Electrochemical Behavior. The irreversible oxidation waves observed for the complexes and not present for the free ligands can be attributed to oxidation of the metal ion. The highly positive oxidation potentials (compared, e.g., to those of polypyridine complexes[4]) are in agreement with the electron-withdrawing effect of the CO ligands. Since oxidation is irreversible, we prefer to avoid any mechanistic speculation. We would only like to note that the dimetallic complexes exhibit only one (irreversible) oxidation wave, at slightly higher potentials compared to those of the monometallic species, indicating that there is scarce communication between the two metal centers, as was previously observed for other dimetallic carbonyl compounds.[31]

The first reduction potential is reversible for all complexes, indicating that reduction occurs in the aromatic ligand. The noticeable displacement toward less negative potentials in going from the free ligand to the monometallic and dimetallic species (Table III) was expected because the electron density on the ligands decreases on coordination to the electron-poor Ru atom of the $Ru(CO)_2Cl_2$ moiety. The correlation between the reduction potentials and the energies of the MLCT absorption bands (Figure 8) has been discussed above.

Conclusions

The monometallic and bimetallic complexes examined in this paper exhibit several interesting properties. The unusual combination of polypyridine, carbonyl, and chloride ligands leads to the presence of closely lying LC, MLCT, and MC excited states. The interplay between these three types of levels on changing temperature results in the presence of a strong LC luminescence at low temperature and of a strong photosensitivity (accompanied in one case by MLCT emission) at room temperature. The properties related to the aromatic bridging ligands (e.g., the reduction potentials) are strongly affected by coordination to the metal moieties, but the two $Ru(CO)_2Cl_2$ moieties practically do not communicate in the bimetallic complexes because of the strong withdrawing effect of the CO ligands.

Note Added in Proof. After submission of this work, a paper has appeared (Thomas, N. C.; Cox, J. *Polyhedron* **1988**, *7*, 731) on Ru(2,3-dpp)$(CO)_2Cl_2$ and (μ-2,3-dpp)$[Ru(CO)_2Cl_2]_2$. Absorption maxima are given at 538 nm for the former and at 596 and 448 nm for the latter. These data are in disagreement with our results (Table III) and seem to refer to partly photolyzed solutions.

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Registry No. 2,3-dpp, 25005-96-3; 2,5-dpp, 54266-39-6; Ru(2,3-dpp)$(CO)_2Cl_2$, 117247-58-2; (μ-2,3-dpp)$[Ru(CO)_2Cl_2]_2$, 116086-31-8; Ru(2,5-dpp)$(CO)_2Cl_2$, 120362-23-4; (μ-2,5-dpp)$[Ru(CO)_2Cl_2]_2$, 120362-24-5; $Ru(CO)_2Cl_2$, 16369-40-7.

Contribution from the Institut für Theoretische Chemie
der Universität Düsseldorf, D-4000 Düsseldorf 1, FRG

Far-IR Spectra and Normal-Coordinate Analyses of Halogenopentaamminechromium(III) Complexes

Hans-Herbert Schmidtke* and Manuela Rosner

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The infrared spectra in the 60–500-cm^{-1} region of $[Cr(NH_3)_5X]^{2+}$ salts (X = F, Cl, Br, I) and their deuterated analogues have been recorded down to 35 K temperature. Normal-coordinate analyses performed on the CrL_5X skeleton by using a modified valence force field (MVFF) as proposed by Labonville et al. are able to reproduce the measured vibrational fundamentals very well. The calculated force constants for corresponding atomic group vibrations can be transferred to a good approximation from one compound to another. Appreciable intermixing of symmetry vibrations occurs only for some vibrational modes. Deviations from C_{4v} selection rules indicate larger distortions in the crystals of heavier halogeno compounds.

Introduction

Pentaamminechromium(III) complexes are currently used as sample compounds for studying low-symmetry effects on electronic energy level schemes derived from optical spectra.[1-3] Band assignments usually face the problem of how electronic level splittings due to lower symmetry can be distinguished from vibrational fine structure. For a solution of this problem the vibrational level scheme of the complex molecule must be available together with the symmetry assignments, which are usually obtained by normal-coordinate analysis of the vibrational spectra.

