Contribution from the Institut für Theoretische Chemie der Universität Düsseldorf,
D-4000 Düsseldorf, West Germany

Electronic and Vibrational Levels in (Isocyanato)pentaamminechromate(III) Obtained from an Analysis of Vibronic and Far-Infrared Spectra

THOMAS SCHÖNHERR and HANS-HERBERT SCHMIDTKE*

Received February 26, 1979

The far-infrared, Raman, and vibronic spectra in absorption and emission of $[Cr(NH_3)_5(NCO)](NO_3)_2$ and its deuterated compound at low temperature have been recorded. A complete assignment of band peaks leads to a normal-mode analysis by comparison with results from smaller analogues using the different selection rules for vibrational and vibronic transitions appropriate to each of the various techniques. Some discrepancies in the literature concerning the assignment of the first spin-forbidden zero-phonon (quartet–doublet ligand field) transitions of low symmetry have been removed. It is concluded that conventional ligand field theory does not properly account for the magnitude of energy level splitting due to low-symmetry fields.

Introduction

The low-energy vibronic spectra of d^3 complexes in absorption and emission at cryogenic temperatures are usually well resolved. This is (at least for coordination compounds for which ligand field theory is able to explain the electronic structure) attributed to the fact that the electronic ground state $^4A_{2g}$ (in octahedral notation) and the lowest excited states ^2E_g and $^2T_{1g}$ result from the same electron configuration $t_{2g}{}^3$. By comparison with infrared and Raman data, a vibrational analysis of the electronic spectra can be carried out which allows for a peak assignment either to vibrations of groups of atoms or, in the most favorable case, to normal vibrations of the complex molecule. A complete assignment to normal vibrations from an analysis primarily on the basis of vibronic and vibrational spectra has been obtained only for octahedral compounds, e.g., for hexahalogeno complexes of Re(IV),[1,2] Os(IV),[3,4] and Mn(IV).[5] Some partial vibrational assignments for Cr(III) compounds have been made, e.g., $[Cr(NCS)_6]$.[3-6] For low-symmetry compounds the only vibrational analysis of vibronic spectra which has been carried out is for Cr(III) pentaammines.[7] From these spectra only some of the normal modes could be assigned. In the case of low symmetry, this assignment is difficult to make in view of the large number of electronic and vibrational states. Nevertheless, since the selection rules work more effectively for low symmetry and since they are different for different spectroscopic techniques, a characterization of the electronic and vibrational levels can be obtained. A more detailed investigation of some acidopentaamminechromium(III) complexes has been carried out by Forster,[8] by Flint,[7] and lately by Güdel[9] (together with their co-workers). A disagreement emerges on the assignment of the zero-phonon transitions to the electronic levels, which belong to the low-symmetry components of the octahedral ^2E_g term. Since Flint[7] and Güdel[9] disagree in assuming different magnitudes for this splitting, the assignment of the higher spin-forbidden transitions also becomes doubtful. This problem is pertinent for all other low-symmetry Cr(III) compounds. Reliable results on the splitting of the higher $^2T_{1g}$ due to lower symmetry on the basis of spectroscopic data for the pentaammines have up to this time been very meager.

Since the absorption spectrum of $[Cr(NH_3)_5(NCO)]^{2+}$, which has been recently synthesized,[10] is highly resolved, it can contribute, with consideration of far-infrared and Raman data as well, to a solution to this question. In addition, a complete, but for some peaks still tentative, assignment to normal vibrations of the $CrN_5(NCO)$ chromophore is reported here. This analysis made use of comparison spectra from deuterated materials.

Table I. Symmetries and Selection Rules of Normal Vibrations of $[Cr(NH_3)_5X]$ and $[Cr(NH_3)_5(NCO)]$ Molecules of Symmetry C_{4v}

	a_1	a_2	b_1	b_2	e
$\sigma(Cr-NH_3)$	ν_1, ν_2		ν_3		ν_4
$\sigma(Cr-X)$	ν_5				
$\delta(H_3N-Cr-NH_3)$	ν_6		ν_7	ν_8	ν_9, ν_{10}
$\delta(H_3N-Cr-X)$					ν_{11}
$\delta(Cr-N-H)$	ν_{12}	ν_{13}	ν_{14}	ν_{15}	$\nu_{16}-\nu_{18}$
$\delta(Cr-N-C)$					ν_{19}
$\delta(N-C-O)$					ν_{20}
$\sigma(N-C-O)$	ν_{21}, ν_{22}				
activity IR	×				×
activity Raman	×		×	×	×

Experimental Section

(a) Synthesis. $[Cr(NH_3)_5(NCO)](NO_3)_2$ was prepared by heating chromium(III) nitrate in molten urea by use of a procedure described previously.[10] The chloride, bromide, iodide, and perchlorate salts were obtained by metathesis of low-temperature saturated solutions of the respective alkali salts. Single crystals of a quality appropriate for spectroscopic investigation were not obtained.

