Inorg. Chem. **1987**, *26*, 2747–2750 **2747**

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Site-Selective Luminescence and Excitation Spectroscopy in Tris(μ-hydroxo)bis[(1,5,9-triazacyclododecane)chromium(III)] Tribromide Dihydrate

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Received January 23, 1987

Single crystals of the title compound were studied by low-temperature absorption and site-selective luminescence and excitation spectroscopy. The luminescence spectra of the two inequivalent crystallographic sites could selectively be excited whereby the luminescence lines were considerably narrowed. Thus an accurate determination of the ground-state splitting was possible. The exchange parameter J was found to be slightly but significantly different for the two sites: $J = -49.5$ cm^{-1} (site A) and -52.5 cm^{-1} (site B). The exchange splitting of the ground and the singly excited states is compared with that found in tris(μ-hydroxo)bis[(1,4,7-trimethyl-1,4,7-triazacyclononane)chromium(III)] triperchlorate. Exchange parameters are reduced by approximately 20% in the title compound.

Introduction

The structural, electronic, and magnetic properties of μ-hydroxo binuclear chromium(III) complexes have been intensively investigated in recent years.[2-4] In contrast to the case for mono(hydroxo)- and bis(hydroxo)-bridged complexes the first tris(hydroxo)-bridged chromium(III) complex was synthesized only recently.[5] A detailed analysis of the highly resolved optical spectrum of tris(μ-hydroxo)bis[(1,4,7-trimethyl-1,4,7-triazacyclononane)chromium(III)] triperchlorate (in the following abbreviated by $[9](ClO_4)_3$) has been possible.[6,7] In the title complex the ligand 1,4,7-trimethyl-1,4,7-triazacyclononane is replaced by the larger 1,5,9-triazacyclododecane but the $Cr(OH)_3Cr$ bridge is essentially the same. The two dinuclear complexes will be abbreviated by $[9]^{3+}$ and $[12]^{3+}$ in the following. The title compound, $[12]Br_3{\cdot}2H_2O$, crystallizes in the orthorhombic space group $P2_12_12_1$, and the trigonal symmetry of the dinuclear complex is slightly distorted.[8] The three OH bridges are no longer exactly equivalent. There are two crystallographically nonequivalent sites of the complex cation in the crystal. Magnetic susceptibility measurements have revealed[8] that the exchange coupling is smaller by approximately 25% in $[12]Br_3{\cdot}2H_2O$ than in $[9](ClO_4)_3$. However, a bulk technique such as a susceptibility measurement is not able to reveal differences between inequivalent sites. Thus, if the exchange splittings of the ground state are different for the two inequivalent binuclear complexes in $[12]Br_3{\cdot}2H_2O$, only averaged values are determined. In contrast, site-selective spectroscopy and the technique of luminescence line narrowing[9] allow a very precise probing of the ground-state splitting of individual sites and even subsets of sites. This was recently shown for two other dinuclear chromium(III) complexes: $[(NH_3)_5CrOHCr(NH_3)_5]Cl_5{\cdot}H_2O$[10] and $[(bispicam)Cr(OH)_2(SO_4)Cr(bispicam)]S_2O_6{\cdot}3H_2O$[11] (bispicam = bis(2-pyridylmethyl)amine).

The present work is an illustration of the potential of such spectroscopic techniques. The ground-state energy splittings of the binuclear complexes in $[12]Br_3{\cdot}2H_2O$ are evaluated and discussed. A comparative analysis of the exchange splittings in the singly excited states of $[12]Br_3{\cdot}2H_2O$ and $[9](ClO_4)_3$ is given. Orbital exchange parameters are determined and discussed.

Experimental Section

$[12]Br_3{\cdot}2H_2O$ was prepared as described elsewhere.[8] Crystals suitable for optical spectroscopy were grown from a 0.2 M aqueous solution of NaBr. The crystals were checked by powder X-ray diffraction. The diagrams were found to agree with the structure published in ref 8.