Concerning chromium(III) ammine complexes, such an analysis has been reported only for $[Cr(NH_3)_6]^{3+}$.[4-6] From systems of lower symmetry, some IR spectra covering the usual frequency region have been reported.[7,8] We want to add to these results some normal-coordinate analyses that we performed on the basis of far-IR and Raman spectra of halogenochromiumpentaammines and their deuterated analogues measured at low temperature. With use of the experience obtained on the hexaammine complex, the results are taken as the starting point for the low-symmetry cases allowing comparison of high- and low-symmetry vibrational level systems. All analyses were carried out for a CrL_5X skeleton of the chromophores in which the ammonia ligands are substituted by one-center units of 17 (NH_3) or 20 (ND_3) amu. This assumption already proposed earlier for other ammonia complexes[9] turned out to be a good approximation, yielding in the case of $[Cr(NH_3)_6]^{3+}$, for frequencies lower than 500 cm^{-1}, deviations of less than 2% compared to calculations performed for the entire complex with molecular NH_3 ligands. Correspondingly, coupling between internal NH_3 and ML_5X skeleton vibrations is found to be very small. For all calculations the point symmetry was assumed as C_{4v}, which is based on an X-ray structure analysis carried out only on $[Cr(NH_3)_5Cl]Cl_2$ and its Co and Rh homologues.[10]

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Table I. Experimental[1,5] and Calculated Frequencies (cm^{-1}) for $[Cr(NH_3)_6]^{3+}$ and Its Deuterated Analogue

H		D		main sym coord
$\tilde{\nu}_{exp}$	$\tilde{\nu}_{calc}$	$\tilde{\nu}_{exp}$	$\tilde{\nu}_{calc}$	
467	467.2	431	431.1	$S_3(T_{1u})$
461	461.4		406.2	$S_1(A_{1g})$
412	412.2	380	379.7	$S_2(E_g)$
296	296.2		271.9	$S_5(T_{2g})$
264	263.3	245	244.9	$S_4(T_{1u})$
230	228.9	202	201.3	$S_6(T_{2u})$

From the Co series a normal-coordinate analysis using a modified Urey–Bradley force field (MUBFF) has been reported.[4] The present analysis uses the Wilson GF matrix method, applying a modified valence force field (MVFF) similar to that proposed by Labonville et al.[11] for octahedral hexahalogeno complexes, which allows for keeping the set of force constants lower than the number of frequencies available from the measured spectra. This requirement attributes higher physical significance to the calculation.

Experimental Section

The complex salts $[Cr(NH_3)_5X](NO_3)_2$ and $[Cr(NH_3)_5X]X_2$ with X = Cl, Br, and I and $[Cr(NH_3)_5F](ClO_4)_2$ were synthesized by using common procedures as described in the literature.[12-14] Before the spectra were recorded, the compounds were purified by recrystallization.

Deuteration by usual methods such as crystallizing the compounds from D_2O solution or precipitating from a saturated heavy water sodium salt solution of the respective anions does not lead to completely deuterated materials. In the case of the chloropentaammine complexes, optimal deuteration obtained was only 80%. Performing a normal-coordinate analysis on the basis of spectra measured from partially deuterated compounds has not been very successful.[15] Completely deuterated compounds can be obtained, however, by reacting $[Cr(ND_3)_5NCO](NO_3)_2$ with a DX solution in D_2O. The cyanato complex was synthesized by melting $Cr(NO_3)_3$ with deuterated urea using a prescription as given earlier.[16] If this compound is heated with DX solutions (X = Cl, Br, I), substitution of the cyanate ligand by halogen occurs, yielding $[Cr(ND_3)_5X]X_2$ by precipitation. The IR spectra do not show any trace of N–H or C–O bands; instead, the N–D stretching and bending frequencies appear in the expected regions.

The far-IR spectra were recorded by using a Beckman interferometer, Model IR-720, from microcrystalline compounds pressed in polyethylene pellets (concentration 2–3 mg in 100 mg of polyethylene). Low-temperature measurements were performed by using a liquid nitrogen cryostat, Air Products Model LC-1110; cooling to 35 K was achieved by an evaporating cryostat, Model LT-3-110C, from the same supplier. The temperature was monitored by a chromel/gold thermocouple.

The low-temperature Raman spectrum of $[Cr(NH_3)_5Cl](NO_3)_2$ has already been reported in ref 3; spectra from other compounds could not be recorded due to ease of decomposition.

Vibrational Force Field

For the octahedral parent molecule ML_6 the diagonal force constants of stretching and angular vibrations will be denoted by F_R and F_α, respectively. In the Labonville force field,[11] finite off-diagonal elements are F_{RR^c} and F_{RR^t} for the interactions between bonds in cis and trans positions, respectively, $F_{\alpha\alpha}$ and $F_{\alpha\alpha'}$ for interactions when corresponding bond angles are either in a common plane or in a different plane and have one bond in common, and $F_{R\alpha}$ referring to the situation where a bond R forms one leg of the angle α. All other force constants are set equal to zero. With this simplified force field, which differs from that of Labonville et al.[11] only by the fact that $F_{\alpha\alpha}$ and $F_{\alpha\alpha'}$ are allowed to vary separately, the **GF** matrix method can reproduce the experimental data[1,6] of $[Cr(NH_3)_6]^{3+}$ quite well (see Table I). The force constants obtained are listed in Table II.

