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Electronic Spectrum of Hydroxopentaamminechromium(III)

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Absorption, luminescence, and luminescence excitation spectra of single crystals and powders of [Cr(NH₃)₅OH](ClO₄)₂ have been measured between 7 K and room temperature. [Cr(NH₃)₅OH]²⁺ takes a unique position within the series [Cr(NH₃)₅X]ⁿ⁺ (X = I⁻, Br⁻, Cl⁻, F⁻, H₂O, OH⁻). The great capacity of the OH⁻ ligand to destabilize z², xz, and yz orbitals leads to a large tetragonal crystal field component. This causes a large tetragonal splitting of the second spin-allowed band as well as a reversal of the order of the lowest lying doublet states. The lowest excited state, from which luminescence is observed, is not a component of ²E_g as in "normal" chromium(III) complexes but is the ²E component (C_{4v} notation) of ²T_{1g}. A progression in the totally symmetric Cr-O stretching frequency of 570 cm⁻¹ is observed in the luminescence spectrum. The positions of nine experimentally located electronic states could be rationalized by a crystal field calculation.

1. Introduction

There have been a number of spectroscopic investigations of complexes of the type [CrN₅X]ⁿ⁺ and [CrN₄X₂]ⁿ⁺ (N = nitrogen ligand; X = I⁻, Br⁻, Cl⁻, F⁻, H₂O, OH⁻) in recent years.¹⁻⁵ Low-temperature single-crystal absorption spectra, luminescence spectra, and EPR spectra have led to a better understanding of the electronic structure in these classes of compounds.

No single-crystal study of the complex [Cr(NH₃)₅OH]²⁺ has been performed so far, and the powder luminescence and diffuse reflectance spectra of [Cr(NH₃)₅OH](ClO₄)₂ have been measured at 77 K under rather poor resolution.⁶ On the other hand, as far as its electronic properties are concerned, the hydroxopentaamminechromium(III) complex is expected to take quite a unique position within the series [Cr(NH₃)₅X]ⁿ⁺. This expectation is based on the great capacity of the hydroxo ligand for both σ and π bonding,^{7,8} which should lead to a large tetragonal crystal field component. A large splitting of the second spin-allowed band is observed in a solution and diffuse reflectance spectrum of this complex. Our main interest in the hydroxopentaamminechromium(III) complex arose from our studies of hydroxo- and oxo-bridged polynuclear chromium(III) complexes.^{9,10} In order to un-

derstand the spectroscopic properties of dinuclear [(NH₃)₅CrOHCr(NH₃)₅]⁵⁺ (acid rhodo chromium) and [(NH₃)₅CrOOCr(NH₃)₅]⁴⁺ (basic rhodo chromium) it is necessary to get a feeling about the electronic properties of the constituent single ions. Since exchange interactions cannot simply be switched off, some suitable mononuclear complex has to be used as a reference. It was thought that, as far as the strength of both σ and π bonding within the Cr-O bond was concerned, [Cr(NH₃)₅OH]²⁺ would lie in between the two dinuclear complexes [(NH₃)₅CrOHCr(NH₃)₅]⁵⁺ and [(NH₃)₅CrOOCr(NH₃)₅]⁴⁺. In [(NH₃)₅CrOHCr(NH₃)₅]⁵⁺ ²E_g is the lowest lying excited state, from which luminescence is observed.⁹ On the other hand it was not possible to detect any luminescence from [(NH₃)₅CrOOCr(NH₃)₅]⁴⁺ even at very low temperatures.¹⁰ This behavior is quite unusual for a chromium complex, and one possible explanation is that due to the very large tetragonal crystal field component the ²E component (C_{4v} notation) of the ²T_{1g} state has been pushed way below ²E_g, thus leading to a situation where luminescence is expected to be rather broad and lie in the infrared region where detection becomes a problem.