(b) Far-IR Measurements. The far-infrared spectra have been recorded on a Beckman 720 Fourier spectrometer. The resolution was about 3 cm^{-1}. The probes were pressed into polyethylene disks. For low-temperature measurements a helium cryostat from Air Products was mounted in an evacuable chamber, constructed in this laboratory, avoiding the necessity of additional windows. Temperatures down to 15 K were measured by a thermocouple, which was affixed to the sample.

(c) Absorption Spectra. These were measured on transparent KBr disks by using a Cary 17 spectrophotometer provided with a GaAs detector, which yields a resolution better than 1 cm^{-1}. For cooling, a helium flow cryostat CF 100 from Oxford Instruments has been used, by which temperatures down to 25 K were reached at the sample.

(d) Emission Spectra. Essential parts of the luminescence apparatus are an 0.5-m double monochromator (McPherson Model 285), a GaAs photomultiplier, and an argon laser (Spectra Physics Model 165). The crystal powders or KBr disks were cooled to 10 K by a helium closed-cycle cryostat (Air Products Model CSW 202).

(e) Computer Programming. Band analyses, in particular for absorption spectra, have been carried out in order to obtain reliable Lorentzian band parameters, i.e., positions of band maxima, intensities, and half-widths. In all cases the spectra are simulated with a least-squares fit by independent variation of all band parameters for a minimal number of bands. Ligand field calculations have been carried out by using the perturbation matrices of quadratic symmetry given by Perumareddi.[11]

Vibrational Spectra

The infrared spectrum in the region 4000–300 cm^{-1} has been reported earlier,[10] together with an assignment to stretching and angular vibrations of atomic groups. The peaks at 463 and 438 cm^{-1} are assigned to $\sigma(Cr-NH_3)$ stretching vibrations. The 463-cm^{-1} band is more intense and is split by 4 cm^{-1} in the $[Cr(NH_3)_5(NCO)]Cl_2$ compound, where hydrogen bonding to chloride ions may occur.[12] Therefore, this peak is assigned to the degenerate mode ν_4(e). In Table I the notation for the possible vibrations belonging to various

0020-1669/79/1318-2726$01.00/0 © 1979 American Chemical Society

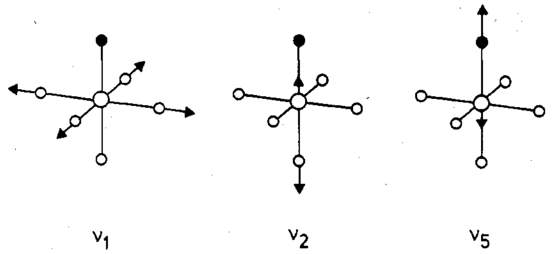

Figure 1. Symmetry vibrations of ν_1, ν_2, and ν_5, all belonging to a_1.

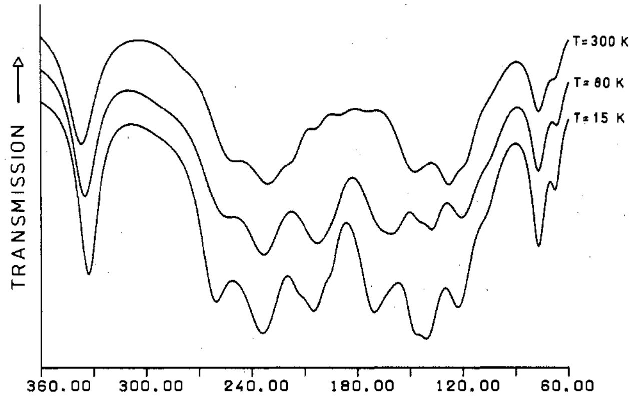

Figure 2. Far-infrared spectrum of $[Cr(ND_3)_5(NCO)](NO_3)_2$ at various temperatures in polyethylene disks.

representations of the C_{4v} group is given. According to the selection rules, two a_1 $\sigma(Cr–NH_3)$ stretching modes are allowed, which are denoted ν_1 and ν_2. The other peak (i.e., the 438-cm^{-1} band) must contain a large contribution from the $\nu_2(a_1)$ symmetry mode, since only this vibration gives rise to a change of dipole moment (cf. Figure 1).

(a) Far-Infrared. Figure 2 shows the far-infrared spectrum of $[Cr(ND_3)_5(NCO)](NO_3)_2$ at various temperatures. It demonstrates the importance of low-temperature measurements for locating peaks in vibrational spectra when they are used as a basis for assigning normal modes. The peaks obtained at 15 K for the deuterated and undeuterated compound are compiled in Table II together with their relative intensities, and the band shifts on deuteration are given by the frequency relation.