Absorption spectra were recorded on a Cary 17 spectrometer. The samples were cooled in a helium flow tube.[12] A Kr^+ ion laser (Coherent CR-500K) and a dye laser (Spectra-Physics 375; spectral bandwidth, 30 GHz; dye DCM Exciton in propylene carbonate/ethylene glycol (2:3)) pumped by an Ar^+ ion laser (Spectra Physics 166) were used as excitation sources for luminescence and excitation spectra. In these experiments a liquid-helium-bath cryostat (Oxford Instruments MD4) was used to cool the sample.

Results

In Figure 1 we show the temperature dependence of the absorption spectrum of $[12]Br_3{\cdot}2H_2O$ in the region of $^4A_2{}^4A_2 \rightarrow {}^2E^4A_2$, $^2T_1{}^4A_2$ excitations. Three distinct temperature dependences, which are due to a Boltzmann population of the exchange-split spin levels $S = 0, 1, 2$ in the $^4A_2{}^4A_2$ ground state, are clearly recognized. The peaks are labeled accordingly. The absorption spectrum consists of two overlapping individual spectra corresponding to the two inequivalent binuclear chromium(III) complexes. For comparison the absorption spectrum of $[9](ClO_4)_3$ is presented in Figure 2 in the same spectral region and also at three temperatures. Similar features can be seen in the spectra of the two compounds. $[9](ClO_4)_3$ crystallizes in the hexagonal space group $P6_3/m$,[13] containing only one site for the binuclear cation. Due to this high symmetry, the sharpness of the lowest energy excitations, and the complete polarization of all prominent transitions, a detailed analysis of the absorption spectrum of this compound is much easier than for $[12]Br_3{\cdot}2H_2O$. Our interpretation of the title compound will therefore rely heavily on ref 7, where the spectrum of $[9](ClO_4)_3$ was analyzed.

The luminescence spectrum of $[12]Br_3{\cdot}2H_2O$ can be separated into the individual spectra of site A (higher in energy) and site B (lower in energy) by selective excitation as is illustrated in Figure 3. As a further result of the selective excitation, luminescence lines are considerably narrowed at low temperatures. The quantum efficiency of the luminescence is only on the order of 1% at 1.5 K for either site. This is usually found for complexes containing high-frequency vibrations.[14] The luminescence is rapidly quenched with increasing temperature.

In Figure 4 we show individual excitation spectra of the two sites in the region of the cold $^4A_2{}^4A_2 \rightarrow {}^2E^4A_2$, $^2T_1{}^4A_2$ transitions together with the 7 K absorption spectrum. The excitation spectra were obtained by monitoring the luminescence at 14 431.2 cm^{-1} (site A) and 14 301.8 cm^{-1} (site B) (cf. Figure 3). The selectivity is more complete in the spectrum of site A. Vibronic sidebands of the strongest electronic transition in the luminescence spectrum

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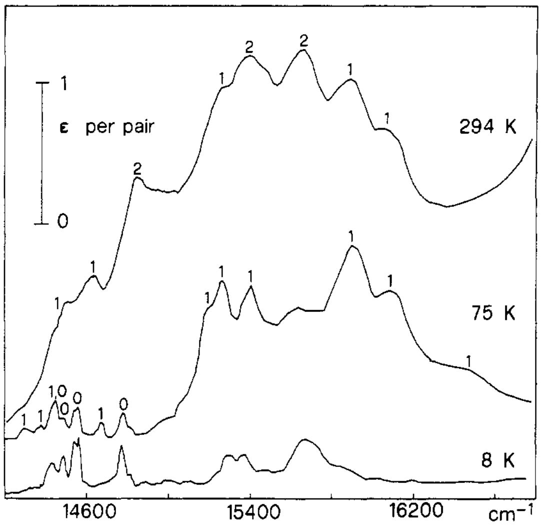

Figure 1. Unpolarized crystal absorption spectra of [12]Br$_3$·2H$_2$O in the region of $^4A_2{}^4A_2 \rightarrow {}^2E^4A_2$, $^2T_1{}^4A_2$ excitations. Spin quantum numbers of the ground levels are indicated. Polarized spectra of this (unidentified) crystal face showed practically no dichroism.