2. Experimental Section

[Cr(NH₃)₅OH](ClO₄)₂ was prepared by the method of Linhard.¹¹

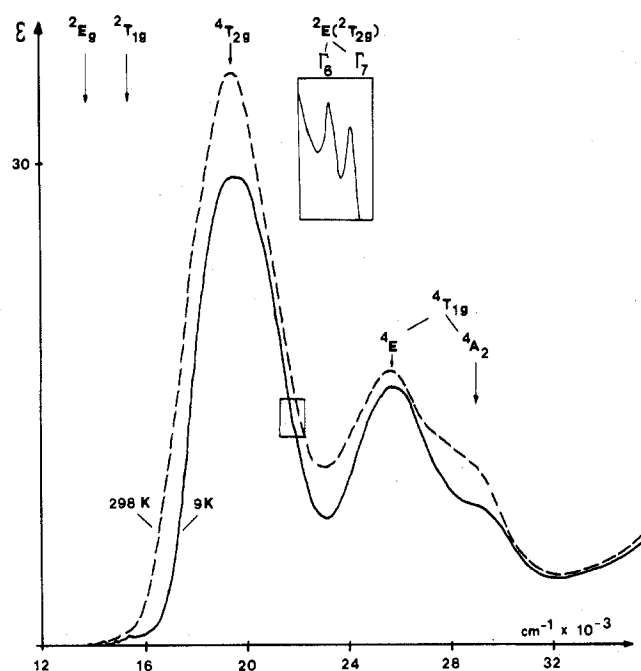


Figure 1. Single-crystal absorption spectra of $[\text{Cr}(\text{NH}_3)_5\text{OH}](\text{ClO}_4)_2$ at 9 and 298 K. The incident beam is parallel to the threefold axis of the crystal (axial spectrum).

Single crystals of a suitable size for x-ray diffraction and optical spectroscopic measurements were grown by slow mixing of saturated solutions of $[\text{Cr}(\text{NH}_3)_5\text{OH}](\text{ClO}_4)_2$ and NaClO_4 .

X-ray diffraction measurements were made with a Burger precession camera using Mo radiation. Single-crystal absorption spectra were measured on a Cary 17 spectrophotometer equipped with a red-sensitive GaAs photocathode.¹² For the measurement of luminescence spectra the exciting light from a 150-W sealed beam Xe lamp was filtered with a Spex minimate monochromator, while the luminescence was dispersed by means of a 0.75-m Spex monochromator. A red-sensitive photomultiplier tube (RCA C31034, cooled to -30°C) was used for detection. In the luminescence excitation experiments light from the Xe lamp was dispersed with a 0.82-m Spex double monochromator, and the luminescence was measured directly, with only a suitable cutoff filter between the sample and the detector. For all experiments between 6 K and room temperature a helium flow tube technique was used for cooling purposes.

Energy level and magnetic dipole transition probability calculations were carried out using a computer program which sets up the crystal field, spin-orbit coupling, and magnetic moment operator matrices according to the equations of ref 13. Reduced matrix elements tabulated by Nielson and Koster¹⁴ were used.

3. Results and Discussions

Symmetry. Crystals of $[\text{Cr}(\text{NH}_3)_5\text{OH}](\text{ClO}_4)_2$ belong to the trigonal crystal system. The trigonal axis is perpendicular to the well-developed hexagonal plates. Single-crystal spectroscopic experiments in transmission could only be performed with the light parallel to the c axis.

Since the crystal structure has not been determined, the exact symmetry and orientation of the $[\text{Cr}(\text{NH}_3)_5\text{OH}]^{2+}$ complexes with respect to the threefold axis are not known. But C_{4v} symmetry is certainly a good approximation for the chromophore; and in the following the symmetry arguments are based on point group C_{4v} . The symmetry symbols with and without a subscript g refer to the point groups O_h and C_{4v} , respectively.

Spin-Allowed Transitions. Figure 1 shows the 9-K absorption spectrum of a single crystal of $[\text{Cr}(\text{NH}_3)_5\text{OH}](\text{ClO}_4)_2$. The two tetragonal components of the second spin-allowed band are nicely resolved. The splitting of 3100 cm^{-1} is larger than in any other known $[\text{Cr}(\text{NH}_3)_5\text{X}]^{n+}$ complex.^{7,15}

The splitting of the first spin-allowed band is too small to be resolved even at very low temperatures. This situation of a small splitting in the first band and a large splitting in the second band has been discussed in terms of the angular overlap model.⁷ The hydroxo ligand has a greater destabilizing effect on both σ - and π -antibonding orbitals (z^2 , xz , and yz where z is along Cr-O) than the ammonia ligand. This leads to a big positive value for the crystal field parameter Ds ,¹⁶ and since the splitting of the second spin-allowed transition ${}^4A_{2g} \rightarrow {}^4T_{1g}$ is predominantly determined by the value of Ds , the two components can be assigned as indicated in Figure 1.