The assignment of the 342-cm^{-1} peak to the Cr–NCO stretching mode $\nu_5(a_1)$ has been discussed in the preceding paper.[10] It is made by comparison to other isocyanate complexes. The angular vibrations, which follow the stretching modes in Table I, have decreasing isotope shifts, which are due to the smaller content of hydrogen atoms in the series $\delta(H_3N–Cr–NH_3) > \delta(H_3N–Cr–NCO) > \delta(Cr–N–C)$. There are five bands with shift quotients between 1.07 and 1.10, which are candidates for $\delta(H_3N–Cr–NH_3)$ deformations; all others have much smaller isotope effects. Three of them, 281, 255, and 220 cm^{-1}, are rather intense; two others, 236 and 158 cm^{-1}, are weak. It is reasonable to assign the weaker bands to b_1 and b_2 symmetries since they are forbidden in the infrared. The more intense peaks must then belong to a_1 or e symmetry. In order to obtain the correct sequence, we made a comparison with corresponding modes in octahedral complexes, where the series of vibrational energy quanta is given by[13] $t_{1u} > t_{2g} > t_{2u}$. If the symmetry is decreased to C_{4v}, each of these terms decomposes into e and into $a_1 > b_2 > b_1$, respectively, which, since they do not combine, should follow the same sequence of terms. An identical series is found in halogenopentaammines of Rh, Ru, and Ir.[14] Following these arguments, the 158-cm^{-1} peak is assigned to $\nu_7(b_1)$ and the 236-cm^{-1} peak to $\nu_8(b_2)$. It is also concluded that either the 281-cm^{-1} or the 255-cm^{-1} band belongs to a_1. Since there remains only one a_1 and two e modes in the table of $\delta(H_3N–Cr–NH_3)$ deformations, the peak at 220 cm^{-1} must belong to e and may be denoted by ν_9. At this stage of discussion the assignment of 281 and 255 cm^{-1} to either a_1 or e is open; vide infra.

Table II. Far-Infrared Spectra of the Undeuterated (H) and Deuterated (D) Nitrate Compound at 15 K

H		D		
$\bar{\nu}$, cm^{-1}	I^a	$\bar{\nu}$, cm^{-1}	I^a	$\bar{\nu}(H)/\bar{\nu}(D)$
342	100	333	100	1.03
281	85	262	80	1.07
255	90	235	85	1.08
236	40	214	30	1.10
220	70	204	75	1.08
195	35	195	25	1.0
177	60	172	75	1.03
158	45	148	40	1.07
140	70	140	75	1.0
122	90	122	85	1.0
102	20	106	30	0.96
77	70	77	75	1.0
67	25	67	35	1.0

^{a} I is the relative intensity.

The peak at 177 cm^{-1}, with an isotope shift slightly lower than the preceding bands, is then assigned to $\delta(H_3N–Cr–NCO)$, which according to Table I is $\nu_{11}(e)$. The remaining angular vibration $\delta(Cr–N–C)$ must belong to one of the bands showing no isotope effect. Since none of the long-wavelength peaks at 67, 77, 122, and 140 cm^{-1} show an isotope shift nor an appreciable change in intensity, these bands should be due to lattice vibrations. This leads toward the conclusion that either 195 cm^{-1} or 102 cm^{-1} is due to $\delta(Cr–N–C)$. Following arguments brought forward for a thiocyanate complex, i.e., Reinecke salt,[15] the assignment of the 195-cm^{-1} peak to $\delta(Cr–N–C)$, i.e., $\nu_{19}(e)$, is more likely. Then the 102-cm^{-1} band must be a lattice vibration. This assignment also agrees with the results obtained for $[Cr(NCS)_6]^{3-}$.[6]

(b) Raman. These were recorded by Preetz[16] on an apparatus equipped with a spinning sample holder and excited with the 514-nm line of an argon laser. Probably due to the high absorptivity of the compound at this wavelength, the resulting spectrum was not very good. Only two prominent peaks were present in the region 500–100 cm^{-1}, at 480 and 448 cm^{-1} for the undeuterated and 440 and 416 cm^{-1} for the deuterated compound. Due to their high frequency, both peaks should be assigned to $\sigma(Cr–NH_3)$ stretches. Since $\nu_2(a_1)$ and $\nu_4(e)$ were assigned from infrared spectroscopy, the remaining possibilities for these bands are $\nu_1(a_1)$ and $\nu_3(b_1)$. In other acidopentaammine complexes, the most intense $\sigma(M–NH_3)$ Raman peak is usually ν_1, which is also found at higher energy than ν_3. Since in our case the 480-cm^{-1} peak is the more intense, it can be rather safely assigned to $\nu_1(a_1)$, and the 448-cm^{-1} band is $\nu_3(b_1)$.[13,14]

Vibronic Spectra

(a) Emission. The luminescence spectrum of powder samples shows about 30 peaks with half-widths of 20–50 cm^{-1} (the instrumental resolution was better than 1 cm^{-1}) and is displayed in Figure 3. The most intense peak, at 14680 cm^{-1}, and the band at 14885 cm^{-1} represent zero-phonon transitions. They remain essentially unshifted upon deuteration, and no vibrational frequency at 205 cm^{-1} was apparent, which might have explained the 14885-cm^{-1} line as a hot band. The line is still present at 10 K and more intense than would result from a Boltzmann distribution due to thermal population. The higher electronic state, therefore, must be populated from higher states in the deactivation cascade.