Table II. Comparison of Calculated Force Constants ($N\ cm^{-1}$) for $[Cr(NH_3)_5X]^{n+}$

O_h		C_{4v}			
		slight distortion		larger distortion	
X = NH_3		X = F^-	X = Cl^-	X = Br^-	X = I^-
F_R = 1.47	F_1	1.75	1.748	1.799	1.765
	F_2	1.49	1.509	1.546	1.560
	F_3	2.50	1.261	0.802	0.700
F_α = 1.08	F_4	0.73	0.566	0.521	0.466
	F_5	0.69	0.511	1.088	1.110
	F_6	1.10	1.152	1.171	1.060
F_{RR^c} = 0.07	F_7	0.07	0.07	0.025	0.062
F_{RR^t} = 0.37	F_8	0.55	0.373	0.398	0.446
	F_9	0.26	0.278	0.337	0.323
$F_{\alpha\alpha}$ = 0.01	F_{10}	0.11	0.122	0.164	0.147
$F_{\alpha\alpha'}$ = −0.08	F_{11}	−0.25	−0.18	−0.277	−0.256
$F_{R\alpha}$ = 0.004	F_{12}	0.001	0.022	0.022	0.030

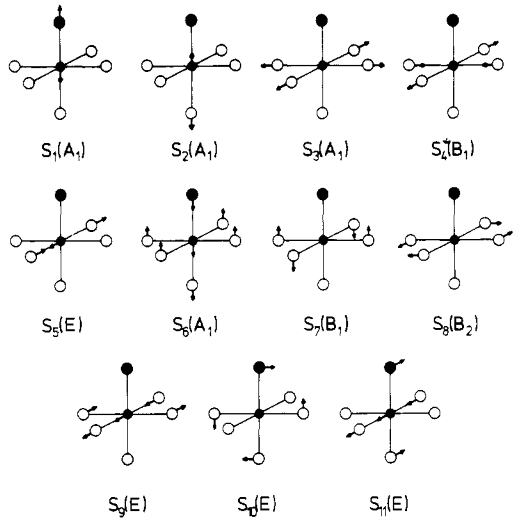

Figure 1. Symmetry vibrations for ML_5X molecules and their irreducible representations in the C_{4v} point group.

The corresponding calculation performed for the deuterated compound supplies similarly good results, yielding force constants that differ only slightly from those of the protonated complex. Therefore, applying identical force fields for both isotopes seems to be justified. In variance to an earlier analysis[6] the $F_{R\alpha}$ force constant is found to be very small in accordance with preceding assumptions where it has been neglected.[5]

For ML_5X molecules of C_{4v} symmetry 11 different symmetry vibrations are possible as depicted in Figure 1 from which corresponding symmetry coordinates S_i (i = 1–11) can be derived. The relevant force field must be specified in more detail considering interactions of different types between M–X, M–L_{trans}, and M–L_{cis} metal–ligand vibrations. Instead of two different diagonal elements F_R and F_α pertinent to the O_h force field matrix, we now have six

$$F_1 = F_{R_{14}} \qquad F_4 = F_{\alpha_{34}}$$
$$F_2 = F_{R_{13}} \qquad F_5 = F_{\alpha_{23}}$$
$$F_3 = F_{R_{12}} \qquad F_6 = F_{\alpha_{36}} \tag{1a}$$

(atom notations: 1 for the central metal, 2 for the hetero atom X, 3 and 5–7 for L in cis positions and 4 for L in the trans position to X). Nondiagonal elements are chosen identical with those in O_h symmetry except for F_{RR^t}, which is split into two

$$F_8 = F_{R_{12}R_{14}}$$
$$F_9 = F_{R_{13}R_{15}} \tag{1b}$$

referring to different interactions between M–X and M–L_{trans} and between two of the M–L_{cis} coordinates, respectively. Since cis interactions of this kind are calculated to be small compared to trans interactions a further differentiation of F_{RR^c}, $F_{\alpha\alpha}$, $F_{\alpha\alpha'}$, and

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Table III. Measured Raman (20 K) and Infrared (100 K) Frequencies (cm^{-1}) for $[Cr(NH_3)_5Cl]Y_2$

Raman	IR		Raman	IR	
$Y = NO_3^-$	$Y = NO_3^-$	$Y = Cl^-$	$Y = NO_3^-$	$Y = NO_3^-$	$Y = Cl^-$
471	472	472	189		
460	460	462	170	170	170
434	433	434	147		*a*
406			137	140	*a*
301	302	306	125	124	126
285	285		120		*a*
252	255	255	114	114	114
217			110		*a*
198	200		105		*a*

[a] Lattice vibration.