There is a remarkable increase in intensity of the first spin-allowed band in the series $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ ($\epsilon_{\text{max}} \approx 10$),¹⁷ $[\text{Cr}(\text{NH}_3)_5\text{OH}]^{2+}$ ($\epsilon_{\text{max}} \approx 30$), and $[(\text{NH}_3)_5\text{Cr}(\text{O})\text{Cr}(\text{NH}_3)_5]^{4+}$ ($\epsilon_{\text{max}} \approx 60$),¹⁰ i.e., with increasing anisotropy of the CrN_5O system. The second band, on the other hand, has about the same intensity in all three complexes ($\epsilon_{\text{max}} \approx 10$ – 15). This increase can be due either to an increasing electric dipole transition moment or to an increase in the vibronic intensity of the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition.

Spin-Forbidden Transitions. Figure 2 shows the 9-K luminescence spectrum of $[\text{Cr}(\text{NH}_3)_5\text{OH}](\text{ClO}_4)_2$, including a vibrational analysis. The luminescence excitation spectrum in the region of the ${}^4A_{2g} \rightarrow {}^2E_g, {}^2T_{1g}$ transitions is given in Figure 3.

The two sharp bands at 13763 and 13675 cm^{-1} are the common origins of the luminescence and absorption spectra; and they can therefore unambiguously be assigned as electronic origins. Both bands are of comparable intensity in the absorption spectrum, and Figure 3 shows that they are relatively weak in comparison with a number of bands to higher energy. In the emission spectrum the 13763-cm^{-1} band is a hot band as expected. The temperature dependence of the two origins in the emission spectrum is consistent with a Boltzmann distribution between two levels of the same multiplicity separated by 88 cm^{-1} .

The luminescence spectrum as well as the excitation spectrum exhibits a rich fine structure. The most striking feature of the luminescence spectrum is a progression in the totally symmetric $\nu(\text{Cr-O})$ stretching mode of 570 cm^{-1} . It is built on the electronic origin at 13675 cm^{-1} as well as a great number of vibronic origins between 13609 and 13227 cm^{-1} . The occurrence of such a progression is unusual for the luminescence spectrum of a chromium(III) complex. It is certainly not expected for a pure spin-flip transition like ${}^2E_g \rightarrow {}^4A_{2g}$. We can therefore take it as a strong indication that we are observing luminescence from the 2E component of ${}^2T_{1g}$, the potential surface of which is slightly displaced with respect to the electronic ground state. The two states 13675 and 13763 cm^{-1} above the ground state are then the two spin-orbit components Γ_7 and Γ_6 , respectively, of 2E .

This assignment is strongly supported by the fact that in comparison with a number of bands to higher energy the 13763 - and 13675-cm^{-1} bands are relatively weak in the luminescence excitation spectrum. Since the transitions to the 2B_1 and 2A_1 components of 2E_g are expected to be more intense than the transitions to ${}^2T_{1g}$ (cf. Table I), the strong spectral features in the excitation spectrum have to be associated with ${}^4B_1 \rightarrow {}^2B_1, {}^2A_1$ transitions. We tentatively assign the two prominent bands at 14261 and 14322 cm^{-1} as electronic origins of the transitions ${}^4B_1 \rightarrow {}^2B_1$ and ${}^4B_1 \rightarrow {}^2A_1$, respectively. The 14322-cm^{-1} band is overlapping with a vibronic origin. Even though some regularities in the vibronic structure of these two transitions are evident, the present data are not sufficient for a complete analysis. In particular it is not possible to locate the 2A_2 component of ${}^2T_{1g}$. According to the quartet character of the ${}^4B_1 \rightarrow {}^2A_2$ transition (Table I) it is not expected to be as intense as the ${}^4B_1 \rightarrow {}^2B_1, {}^2A_1$

