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Far-Infrared Assignments for Bridging Cobalt–Halogen Stretching Vibrations in Several Coordination Compounds[1a]

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Some coordination compounds of cobalt(II) of the type $\mathrm{CoL_2X_2}$ (L = py, 4-Cl(py), or 4-Br(py); X = Cl or Br) are known to exist in polymeric and monomeric forms. By following the appearance and disappearance of bands in the low-frequency spectra of both forms and by studying the effects of high pressure on these bands, assignments of bridging CoX stretching vibrations (ν_bCoX) have been made for the first time. The ν_bCoCl vibrations occur in the 155–186-cm^{-1} region. The ν_bCoBr vibrations occur in the 118–143-cm^{-1} region. The terminal CoX stretching vibrations (ν_tCoCl) occur in the 306–347-cm^{-1} region; the ν_tCoBr occur at 265 cm^{-1}.

Introduction

Halogens are common ligands in coordination chemistry, forming coordinate bonds with metals readily. Metal–halogen (M–X) stretching bands show a strong absorption in the far-infrared region and can be assigned empirically without much ambiguity. Thus, extensive infrared studies have already been carried out on M–X stretching bands by many investigators.[2] However, most of the previous investigations have concentrated on terminal M–X stretching bands, and very little information is available on bridging M–X stretching frequencies. Thus far, bridging M–X stretching frequencies have been reported for Pt(II), Pd(II),[3,4] Cu(II),[5–7] Al(III),[8,9] and some transition metal [M(II)] complexes[10,11] containing halogen bridges. A primary cause for the lack of investigation of bridged M–X frequencies was their location below 200 cm^{-1}, an instrumental limitation until recently.

Co(II) complexes of the type $\mathrm{CoL_2X_2}$, where X is Cl or Br and L is pyridine or a substituted pyridine,[12,13] exist in two forms: the monomeric tetrahedral form (blue or green) and the polymeric octahedral form (lilac). The crystal structure of the polymeric form was established by Dunitz.[14] In most cases, only one of the two forms is obtained as crystals at room temperature. Although the polymeric octahedral form is more stable than the monomeric tetrahedral form, this trend is reversed as the size of X increases in the order Cl < Br < I. If the polymeric octahedral form is obtained, it is often possible to produce the unstable monomeric tetrahedral form either by heating or by changing the solvent. In this paper, we report the far-infrared spectra of five complexes of the type $\mathrm{CoL_2X_2}$ in both the polymeric and the monomeric forms. By comparing the far-infrared spectra and studying the effects of pressure on the spectra of both forms for each compound, we have been able to assign both bridging and terminal Co–X stretching vibrations, the former not previously located in complexes of this type.

Experimental Section

Preparation of Compounds. Ligands.—4-Chloropyridine (4-Cl(py)) and 4-bromopyridine (4-Br(py)) were prepared by neutralizing the corresponding HCl salts with cold KOH solution. The latter was purchased from Aldrich Chemical Co., Milwaukee, Wis.

Complexes.—$\mathrm{Co(py)_2Cl_2}$ (polymeric form), $\mathrm{Co(4\text{-}Cl(py))_2Cl_2}$ (polymeric form), $\mathrm{Co(4\text{-}Cl(py))_2Br_2}$ (polymeric form), $\mathrm{Co(4\text{-}Br(py))_2CoCl_2}$ (polymeric form), and $\mathrm{Co(4\text{-}Br(py))_2Br_2}$ (monomeric form) were prepared according to the method described by Graddon, *et al.*[13] Cobalt halide hexahydrate was dissolved in *sec*-butyl alcohol, and an appropriate amount of 2,2-dimethoxypropane was added as a dehydrating agent. The solution was boiled for several minutes, and 4-chloropyridine or 4-bromopyridine was added to the boiling solution in 1:2 molar ratio (Co:ligand). After cooling, the precipitate was filtered and recrystallized from *sec*-butyl alcohol (dried with 2,2-dimethoxypropane).

$\mathrm{Co(4\text{-}Br(py))_2Br_2}$ (polymeric form) was prepared in the following manner. The monomeric form obtained above was dissolved in hot *sec*-butyl alcohol, and a small amount of 2,2-dimethoxypropane was added. To this solution a few small crystals of $\mathrm{Co(4\text{-}Cl(py))_2Br_2}$ (polymeric form) were added as seeds. The solution yielded a mixture of lilac (polymeric form) and blue (monomeric form) crystals. The lilac crystals were manually separated from the blue crystals.