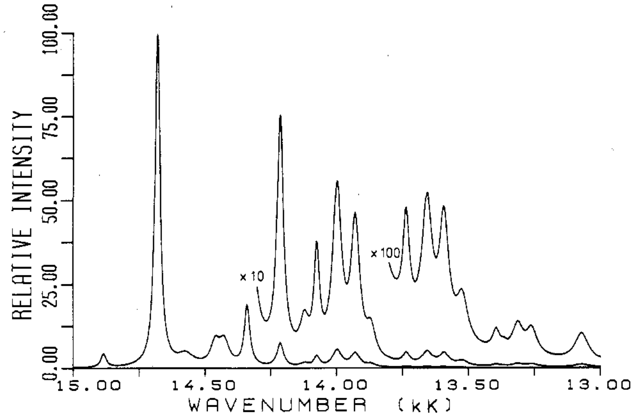

Figure 3. Emission spectrum of $[Cr(NH_3)_5(NCO)](NO_3)_2$ at 80 K, from a powdered sample.

Table III. Vibrational Fundamentals Obtained from the Luminescence Spectrum of the Undeuterated (H) and Deuterated (D) Compound

H	D	assignt	
106	110	lattice (?)	
220	192	ν_9(e)	$\delta(H_3N\text{-}Cr\text{-}NH_3)$
254	224	ν_{10}(e)	$\delta(H_3N\text{-}Cr\text{-}NH_3)$
341	335	$\nu_5(a_1)$	σ(Cr-NCO)
467	430	ν_4(e)	$\sigma(Cr\text{-}NH_3)$
606	610	ν_{20}(e)	δ(N-C-O)
684	535	ν_{17}(e)	δ(Cr-N-H)
752	600	ν_{18}(e)	δ(Cr-N-H)
1315		$\nu_{21}(a_1)$	σ(NC-O)
1610			$\delta_d(NH_3)^a$
2230		$\nu_{22}(a_1)$	σ(N-CO)

[a] Internal NH_3 vibration.

Table IV. Selection Rules for Vibronic Transitions of Electronic Origins $B_1 \rightleftarrows \Gamma_e$ in C_{4v} Symmetry

	Γ_e			
Γ_v	A_1	A_2	B_1	E
a_1	−	−	+	+
a_2	−	−	−	+
b_1	+	−	−	+
b_2	−	+	−	+
e	+	+	+	+

Table V. Relative Intensities of Combination Bands in the Luminescence Spectrum of the H Compound

$\nu_f{}^a$	$I(\nu_5 + \nu_f)$	$I(2\nu_5 + \nu_f)$	$I(\nu_{22} + \nu_f)$	$I(\nu_5 + \nu_{22} + \nu_f)$
ν_4	0.12	0.019	$+^b$	+
ν_9	0.14		+	
ν_{17}	0.08	0.017	+	+
ν_{18}	0.09	0.019		
ν_{20}	0.10	0.019	+	+

[a] Intensity of the fundamental ν_f was set equal to 1. [b] Extremely low intensity; intensity was not evaluated due to the errors resulting from the photomultiplier characteristics within large spectroscopic regions.

All other peaks represent vibronic side bands belonging to the 14680-cm^{-1} electronic origin. The most prominent fundamentals which can be detected in luminescence are listed in Table III. Assignments can be made in correspondence with results from vibrational spectroscopy. Since, obviously, only a_1 and e vibrations can be detected, the selection rules (Table IV) would indicate that the 14680-cm^{-1} origin is either a $^2B_1 \rightarrow {}^4B_1$ or a $^2E \rightarrow {}^4B_1$ transition in C_{4v} symmetry notation.[9]

In addition, some combinations with the most distinct totally symmetric modes ν_5 and ν_{22} can be identified (see Table V). The relative intensities of such progressions provide an estimate of the shift of potential energy curves in the excited electronic state relative to the ground state along the corresponding a_1 normal coordinate.[17] For the a_1 coordinate belonging to the ν_5 mode a shift of $\Delta Q_5 = 0.15$ Å was calculated.

