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Perrhenato Complexes of Bivalent Cations

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A series of complexes of the general formula $[ML_4(ReO_4)_2]$ *were prepared and studied: M = cobalt(II), copper(II), manganese(II), nickel(II) and zinc(II); L = pyridine(py) or 4-methylpyridine(4-mepy). Magnetic susceptibility measurements, infrared spectra (2.5 - 50μ), and near-infrared and visible spectra indicate coordination of the perrhenate groups to form tetragonally distorted octahedral complexes. Metal-ligand vibrations were assigned from the far-infrared spectral data, and Ds, Dt,* Dq_{xy} *and* Dq_z *values of the nickel compounds were calculated from the near-infrared and visible spectral data. These studies indicate that the perrhenate anion coordinates more strongly than the perchlorate and tetra-fluoroborate anions and less strongly than the bromide and chloride anions.*

Introduction

At one time it was believed that the perrhenate anion in solution should be represented as the octahedral ReO_6^{5-} species.[1] However, it has been conclusively shown that in solution the ion exists as ReO_4^- with a tetrahedral structure,[2,3] as in the alkali perrhenate crystals.[4]

The perrhenate salts of several first-row transition metal ions have been prepared, and their properties described.[5]

Since perrhenic acid is not as strong an acid as perchloric acid, the perrhenate ion should coordinate more readily than the perchlorate ion. It seemed desirable to prepare and study a series of perrhenate compounds analogous to the reported perchlorate-pyridine base complexes.[6,7] Only one previous account of perrhenate coordination to a metal ion has been described.[8]

Results and Discussion

Analytical data and magnetic moments of the synthesized compounds are summarized in Table I. The μ_{eff} is representative of high-spin octahedral type complexes and not typical of tetrahedral structures in cases of the cobalt, manganese and nickel materials.

All the compounds were either insoluble in or reacted with such solvents as chloroform, dichloromethane, nitromethane and acetonitrile.

Infrared Spectra. The pyridine bands in the 2.5-15 μ region are typical of complexes containing pyridine.[9] The infrared data along with tentative assignments of bands due to the perrhenate group and central metal-ligand vibrations are listed in Table II.

The vibrational spectrum of the T_d perrhenate ion consists of two infrared and four Raman bands. Only ν_3 and ν_4 are infrared active, while all vibrational modes are Raman active.

It has been shown that a symmetry reduction from T_d to local C_{3v} (C_s symmetry if the M–O–Cl group in the $M{-}OClO_3$ system is not linear) accompanies monodentate coordination of the perchlorate ion through an oxygen atom.[10] Further reduction to local C_{2v} symmetry occurs with bidentate ligand attachment. This behavior is likewise expected for mono- and bidentate perrhenate coordination. Symmetry reduction to local C_{3v} of a monodentate perrhenate group should result in three infrared bands in the 850-950 cm^{-1} region. These three bands correspond to two A_1 and an E species resulting from the splitting of ν_3 and the activation of ν_1 in the infrared.

The infrared and Raman spectra of solid $KReO_4$ have been presented by several authors.[11,12] Based upon S_4 site symmetry, the most intense Raman line at 966 cm^{-1} has been assigned as an A species (ν_1) and the 924 and 897 cm^{-1} lines as the B and E species (ν_3), respectively. The 924 cm^{-1} line was distinguished from the 897 cm^{-1} line as a B species because of its lesser intensity.

In the 850-950 cm^{-1} region, three infrared bands (Figure 1) due to vibrations of the perrhenate group are observed for all complexes except $[Ni(4{-}mepy)_4(ReO_4)_2]$. Two bands, both fairly broad, are observed for this complex. Thus by analogy with the assignments made for S_4 site symmetry, it appears reasonable to tentatively identify the highest energy perrhenate infrared band as an A_1 species and the two lower energy bands as A_1 and E species for local C_{3v} symmetry.