The monomeric forms of $\mathrm{Co(py)_2Cl_2}$ and $\mathrm{Co(4\text{-}Br(py))_2Br_2}$ were prepared by heating the corresponding polymeric forms in a polyethylene matrix near the color transition using a polyethylene pellet press.[15] In the case of $\mathrm{Co(4\text{-}Cl(py))_2Cl_2}$, $\mathrm{Co(4\text{-}Br(py))_2Cl_2}$, and $\mathrm{Co(4\text{-}Cl(py))_2Br_2}$ the spectra indicated some decomposition took place during the course of preparation. Whenever the complex is stable, this method of preparation of the monomer could be quite useful. The monomer can be prepared in a matrix ready for low-frequency measurements. In the case of $\mathrm{Co(py)_2}$-

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Cl_2 the polyethylene pellet of the monomer was stable for months. Normally the monomer reverts to the polymer very quickly.

The Co(dipy)Cl_2 complex (dipy = 2,2′-dipyridyl) was prepared by the method of Ocone, *et al.*,[16] rather than by the decomposition of Co(dipy)$Cl_2 \cdot H_2O$ described by Lee, *et al.*[17] Microanalysis for C, N, and H gave nonreproducible results. Macroanalysis was performed by the Analytical Section of Argonne National Laboratory. *Anal.* Calcd for Co(dipy)Cl_2: Co, 20.58; Cl, 24.8. Found: Co, 20.57; Cl, 24.3.

The results of microanalyses of the complexes are tabulated in Table I. They were performed by Micro-Tech Laboratories, Inc., Skokie, Ill.

TABLE I

MICROANALYTICAL RESULTS FOR COMPLEXES

	Theory			Found		
	% C	% H	% N	% C	% H	% N
Co(py)$_2$Cl$_2$	41.7	3.5	9.7	41.1	3.5	9.6
Co(4-Cl(py))$_2$Cl$_2$	33.7	2.3	7.9	33.4	2.2	7.8
Co(4-Br(py))$_2$Cl$_2$	26.9	1.8	6.3	26.9	1.8	6.5
Co(4-Cl(py))$_2$Br$_2$	26.9	1.8	6.3	27.2	1.8	6.4
Co(4-Br(py))$_2$Br$_2$	22.5	1.5	5.2	22.5	1.5	5.2

Infrared Measurements.—The infrared measurements were made using the Beckman IR-11 and the Perkin-Elmer Model No. 301 spectrophotometers. Spectra were obtained on Nujol mulls using high-density polyethylene plates, on polyethylene pellets,[15] and in a high-pressure diamond cell. Details of the high-pressure technique in the low-frequency region are available in recent literature.[18–20]

Results and Discussion

The cobalt complexes of the type CoL_2X_2, where L is pyridine or a substituted pyridine, exist in monomeric and polymeric forms. The polymeric form contains halide bridging, whereas in the monomeric form only terminal halides are involved. Thus, by comparing the far-infrared spectra and noting the appearance and disappearance of bands, it should be possible to distinguish the bridged cobalt–halide stretching vibrations (ν_bCoX) from the terminal cobalt–halide stretching vibration (ν_tCoX). The following criteria have been used in making the assignments described in this paper.

(1) The assignments for ν_tCoX are consistent with those made for similar vibrations in related T_d complexes.[12] These vibrations are absent in the polymer.

(2) The assignments for the ν_bCoX are made for the first time and are based on the supposition that the bridging metal–halide vibrations should appear at lower frequency than the terminal metal–halide vibrations. This expectation has been realized in the case of complexes of Pt(II), Pd(II), Cu(II), and Al(III), and transition metals [M(II)] containing halogen bridges.[3–11] These bridged vibrations are absent in the monomer.

(3) The ν_{CoN} in a T_d monomer should be at slightly higher frequency than this vibration in an O_h polymer; the effects of coordination number have previously been cited by Clark.[2a]

(4) Ligand spectra in the low-frequency region were obtained and considerations of ligand bands in this region were made. These vibrations are generally observed to shift toward higher frequency upon complexation. Pyridine is free of vibrations in the metal–ligand region.