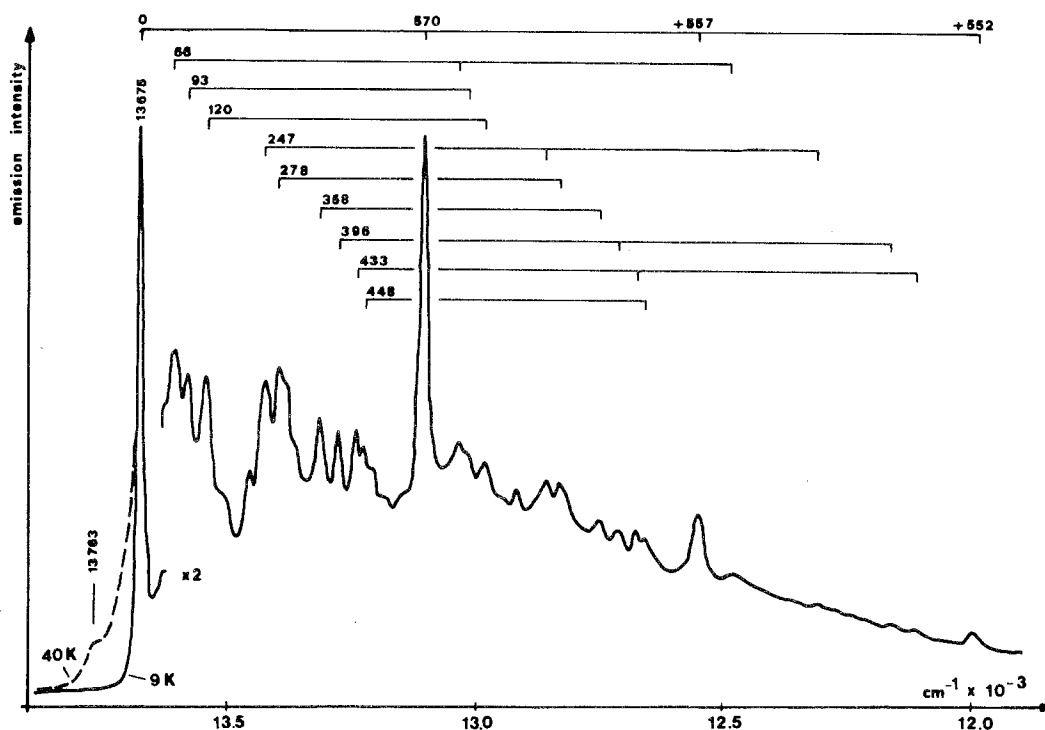


Figure 2. The 9-K luminescence spectrum (unpolarized) of $[\text{Cr}(\text{NH}_3)_5\text{OH}](\text{ClO}_4)_2$; excitation wavelength 510 nm.

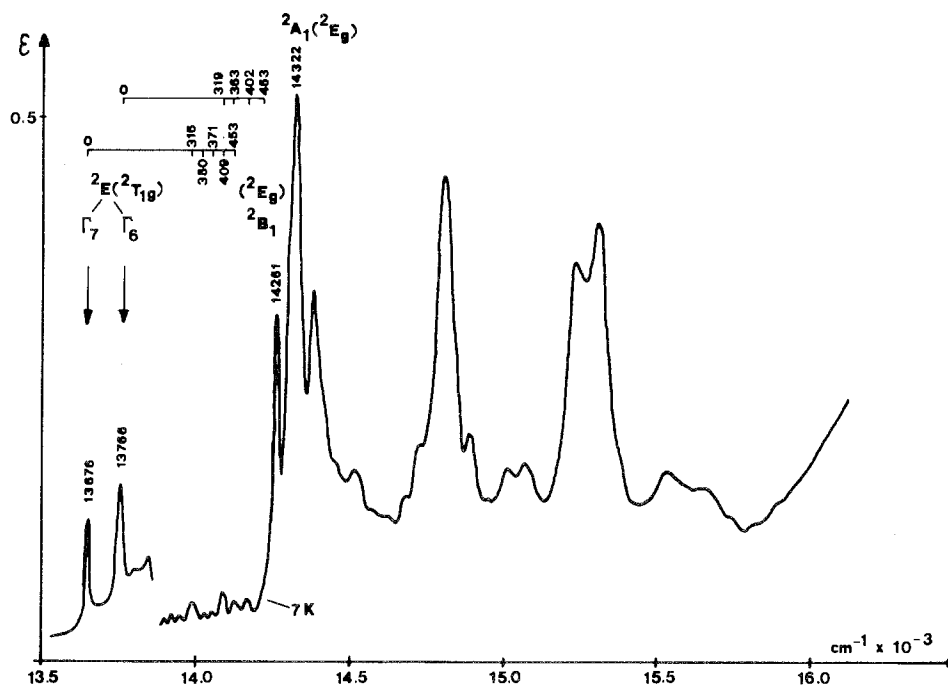


Figure 3. The 7-K luminescence excitation spectrum (unpolarized) of $[\text{Cr}(\text{NH}_3)_5\text{OH}](\text{ClO}_4)_2$. Between 13 676 and 13 850 cm^{-1} , a region in which the excitation spectrum could not be measured, the single-crystal absorption spectrum is given.

transitions. And since these latter transitions and their vibronics appear to dominate the region above 14 261 cm^{-1} , the ${}^4\text{B}_1 \rightarrow {}^2\text{A}_2$ transition is likely to be swamped.

