ClO$_4$·nH$_2$O (M = Co, Ni, Zn), and Cu((py)$_2$PhCO)ClO$_4$ have been prepared. The last complex may contain the cubane-like Cu$_4$O$_4$ structural unit.

Introduction

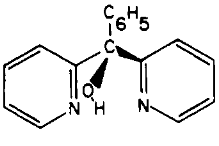
In recent years, a great deal of research has focused on the synthesis and characterization[1-19] and electrochemical[20,21] properties of a group of metal complexes containing potential tridentate ligands (1). Part of this interest has resulted from attempts to employ these ligands ((py)$_3$COH) as model systems for the active site in several enzymes.[15] It has been established that the predominant mode of coordination is as a tridentate ligand (N,N,N coordination) with first-row transition metals and methylmercury(II).[16] However, other modes of coordination are possible, as tris(2-pyridyl)amine ((py)$_3$N) can coordinate as a bidentate[18,19] as well as a tridentate ligand to copper(II).



Py$_3$X , X = N,P,P(O),As,COH

(1)

A cobalt(III)–(py)$_3$COH complex has the two ligands coordinated in two different modes, one in the N,N,N mode and the second in the N,N,O mode with the –COH group being deprotonated.[1,17] After this finding, it was of interest to us to determine if the carbinol group could be forced upon other first-row transition elements. We chose to investigate this with a similar ligand, bis(2-pyridyl)phenylcarbinol ((py)$_2$PhCOH, 2), as steric requirements for this ligand and (py)$_3$COH should be similar but N,N,N coordination is prevented by the replacement of one pyridyl ring with a phenyl ring. Complexes of the stoichiometry ML$_2^{n+}$ (N,N coordination, tetrahedral geometry, or N,N,O coordination, octahedral geometry) or ML$_3^{2+}$ (N,N coordination, octahedral geometry) were anticipated.



Py$_2$phCOH

(2)

Complexes isolated did contain the metal in an approximate octahedral geometry and the ligand coordinated in the N,N,O mode. However, complexes of three different stoichiometries were obtained. The results of this investigation are reported herein.

Experimental Section

Reagents. All reagents are commercially available and were used as received unless noted below.

Syntheses. (1) Ligand. This was prepared by the reaction of phenylmagnesium bromide and di-2-pyridyl ketone (recrystallized from diethyl ether) or by the reaction of 2-lithiopyridine and 2-benzoylpyridine.[22b] Melting points of the products agreed with literature values.

(2) Complexes. Method A. The complexes were prepared by dissolving 0.50 mmol of the hydrated metal perchlorate in a 1:1 mixture of ethanol (95%) and 2,2-dimethoxypropane (ca. 5 mL of each), heating gently for 15 minutes, and then slowly adding 1.5 mmol of the ligand dissolved in 10 mL of ethanol (95%). The mixture was allowed to cool to room temperature, and if no precipitate formed, the solution was boiled to half its volume and cooled in a refrigerator, and if necessary, a small quantity (10 mL) of diethyl ether added to induce precipitation.

Method B. This method is the same as above except that after the initial cooling of the reaction mixture, if no precipitate formed, a large quantity (>100 mL) of diethyl ether (anhydrous) was added to induce precipitation.

Physical Measurements. IR spectra were recorded as Nujol and hexachlorobutadiene mulls with a Perkin-Elmer 1430 ratio-recording spectrophotometer. In regions in which both mulling agents are transparent, no differences in spectra were noted. UV–visible spectra were recorded with a Perkin-Elmer 552 or a Perkin-Elmer 330 spectrophotometer. The ESCA spectra were recorded with a Du Pont spectrometer. Magnetic susceptibility measurements were obtained at room temperature by the Faraday method at four different field strengths. Diamagnetic corrections were made by using Pascal's constants. Resistance measurements were taken at 25 °C with a YSI 31 conductivity bridge (cell constant 1.394).