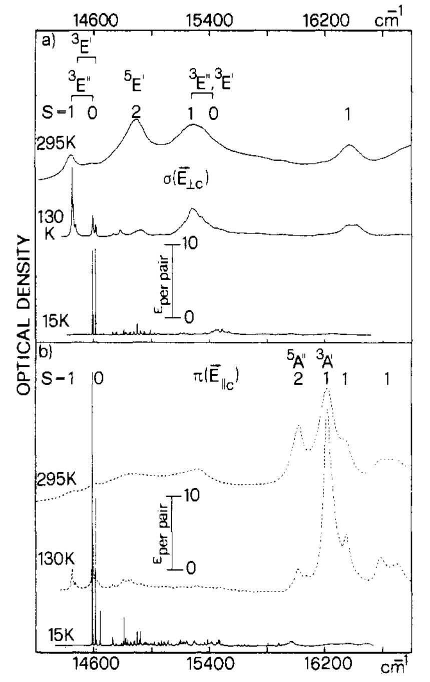

Figure 2. Polarized absorption spectra of [9](ClO$_4$)$_3$ in the same spectral region as for Figure 1: (a) $\sigma(E_{\perp c})$; (b) $\pi(E_{\parallel c})$.

of site A, which coincide with the electronic transition of site B at 14 301.8 cm^{-1}, are likely responsible for this. The sharp lowest energy transitions in these spectra were used to get the selectively excited luminescence spectra as is illustrated in Figure 3. In the region of these lowest energy transitions the excitation spectra are sharp and comparable to the absorption spectra of [9](ClO$_4$)$_3$.

Discussion

Ground-State Exchange Parameters. In Figure 5 we schematically represent the relevant transitions in our site-selective spectroscopy and luminescence line narrowing experiments. The situation shown is typical for an antiferromagnetically coupled tris(μ-hydroxo) binuclear chromium(III) complex: the lowest energy excited level is a spin triplet ($S^* = 1$). At sufficiently low temperatures only the $S = 0$ ground-state level is populated. We used the lowest energy $S = 0 \rightarrow S^* = 1$ transition to selectively excite the luminescence spectra of the two inequivalent sites. The broadening of the luminescence lines is partially resolved by using these selective excitations, clearly demonstrating that it is due to inhomogeneity. Crystal defects and slight modifications in the

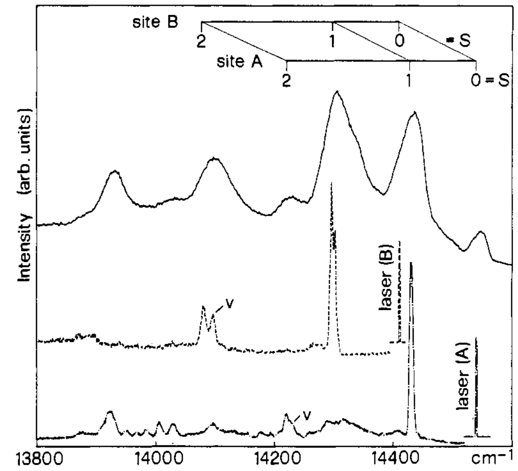

Figure 3. Nonselectively excited (Kr$^+$ ion laser line at 19 196 cm^{-1}) luminescence spectrum (—) in comparison with the spectra excited at 14 411.7 cm^{-1} (- - -, $S = 0 \rightarrow S^* = 1$, site B) and 14 540.5 cm^{-1} (-·-, $S = 0 \rightarrow S^* = 1$, site A) at 1.5 K. v denotes a 200-cm^{-1} vibrational sideband of the $S^* = 1 \rightarrow S = 1$ transitions. The laser lines used for the selective excitation are included.