The two sharp bands at 21 871 and 21 905 cm^{-1} , respectively, observed on the high-energy slope of the first spin-allowed band in the low-temperature absorption spectrum, correspond to the spin-forbidden transition ${}^4\text{A}_{2g} \rightarrow {}^2\text{T}_{2g}$. Their small separation of 34 cm^{-1} and the fact that their vibronics are very weak enable us to make a definite assignment of these bands. They correspond to transitions to the two spin-orbit components Γ_6 and Γ_7 , respectively, of ${}^2\text{E}({}^2\text{T}_{2g})$.

Crystal Field Calculations. In their study of a series of $[\text{Cr}(\text{NH}_3)_5\text{X}]^{n+}$ complexes and their spectroscopic properties

Flint et al.² came to the conclusion that "conventional ligand field theory is not able to account for the observed splitting of the ${}^2\text{E}_g(t_2^3)$ of acido- and aquopentaamminechromium(III) compounds". 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 the above statement is quite disturbing. We therefore performed an energy level calculation in order to check whether the nine experimentally located electronic excited states of $[\text{Cr}(\text{NH}_3)_5\text{OH}]^{2+}$ could be reasonably reproduced within the framework of this model. The calculated and experimental numbers are compared in Table I. The agreement is as good as can be expected from crystal field theory. There is certainly

Table I. Calculated and Experimental Energies of Electronically Excited States of $[\text{Cr}(\text{NH}_3)_5\text{OH}]^{2+}$ ^a

Electronic state notation		Energies, cm ⁻¹		Quartet character
<i>O_h</i>	<i>C_{4v}</i>	Exptl	Calcd	
² T _{1g}	² E (Γ ₇)	13 676	14 064	0.0005
² T _{1g}	² E (Γ ₆)	13 766	14 143	0.0004
² E _g	² B ₁	14 261	14 220	0.0006
² E _g	² A ₁	14 322	14 318	0.0013
² T _{1g}	² A ₂		15 036	0.0004
⁴ T _{2g}	⁴ E	19 600	18 800	0.9992
⁴ T _{2g}	⁴ B ₂		20 600	0.9985
² T _{2g}	² B ₂		21 807	0.0014
² T _{2g}	² E (Γ ₆)	21 871	22 383	0.0025
² T _{2g}	² E (Γ ₇)	21 905	22 424	0.0014
⁴ T _{1g}	⁴ E	25 900	25 735	0.9994
⁴ T _{1g}	⁴ A ₂	29 000	28 862	0.9981

^a The following set of parameters was used for the calculations: $B = 765$, $C/B = 3.6$, $\alpha = 0.08B$ (Tree's correction), $Dq = 2060$, $Ds = 600$, $Dt = -200$, $\zeta = 125$. Dq was determined from the position of ⁴T_{2g}, Ds and Dt were determined from the observed tetragonal splittings of ⁴T_{1g} and ⁴T_{2g}, respectively, and the value for ζ was determined from the observed spin-orbit splittings of the ²E(²T_{1g}) and ²E(²T_{2g}) components. It is well-known that the experimental energy levels of the free Cr³⁺ ion are badly reproduced by theory. Particularly the ²F term is calculated 5000 cm⁻¹ too high.¹⁹ This is the main reason for the fact that in the present calculation both ²T_{1g} and ²T_{2g} are calculated too high. If the diagonal energy of ²F is artificially lowered, the agreement becomes very good.

no need to introduce any further corrections. The spin-orbit coupling parameter ζ can be accurately determined from the measured spin-orbit splittings of ²E(²T_{1g}) and ²E(²T_{2g}). That a large positive value for Ds is physically meaningful for the chromophore $[\text{Cr}(\text{NH}_3)_5\text{OH}]^{2+}$ has been shown by using arguments of the so-called angular overlap model.⁷ Because the hydroxo ligand has a greater destabilizing effect on both e_g and t_{2g} metal orbitals than the ammonia ligand, Ds has to be large and positive, thus directly determining the order of the tetragonal splitting of the second spin-allowed band. A series of calculations with different Ds and Dt values revealed that it is mainly the negative sign of the ratio Ds/Dt which is responsible for the reversed order of the lowest excited doublet states. A calculation of magnetic dipole intensities revealed that no appreciable contribution to the intensity of any transition due to a magnetic dipole mechanism is to be expected. For the transitions to ⁴T_{2g} and the doublets the calculated MD intensities were about one order of magnitude smaller than the observed intensities, while the ⁴T_{1g} transition is purely electric dipole.