Analyses. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

Results and Discussion

The ligand, bis(2-pyridyl)phenylcarbinol ((py)$_2$PhCOH), is prepared by the reaction of phenylmagnesium bromide on di-2-pyridyl ketone or by the reaction of 2-lithiopyridine on 2-

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Table I. Selected Infrared Spectral Data (cm^{-1})

ligand or complex	ν(OH)	pyridyl or phenyl bands	perchlorate bands
$(py)_2PhCOH$	3370 m	1590 s, 1572 s, 1492 m, 1468 s, 1450 m, 1433 s, 998 s, 990 s, 775 s, 763 s, 742 s	
$Ni((py)_2PhCOH)_2(ClO_4)_2\cdot{}^1/_2H_2O$	3200 s	1605 s, 1575 w, 1500 w, 1475 m, 1465 s, 1440 s, 1005 w, 803 m, 765 s, 725 w, 708 s	1120 s, 1105 s, 620 s
$Co((py)_2PhCOH)((py)_2PhCO^-)(ClO_4)\cdot1^1/_2H_2O$		1600 sh, 1595 s, 1565 m, 1490 m, 1468 s, 1445 sh, 1435 s, 1010 m, 995 m, 775 s, 755 s, 720 w, 705 s	1080 s, 620 s
$Ni((py)_2PhCOH)((py)_2PhCO^-)(ClO_4)\cdot2^1/_2H_2O$		1600 s, 1590 s, 1565 m, 1490 m, 1465 s, 1445 m, 1435 s, 1015 m, 1000 m, 775 s, 755 s, 735 w, 720 w, 705 s	1085 s, 602 s
$Zn((py)_2PhCOH)((py)_2PhCO^-)(ClO_4)\cdot H_2O$		1600 s, 1570 m, 1490 m, 1470 s, 1445 sh, 1433 s, 1025 m, 1010 m, 780 s, 765 s, 750 s, 720 s, 695 s	1085 s, 618 m
$Cu((py)_2PhCO^-)(ClO_4)$		1605 s, 1570 m, 1490 m, 1472 s, 1442 s, 770 s, 755 m, 720 m, 710 s, 692 m	1080 s, 620 s

Table II. Physical Data for the Complexes

complex	method of prepn	elemental analyses calcd (found)	Λ_m (solvent)[a]	λ_{max} (ϵ) (solvent)[b]	μ, μ_B
$Ni((py)_2PhCOH)_2(ClO_4)_2\cdot{}^1/_2H_2O$	B	% C 51.61 (51.77) % H 3.69 (3.76) % N 7.08 (7.05) % Cl 8.96 (8.80)	272 (CH_3CN) 145 (CH_3NO_2)	540 (7), 590 (7), 930 (7), (CH_3CN) 500 (10), 600 (7), 880 (7) (CH_3NO_2)	3.20
$Co((py)_2PhCOH)((py)_2PhCO^-)(ClO_4)\cdot 1^1/_2H_2O$	A, B	% C 57.60 (57.38, 57.22) % H 4.27 (4.31, 4.29) % N 7.90 (7.90, 7.86) % Cl 5.00 (5.11)	141 (CH_3CN) 91 (CH_3NO_2)	469 (28), 488 (29), 510 (27), 1030 (8) (CH_3CN) 465 (34), 490 (34), 505 (33) (CH_3NO_2) 460, 490, 520 (solid state)	4.86
$Ni((py)_2PhCOH)((py)_2PhCO^-)(ClO_4)\cdot 2^1/_2H_2O$	A	% C 56.19 (56.14, 56.08) % H 4.58 (4.45, 4.40) % N 7.71 (7.54) % Cl 4.88 (4.89)	144 (CH_3CN) 93 (CH_3NO_2)	600 (17), 1040 (12) (CH_3CN) 605 (23) (CH_3NO_2) 590 (solid state)	3.39
$Zn((py)_2PhCOH)((py)_2PhCO^-)(ClO_4)\cdot H_2O$	A, B	% C 57.81 (57.54, 54.52) % H 4.14 (3.98, 3.95) % N 7.93 (7.87) % Cl 5.02 (5.03)	135 (CH_3CN)		
$Cu((py)_2PhCO^-)(ClO_4)$	A	% C 48.01 (48.77, 48.31) % H 3.32 (3.42, 3.42) % N 6.59 (6.46, 6.36) % Cl 8.34 (8.09)		690 (CH_3CN) 660 (solid state)	1.85

[a] Concentration is 10^{-3} M. [b] Concentration is between 1.0×10^{-3} and 5.0×10^{-3} M.

benzoylpyridine.[22b] The melting point and elemental analyses confirm the identity of the product.