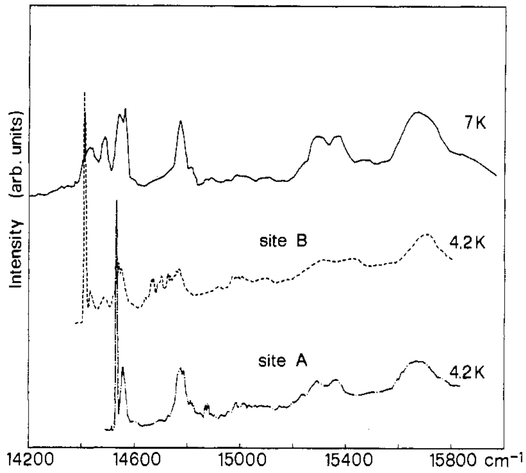

Figure 4. Excitation spectra of [12]Br$_3$·2H$_2$O at 4.2 K. The luminescence line $S^* = 1 \rightarrow S = 1$ was observed at 14 301.8 cm^{-1} (- - -, site B) and at 14 431.2 cm^{-1} (-·-, site A). The 7 K absorption spectrum is shown for comparison.

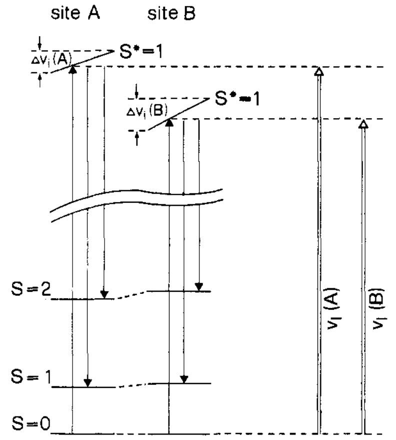

Figure 5. Schematic representation of the site-selective luminescence and luminescence line-narrowing experiments. $\Delta\nu_l$(A) and $\Delta\nu_l$(B) indicate the inhomogeneous broadening of the $S = 0 \leftrightarrow S^* = 1$ transition of the two sites. ν_l is the laser frequency.

neighborhood of the complex are the likely reasons for the inhomogeneous broadening.[9] The fact that luminescence spectra of site A and site B can selectively be excited under CW excitation in the temperature range 1.5–15 K shows that energy transfer

Table I. Energies (in cm^{-1}) of Selectively Excited Luminescence Lines within the Inhomogeneously Broadened Transitions of Sites A and B[a]

excitation energy (laser) $S = 0 \rightarrow S^* = 1$	$S^* = 1 \rightarrow S = 1$	$S^* = 1 \rightarrow S = 2$	site	J	j
14540.5	14430.3	14220.5	A	−49.4	1.8
14545.4	14436.1	14226.0		−50.1	1.4
14549.1	14439.9	14229.8		−50.1	1.4
14551.9	14444.1	14235.2		−50.3	1.0
14556.4	14449.1	14242.5		−49.3	1.3
14407.2	14294.0	14075.4	B	−52.4	1.3
14411.7	14299.0	14080.6		−52.6	1.2
14414.9	14303.0	14083.9		−53.4	0.8
14421.2	14309.4	14091.7		−52.7	1.0
14426.5	14314.8	14097.8		−52.4	1.1

[a] The parameters J and j were calculated by using eq 1.

between the two sites is not competitive with the nonradiative deactivation rate of the excitation at these temperatures. The same is true for the near-resonant spectral energy transfer[9] between subsets within the inhomogeneous width of a given site. This can be directly concluded from the luminescence line narrowing.[10]

From the energy differences between the exciting laser frequency ($S = 0 \rightarrow S^* = 1$) and the two luminescence lines $S^* = 1 \rightarrow S = 1$ and $S^* = 1 \rightarrow S = 2$ the exchange parameters J and j can be calculated according to the eigenvalues of the well-known Hamiltonian (1). The results are summarized in Table I. The

$$\hat{\mathcal{H}} = -2J(\vec{S}_1 \cdot \vec{S}_2) - j(\vec{S}_1 \cdot \vec{S}_2)^2 \qquad (1)$$

two sites A and B have significantly different J values. The differences between the subsets of a given site, on the other hand, are within the experimental error. The smaller J value for site A is reasonable since the Cr–Cr separation was found to be slightly different for the two sites, 2.667 vs. 2.653 Å for sites A and B, respectively.[8] The susceptibility measurement yielded $J = -48 \pm 2$ cm^{-1} and $j = 2$ cm^{-1}.[8] The power of the spectroscopic technique lies in the higher accuracy of the exchange parameters, and, perhaps more importantly, in the ability to selectively determine the parameters of individual sites.