Since it seemed to us to be very unlikely that within the series $[\text{Cr}(\text{NH}_3)_5\text{X}]^{n+}$ the complex $[\text{Cr}(\text{NH}_3)_5\text{OH}]^{2+}$ was the only one with "normal" spectroscopic properties, we measured the emission and absorption spectra of single crystals of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$. We identified three electronic origins at 15042 cm⁻¹ (cold), 15062 cm⁻¹ (hot), and 15256 cm⁻¹ (hot), respectively. The tetragonal splitting of the ²E_g state is 20 ± 10 cm⁻¹. From an 80-K spectrum Flint et al.² reported a splitting of 205 cm⁻¹. Since both emission and absorption bands are rather broad in this compound, it was obviously not possible to detect the relatively small splitting in an 80-K spectrum. The electronic state lying approximately 205 cm⁻¹ above the ²E_g doublet must belong to ²T_{1g}. With an experimental splitting of ²E_g of approximately 20 cm⁻¹ all of the experimentally determined electronic states of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ can be accounted for by ligand field theory. And this may be an indication that the large splittings of ²E_g found for the other members of the series $[\text{Cr}(\text{NH}_3)_5\text{X}]^{n+}$ are artifacts due to poor spectral resolution.^{2,18} The splitting which was interpreted as the tetragonal splitting of the ²E_g state may in fact be the splitting between an unresolved ²E_g doublet and the lowest component of ²T_{1g}.

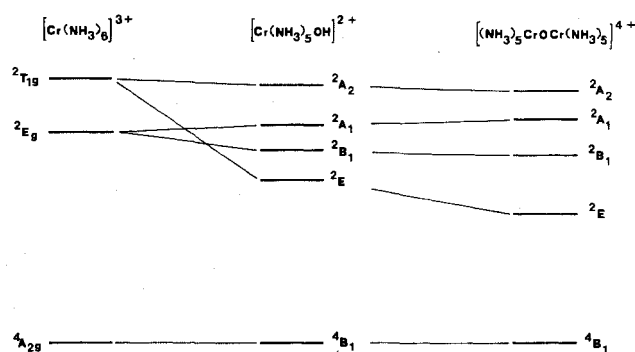


Figure 4. Schematic representation of the reversal of the order of the first excited doublet states upon substitution of one ammonia in $[\text{Cr}(\text{NH}_3)_6]^{3+}$ by a ligand with a large capacity to destabilize z^2 , xz , and yz orbitals, respectively. The ²E component of ²T_{1g} is pushed below the two ²E_g components, thus becoming the lowest lying excited state. Luminescence from ²E(²T_{1g}) is observed in the case of $[\text{Cr}(\text{NH}_3)_5\text{OH}]^{2+}$. No luminescence has been observed so far in $[(\text{NH}_3)_5\text{CrOCr}(\text{NH}_3)_5]^{4+}$.

4. Conclusions

There are some conclusions we can draw from the present results with respect to the electronic properties of the two dinuclear complexes $[(\text{NH}_3)_5\text{CrOHCr}(\text{NH}_3)_5]^{5+}$ and $[(\text{NH}_3)_5\text{CrOCr}(\text{NH}_3)_5]^{4+}$, respectively. The intuitive assumption that as far as destabilization of z^2 , xz , and yz orbitals in the unit CrN_5O (z along Cr–O) is concerned $[\text{Cr}(\text{NH}_3)_5\text{OH}]^{2+}$ lies somewhere between the two dinuclear complexes is fully confirmed (Figure 4). It can therefore be expected that in the basic rhodo chromium complex there is a very low-lying doublet state ²E(²T_{1g}), which has not been found so far because of detection problems in the infrared. There seems to be no doubt that in the acid rhodo chromium complex the lowest lying excited state is ²E_g, but the present study indicates that in the dinuclear complex ²E(²T_{1g}) may lie very close to ²E_g and that, therefore, some mixing of the two states under the influence of exchange interactions could occur. This may be one of the reasons that so far a full analysis of the ⁴A_{2g} → ²E_g, ²T_{1g} transitions in $[(\text{NH}_3)_5\text{CrOHCr}(\text{NH}_3)_5]^{5+}$ has not been possible.

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Registry No. $[\text{Cr}(\text{NH}_3)_5\text{OH}](\text{ClO}_4)_2$, 34076-60-3; $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$, 32700-25-7.

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