Infrared spectral data are especially useful for determining the mode of coordination of the ligand. The OH stretch, ν(OH), of the carbinol group appears as a band of medium intensity at 3370 cm^{-1} (Table I). The remaining portion of the ligand is basically a 2-substituted pyridyl or monosubstituted phenyl ring; extensive correlations between infrared spectral data and coordination by the pyridyl rings are available. An increase in the wavenumber of the highest energy pyridyl band near 1590 cm^{-1} and the wavenumber of a ring-breathing mode between 1000 and 990 cm^{-1} compared to the case of the free ligand is indicative of pyridyl coordination.[18,23] The presence of only four pyridyl bands between 1600 and 1400 cm^{-1} and the pattern of C–H and ring deformations between 800 and 700 cm^{-1} are useful in determining the equivalence or nonequivalence on the pyridyl rings.[1,23] There are, of course, absorptions due to the phenyl ring in the same regions as those of the pyridyl rings, but in several cases, comparison of the spectrum of bis(2-pyridyl)phenylcarbinol to that of tris(2-pyridyl)carbinol ($(py)_3COH$)[1] allows the assignment of bands. For example, the two more intense of the four bands between 1500 and 1400 cm^{-1} (at 1468 and 1433 cm^{-1}) and the ring deformations at 763 and 742 cm^{-1} can be assigned to the pyridyl rings on the basis of bands of nearly the same wavenumber for $(py)_3COH$. The bands at 1492, 1450, and 775 cm^{-1} are more likely due to the phenyl group, as these are absent in the spectrum of $(py)_3COH$. Interaction of the perchlorate anion resulting in the reduction of symmetry from T_d may cause some splitting in the perchlorate bands near 1100 and 620 cm^{-1} [24] although splitting without coordination has been observed.[1,25]

The complexes isolated and their methods of preparation, elemental analyses, single-concentration conductivity values, room-temperature magnetic moments, and visible–near-infrared and infrared spectral data are given in Tables I and II. As is evident from these data, complexes of different stoichiometries can be obtained depending upon the metal ion or method of preparation used. The complexes will be discussed according to their stoichiometry.

$Ni((py)_2PhCOH)_2(ClO_4)_2\cdot{}^1/_2H_2O$. This complex is precipitated from solution as a nearly colorless (light gray) solid by the addition of ether to the reaction mixture. The visible–near-infrared spectra in acetonitrile and nitromethane (Table II) suggest an octahedral geometry around the nickel(II). Absorption bands for the solid could not be identified with certainty due to the almost total absence of color in the solid state. Octahedral nickel(II) normally has three d–d bands, each with a molar absorptivity value less than 20.[26,27] In octahedral symmetry, these bands can be assigned to the ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions, listed in increasing energy. Only the two lower energy bands are observed due to intense ligand bands below 400 nm. Splitting of the middle ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ band is common in nickel(II) complexes[1,28] and has been attributed to spin–orbit coupling or the presence of a spin-forbidden (${}^3A_{2g} \rightarrow {}^1E_g(D)$) transition.

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Reduction from pure octahedral symmetry will remove the degeneracy of the two excited states and may also produce some splitting of either or both bands. The single-concentration conductivity value is indicative of a 2:1 electrolyte in both acetonitrile and nitromethane.[29]

The infrared spectrum of this complex indicates that the pyridyl groups are coordinated, as the 1590-cm^{-1} band of the free ligand is increased to 1602 cm^{-1} and the two bands at 998 and 990 cm^{-1} in the free ligand are absent in the complex. The fairly simple pattern of the bands between 1500 and 1400 cm^{-1} confirms the near equivalence of the pyridyl rings. The ν(OH) of the ligand is a broad band at 3200 cm^{-1}. There is a definite splitting of the perchlorate band near 1100 cm^{-1} and a broadening of the one near 620 cm^{-1}, indicating coordination of the anion or reduction of the symmetry from T_d.