(5) Observation of the pressure effects on the low-frequency vibrations were made. In compounds related to those studied in this paper, the ν_tCoX vibrations behave quite normally for internal vibrations with the symmetric vibration becoming less intense with increasing pressure relative to the asymmetric.[21] The ν_bCoX in a chain polymer, such as we are dealing with here, ought to show pseudo-lattice-like behavior and a lattice-like response to pressure (large blue shifts).[18–22]

Table II tabulates the assignments made for several pairs of complexes (polymers and monomers). The ν_tCoCl vibrations can be assigned in the 306–347-cm^{-1} region. This is quite reasonable and in agreement with previous assignments made for related T_d complexes.[12] The ν_bCoCl vibrations are assigned in the 155–186-cm^{-1} region. In disagreement with our assignment, Nuttall[2b] assigned this mode at *ca.* 240 cm^{-1}. The ν_{CoN} vibrations are assigned at 235–243 cm^{-1} in the O_h polymers and at 236–253 cm^{-1} in the T_d monomers and are consistent with Clark and Williams' observations.[12] The ν_tCoBr in Co(4-Br(py))$_2$Br$_2$ is assigned at 265 cm^{-1}, the analogous CoCl$_2$ complex being free of absorption here. For Co(4-Br(py))$_2$Br$_2$ monomer, Gill and Kingdon[23] assigned two bands at 262 and 217 cm^{-1} to ν_tCoBr modes. Because of the reasons we pointed out in our previous paper,[21] we have assigned only the 265-cm^{-1} (262 cm^{-1} in their paper) band to the Co–Br stretching vibration. The ν_bCoBr vibrations were assigned at 118–143 cm^{-1}. The ν_{CoN} assignments in the cobalt–bromide complexes agree with those in the chloride complexes. Figures 1 and 2 illustrate several spectra in the metal–ligand region.

The Co(dipy)Cl_2 complex is polymeric with halide bridging and demonstrates a similar infrared spectrum from 200 to 430 cm^{-1} with that reported by Clark[24] with no Co–Cl stretching vibrations observed in the 300–340-cm^{-1} region. Repeated attempts to convert the polymer to the monomer by heating, reported to occur at 220°,[17] failed to give a pure compound. Thermal gravimetric studies indicate that loss of weight starts at 280° and that Co(dipy)$_{0.5}$Cl$_2$ is the only product formed in agreement with similar studies previously reported.[16]

The spectrum of this compound shows sharp ligand bands at 653 (ms), 631 (m), and 419 (s) cm^{-1}. The bands at 271 (s), 260 (s), and 252 (sh) cm^{-1} are assigned to the ν_{CoN} vibrations and are very similar to those as-

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TABLE II

ASSIGNMENTS (CM^{-1}) MADE FOR ν_tCoX, ν_bCoX, AND ν_{CoN} IN SEVERAL COBALT COMPLEXES

Compound		$\nu_t(\mathrm{CoX_2})$	$\delta(\mathrm{CoX_2})$	$\nu(\mathrm{CoN})$	$\nu_b(\mathrm{CoX_2})$	Ligand
$\mathrm{Co(py)_2Cl_2}$	monomer	347, 306	190	253	...	225,[d] 144[d]
	polymer	...	...	243, 235	186, 174	225[d]
$\mathrm{Co(4\text{-}Cl(py))_2Cl_2}$	monomer[a,b]	318[c]	?	242	...	213
	polymer	...	...	241	185, 165	322, 217
$\mathrm{Co(4\text{-}Br(py))_2Cl_2}$	monomer[a,b]	318[c]	?	236	...	...
	polymer	...	...	232	178, 155	290, 207
$\mathrm{Co(4\text{-}Cl(py))_2Br_2}$	monomer	←——	——	decomposition	——	——→
	polymer	...	...	238	138, 118	322, 207
$\mathrm{Co(4\text{-}Br(py))_2Br_2}$	monomer	265	157	240	...	285, 205, 221,[d] 219,[d] 138,[d] 84[d]
	polymer	...	...	228	143, 128	290, 195
$\mathrm{Co(dipy)Cl_2}$	polymer	...	...	271, 260, 252	169, 152	238,[d] 123,[d] 106 w

[a] Obtained by heating in polyethylene. [b] Some indication of decomposition by heating occurred. [c] Contains ligand band also. [d] Unassigned.