Table IV. Comparison of Experimental Infrared Frequencies in (cm^{-1}) for $[Cr(NH_3)_5X]Y_2$ at 100 K[a]

		X, Y						
		F^-, ClO_4^-	Cl^-, Cl^-	Cl^-, NO_3^-	Br^-, Br^-	Br^-, NO_3^-	I^-, I^-	I^-, NO_3^-
σ(Cr-N)	A_1	470	472	472	470	474	467	463
σ(Cr-N)	E	462	462	460	453	463	454	457
σ(Cr-N)	A_1	428	434	433	438		442	440
σ(Cr-N)	B_1	399			427	425	417	415
σ(Cr-X)	A_1	540	306	302	206	204	195	184
δ(N-Cr-N)	B_2	275		285	274	287	261	260
δ(N-Cr-N)	E	260	255	255	259	265	248	250
δ(N-Cr-N)	B_1	238		200	248	250	238	240
δ(N-Cr-X)	E	214	170	170	171	172	168	172
δ(N-Cr-X)	E	184	126	124	122	122	112	116
δ(N-Cr-N)	A_1	114	114	114	114	110	103	

[a] Key: σ, stretching vibration; δ, angular vibration.

$F_{R\alpha}$ was not carried out. A splitting of, e.g., $F_{RR'}$ parameters by adapting them to lower symmetry did not add to the quality of the results. The resulting 12 force constants then can be fitted to the experimental frequencies by using also data from the deuterated compounds. All computational calculations are carried out using Program No. 342 of the Quantum Chemistry Program Exchange.[17] The nuclear coordinates necessary for performing normal-coordinate analyses were calculated from bond distances Cr–N = 2.07 Å, Cr–F = 1.9 Å, Cr–Cl = 2.3 Å, Cr–Br = 2.5 Å, and Cr–I = 2.7 Å and 90° for all bond angles obtained on the basis of X-ray data[10,18] or by adopting ionic radii[19] if structural data are not available. A calculation with the correct geometry parameters reported[10] for $[Cr(NH_3)_5Cl]Cl_2$ with a symmetry slightly lower than C_{4v} leads to a splitting of E modes of only 0.2 to 0.5 cm^{-1}.

Far-Infrared Spectra

Figure 2 presents the far-infrared spectra recorded at room temperature and at about 100 K of $[Cr(NH_3)_5F](ClO_4)_2$ and $[Cr(NH_3)_5X]X_2$.

Lowering the temperature down to about 35 K adds to the quality of resolution; peak positions largely remain, however, unchanged. Comparison with corresponding nitrate complexes shows that the frequencies of the chromophore do not change significantly for different salts of the same complex. This is seen for the example of the chloro complex in Table III, which in addition reports the 20 K Raman spectrum of the nitrate salt.[3]

Peaks in the Raman spectrum are more numerous since in C_{4v} all possible normal modes are Raman active while in IR only A_1 and E vibrations are allowed. Measured band peaks of all compounds are compiled in Table IV, which also lists the assignments to atomic group vibrations and symmetries of normal vibrations resulting from normal-coordinate analyses (see Discussion).