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Table I. Analytical Data and Magnetic Moments

Compound	Found (%) C	H	N	Required (% C	H	N	$\mu_{eff.}$ [a] (B.M.)
[Co(py)$_4$(ReO$_4$)$_2$]	27.67	2.39	5.68	27.43	2.31	6.40	5.19
[Cu(py)$_4$(ReO$_4$)$_2$]	27.81	2.24	5.71	27.28	2.29	6.36	1.94
[Mn(py)$_4$(ReO$_4$)$_2$]	27.33	2.26	6.17	27.55	2.32	6.43	6.02
[Ni(py)$_4$(ReO$_4$)$_2$]	27.68	2.28	5.50	27.43	2.31	6.40	3.25
[Ni(4-mepy)$_4$(ReO$_4$)$_2$]	30.64	2.84	5.78	30.94	3.04	6.02	3.42
[Zn(py)$_4$(ReO$_4$)$_2$]	27.42	2.18	6.42	27.23	2.29	6.35	

[a] All magnetic data were obtained at 23±2°C. Analyses performed by Weiler and Strauss Laboratories, Oxford, England, and Galbraith Laboratories, Knoxville, Tennessee.

Table II. Infrared Spectra Showing Re—O and Metal-Ligand Frequencies (cm^{-1})

Compound	ν_1	ν_2	ν_3	ν_4	M—N	M—O
KReO$_4$ [a]	 (966) [b]	362 s (361 m)	915 s, br (898 s) (915 s)	~310 vs, br (304 s) (317 s)		
[Co(py)$_4$(ReO$_4$)$_2$]	936 s	338 m 342 m	905 s 923 s	311 vs 319 sh 322 m	225 sh 233 s	
[Cu(py)$_4$(ReO$_4$)$_2$]	928 s	339 m	900 s 907 w 918 s	310 vs 320 s 325 s	276 m 260 m	229 m
[Ni(py)$_4$(ReO$_4$)$_2$]	935 s	343 s	903 s 921 s	314 vs 321 s 326 s 329 s	245 sh 256 s	
[Mn(py)$_4$(ReO$_4$)$_2$]	940 s	336 m 342 m	898 s 928 m	310 vs 317 s 321 s 325 sh	~212 m, br	
[Zn(py)$_4$(ReO$_4$)$_2$]	935 s	338 m 342 m	900 s 922 s	311 vs 319 s 322 s 325 sh	~200 m, br	
[Ni(4—mepy)$_4$(ReO$_4$)$_2$]	928 s	338 m	903 s 928 s	320 s 326 sh 329 vs	221 m 230 m	264 m

[a] Literature values in parenthesis (Refs. 10 and 11). [b] Raman line. Intensities: s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad.

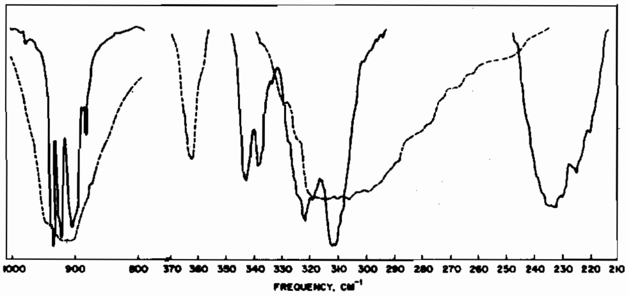

Figure 1. The infrared spectra of [Co(py)$_4$(ReO$_4$)$_2$] (———), and KReO$_4$ (- - -). The band of medium intensity at 880 cm^{-1} arises from pyridine.

Although only two bands are observed for [Ni(4—mepy)$_4$(ReO$_4$)$_2$], we feel that the perrhenate groups are cordinated and probably have local C_{3v} symmetry. The relatively broad band at 928 cm^{-1} most likely consists of the coincidence of two of the expected perrhenate bands which are unresolved.

It should be pointed out that the splitting of the ν_3 band of the perrhenate ion upon cordination observed in this study is much less than that reported by Lenz and Murmann[8] for [Co(NH$_3$)$_5$ReO$_4$]$^{2+}$. We feel that these authors probably incorrectly assigned their observed lower energy peak at about 835 cm^{-1} to a coordinated perrhenate group vibration. We believe this vibration to be due to a rocking mode of the coordinated ammine groups which are observed in this region for ammine complexes of cobalt(III).[13] The broad band centered around 930 cm^{-1} observed in this earlier study is believed to be the unresolved bands due to coordinated perrhenate ion.