(b) Absorption Spectra and Ligand Field Calculations. The investigation of the absorption spectrum contributes primarily to the problem of assigning the lowest zero-phonon transitions to the spin-forbidden transition of the electronic level scheme in C_{4v} symmetry. The research groups of Flint,[7] Forster,[8] and Güdel[9] disagree on the question of the extent of splitting of the lowest excited doublet $^2E_g(O_h)$ of $[Cr(NH_3)_5X]$ complexes due to the low-symmetry component of the ligand field. If no splitting is experimentally detectable in the quartet bands ($^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4T_{1g}$), a conventional ligand field calculation (for a relatively small quartet splitting) is not able to explain a low-symmetry splitting for $^2E_g(O_h)$ larger than 50 cm^{-1}. This can be demonstrated for any low-symmetry parameter set, *Ds* and *Dt*, which allows a splitting of the spin-allowed bands no larger than 1500 cm^{-1}. In this calculation, the *B*, *C*, and *Dq* parameters can be varied within a reasonable range. This result is not changed when spin–orbit coupling and other extensions of ligand field theory are also considered.[7,18] Ligand field calculations, which include spin–orbit coupling, supply ^2E_g splittings of only a few wavenumbers.[19] Since there are usually two intense zero-phonon transitions in the spectrum, 100–300 cm^{-1} apart, which are attributed by Forster[8] and Flint[7] to the two low-symmetry components $^2B_1$ and $^2A_1$ resulting from $^2E_g(O_h)$, Flint[7] came to the conclusion, "conventional ligand field theory is not able to account for the observed splitting of the ^2E_g of acido- and aquopentaamminechromium(III) compounds". Güdel and co-workers,[9] however, in view of the fact that ligand field theory has been most successful in rationalizing the spectroscopic properties of a great number of chromium(III) compounds, found this situation "quite disturbing". They claimed that the splitting of $^2E_g(O_h)$ is much smaller, as a matter of fact indetectably small for most of the pentaammines. They assigned the $^2B_1$ and $^2A_1$ levels in the excitation spectrum of $[Cr(NH_3)_5OH](ClO_4)_2$ to peaks which are only 61 cm^{-1} apart. The assigned splitting in the case of the $[Cr(NH_3)_5H_2O]^{3+}$ complex is 205 cm^{-1} (Flint[7]) and 20 ± 10 cm^{-1} (Güdel[9]). This different viewpoint would also change the assignments of all higher levels which originate from $^2T_{1g}$ in octahedral symmetry. $^2T_{1g}$ in C_{4v} symmetry yields an A_2 and an E level. Spin–orbit coupling splits E into Γ_6 and Γ_7 (Bethe notation) by several 10 cm^{-1}.[6,9,18] Following Güdel, the second zero-phonon transition would be due to a lower energy component of $^2T_{1g}$, which for the aquo complex should be about 200 cm^{-1} higher in energy. However, a ligand field calculation performed for a reasonable set of *Dq* and Racah parameters, *B* and *C*, with two restrictions imposed on the splittings, (1) for quartets not larger than 1500 cm^{-1} and (2) for the $^2E_g(O_h)$ level not larger than 30 cm^{-1}, is not able to explain the Güdel assignment either: for any set of parameters *Ds* and *Dt*, the difference between either of the split components $^2A_1$ and $^2B_1$ arising from $^2E_g(O_h)$ and the lower component $^2E(C_{4v})$ resulting from $^2T_{1g}(O_h)$, is somewhere between 350 and 530 cm^{-1}, i.e., never in the range 100–300 cm^{-1}, as has been found for any of the acido- or aquopentaammines of chromium(III). Also, the calculation cannot reproduce, in the case of the Güdel assignment, the general trend of the experimental splittings. For example, in the series of halogenopentaammines the calculated energy difference of $^2A_1$ and $^2B_1$ increases from Cl, Br to I in accordance with the band peak assignment of Flint. For the Güdel assignment, however, a decrease is calculated for this difference of peaks, which is due to the stabilization of the $^2E(^2T_{1g})$ state in this series of compounds. Therefore, it

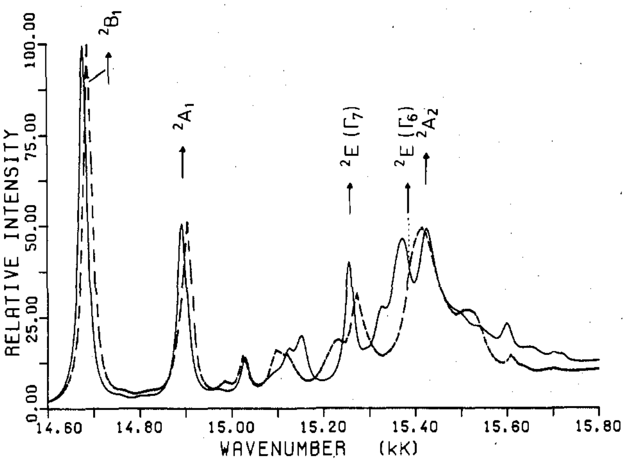

Figure 4. Absorption spectrum of $[Cr(NH_3)_5(NCO)](NO_3)_2$ (—) and the corresponding deuterated compound (- - -) in transparent KBr disks at 25 K.