Exchange Splittings in Singly Excited States. The overlap of the two individual spectra of sites A and B in the absorption spectrum complicates the situation considerably. Except for the very lowest excitations all the bands consist of superimposed transitions. In comparison with the case for $[9](ClO_4)_3$ there is the additional complication that, as a result of the lower symmetry, the number of vibrational sidebands is much larger. Therefore, even the selective excitation spectra of sites A and B (Figure 4) are much less informative than the absorption spectrum of $[9](ClO_4)_3$. However, by comparing the spectra of $[12]Br_3 \cdot 2H_2O$ and $[9](ClO_4)_3$, and by making use of the detailed analysis of $[9](ClO_4)_3$, we arrive at a reliable estimate of the relevant orbital exchange parameters.

First of all we note that the total energy range covered by the $^2E^4A_2$ and $^2T_1{}^4A_2$ singly excited states is approximately 15% smaller in $[12]Br_3 \cdot 2H_2O$ than in $[9](ClO_4)_3$ (Figures 1 and 2). This may be the result of slightly different ^2E and $^2T_1$ single-ion energies or slightly different orbital exchange parameters. Since the ground state J is approximately 20% smaller in $[12]Br_3 \cdot 2H_2O$, we suspect the latter and assume equal single-ion energies. In $[9](ClO_4)_3$ the $^4A_2{}^2E$ and $^4A_2{}^2T_{1a\pm}$ singly excited states were found to be strongly mixed by the exchange interactions. Energies of the pair levels in these excited states are given in terms of the single-ion energies and the two orbital exchange parameters J_a and J_e. These exchange parameters can be expressed in terms of one-electron transfer integrals $h(\mathrm{i} \leftarrow \mathrm{j})$ and the electron-transfer energy U:[15]

$$J_a = J(t_{2x0}t_{2x0}, t_{2x0}t_{2x0}) \cong -2(h(t_{2x0} \leftarrow t_{2x0}))^2/U$$

$$J_e = J(t_{2x\pm}t_{2x\pm}, t_{2x\pm}t_{2x\pm}) \cong -2(h(t_{2x\pm} \leftarrow t_{2x\pm}))^2/U \qquad (2)$$

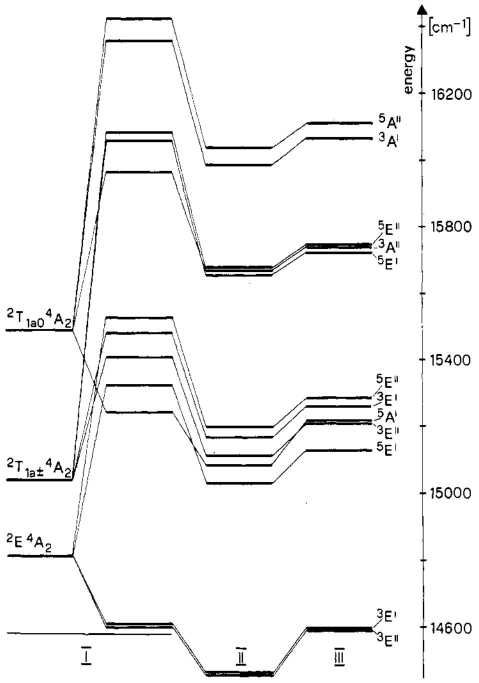

Figure 6. Calculated energy pattern in the region of the $^2E^4A_2$ and $^2T_1{}^4A_2$ pair states.[7] Pattern I corresponds to the situation as found in $[9](ClO_4)_3$. Patterns II and III were calculated by using the same single-ion energy differences $R(^2T_{1a\pm}) - R(^2E)$ and $R(^2T_{1a0}) - R(^2E)$ but reducing the exchange parameters to 81% and 76%, respectively. The absolute energy of II and III was chosen such that the calculation reproduces the experimental energies of the lowest energy $^3E''$, $^3E'$ levels of sites A and B, respectively.

t_{2x0} and $t_{2x\pm}$ are trigonally quantized t_2 orbitals. In $[9](ClO_4)_3$ J_e was found to be 1–3% of J_a. The corresponding calculated energy splitting pattern, which is in very nice agreement with the experiment, is shown in column I of Figure 6. For the calculations in columns II and III the exchange parameters were reduced by the factors 1.23 and 1.32, respectively, so as to roughly reproduce the observed energy splittings of sites B and A in $[12]Br_3 \cdot 2H_2O$. This procedure is only approximate, because the ^2E and $^2T_1$ single-ion energies were assumed to be the same as in $[9](ClO_4)_3$.