The far-infrared[12] and the Raman[11] perrhenate spectra of solid KReO$_4$ reveal a splitting of ν_4 and an activation of the ν_2 vibration in the infrared which suggests a symmetry reduction of the T_d perrhenate ion. The vibrational spectra of some perrhenate complexes were compard with those of the analogous perchlorate compounds in order to distinguish metal-ligand vibrations from those of the perrhenate group. All perrhenate compounds show four to six perrhenate bands (Figure 1) in the 310- 350 cm^{-1} region indicating in some cases a complete removal of the degeneracies expected with C_{3v} symmetry. This symmetry reduction may be due to distorsions within the cry-

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stalline lattice.* The band around 340 cm^{-1}, which is split for the cobalt, manganese and zinc compounds, arises from the activation of ν_2 and is assigned as an E species. The remaining bands in this region result from the splitting of the ν_4 mode. Although the splittings of ν_2 and ν_4 indicate a symmetry lower than C_{3v}, it is believed that the perrhenate groups are coordinated through only one oxygen and thus are monodentate in these compounds.

There exists one metal-to-pyridine nitrogen infrared vibration for *trans*-octahedral compounds of the ML_4X_2 type.[14] This mode, and E_u species in D_{4h} symmetry, has been placed near 200 cm^{-1} and may be split due to solid state effects among other things.[14,15] The assignments of the skeletal vibrations were based upon comparison with some analogous perchlorate materials and literature values for similar compounds.[14-17]

The metal-nitrogen frequencies form a trend, Cu > Ni > Co > Mn > Zn, similar to the Irving-Williams stability series.[18]

It appears reasonable to assign the 229 cm^{-1} band of the [Cu(py)$_4$(ReO$_4$)$_2$] as a copper-oxygen vibration. That this band is not observed in the other pyridine compounds suggests that it may occur below 200 cm^{-1} and supports the trend found in the metal-nitrogen frequencies.

In summary, the infrared and far-infrared data are consistent with monodentate perrhenate groups in these complexes. This is also supported by the magnetic moment data and the electronic spectral data given below.

Visible and Near-Infrared Spectra. Since component vibrational transitions accompany electronic transitions observed in the solid state, transitions to excited electronic levels differing by less than about 1500 cm^{-1} may not be resolved at room temperatures.[19] Thus in order to reduce band broadening, electronic spectra were obtained on all the compounds at temperatures approaching that of liquid nitrogen.

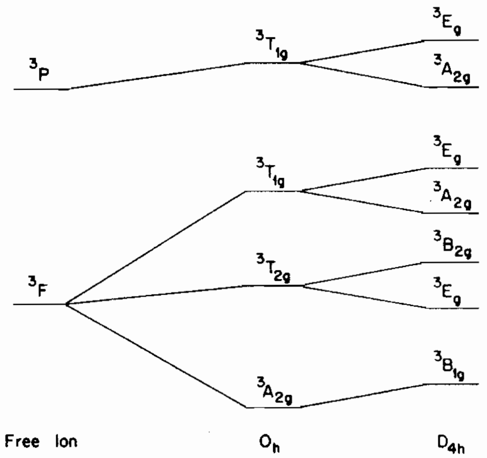

Figure 2. Correlation diagram for a d^8 configuration in crystal fields of O_h and D_{4h} symmetry.

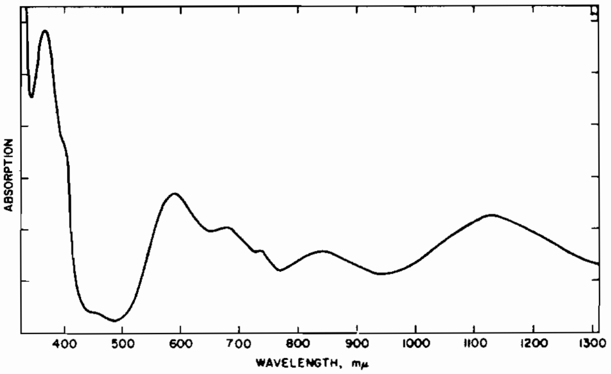

Figure 3. Low temperature electronic spectrum of [Ni(4–mepy)$_4$(ReO$_4$)$_2$] as a Kel-F mull.