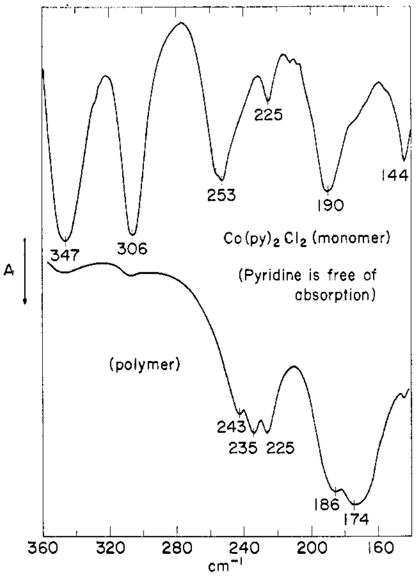

Figure 1.—Comparison of the spectrum of the $\mathrm{Co(py)_2Cl_2}$ monomer with that of the $\mathrm{Co(py)_2Cl_2}$ polymer in the 140–360-cm^{-1} region.

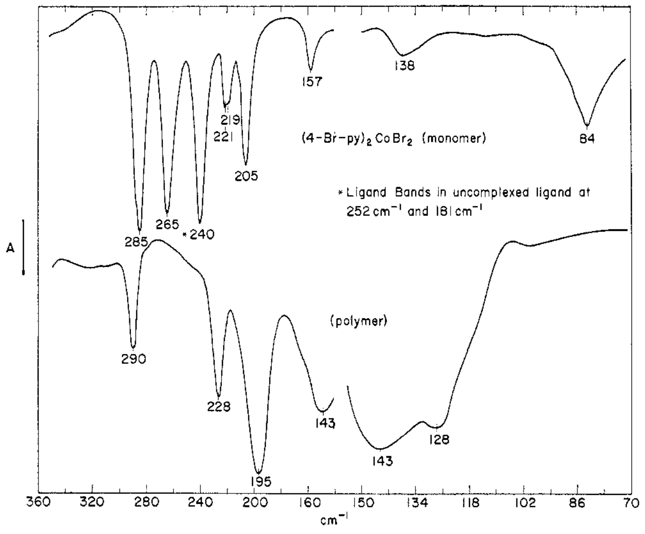

Figure 2.—Comparison of the spectrum of the $\mathrm{Co(4\text{-}Br(py))_2Br_2}$ monomer with that of the $\mathrm{Co(4\text{-}Br(py))_2Br_2}$ polymer in the 70–360-cm^{-1} region.

signed for this vibration in $\mathrm{Co(py)_2Cl_2}$. The metal–chloride bridging stretching is assigned at 169 (m) and 152 (ms) cm^{-1}. These frequencies are at slightly lower positions than frequencies assigned for the other bridged halides and may reflect the nonplanar bridging in the dipyridyl complex. Uncomplexed dipyridyl has a fairly strong peak at 164 cm^{-1}; however, in dipyridyl complexes it appears only as a weak band.[25,26] Unassigned bands are also found at 125 (w) and 106 (w) cm^{-1}.

A. High-Pressure Studies.—The behavior of terminal ν_{MX} vibrations with pressure, where two peaks are resolved (the asymmetric and symmetric vibrations), has previously been demonstrated.[21] In the monomeric complex $\mathrm{Co(py)_2Cl_2}$ the symmetric vibration (306 cm^{-1}) decreases in intensity to a greater extent relative to the asymmetric mode at 347 cm^{-1}. In monomeric $\mathrm{Co(4\text{-}Br(py))_2Br_2}$ the terminal cobalt–bromide stretching vibration at 265 cm^{-1} fails to shift with pressure. The ν_tCoX vibrations in the other two monomers reported in this paper were not studied by pressure, since the monomers could only be prepared by the polyethylene pellet technique. The bridged cobalt–halide stretching vibrations should be pseudo-lattice-like in their behavior to pressure, since the polymer involves long chains of cobalt–halide bridges. Thus, they should show appreciable blue shifts, and this has been verified. The most pressure-sensitive bands in the far-infrared region for these complexes are the ν_bCoX vibrations. Additionally, two bridged vibrations are assigned, as expected theoretically. Figure 3 shows the effect of pressure on the spectrum of the polymeric form of $\mathrm{Co(4\text{-}Cl(py))_2Cl_2}$.