In conclusion we can say that the exchange interactions in $[12]Br_3 \cdot 2H_2O$ are weaker than in $[9](ClO_4)_3$ by approximately 20%. This is true for the ground-state exchange parameter J as well as the orbital parameters J_a and J_e derived from the excited-state splittings.

In both tris(hydroxo)-bridged Cr(III) complexes J_a dominates J_e by roughly 2 orders of magnitude. This is qualitatively understood on the basis of simple overlap arguments. The trigonal a orbitals are pointing in the Cr–Cr direction; they are thus favorably oriented for direct overlap. On a more quantitative level, J_a and J_e can be related to energy differences of bonding and antibonding molecular orbitals built from the a and e magnetic orbitals on the two Cr(III) ions. Using an extended Hückel calculation to estimate MO energies, we obtained $J_a/J_e = 30$ for $[9](ClO_4)_3$.[7] This is in exact agreement with the experimental ratio obtained for $^2T_{1a0}{}^4A_2$, which is clearly fortuitous. But there is not doubt about the general trend.

The reduction of exchange parameters by approximately 20% in $[12]Br_3 \cdot 2H_2O$ compared to those in $[9](ClO_4)_3$ can be correlated with differences in the molecular structure as follows. According to the X-ray diffraction results and considering standard deviations, the Cr–Cr separations lie within the range 2.66 ± 0.01 Å in both compounds. Cr–O distances range from 1.98 to 2.05 Å in $[12]Br_3 \cdot 2H_2O$,[8] compared to a Cr–O bond length of 1.98 Å in $[9](ClO_4)_3$.[13] Accordingly, Cr–O–Cr angles are somewhat smaller in $[12]Br_3 \cdot 2H_2O$, and the oxygen atoms are further removed from the Cr–Cr axis. This leads to a reduction of J_a despite the equal Cr–Cr separation. The a molecular orbitals are not combinations of pure metal d orbitals. They have contributions from oxygen

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s and p orbitals, which are altered by the change in Cr–O bond lengths. The term "direct exchange" for J_a is misleading in this respect. We should also realize that a change of only 0.01 Å in the Cr–Cr separation can result in a 10% change of J_a and J. This is the result of recent experiments with $[9](ClO_4)_3$ under hydrostatic pressure.[16] A difference of 0.01 Å in the Cr–Cr separation between $[9](ClO_4)_3$ and $[12]Br_3 \cdot 2H_2O$ cannot be ruled out on the basis of the X-ray diffraction results. It may account for part of the observed difference in J.

Acknowledgment. We acknowledge financial support of this work by the Swiss National Science Foundation.

Registry No. $[12]Br_3 \cdot 2H_2O$, 109306-30-1.

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Contribution from the Istituto di Teoria e Struttura Elettronica, CNR, 00016 Monterotondo Scalo (Roma), Italy,
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Optical Spectroscopy of One- and Two-Dimensional Ionic Magnets of Cr^{2+}: $CsCrCl_3$, $(CH_3)_4NCrCl_3$, $(CH_3)_4NCrBr_3$, $CrCl_2$, $(C_2H_5NH_3)_2CrCl_4$, and $(C_2H_5NH_3)_2CrBr_4$