Expressions relating transition energies to the radial parameters Ds, Dt, Dq_{xy}, and Dq_z have been developed from crystals field theory[20] by several authors for d^6, d^3 and d^8 *trans* ML_4X_2 type complexes.[19] The three spin-allowed excited electronic states of an O_h d^8 configuration become split (Figure 2) as the molecular symmetry is lowered to D_{4h} by tetragonal distorsion, thus permitting six spin-allowed transitions. The low temperature spectrum of [Ni(4–mepy)(ReO$_4$)$_2$] is shown in Figure 3. Equating the energy of the $^3B_{1g}$ ground state to zero, the energies of the first two excited states are to a first order approximation[21]

$$
\begin{aligned}
E(^3B_{2g}) &= 10\,Dq_{xy}\\
E(^3E_g) &= 10\,Dq_{xy}-35/4\,Dt\\
E(^3A_{2g}) &= 10\,Dq_{xy}+12\,B-4\,Ds-5\,Dt\\
E(^3E_g) &= 10\,Dq_{xy}+12B+2Ds-25/4\,Dt.
\end{aligned}
$$

The $^3B_{1g}\rightarrow{}^3B_{2g}$ transition is dependent only on the in-plane ligand field strength Dq_{xy}. The splitting of the first excited state ($^3T_{2g}$, O_h) is 35/4 Dt, while that of the second ($^3T_{1g}$, O_h) is 6Ds - 5/4 Dt. The sign of Dt was determined through consideration of the relative strengths of the in-plane and out-of-plane ligand fields. A weak axial field results in the ^3E_g being of lower energy than the $^3B_{2g}$ state. Also, the lower energy component of the first split band is the more intense and should be assigned as the E_g, as the higher energy component of the second split band is the more intense and is therefore the E_g band. These assignments produce reasonable results. Once Dq_{xy} and Dt are obtained calculation of the axial field parameter, Dq_z, is possible from the expression, $Dt = 4/7\,(Dq_{xy}-Dq_z)$, assuming the absence of configurational interaction.[19]

(*) As was kindly pointed out by one of the referees, the splitting of the for infrared bands may be due to coupling effects between the two perrhenate groups in a molecule and/or between perrhenate groups within the unit cell.

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The spectra of [Ni(py)$_4$(ReO$_4$)$_2$] and [Ni(4—mepy)$_4$(ReO$_4$)$_2$] are very similar. In most instances assignments of the spin-allowed transitions were straight forward, although the low intensity spin-forbidden bands[22,23] added some complications (Table III).

Comparison of Dt values calculated from the electronic spectral data for pyridine complexes[23] by the procedure presented in this study indicates that the perrhenate anion (Table IV) coordinates more strongly than the perchlorate (577 cm^{-1}) and tetrafluoroborate (625 cm^{-1}) anions but less strongly than the bromide (349 cm^{-1}) and chloride (307 cm^{-1}) ions.

Table III. Visible and Near-Infrared Spectral Data (cm^{-1})

[Ni(py)$_4$(ReO$_4$)$_2$]	[Ni(4—mepy)$_4$(ReO$_4$)$_2$]	Assignment
8,780 s	8,840 s	$^3B_{1g} \rightarrow {}^3E_g$
12,000 s	11,800 m	$\rightarrow {}^3B_{2g}$
13,300 w	13,500 w	$\rightarrow {}^1A_{1g}, B_{1g}(^1D)$
15,000 m	14,400 w	$\rightarrow {}^3A_{2g}$
17,700 s	17,100 m	$\rightarrow {}^3E_g$
21,700 vw	21,400 vw	$\rightarrow {}^1A_{1g}(^1G), {}^1E_g(^1D)$
25,600 sh	24,800 sh	$\rightarrow {}^3A_{2g}(^3P)$
27,500 vs	27,200 vs	$\rightarrow {}^3E_g(^3P)$
[Co(py)$_4$(ReO$_4$)$_2$]		
7,900 w		$^4T_{1g} \rightarrow {}^4T_{2g}$
10,000 m		
15,500 m		
16,700 m		
17,600 sh		
18,500 sh		$^4T_{1g} \rightarrow {}^4T_{1g}(P)$
19,600 vs		
20,600 s		
21,400 sh		
25,800 sh		

Intensities: w, weak; m, medium; s, strong; v, very; sh, shoulder.