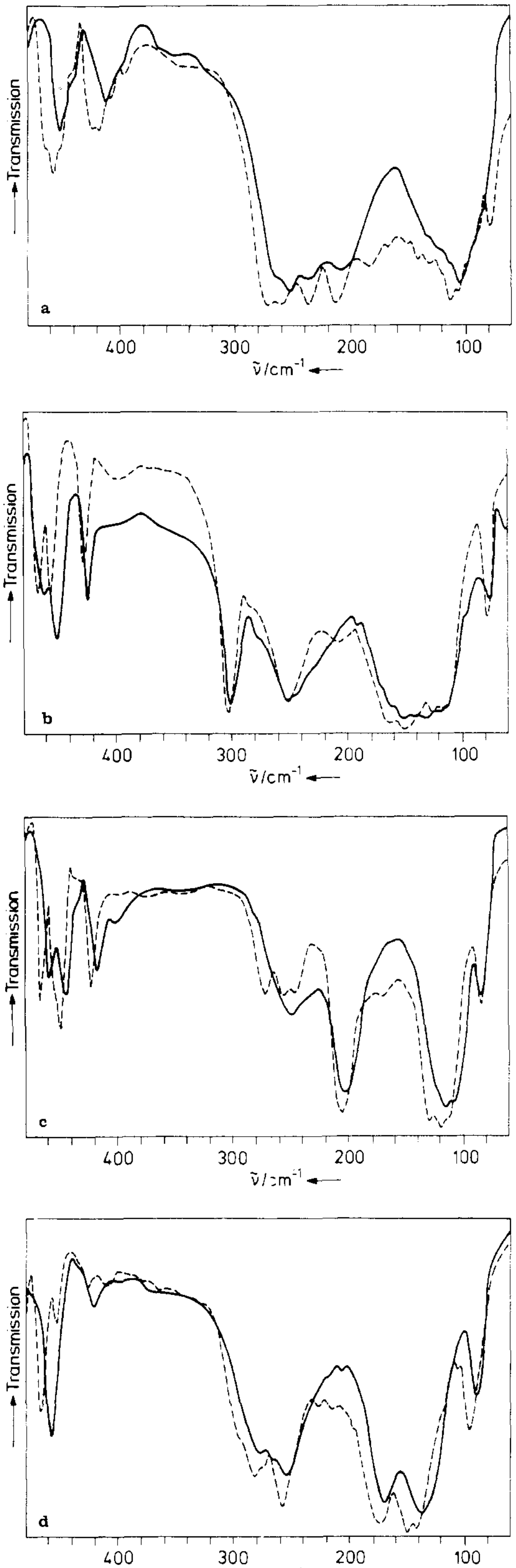

Figure 2. Far-infrared spectra of $[Cr(NH_3)F](ClO_4)_2$ (a) and $[Cr(NH_3)_5X]X_2$ for X = Cl (b), Br (c), and I (d) at 293 (—) and 100 K (---) pressed in polyethylene pellets.

Discussion

Preliminary assignments of measured peaks can be obtained by inspecting isotope shifts comparing spectra of corresponding deuterated and protonated compounds. Low-frequency absorptions at 110, 140, and 150 cm^{-1} of the chloropentaammine showing virtually no isotopic shift must be assigned to lattice vibrations; also, the only molecular vibration at 301–306 cm^{-1} (cf. Table III)

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exhibiting no isotope effect can be assigned to a stretching vibration localized on the Cr–Cl bond, which is represented by the $S_1(A_1)$ symmetry coordinate of Figure 1. Corresponding peaks in the bromo- and iodopentaammine spectra of negligible isotope shifts are at 204–206 and 184–195 cm^{-1}, respectively (Table IV). Since only A_1 and E vibrations are infrared active in C_{4v} symmetry, we may expect at least eight peaks in each spectrum to be investigated, four belonging to stretching vibrations and four others belonging to angular vibrations. All vibrations except that belonging to σ(Cr–X) should have deuterium shifts. For compounds with symmetries lower than C_{4v}, B_1 and B_2 vibrations are also detected in the IR spectra. Since $[Cr(NH_3)_5Cl]Cl_2$ supplies a molecular spectrum with only eight peaks, lacking those three that are detectable in the other spectra (cf. Table IV), we can conclude that only this compound has actual C_{4v} chromium site symmetry while the other systems supply lower symmetry, the extra peaks being due to B_1 and B_2 vibrations.

A further classification of bands prior to carrying out a normal-coordinate analysis can be obtained by comparing spectra of low symmetry with those of octahedral compounds and considering the decrease of symmetry by perturbation on the high symmetry vibrational levels. Since in O_h only T_{1u} vibrations are allowed in the IR, in general giving rise to very intense absorption, also the A_1 and E vibrations resulting in C_{4v} should have high intensity at frequencies similar to T_{1u} of CrL_6. Indeed, from the symmetry coordinate $S_3(T_{1u})$ (Table I) belonging to the Cr–L stretching vibration, the coordinates $S_2(A_1)$ and $S_5(E)$ of C_{4v} symmetry in Figure 1 will result, explaining the splitting of the 466-cm^{-1} band[20] of $[Cr(NH_3)_6]^{3+}$ into the strong peaks at 460 and 471 cm^{-1} of $[Cr(NH_3)_5Cl]^{2+}$. Similar arguments can be used for assigning the vibrations arising from the octahedral T_{1u} angular vibration belonging to S_4 in Table I. The 434-cm^{-1} band (Table III), which is strong in the IR and Raman spectra, can be derived from the A_{1g} mode in O_h symmetry, giving rise to a strong peak also in the $[Cr(NH_3)_6]^{3+}$ Raman spectrum.[20] Classification of angular vibrations with arguments from the descent of symmetry can be carried out in a similar way; they are, however, not always as straightforward.