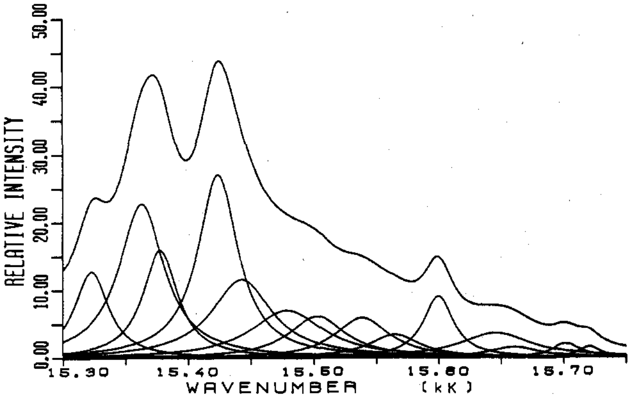

Figure 5. A portion of the absorption spectrum of Figure 4, with band decompositions into Lorentzian curves.

must be concluded that for either assignment, ligand field theory is not able to explain the experimental facts.[7,8] Flint's statement, as quoted above, must be accepted as being correct. Arguments for a correct assignment must rather be obtained from experimental results.

Since the absorption spectrum of $[Cr(NH_3)_5(NCO)](NO_3)_2$ in KBr at 25 K (Figure 4) is well resolved, it can serve to obtain reliable peak assignments to electronic origins. The nitrate salt exhibits a better resolved spectrum than the halide or perchlorate salts. By band analysis the positions of more than 30 bands can be identified. Figure 5 shows the accuracy which can be obtained from a decomposition into Lorentzian distributions. For the deuterated compound such a band analysis is carried out with equally good results.

A careful inspection of the intense bands at 14 678 and 14 891 cm^{-1} (cf. Figure 4) shows no splitting of these bands with an instrumental resolution of 1 cm^{-1}. The half-widths of these bands obtained from a band analysis are 21 and 22 cm^{-1}, respectively. The four most intense bands at 14 678, 14 891, 15 256, and 15 424 cm^{-1} and the band at 15 378 cm^{-1}, which is determined by band analysis, are assigned to pure electronic (zero-phonon) transitions since they are also found at similar positions in the deuterated compound (see Table VI). As in luminescence, the totally symmetric σ(Cr–NCO), i.e. ν_5, vibration gives rise to intense sidebands belonging to the 14 678-, 15 256-, and 15 378-cm^{-1} origins. Since, according to Table IV, an a_1 vibration can only combine with a transition from the ground state $^4B_1$ to the states $^2B_1$ and $^2E(\Gamma_6, \Gamma_7)$, these bands must correspond to these electronic transitions. With the zero-phonon band assignment as given in Table VI, all other vibronic transitions can also be interpreted as fundamentals which combine with the respective electronic transitions in accordance with the selection rules of Table IV. This assignment is in complete agreement with the interpretation of spin-forbidden d–d bands as given by Flint[7] and Forster,[8] confirming their interpretation of low-symmetry level splittings of ligand field doublets. In absorption, no progressions were detected. Their intensities are obviously so low that they are covered by vibronic bands of other electronic transitions.

Table VI. Absorption Spectrum (cm^{-1}) from a Band Analysis and Assignment of Its Structure[a]

$\bar{\nu}$(H)	$\bar{\nu}$(D)	assignts for H (D)	
14 678	14 688	$^4B_1 \rightarrow {}^2B_1$	$0\text{–}0_A$
14 755	14 765	A + 77 (77)	lattice
14 800	14 810	A + 122 (122)	lattice
14 820	14 830	A + 142 (142)	lattice
14 891	14 906	$^4B_1 \rightarrow {}^2A_1$	$0\text{–}0_B$
14 903	14 890	A + 224 (202)	ν_9(e)
14 970	14 983	B + 79 (77)	lattice
15 029	15 026	A + 351 (338)	$\nu_5(a_1)$
15 092	15 096	B + 201 (190)	ν_{19}(e)
15 123	15 096	A + 444 (408)	$\nu_2(a_1)$
15 146	15 140	B + 255 (233)	ν_{10}(e)
15 154	15 121	A + 476 (433)	ν_4(e)
15 256	15 270	$^4B_1 \rightarrow {}^2E(\Gamma_7)$	$0\text{–}0_C$
15 291	15 313	A + 613 (625)	ν_{20}(e)
15 323	15 200	A + 645 (512)	ν_{16}(e)
15 323	15 340	C + 67 (70)	lattice
15 363	15 228	A + 685 (540)	ν_{17}(e)
15 378	15 390	$^4B_1 \rightarrow {}^2E(\Gamma_6)$	$0\text{–}0_{C'}$
15 424	15 420	$^4B_1 \rightarrow {}^2A_2$	$0\text{–}0_D$
15 443	15 288	A + 765 (600)	ν_{18}(e)
15 479	15 474	C + 223 (204)	ν_9(e)
15 503	15 500	D + 79 (80)	lattice
15 539	15 409	B + 648 (503)	ν_{16}(e)
15 539	15 535	C + 283 (265)	$\nu_6(a_1)$
15 565	15 446	B + 674 (540)	ν_{17}(e)
15 600	15 610	C + 344 (340)	$\nu_5(a_1)$
15 646	15 517	B + 755 (610)	ν_{18}(e)
15 661	15 636	D + 237 (216)	$\nu_8(b_2)$
15 702	15 686	C + 446 (416)	$\nu_3(b_1)$
15 722	15 720	C' + 344 (330)	$\nu_5(a_1)$
15 885	15 850	D + 462 (430)	ν_4(e)
15 965	15 686	A + 1287 (998)	$\delta_s(NH_3)$
16 020	15 870	C + 764 (600)	ν_{18}(e)
16 035	16 040	D + 612 (620)	ν_{20}(e)
16 310	15 870	A + 1632 (1182)	$\delta_d(NH_3)$
16 515	16 090	B + 1624 (1184)	$\delta_d(NH_3)$
16 890	16 450	C + 1634 (1180)	$\delta_d(NH_3)$