The effects of pressure on the other vibrations in the polymeric complexes are tabulated in Table III. The ligand vibrations show only small blue shifts of the order of a few reciprocal centimeters. The ν_{CoN} vibration shows larger effects but not as large as the ν_bCoX vibrations. Some vibrations disappear with an increase in pressure.

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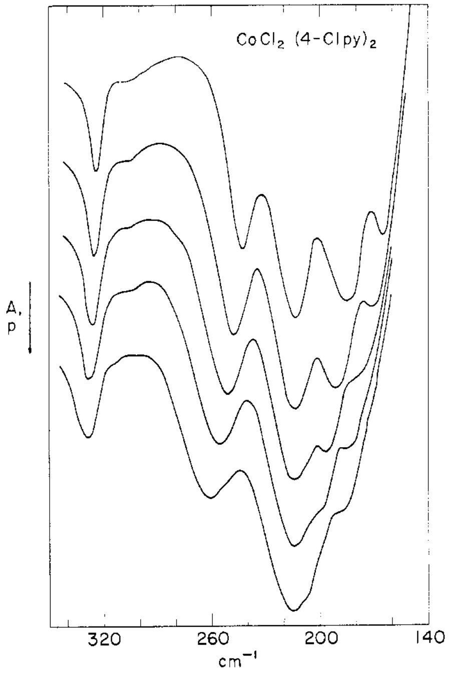

Figure 3.—Effect of pressure on the spectrum of polymeric Co(4-Cl(py))$_2$Cl$_2$.

TABLE III

PRESSURE EFFECTS ON LOW-FREQUENCY INFRARED VIBRATIONS—BRIDGING, METAL–LIGAND, AND LIGAND MOTIONS

Polymeric compound	Assignment	Ambient pressure	Nonambient pressure[a]	Shift, cm^{-1}
Co(py)$_2$Cl$_2$	ν_{CoN}	243	260	17
		235	Disappears	. . .
	L[b]	225	Disappears	. . .
	ν_bCoCl	174	220	46
		186	Disappears	. . .
Co(4-Br(py))$_2$Br$_2$	ν_bCoBr	143	173	31
		128	142	14
	L	195	199	4
	ν_{CoN}	228	230	2
	L	290	292	2
Co(4-Br(py))$_2$Cl$_2$	ν_bCoCl	155	Disappears	. . .
		178	200	22[c]
	L	207	208 sh	1
	ν_{CoN}	232	240, 247	11
	L	290	293	3
Co(4-Cl(py))$_2$Cl$_2$	ν_bCoCl	165	190	~35
		185	Shifts into 217 band	~32[c]
	L	217	217	0
	ν_{CoN}	241	259	18
	L	322	326	4
Co(4-Cl(py))$_2$Br$_2$	ν_bCoBr	118 sh	146	14
		138	175	37
	L	207	209, 223 sh	2
	ν_{CoN}	238	245	7
	L	322	323	1

[a] All pressures are 28 kbars, except for Co(py)$_2$Cl$_2$ where 36-kbar pressures were used. [b] L = ligand. [c] Estimated.

A study of the interconversion of the Co(py)$_2$Cl$_2$ monomer–polymer system with pressure has been made. At room temperature the application of pressure to either the monomer or the polymer caused no conversion from one form to the other. At 130°, where the interconversion is rapid, application of pressure converts the monomer to polymer. Upon release to atmospheric pressure, the monomer is re-formed.