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Received March 5, 1987

The title compounds were synthesized and grown as single crystals. Absorption spectra were measured between 10 and 300 K in the visible and near-infrared range. Spin-allowed transitions were assigned to the near-IR bands. The linear-chain compounds $ACrX_3$ (A = Rb^+, Cs^+, $(CH_3)_4N^+$; X = Cl^-, Br^-) and $CrCl_2$ show a large number of sharp spin-forbidden bands between 16000 and 24000 cm^{-1}, whereas the layer compounds A_2CrX_4 (A = Rb^+, Cs^+, $C_nH_{2n+1}NH_3^+$; X = Cl^-, Br^-) show only two band systems around 16000 and 19000 cm^{-1}. This difference is interpreted in terms of an exchange intensity mechanism, and the bands observed near 16000 and 19000 cm^{-1} are assigned as ${}^5B_{1g} \rightarrow {}^3B_{1g}({}^3H)$ and ${}^3B_{1g}({}^3F)$ transitions. The small number of spin-forbidden bands in A_2CrX_4 is due to a lack of orbital overlap between the magnetic orbitals on nearest-neighbor Cr^{2+} ions. It is thus correlated to the observed ferromagnetic ground state in these compounds. In contrast, the crystal structures of $ACrX_3$ and $CrCl_2$ are more favorable for orbital overlap. As a consequence, these compounds are antiferromagnets and exhibit a larger number of spin-forbidden excitations within the ground-state electron configuration.

1. Introduction

Ternary chromium(II) halides of the general composition $ACrX_3$ (A = Rb^+, Cs^+, $(CH_3)_4N^+$; X = Cl^-, Br^-) crystallize in structures derived from the well-known hexagonal $CsNiCl_3$ structure.[1-4] Since Cr^{2+} is subject to $E \otimes e$ Jahn–Teller distortions, the local coordination geometry is approximately D_{4h}. Structural phase transitions resulting from a cooperative Jahn–Teller effect have been observed and investigated in $RbCrCl_3$, $CsCrCl_3$, $CsCrBr_3$, and $(CH_3)_4NCrCl_3$.[1] In the high-temperature phase the directions of the elongated Cr–Cl bonds are considered to be disordered along the chains, thus retaining the overall hexagonal symmetry of the $CsNiCl_3$ structure. The low-temperature phases correspond to superstructures with ordered directions of the elongated Cr–Cl bonds and correspondingly lower symmetry space groups. The magnetic and caloric properties of $ACrX_3$ compounds show typical features of one-dimensional antiferromagnets.[2-5] $(CH_3)_4NCrCl_3$ (TMCC) shows a transition to three-dimensional magnetic order at 7 K.[2] In this respect it resembles $(CH_3)_4NMnCl_3$ (TMMC), the prototypical one-dimensional antiferromagnet.

Detailed single-crystal optical spectra have been reported for $RbCrCl_3$ and $CsCrCl_3$ as well as their diluted analogues $RbMg_{1-x}Cr_xCl_3$ and $CsMg_{1-x}Cr_xCl_3$.[1,6-8] Some authors have assumed local O_h symmetry in the assignment of the spin-allowed absorption bands, while other analyses are based on the more realistic assumption of a local D_{4h} distortion.[1,8] Spin-forbidden bands have only been interpreted in O_h.

$CrCl_2$ has a chain structure with edge-sharing octahedra along the c axis of the orthorhombic unit cell.[9] The elongated Cr–Cl bonds are not involved in the bridging between nearest-neighbor Cr^{2+} ions in the chains.[10] A transition to three-dimensional antiferromagnetic order was observed at 20 K. Unpolarized single-crystal absorption spectra in the near-infrared and visible region have been reported and interpreted.[11]

Ternary chromium(II) halides of the composition A_2CrX_4 (A = Rb^+, Cs^+, RNH_3^+; X = Cl^-) crystallize in a distorted K_2NiF_4 layer structure. Recently several A_2CrBr_4 compounds (A = $C_2H_{2n+1}NH_3^+$) have been synthetsized and characterized.[12,13] They are all two-dimensional ferromagnets. As a result of the ferromagnetic exchange coupling within the layers they exhibit very interesting and quite unique physical properties at low temperatures. Their structural, magnetic, and spectroscopic properties have therefore been studied in much more detail than for the corresponding CrX_2 and $ACrX_3$ compounds.[14] Optical spectroscopists have focused on two absorption band systems, which show a very distinct temperature dependence typical of two-dimensional ferromagnets.

The visible part of the absorption spectrum of Cr^{2+} with chloro or bromo coordination consists of spin-forbidden transitions. The

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