A more reliable interpretation is obtained from the normal-coordinate analysis, which supplies not only the symmetries of each of the vibrations but also potential energy distributions (PED)[21] on symmetry coordinates belonging to it. The latter are connected to the normal coordinates Q_i.

In Table V the corresponding results obtained for the four complexes considered are listed. Comparisons of experimental and calculated frequencies indicate that some of the measured peaks, in particular at lower energy, could not be reproduced very well on the basis of the applied force field. In general, agreement is quite satisfactory, and this is also true for the results obtained for the deuterated compounds performed with equal sets of force constants as they are listed in Table II. Due to the space presently available, these results cannot be given in this report; errors and PEDs of normal coordinates obtained are, however, very similar to those of the protonated species. Owing to the limited experimental material available for $[Cr(NH_3)_5F]^{2+}$ (only the perchlorate has been investigated in the present study), the normal-coordinate analysis has not been carried out to the same standard as for the other compounds (cf. Table Vd). The calculation in this case was started from the force fields of $[Cr(NH_3)_5Cl]^{2+}$ or $[Cr(NH_3)_6]^{3+}$ adapting the experimental frequencies by subsequent change of some of the force constants in various cycles until agreement could not be essentially improved.

For evaluation of the results, it is worth comparing the force constants (Table II) and frequencies (Table IV) obtained in the series of compounds considered. As expected, the most drastic change is observed in the σ(Cr–X) frequency reflected in the force constant F_3 (eq 1a), which varies from 2.50 (F) to 0.70 N cm^{-1} (I). The Cr–F stretching frequency of 540 cm^{-1} is relatively high and so mixing with angular vibrations, such as $S_6(A_1)$, while being large for the bromo and iodo complex (cf. Table V), is negligibly small for the fluoro complex. The corresponding vibrations are localized on the $S_1(A_1)$ symmetry coordinate. The PED results indicate that most of the symmetry coordinates are not or only slightly intermixed. Appreciable mixing of $S_2(A_1)$ and $S_3(A_1)$ is observed in Q_1 and Q_4 and of $S_{10}(E)$, $S_{11}(E)$, and partially $S_9(E)$ in Q_{11} and Q_{13}, in general increasing with heavier halogeno compounds. This is certainly due to the similar vibrational energies belonging to equal symmetries (A_1 and E) or arises, in terms of force fields, from similar force constants for F_1 and F_2 referring to S_2 and S_3 vibrations and correspondingly for F_4, F_5, and F_6, which belong to S_9, S_{10}, and S_{11} vibrations (see Table II and Figure 1 for the definition of symmetry coordinates).

Table V. Normal-Coordinate Analyses for $[Cr(NH_3)_5X]^{2+}$[a]