[a] The spectrum is recorded from a transparent KBr disk at 25 K.

Very intense sidebands, with frequencies 645, 685, and 765 cm^{-1} for H and 512, 540, and 600 cm^{-1} for D, exhibit a rather large deuterium shift (quotient ~1.27). Due to the fact that they combine with several of the zero-phonon transitions, it can be concluded that these frequencies originate from NH_3 rocking vibrations of symmetry e. In accordance with Table I, we may assign ν_{16}(e) 645 cm^{-1}, ν_{17}(e) 685 cm^{-1}, and ν_{18}(e) 765 cm^{-1} to δ(Cr–N–H).

Finally, the assignment of ν_6 and ν_{10} from the far-infrared spectrum remains to be discussed. In absorption, ν_6 is observed only in combination with the ^2E electronic state. Since all vibrational symmetries are allowed to combine with this state (cf. Table IV), no classification is possible for this frequency. However, since ν_{10} is observed only in combination with $^2A_1$ (cf. the 15 146-cm^{-1} band), the vibronic selection rule would indicate ν_{10} to be either b_1 or e. In the infrared spectrum, ν_{10} is active only if it belongs to a_1 or e symmetry. Therefore, we conclude that ν_{10} must belong to e, whence it follows from the far-infrared arguments that ν_6 must have a_1 symmetry.

In addition, attention should be directed to an interesting point concerning the variation of the totally symmetric σ-(Cr–NCO) stretch, ν_5, in the excited electronic state as

Table VII. Complete Assignment of Normal Modes to C_{4v} Symmetry Notations and Atomic Group Vibrations

	symm	arguments from	H	D	assignt
ν_1	a_1	R	480	440	σ(Cr-NH$_3$)
ν_2	a_1	IR	438	413	
ν_3	b_1	R	448	416	
ν_4	e	IR	463	432	
ν_5	a_1	far-IR	342	333	σ(Cr-NCO)
ν_6	a_1	abs	281	235	δ(H$_3$N-Cr-NH$_3$)
ν_7	b_1	far-IR	158	148	
ν_8	b_2	far-IR	236	214	
ν_9	e	far-IR	220	204	
ν_{10}	e	abs	255	235	
ν_{11}	e	far-IR	177	172	δ(H$_3$N-Cr-NCO)
ν_{16}	e	abs	645	512	δ(Cr-N-H)
ν_{17}	e	abs	685	540	
ν_{18}	e	IR + abs	760	600	
ν_{19}	e	far-IR	195	195	δ(Cr-N-C) (?)
ν_{20}	e	IR	605	609	δ(N-C-O)
ν_{21}	a_1	IR	1315	1292	σ(NC-O)
ν_{22}	a_1	IR	2240	2220	σ(N-CO)

compared to the ground state. From infrared, Raman, and vibronic data in absorption and emission, it is certain that the ν_5 frequency in the excited electronic states is greater than in the ground state, with a frequency factor[17] of $\beta = 351/342 = 1.02$ if, e.g., the vibronic $^2A_1$ sideband of the undeuterated compound (cf. see Tables II, III, and VI) is considered. This is quite unusual: generally, the potential curves of excited states indicate force constants which are lower than those in the ground state.[2,7] The steeper potential curve in the excited state may be explained by coupling of a large number of electronic states by virtue of the low symmetry.

Conclusions

In Table VII the results obtained from the above discussion on symmetry assignments to band peaks, using different spectroscopic techniques, are compiled. The assignment to vibrations of atomic groups as derived from symmetry vibrations (see Table I) is also included. While most of these assignments appear certain, some others are still tentative. Further investigations with other techniques or a complete normal-coordinate analysis must be carried out if more definite assignments are to be made. The other main concern of this paper is the determination of the order of doublet energy level splittings resulting from the low-symmetry, in order to come to a decision on the inconsistencies in the literature. All results support the view that convential ligand field theory is unable to explain the large low-symmetry effects on energy levels of low multiplicity found experimentally.