With both pyridyl rings from each ligand coordinated and with an octahedral geometry around the nickel(II), there are still two coordination sites not accounted for. Conductivity data suggest neither carbinol group is ionized, yet the sharp decrease in the ν(OH) band suggests some interaction of this group. We believe the data can best be rationalized by suggesting that the oxygen of the carbinol group is both protonated and coordinated. Coordination would weaken the O–H bond, thus decreasing its stretching frequency. Interaction of the hydrogen with the perchlorate group ($O–H\cdots O–ClO_3^-$) would further weaken this bond and at the same time cause a reduction of the symmetry of the perchlorate anion. A similar but smaller decrease in ν(OH) and some splitting of the perchlorate band at 1100 cm^{-1} were observed in several complexes of $(py)_3COH$.[1] The simple pattern for the pyridyl bands between 1500 and 1400 cm^{-1} would suggest a trans arrangement of the carbinol oxygens, as the pyridyl groups should then be equivalent. Molecular models show that this arrangement has the least steric interactions although a cis arrangement is possible. Since the carbinol groups remain protonated, they should not be strongly coordinating, and partial replacement by solvent molecules (CH_3CN or CH_3NO_2) would explain the minor differences in the visible–near-infrared solution spectra.

In summary, the $(py)_2PhCOH$ can act as a tridentate ligand (N,N,O coordination) regardless of whether the carbinol is protonated or not.

$M((py)_2PhCOH)((py)_2PhCO^-)(ClO_4)\cdot nH_2O$. Cobalt(II) and zinc(II) complexes of this stoichiometry were isolated regardless of the method of preparation. The cobalt(II) complex was prepared under a nitrogen atmosphere because of the ease of oxidation of the similar complex with $(py)_3COH$.[1]

The visible–near-infrared spectra of the cobalt(II) and nickel(II) complexes (Table II) are typical of an approximate octahedral geometry. Further, they are nearly identical in both the solid state and solution. In octahedral symmetry for cobalt(II), the higher energy band(s) are assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition and the lower energy band to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ transition.[26] The two bands in the nickel(II) spectrum can be given the same assignments as in the previous nickel(II) complex. Conductivity data for both complexes in acetonitrile and nitromethane are typical of 1:1 electrolytes.[29] The infrared spectra of these two complexes are virtually identical. There are an increase in wavenumber and some broadening or splitting of the 1590-cm^{-1} band and an increase in wavenumber of the 990-cm^{-1} band of the free ligand. The similarity of the pyridyl bands between 1500 and 1400 cm^{-1} in the ligand and the complexes indicates no pronounced structural differences. The complexes contain water of hydration, as seen from their elemental analyses and the broad bands near 3600 cm^{-1} (ν(OH)) and 1640 cm^{-1} (H–O–H bending). There is some structure on the former band at 3540 cm^{-1}, and it could be argued that this is the OH stretch of the ligand superimposed upon the hydrate water band. However, the zinc(II) complex (vide infra) contains little water of hydration, and no band assignable to the ligand can be found in this region. The perchlorate bands centered at 1080 and 620 cm^{-1} are fairly broad, but no splitting is evident.

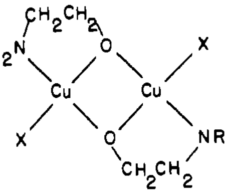
With only two ligands per metal ion and an octahedral geometry indicated by the visible–near-infrared spectra, N,N,O coordination is again indicated. The band positions in the visible–near-infrared spectra are consistent with a mixture of nitrogen and oxygen donor atoms.[26,30,31] From this, coupled with the conductivity data (1:1 electrolyte), it appears that both carbinol groups are coordinated but with only one group remaining protonated. The inability to locate the ligand OH stretch in either complex is a logical consequence of the proposed structure in that one carbinol is deprotonated while the second, although protonated, is complexed, leading to a decrease in both the frequency and intensity of the band.

The infrared spectrum of the zinc(II) complex indicates a similar coordination mode. The perchlorate band at 1080 cm^{-1} has some structure, but coordination is not indicated due to the absence of similar splitting of the 615-cm^{-1} band. The conductivity is consistent with a 1:1 electrolyte.

