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Cooperative Absorptions in the Electronic Spectrum of K_2TcCl_6

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In a recent paper, cooperative absorptions, involving the simultaneous excitation of two coupled $ReCl_6^{2-}$ ions and occurring at energies which are the sum of lower energy $t_{2g}^3 \rightarrow t_{2g}^3$ transitions, have been detected and assigned in the electronic spectra of the pure crystals K_2ReCl_6 and Cs_2ReCl_6.[2] It is interesting to extend the study of these cooperative absorptions to other pure crystals of the MX_6^{2-} ions (where M = second-, or third-row transition-metal ion and X = halide ion). K_2TcCl_6 is an ideal compound for this extension. It is isostructural with K_2ReCl_6 and Cs_2ReCl_6, and the $4d^3$ ion Tc^{4+} has the same t_{2g}^3 strong-field configuration as $5d^3$ Re^{4+}. The ordering of the crystal field energy levels of $TcCl_6^{2-}$ is accordingly similar to that of $ReCl_6^{2-}$. From the spectral data for $TcCl_6^{2-}$ in transparent host crystals,[3] the cooperative absorptions for K_2TcCl_6 are expected to fall in a spectral region in proximity to the $\Gamma_8(^4A_{2g}) \rightarrow \Gamma_7, \Gamma_8(^2T_{2g})$ transitions without overlapping them; the interconfigurational ($t_{2g} \rightarrow e_g$) and charge-transfer transitions lie sufficiently distant to allow their detection.

In this note, we report the observation and assignment of the cooperative absorptions for K_2TcCl_6 and briefly discuss the differences in the spectral behavior with respect to the pure hexachlororhenates.

Experimental Section

K_2TcCl_6 was prepared following standard methods.[4] Relatively large crystals ($1.5 \times 1.5 \times 1.0$ mm^3) were grown by slow evaporation and used for the optical measurements. Absorption spectra in the near infrared and the visible were measured at 9, 80, and 293 K using a Varian 2390 recording spectrophotometer equipped with a CTI-Cryogenics Model 21 refrigerator. The spectral bandwidth was 15 cm^{-1} in the region of interest (17 500–19 500 cm^{-1}) but did not limit the resolution achieved. Standard radiochemical practice was used throughout.

Structural and Magnetic Data. K_2TcCl_6 is cubic at room temperature, space group $Fm3m$ (O_h^5), with $Z = 4$ and $a = 9.82$ Å; the site symmetry is exactly O_h for the Tc^{4+} ions.[4] Structural phase transitions occur at 132[5] and 34 K[6] and the Nêel temperature, $T_N = 7$ K, has been reported.[6] K_2TcCl_6, K_2ReCl_6, and Cs_2ReCl_6 are isostructural at room temperature. The lattice parameter a is 9.840 Å for K_2ReCl_6[7] and 10.225 Å for Cs_2ReCl_6.[8]

Results and Discussion

The 9 K absorption spectrum of K_2TcCl_6 is composed of two strong regions of absorption centered at 9500 and 14 300 cm^{-1} and a third medium-intensity set of bands centered at 18 500 cm^{-1}, followed by a rapidly rising absorption edge starting at about 22 500 cm^{-1}. The two former groups of bands are readily assigned to the intraconfigurational $\Gamma_8(^4A_{2g}) \rightarrow \Gamma_8(^2E_g), \Gamma_8(^2T_{1g}), \Gamma_6(^2T_{1g})$ and $\Gamma_8(^4A_{2g}) \rightarrow \Gamma_7(^2T_{2g}), \Gamma_8(^2T_{2g})$ transitions respectively.[9] They feature weak no-phonon magnetic dipole origins and strong electric dipole ν_6, ν_4, and ν_3 vibronic origins with very weak progressions in the ν_1 mode. The bands are rather broad, as already found in the absorption spectra of the pure hexachlororhenates.[2]

Table I. Cooperative Absorptions in the 9 K Spectrum of K_2TcCl_6[a]

	wavenumber/cm^{-1}		
band	obsd	calcd	assign
1	18 000 (sh)	17 668	$\Gamma_8(^2E_g) + \Gamma_8(^2E_g)$
2	18 220 (m)	18 285	$\Gamma_8(^2E_g) + \Gamma_8(^2T_{1g})$
3	18 470 (m)	18 445	$\Gamma_8(^2E_g) + \Gamma_6(^2T_{1g})$
4	18 790 (w)	18 902	$\Gamma_8(^2T_{1g}) + \Gamma_8(^2T_{1g})$
5	19 160 (vw)	19 062	$\Gamma_8(^2T_{1g}) + \Gamma_6(^2T_{1g})$
6	19 510 (vw)	19 222	$\Gamma_6(^2T_{1g}) + \Gamma_6(^2T_{1g})$

[a] The calculated wavenumbers were obtained by using the positions of the $\Gamma_8(^2E_g)$, $\Gamma_8(^2T_{1g})$, and $\Gamma_6(^2T_{1g})$ states, derived from the 9 K near-infrared absorption spectrum.[9] The experimental precision of the observed wavenumbers is ±15 cm^{-1}.