TABLE IV

COMPARISON OF BRIDGED MX STRETCHING VIBRATIONS WITH THE TERMINAL MX STRETCHING VIBRATIONS

		X	ν_bMX/ν_tMX *f*	 *g*
		Dimer		
Pt(II)	R$_2$Pt$_2$X$_6$^{3,4,c}	Cl	0.88[a]	
		Br	0.85[a]	
		I	0.81[a]	
Pt(II)	Pt$_2$X$_4$L$_2$^{3,4,d}	Cl	0.83[b]	
		Br	0.81[b]	
		I	0.84[b]	
Pd(II)	R$_2$Pd$_2$X$_6$^{3,4,c}	Cl	0.83[a]	
		Br	0.70[a]	
		I	0.62[a]	
Pd(II)	Pd$_2$X$_4$L$_2$^{3,4}	Cl	0.80[b]	
		Br	0.70[b]	
Cu(II)	MCuX$_3$$^{5-7}$	Cl	0.74[a]	
		Br	0.63[a]	
Co(II)	Co$_2$X$_4$^{10,11}	Cl	0.74[b]	0.62
Zn(II)	Zn$_2$X$_4$^{10,11}	Cl	0.71[b]	
Al(III)	(AlX$_3$)$_2$^{8,9}	Cl	0.68[e]	
		Polymer		
Co(II)	CoL$_2$X$_2$	Cl		0.55
		Br		0.50

[a] Two ν_tMX and two ν_bMX vibrations are assigned. The average of each of the two vibrations is used to obtain this column. [b] One ν_tMX and two ν_bMX vibrations are assigned, and the average of the two ν_bMX is used. [c] R = cation. [d] L = PCl$_3$, P(OC$_2$H$_5$)$_3$, PR$_3$, TeR$_2$, pyridine, olefin, AsR$_3$, SR$_2$, SeR$_2$ (R = alkyl). [e] Five ν_tMX and five ν_bMX are assigned. Five ν_bMX/ν_tMX values are obtained and these are averaged. [f] This ratio is taken using the ν_bMX and ν_tMX vibrations in the dimer. [g] This ratio is taken using the ν_bMX(polymer) and ν_tMX(monomer) vibrations.

B. Summary.—The ratios of ν_tCoBr/ν_tCoCl and ν_bCoBr/ν_bCoCl in this work are about 0.8. The ratio for the terminal vibrations agrees very well with the results of Clark and Williams.[12] Table IV tabulates the values of ν_bMX/ν_tMX for several complexes of Pt(II), Pd(II), Cu(II), Al(III), several transition metals [M-(II)], and the CoL$_2$Cl$_2$ complexes studied in this paper. The ratios ν_bCoCl/ν_tCoCl and ν_bCoBr/ν_tCoBr are about 0.5. The ratio of ν_bMX(dimer)/ν_tMX(dimer) is greater than the ratio of ν_bMX(polymer)/ν_tMX(monomer). The decrease in frequency of the bridging vibration as compared to the terminal vibration is caused in part by weaker metal–halogen bonding in bridged complexes, since the halogens are shared between two metal atoms.

It is observed that the frequency difference between terminal and bridging vibrations is greatest for the complexes of Co(II) (present study) and least with Pt(II) and Pd(II) complexes. In the dimer complexes shown in Table IV, the terminal and bridging bonds appear in the same molecule. In such complexes no contribution from a change in coordination number (CN) is involved. For the complexes CoL$_2$X$_2$, the comparisons of bridging and terminal frequencies are made for different states of aggregation, the bridged bonds occurring in the polymer (CN = 6) and the terminal bonds occurring in the monomer (CN = 4). Thus, it is expected that a contribution from the change in coordination number would occur.[2a] This may contribute, at least in part, to the difference observed in Table IV between dimer and polymer complexes.

A recent matrix isolation investigation[11] in the far-infrared region for $CoCl_2$ appears to give parallel results to those obtained for the CoL_2Cl_2 complexes. In the dimeric $(CoCl_2)_2$ molecule (CN = 4), the Co–Cl bridge-bond stretchings are observed at 323 and 289 cm^{-1}, and the terminal CoCl stretching is found at $\sim$432 cm^{-1}. Thus, the ν_bCoCl (dimer)/ν_tCoCl(dimer) is about 0.74. In monomeric $CoCl_2$ (CN = 2), the asymmetric ν_{CoCl} is found at 492 cm^{-1} (the symmetrical vibration is not observed in the infrared region). The ratio of ν_bCoCl (dimer)/ν_tCoCl(monomer) is 0.62 and is observed to be less than the ratio ν_bCoCl(dimer)/ν_tCoCl(dimer).

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Interpretation of the Magnetic Properties of Pfeiffer's Cation, $Cr_4(OH)_6(en)_6{}^{6+}$

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Magnetic susceptibility data for $[Cr_4(OH)_6(en)_6](N_3)_6 \cdot 4H_2O$ are reported from 300 to 4.2°K. The observed antiferromagnetic behavior is satisfactorily accounted for on the basis of the Heisenberg–Dirac–Van Vleck spin–spin coupling model derived from a rhomboid arrangement of the four interacting chromium(III) atoms.