An alternate formulation, $M((py)_2PhCOH)_3(ClO_4)_2\cdot nH_2O$ (N,N or N,O coordination), which will give acceptable carbon, hydrogen, and nitrogen analyses, is ruled out by the experimental chlorine analyses and low conductivity values (2:1 electrolytes). The ESCA spectrum (N 1s) of the nickel(II) complex was recorded in an attempt to determine if the pyridyl rings were indeed equivalent, and only one peak was observed. However, the cobalt(III) complex of $(py)_3COH$ in which there are five coordinated and one noncoordinated pyridyl groups[1,19] also gave only one peak although the peak width at half-height was about 20% wider than that of the nickel(II) complex.

In summary, the complexes of stoichiometry $M((py)_2PhCOH)((py)_2PhCO^-)(ClO_4)\cdot nH_2O$ have an octahedral geometry around the metal ion, and both ligands are tridentate via the two pyridyl ring nitrogens and the carbinol oxygen. In this mode of coordination, one of the ligands must remain protonated.

$Cu((py)_2PhCO^-)ClO_4$. The empirical formula of this complex indicates some bridging of the donor atoms of $(py)_2PhCO^-$ between copper(II) ions. There is ample precedent for such bridging, as in the series of complexes consisting of the anion of various (dialkylamino)ethanol derivatives, $R_2NCH_2CH_2O^-$, to yield complexes of the stoichiometry $[Cu(R_2NCH_2CH_2O)X]_n$.[32-36] For $n = 2$, complexes exhibit the structure 3. A feature of these complexes is a diminished, room-temperature magnetic moment <1 μ_B (see ref 33 and references therein). For $n = 4$, complexes exhibit a cubane-like unit Cu_4O_4, 4. For simplicity, the ligand



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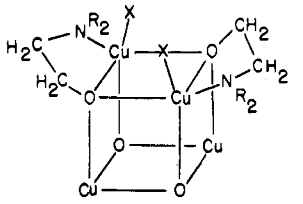

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(except for the oxygen atom) and the anion have been omitted from the bottom portion of **4**. Room-temperature magnetic moments for these complexes are near those for magnetically dilute copper(II) ions, ~1.9 μ_B (see ref 33 and references therein). A recent report[19] has described a Cu_4O_4 complex, $[Cu_4(OH)_4(SO_3CF_3)_2((py)_3N)_4](SO_3CF_3)_2$, which contains tris(2-pyridyl)amine instead of a (dialkylamino)ethanol derivative; the $(py)_3N$ coordinates as a bidentate ligand bound via the pyridyl groups, and the OH^- ions provide the oxygen bridging atoms.

The $(py)_2PhCOH$ ligand can provide both the pyridyl groups for coordination to the copper(II) as in the complex above and the bridging oxygen atom to obtain a cubane-like structure. The data for this complex are consistent with such a Cu_4O_4 unit as (1) the stoichiometry suggests there must be some sharing of the donor atoms between copper(II) ions, (2) limited solubility in both nitromethane and acetonitrile suggests some association of copper(II)–$(py)_2PhCO^-$ units, (3) the room-temperature magnetic moment (Table II) is consistent with the magnetic moments of other Cu_4O_4 clusters, (4) infrared bands in the 1600–1400-cm^{-1}, 1000–980-cm^{-1}, and 800–700-cm^{-1} regions suggest coordinated and nearly equilvalent pyridyl rings while there are no bands above 3200 cm^{-1} assignable to the carbinol group, and (5) perchlorate bands are broad but do not show any pronounced splitting, indicating only slight distortion from T_d symmetry. Molecular models show that steric considerations do not preclude such a structure. We are currently trying to obtain suitable crystals for an X-ray structure analysis to provide an unambiguous assignment to this complex.

Conclusions

This investigation has shown that the ligand bis(2-pyridyl)phenylcarbinol can function as a tridentate ligand (N,N,O) regardless of whether the carbinol group remains protonated. Complexes of varying stoichiometry are easily obtained depending upon the metal ion and/or the reaction conditions employed. Finally, a cluster complex $[M((py)_2PhCO^-)]_4^{4+}$ unique for copper(II) with this particular ligand has been prepared.