$\tilde{\nu}_{exp}$	$\tilde{\nu}_{calc}$	sym		PED
				(a) X = Cl
472	471.6	A_1	Q_1	$0.85S_2 + 0.12S_3 + 0.03S_1$
460	460.1	E	Q_2 (Q_3)	$0.92S_5 + 0.08S_9$
433	433.8	A_1	Q_4	$0.75S_3 + 0.22S_2 + 0.03S_1$
406[b]	405.7	B_1	Q_5	S_4
302	302.3	A_1	Q_6	$0.92S_1 + 0.08S_6$
285	286.6	B_2	Q_7	S_8
255	252.5	E	Q_8 (Q_9)	$0.92S_9 + 0.08S_5$
200	201.7	B_1	Q_{10}	S_7
170	169.1	E	Q_{11} (Q_{12})	$0.54S_{10} + 0.38S_{11} + 0.08S_9$
124	122.1	E	Q_{13} (Q_{14})	$0.66S_{11} + 0.26S_{10} + 0.08S_9$
114	114.9	A_1	Q_{15}	S_6
				(b) X = Br
470	470.5	A_1	Q_1	$0.94S_2 + 0.02S_1 + 0.04S_6$
453	453.3	E	Q_2 (Q_3)	$0.88S_5 + 0.10S_9 + 0.02S_{10}$
438	438.5	A_1	Q_4	$0.96S_3 + 0.04S_2$
427	427.8	B_1	Q_5	S_4
274	276.3	B_2	Q_7	S_8
259	256.2	E	Q_8 (Q_9)	$0.92S_9 + 0.04S_{10} + 0.04S_5$
248	248.0	B_1	Q_{10}	S_7
206	209.6	A_1	Q_6	$0.46S_1 + 0.52S_6 + 0.01S_2$
171	169.7	E	Q_{11} (Q_{12})	$0.78S_{10} + 0.22S_{11}$
122	122.5	E	Q_{13} (Q_{14})	$0.56S_{11} + 0.24S_9 + 0.20S_{10}$
114	120.6	A_1	Q_{15}	$0.80S_6 + 0.19S_1 + 0.01S_2$
				(c) X = I
467	468.2	A_1	Q_1	$0.77S_2 + 0.20S_3 + 0.01S_1 + 0.03S_6$
454	454.8	E	Q_2 (Q_3)	$0.92S_5 + 0.06S_9 + 0.02S_{10}$
442	440.0	A_1	Q_4	$0.64S_3 + 0.35S_2 + 0.01S_1$
417	419.1	B_1	Q_5	S_4
261	263.4	B_2	Q_7	S_8
248	244.9	E	Q_8 (Q_9)	$0.92S_9 + 0.04S_5 + 0.02S_{10} + 0.02S_{11}$
238	242.6	B_1	Q_{10}	S_7
195	194.3	A_1	Q_6	$0.27S_1 + 0.68S_6 + 0.05S_2$
168	165.2	E	Q_{11} (Q_{12})	$0.74S_{10} + 0.22S_{11} + 0.04S_9$
112	112.3	E	Q_{13} (Q_{14})	$0.38S_{11} + 0.34S_{10} + 0.28S_9$
103	109.4	A_1	Q_{15}	$0.48S_6 + 0.44S_1 + 0.06S_2$
				(d) X = F
540	538.7	A_1	Q_6	$0.96S_1 + 0.04S_2$
470	472.3	A_1	Q_1	$0.86S_2 + 0.1S_3 + 0.04S_1$
462	463.3	E	Q_2 (Q_3)	$0.88S_5 + 0.07S_9 + 0.05S_{10}$
428	426.0	A_1	Q_4	$0.88S_3 + 0.18S_2 + 0.02S_1$
399	400.9	B_1	Q_5	S_4
275	282.3	B_2	Q_7	S_8
260	260.2	E	Q_8 (Q_9)	$0.82S_9 + 0.08S_{10} + 0.08S_{11} + 0.02S_5$
238	234.1	B_1	Q_{10}	S_7
214	214.2	E	Q_{11} (Q_{12})	$0.54S_{10} + 0.46S_{11}$
184	171.7	E	Q_{13} (Q_{14})	$0.36S_{11} + 0.32S_{10} + 0.32S_9$
114	128.5	A_1	Q_{15}	S_6

[a] Frequencies in cm^{-1}; symmetry symbols of C_{4v} point group. PED = potential energy distribution. [b] Frequency obtained from Raman spectrum.

All Cr–N frequencies are located in the expected range estimated from the octahedral parent complex; deviations are observed only when strong mixing of the Cr–X vibration with other A_1 modes occurs, see e.g. the S_1 and S_6 intermixing into Q_6 and Q_{15} modes (Table Vb,c).

Concerning the force constants listed in Table II, we note that, as expected from the definition of eq 1a, the F_2 parameter values

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remain close to the F_R parameter of the octahedral species; it does not change very much in the series of compounds, the influence of the hetero ligand perpendicular to the N–Cr–N plane being small. The parameter values of F_1 describing the force along the Cr–N bond trans to the halogen ligand are all increased compared to F_R of O_h, indicating a pronounced trans effect caused by a withdrawal of d electrons in antibonding metal orbitals. This leads to a strengthening of Cr–N bonds, in particular of those in positions trans to the hetero ligand. In the iodo complex, this effect is partially reduced due to the large internuclear distance.

From the angular force constants, it is the F_6 parameter that is closest to F_α of O_h; it belongs to bond angles in the N–Cr–N plane and is hardly affected by the hetero ligand as was equally observed for F_2. The parameter values of F_2 and F_6 and obviously also of some others are similar for different compounds and therefore can be transferred from one compound to another. Force constants that belong to angles containing the trans Cr–N bond (F_4) or the Cr–X bond (F_5) are also similar, as long as the size of the halogen ligand does not exceed the space necessary for the NH_3 ligands and thus restrict the angular vibrations because of steric hindrance. In fact, the F_5 parameters of the bromo and iodo complex are calculated to be much higher, adopting the value of the octahedral complex, which indicates the importance of the ligand size for angular vibrations.

A similar discussion of parameter sequences could not be carried out for the normal-coordinate analysis of the $[Co(NH_3)_5X]^{2+}$ homologues[4] since in these calculations all force constants belonging to the Co–N atom groups are transferred from the hexaammine complex and assumed to be invariant in the series of the halogeno compounds. Since this leads to artificial effects also on the Co–X force constants, they are not comparable with our results.