Acknowledgment. The authors are indebted to the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, Düsseldorf, and the Verband der Chemischen Industrie, Frankfurt, for financial support. We also thank Mr. Rolf Linder, Düsseldorf, for his technical assistance in the construction of some spectroscopic devices.

Registry No. [Cr(NH$_3$)$_5$(NCO)](NO$_3$)$_2$, 68092-88-6.

References and Notes

(1) A. M. Black and C. D. Flint, *J. Chem. Soc., Faraday Trans. 2*, **73**, 877 (1977).
(2) R. Wernicke and H.-H. Schmidtke, *Mol. Phys.*, **37**, 607 (1979).
(3) S. M. Khan, H. H. Patterson, and H. Engstrom, *Mol. Phys.*, **35**, 1623 (1978).
(4) R. Wernicke, G. Eyring, and H.-H. Schmidtke, *Chem. Phys. Lett.*, **58**, 267 (1978).
(5) S. L. Chodos, A. M. Black, and C. D. Flint, *J. Chem. Phys.*, **65**, 4816 (1976).
(6) C. D. Flint and A. P. Matthews, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1301 (1974).
(7) C. D. Flint and A. P. Matthews, *J. Chem. Soc., Faraday Trans. 2*, **69**, 419 (1973).
(8) W. N. Shephard and L. S. Forster, *Theor. Chim. Acta*, **20**, 135 (1971).
(9) S. Decurtins, H. U. Güdel, and K. Neuenschwander, *Inorg. Chem.*, **16**, 796 (1977).
(10) H.-H. Schmidtke and T. Schönherr, *Z. Anorg. Allg. Chem.*, **443**, 225 (1978).
(11) J. R. Perumareddi, *Coord. Chem. Rev.*, **4**, 73 (1969).
(12) N. Tanaka, M. Kamada, J. Fujita, and E. Kyuno, *Bull. Chem. Soc. Jpn.*, **37**, 222 (1964).
(13) K. H. Schmidt and A. Müller, *J. Mol. Struct.*, **22**, 343 (1974).
(14) M. W. Bee, S. F. A. Kettle, and D. B. Powell, *Spectrochim. Acta, Part A*, **30a**, 139 (1974).
(15) P. E. Hoggard, T. Schönherr, and H.-H. Schmidtke, *Spectrochim. Acta, Part A*, **32a**, 917 (1976).
(16) H. Homborg and W. Preetz, *Spectrochim. Acta, Part A*, **32a**, 709 (1976).
(17) H. Kupka, *Mol. Phys.*, **36**, 685 (1978).
(18) C. D. Flint, A. P. Matthews, and P. J. O'Grady, *J. Chem. Soc., Faraday Trans. 2*, **73**, 655 (1977).
(19) R. M. MacFarlane, *J. Chem. Phys.*, **47**, 2066 (1967).

Contribution from the Institut für Anorganische Chemie, Universität Bern, CH-3000 Bern 9, Switzerland,
and the Institut für Reaktortechnik ETHZ, CH-5303 Würenlingen, Switzerland

Electronic Ground-State Properties of Tetranuclear Hexa-μ-hydroxo-bis(tetraamminechromium(III))bis(diamminechromium(III)) Chloride. A Spectroscopic and Magnetochemical Study

HANS U. GÜDEL,* URS HAUSER, and ALBERT FURRER

Received March 20, 1979

Magnetic susceptibility, optical spectroscopic, and inelastic neutron-scattering experiments were performed in order to investigate the exchange coupling in deuterated rhodoso chloride, [Cr$_4$(OD)$_6$(ND$_3$)$_{12}$]Cl$_6$·4D$_2$O. Optical spectra illustrate the splitting of both ground and excited electronic states. By use of neutron inelastic scattering, transitions within the exchange split ground state were measured. Five inelastic peaks were resolved and analyzed in terms of an isotropic exchange Hamiltonian containing three bilinear and two biquadratic coupling parameters. The magnetic susceptibility curve does not contain enough structure to allow the determination of five exchange parameters by a least-squares fit.

Introduction

The tetranuclear rhodoso complex, hexa-μ-hydroxo-bis(tetraamminechromium(III))bis(diamminechromium(III)), first described by Jørgensen[1] almost 100 years ago, has a planar structure with the Cr^{3+} ions forming a regular rhombus (Figure 1).[2] Its structure is closely related to the Pfeiffer cation, [Cr$_4$(OH)$_6$(en)$_6$]$^{6+}$,[3] the magnetic properties of which have been studied in detail.[4-6] No magnetochemical investigation of the rhodoso complex has been reported.

Rather conflicting results have been obtained for the Pfeiffer ion. On the basis of the magnetic susceptibility measurements of the azide, Flood et al.[4] found both J and J' to be antiferromagnetic with a J/J' ratio of 0.53. Iwashita et al.,[5] on

---

*To whom correspondence should be addressed at the Institut für Anorganische Chemie, Universität Bern.

0020-1669/79/1318-2730$01.00/0