Table IV. Electronic Spectral Parameters of Ni^{II} Compounds (cm^{-1})

Parameter	[Ni(py)$_4$(ReO$_4$)$_2$]	[Ni(4—mepy)$_4$(ReO$_4$)$_2$]
Dq_{xy}	1,200	1,180
Dq_z	556	588
Dt	368	338
Ds	527	504
B	577	530

The low temperature mull spectrum of [Co(py)$_4$(ReO$_4$)$_2$] reveals a splitting of the near-infrared band and a visible band containing multiple structure, which is typical of tetragonally distorted octahedral complexes.[24] Splitting in both bands may result from spin-orbit coupling[25,26] and/or symmetry reduction.[27] Spin-forbidden transitions[28] and a ground state to $^4B_{1g}$ (D_{4h}) transition may be responsible for the multiple structure of the visible band. Since at least two distinct peaks are seen in the visible band, it is believed that the perrhenate groups occupy the *trans* position.[27]

General assignments have been postulated (Table III), since definite band assignments are impossible at this point.

The low temperature mull spectrum of the [Cu(py)$_4$(ReO$_4$)$_2$] consists of a broad intense band centered around 16,800 cm^{-1} and a distinctly separate band at 12,000 cm^{-1} of weaker intensity. Because of considerable overlapping, the three transitions expected for tetragonally distorted octahedral copper complexes (D_{4h}) normally appear as a broad asymmetrical band envelope.[29] The two observed bands at 12,000 and 16,800 cm^{-1} are assigned as the $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2B_{2g}$, ^2E_g transitions, respectively.

X-Ray Diffraction. To obtain additional evidence for the coordination of the perrhenate group, X-ray diffraction powder patterns were obtained on all the compounds. The patterns of the cobalt, copper and nickel pyridine compounds are quite similar, and it is reasonable to conclude that these compounds are isostructural. The powder patterns of the manganese and zinc compounds are unique, differing significantly from each other and the patterns obtained for the cobalt, copper and nickel compounds.[30]

Experimental Section

Materials. Reagent grade acetone, methanol, metal carbonates and practical grade 2,2-dimethoxypropane and ether were used as received without further purification. The hydrated metal perrhenates were obtaind by treating the metal carbonates with an excess of perrhenic acid.

Preparation of Complexes. The cobalt(II) and nickel(II) complexes were prepared virtually in the same manner. Approximately 0.006 mole of the hydrated metal perrhenate was dissolved in about 75 ml. of 2,2-dimethoxypropane, which served as a solvent and a dehydrating agent. To this solution was added an excess (0.12 mole) of the appropriate pyridine base. The complex material formed immediately, and the resultant slurry was stirred about an hour.

The copper(II) complex was prepared by dissolving approximately 0.003 mole of the hydrated copper(II) perrhenate in about 50 ml of water. To this solution was added with stirring an excess (0.12 mole) of pyridine. The copper complex formed immediately.

About 0.004 mole of the anhydrous manganese(II) or zinc(II) perrhenate dissolved in about 50 ml of acetone was treated with 10 ml of 2,2-dimethoxypropane. The complex precipitated upon addition of an excess (0.12 mole) of pyridine.

All the metal complexes, except the zinc, were collected by suction filtration, washed with ether and

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(30) Detailed data will be available in the doctoral dissertation of H. G. M., the University of Tennessee (1970).

dried in a vacuum desiccator at room temperatures. The zinc complex was washed with a pyridine containing solution of ether and dried over calcium sulfate in a desiccator.

Measurements. Infrared spectra of the complexes were obtained as Nujol mulls using a Perkin-Elmer 257 recording spectrophotometer equipped with sodium chloride optics. Far-infrared spectra were obtained as Nujol mulls spread on a single piece of polyethylene using a Perkin-Elmer 225 recording spectrophotometer.

Visible and near-infrared spectra were obtained using a Cary Model 14 recording spectrophotometer at low temperatures as mulls spread on a quartz window placed in a dewar filled with liquid nitrogen. The mulls were prepared by grinding the complexes in Nujol or Kel F grease.[22] In an attempt to equalized light scattering, Nujol-saturated filter paper was placed in the reference beam.[31]

Magnetic moments were determined according to the Guoy method. Mercury tetrathiocyanatocobaltate(II) was used as the calibration standard. Molar diamagnetic corrections were made on the molar magnetic susceptibilities.[32,33] The magnetic moments were calculated assuming a Weiss constant of 0° Kelvin using the following equation:

$$\mu_{\text{eff.}} = 2.84\,(\chi_m^{\text{Corr}}\,T)^{1/2}$$

All measurements were made at 23±2°C.

X-Ray diffraction patterns were obtained with a Norelco X-Ray diffractometer. Copper K_α X-rays were employed for an exposure time of approximately 3.5 hours.

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