Nondiagonal **F** matrix elements of the mixed-ligand compounds, in general, are calculated to be larger than the corresponding parameters of the octahedral parent system, indicating enhanced interactions in molecules of lower symmetry and larger environmental effects in the crystal. While F_7 does not differ very much for all compounds, the parameters F_8 and F_9 resulting from $F_{RR'}$ vary from the fluoro to the iodo compound in an unspecific way. Values of F_8 belonging to the force along the hetero axis (eq 1b) grow from Cl, Br, to I in this series possibly due to the increasing halogen polarizability. For $[Cr(NH_3)_5F]^{2+}$, this parameter is the largest which can be attributed to the high electronegativity of F and to the small Cr–F distance. In a similar way, other variations of force constants may be explained from physical properties of halogen ligands.

Conclusions

An assignment of vibrational spectra of low-symmetry complex compounds by normal-coordinate analyses applying a slightly modified Labonville force field on chromophore skeletons can be carried out with some confidence. The frequencies calculated for stretching modes are generally in better agreement with the experiment than those of angular vibrations since, for the latter, off-diagonal elements of the force field matrix are more important relative to diagonal elements. In addition, long wavelength modes are not as well reproduced by the calculation owing to the larger intermixing with lattice modes. Variations of smaller off-diagonal force constants do not add very much to the overall quality of the results. Also, the neglect of ligand vibrations (e.g. rocking vibrations of NH_3 ligands) does not interfere significantly with the results. Force constants belonging to corresponding atom groups can be transferred from one compound to another.

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Registry No. $[Cr(NH_3)_5F](ClO_4)_2$, 22478-31-5; $[Cr(NH_3)_5Cl]Cl_2$, 13820-89-8; $[Cr(NH_3)_5Cl](NO_3)_2$, 57255-94-4; $[Cr(NH_3)_5Br]Br_2$, 13601-60-0; $[Cr(NH_3)_5Br](NO_3)_2$, 57255-97-7; $[Cr(NH_3)_5I]I_2$, 19683-65-9; $[Cr(NH_3)_5I](NO_3)_2$, 100729-49-5; D_2, 7782-39-0.

Contribution from the Departments of Chemistry, Wayne State University, Detroit, Michigan 48202,
and University of Wisconsin at Eau Claire, Eau Claire, Wisconsin 54701

Perturbations of the Low-Energy Doublet Excited State of Chromium(III). Competing Heavy-Atom and Macrocyclic Ligand Effects in Thermally Activated Relaxation Pathways[1]

Ronald B. Lessard,[†] John F. Endicott,*[,†] Marc W. Perkovic,[†] and L. A. Ochrymowycz[‡]

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The thermally activated relaxation of the lowest energy doublet state has been examined in several families of chromium(III) complexes. The effective rate constant for excited-state relaxation can be approximately represented as $k(\text{obsd}) = k^\circ + k(T)$, where k° is a low-temperature limit that is nearly temperature and medium independent, and $k(T)$ can be approximately represented in an Arrhenius form. The repression of the thermally activated pathway (i.e., $k(T) < k^\circ$, for $T \leq 300$ K), which has been reported for *trans*-$Cr^{III}(N_4)X_2$ complexes in which N_4 is a macrocyclic tetraamine ligand and X = NH_3 or CN^-, is not observed when X = Cl^- or Br^-. Rather $k(T)$ dominates the behavior of these and other chloro and bromo complexes, even in glassy matrices at temperatures between 160 and 200 K. The medium dependence of $k(T)$ is dramatically illustrated by the orders of magnitude decrease of its contribution to the decay of $(^2E)Cr(NH_3)_5Cl^{2+}$ doped into a $[Rh(NH_3)_5Cl]Cl_2$ solid matrix. Stereochemical and "heavy-atom" perturbations of the ^2E excited state have been further examined by using macrocyclic ligands containing pyridyl and thioether donor groups. These and related observations require that several different mechanisms (decay channels) can contribute to $k(T)$. The evidence is evaluated for differing contributions of surface crossing channels such as formation of an intermediate in its ground electronic state or the thermal population of a higher energy quartet excited state (BISC). It is inferred that these are plausible competitive decay channels with intermediate formation being important for strong-field ligands (NH_3, CN^-) and BISC being important for weak-field ligands (Cl^-, Br^-).

Introduction

While chromium(III) photochemistry and photophysics have long and distinguished histories,[2] recent studies have turned up some surprising features of the excited-state behavior and provided some important insights into the mechanisms of excited-state

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[†] Wayne State University.
[‡] University of Wisconsin at Eau Claire.

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