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Registry No. $Ni((py)_2PhCOH)_2(ClO_4)_2$, 97633-54-0; $Co((py)_2PhCOH)((py)_2PhCO^-)(ClO_4)$, 97644-25-2; $Ni((py)_2PhCOH)((py)_2PhCO^-)(ClO_4)$, 97644-27-4; $Zn((py)_2PhCOH)((py)_2PhCO^-)(ClO_4)$, 97644-29-6.

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Effect of Equivalent and Nonequivalent Sites on the Kinetics of Equilibration of Thiocyanate with $[Mo_3O_4(H_2O)_9]^{4+}$

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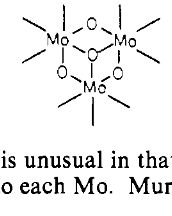
Unique kinetic situations arise in considering substitution reactions of the triangular Mo(IV) ion $[Mo_3O_4(H_2O)_9]^{4+}$. For the condition in which $[NCS^-]$ is in large (≥10-fold) excess a statistically corrected rate constant is used, assuming three equivalent sites on the $Mo_3O_4^{4+}$ ion, and equilibration rate constants k_{eq} can be expressed as $k_{eq} = (k_1/3)[NCS^-] + k_{-1}$. With $[Mo_3O_4(H_2O)_9]^{4+}$ in excess the reaction is constrained by the low $[NCS^-]$ to form only $Mo_3O_4(NCS)^{3+}$, and $k_{eq} = k_1[Mo_3O_4^{4+}] + k_{-1}$. A comparison is made by using different anions, *p*-toluenesulfonate; trifluoromethanesulfonate, and perchlorate, $I = 2.0$ M (Li^+ salt). At 25 °C forward and backward rate constants at $[H^+] = 2.0$ M are $k_1 = 0.78, 1.02, 2.13$ $M^{-1}\ s^{-1}$ and $10^3k_{-1} = 1.57, 1.94, 2.18$ s^{-1} for the three anions, respectively. Rate constants k_1 and k_{-1} (and the aquation step k_{-2}) have $[H^+]$ dependences of the kind $a + b[H^+]^{-1}$, with b dominant for $[H^+] = 0.8$–2.0 M. Solutions containing higher complexes obtained by equilibrating $Mo_3O_4^{4+}$ (1.3×10^{-3} M) with NCS^- (5×10^{-3} M) give, on ion exchange, bands that in order of elution (Mo and NCS^-) analyze for $Mo_3O_4(NCS)_2^{2+}$, $Mo_3O_4(NCS)^{3+}$, and $Mo_3O_4^{4+}$. A fraction not held on the column at $[H^+] = 0.3$ M is believed to contain $Mo_3O_4(NCS)_3^+$ as well as free NCS^-. Two kinetic stages are observed for aquation of $Mo_3O_4(NCS)^{2+}$, which are assigned (for 2 M HPTS) to k_{-1} (here 1.7×10^{-3} s^{-1}) and $k_{-2} = 0.24 \times 10^{-3}$ s^{-1}. Consistent with these assignments, the faster and not the slower rate constant is observed in the aquation of $Mo_3O_4(NCS)^{2+}$. Implications regarding different isomeric forms of $Mo_3O_4(NCS)^{3+}$ and $Mo_3O_4(NCS)_2^{2+}$ are considered.

Introduction

The trimeric Mo_3O_4 core in Mo(IV) is now well characterized, a notable feature being the apical μ_3-oxo ligand.[1-3] The aqua ion $[Mo_3O_4(H_2O)_9]^{4+}$ is unusual in that four different types of O atoms are attached to each Mo. Murmann and colleagues,[4,5] using ^{18}O-labeling techniques, have obtained information regarding exchange rates. At 25 °C and in 1 M methanesulfonic acid (CH_3SO_3H) the half-time for exchange of the μ_3-oxo is 5 days, for the three μ_2-oxo's >3 years, for the three H_2O's trans to the μ_3-oxo 1.1 h, and for the six H_2O's trans to the μ_2-oxo's ~20 min (at 0 °C). We now extend these studies to include NCS^- anation of $[Mo_3O_4(H_2O)_9]^{4+}$ and related aquation reactions. For the duration of the experiments considered the four core O atoms of $Mo_3O_4^{4+}$ can be assumed to be inert. Previous studies from this laboratory on $Mo_3O_4^{4+}$ have been reported.[6-9] The instability



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