Introduction

The interpretation of the temperature dependence of the magnetic susceptibility of "Pfeiffer's cation," $Cr_4(OH)_6(en)_6{}^{6+}$, has been a subject of recent interest. Susceptibility measurements on $[Cr_4(OH)_6(en)_6]I_6 \cdot 4H_2O$ from room temperature to 77°K were originally interpreted[2a] using as a model a trigonal-planar array of four chromium(III) atoms. Although from analogy to Werner's[2b] $Co[(OH)_2Co(NH_3)_4]_3{}^{6+}$ a trigonal-planar model is reasonable, it was subsequently pointed out[3] that the experimental magnetic data down to 77°K could be better explained by a tetrahedral array of four equivalent chromium(III) atoms.

The tetrahedral model, however, failed when susceptibility measurements on $[Cr_4(OH)_6(en)_6](N_3)_6 \cdot 4H_2O$ were carried out from room to liquid helium temperature; these data were presented in a preliminary communication along with the results of an X-ray structural study, which revealed a rhomboid arrangement of the four chromiums.[4] In this paper we present a full report of the magnetic susceptibility data for $[Cr_4(OH)_6(en)_6](N_3)_6 \cdot 4H_2O$ and an associated theoretical interpretation on the basis of the Heisenberg–Dirac–Van Vleck spin–spin coupling model.[5]

Experimental Section

Preparation of $[Cr_4(OH)_6(en)_6](N_3)_6 \cdot 4H_2O$.—Crude $[Cr_4(OH)_6(en)_6](SO_4)_3$ was prepared according to the method of Pfeiffer.[6] To the solid sulfate, a small quantity of water was added to form a paste. Concentrated hydrochloric acid was then added dropwise with mixing until the solid completely dissolved. After filtration, solid reagent grade sodium azide was added to the solution with stirring. A red precipitate of $[Cr_4(OH)_6(en)_6](N_3)_6 \cdot 4H_2O$ formed almost immediately. The solid was washed with absolute ethanol and dried with ethyl ether. It was then dissolved in a minimum quantity of water and reprecipitated by adding solid sodium azide. After washing with water and absolute ethanol and drying with ethyl ether, the azide salt was dissolved again in a minimum amount of water and then diluted with half the original amount of water necessary to dissolve the compound. To the solution solid sodium azide was added and allowed to dissolve; then the solution was cooled to about 5°. After several hours, dark red crystals formed on the sides of the container. These were washed with water, absolute ethanol, and ether, and then air dried. A single-crystal X-ray diffraction study has shown[4] the exact formulation of the crystalline compound to be $[Cr_4(OH)_6(en)_6](N_3)_6 \cdot 4H_2O$.

Spectral Measurements.—Visible spectra were obtained with a Cary Model 14 RI recording spectrophotometer. At liquid nitrogen temperatures, a dewar constructed in these laboratories was used. A sample of $[Cr_4(OH)_6(en)_6][B(C_6H_5)_4]_6$ for low-temperature study was obtained by adding a concentrated aqueous solution of sodium tetraphenylboron to an aqueous solution of the azide salt. The low-temperature (77°K) medium employed was a frozen solution of 2-methyltetrahydrofuran (freshly distilled from $LiAlH_4$) and methanol (degassed) in the volume ratio of 2:1, respectively.

Magnetic Measurements.—Magnetic susceptibilities were determined using a Princeton Applied Research FM-1 vibrating sample magnetometer using a liquid helium dewar obtained from Andonian Associates, Inc. Temperatures were measured on a Leeds and Northrup potentiometer using a copper–constantan thermocouple calibrated at low temperatures against a calibrated carbon resistor. Because of the insensitivity of the thermocouple to temperature changes at very low temperatures, accurate measurements were not possible in the temperature range 30–4.2°K. The liquid helium point, however, could be accurately determined by the final (and maximum) value of the susceptibility.

Theoretical Section

The magnetic properties of the $Cr_4(OH)_6(en)_6{}^{6+}$ cation (en = ethylenediamine) may be quantitatively inter-

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