From a previous work,[9] the energies of the excited states are 8834 cm^{-1} [$\Gamma_8(^2E_g)$], 9451 cm^{-1} [$\Gamma_8(^2T_{1g})$], 9611 cm^{-1} [$\Gamma_6(^2T_{1g})$], $\approx$14 000 cm^{-1} [$\Gamma_7(^2T_{2g})$], and $\approx$14 100 cm^{-1} [$\Gamma_8(^2T_{2g})$]. The ordering of the excited states is based upon the experimental data and the calculations of Flint and Lang for $TcCl_6^{2-}$ in transparent host crystals.[3] Due to the poor spectral resolution, the assignments of the vibronic origins of the transitions to the $^2T_{2g}$ state must be regarded as tentative, and therefore the energies of $\Gamma_7(^2T_{2g})$ and $\Gamma_8(^2T_{2g})$ are only approximate.[9]

When the temperature is raised to 80 and 293 K, the only change in the $t_{2g}^3 \rightarrow t_{2g}^3$ transitions is the appearance of hot vibronic bands. Similarly to what found for K_2ReCl_6,[2] no effect whatsoever is induced in the intraconfigurational spectrum of K_2TcCl_6 by the structural phase transitions. No magnon sideband is observed at 9 K in agreement with the Nêel temperature being 7 K.

At 9 K the medium-intensity group of bands around 18 500 cm^{-1} (Figure 1) is composed of broad and partly overlapped features. In the 293 K spectrum, these bands are superimposed on a rising background and are affected by some thermal broadening but do not show any other difference or shift with respect to the low-temperature spectra. No apparent change of the total intensity is observed in the 9–293 K range.

A corresponding group of bands has been detected in the reflectance spectrum of K_2TcCl_6 at room and liquid-air temperatures by Elder et al.,[10] who assigned them as transitions to low-symmetry components of $^2T_{2g}$ for distorted $TcCl_6^{2-}$ ions. In this case the splitting of $^2T_{2g}(t_{2g}^3)$ would be abnormal ($\approx$5500 cm^{-1}), and there is no reason for such bands to be present in the spectrum measured at 293 K, where the $TcCl_6^{2-}$ ions are exactly octahedral. We therefore find no evidence for this assignment. These bands are weaker than the intraconfigurational transitions and clearly cannot be attributed to interconfigurational ($t_{2g} \rightarrow e_g$) d–d transitions. Moreover, they cannot be assigned to parity-forbidden charge-transfer bands, because these are much more intense and their first maximum lies at much higher wavenumbers (25 970 cm^{-1}) in the aqueous solution spectrum.[11]

On the basis of the analogy of the similar set of bands between 16 000 and 19 000 cm^{-1} in the absorption spectrum of K_2ReCl_6

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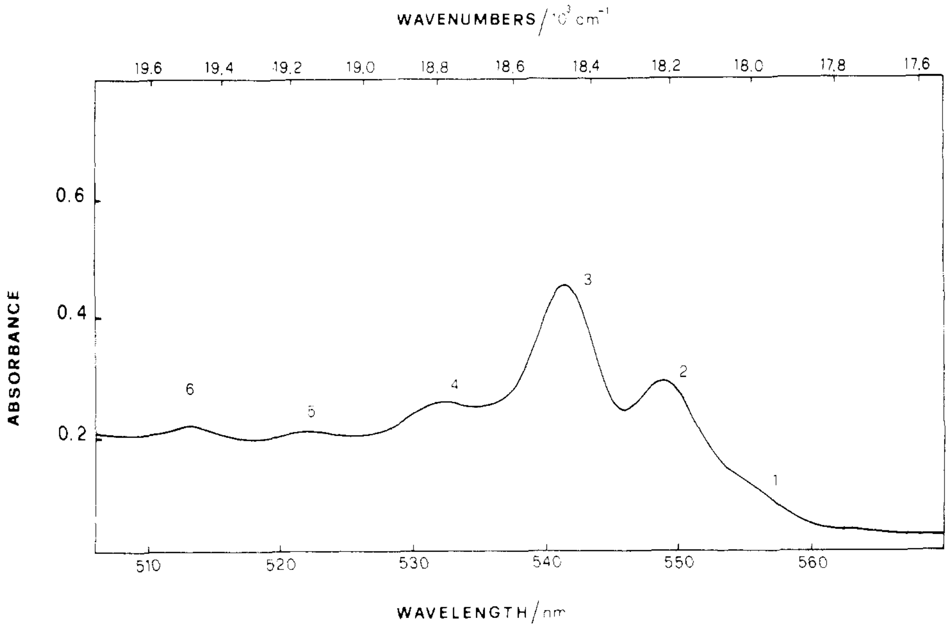

Figure 1. Cooperative absorptions for a K_2TcCl_6 crystal (1.0 mm thick) at 9 K.

and Cs_2ReCl_6, this group of bands centered at 18 500 cm^{-1} is readily assigned as cooperative absorptions.[12] Their energies can be expressed as the sums of the energies of the electronic $\Gamma_8(^2E_g)$, $\Gamma_8(^2T_{1g})$, and $\Gamma_6(^2T_{1g})$ states (Table I), but the difference between the experimental and the calculated positions is bigger than that for the pure hexachlororhenate compounds. Neither progressions in the ν_1 mode nor vibronic origins are observed. This behavior differs from that observed for K_2ReCl_6 and Cs_2ReCl_6, for which the first members of the progressions in the ν_1 mode on the cooperative absorptions are easily measurable.

The total oscillator strength of the band system centered at 18 500 cm^{-1} was calculated on the basis of single $TcCl_6^{2-}$ ions, although the transitions involve a two-center electronic excitation, and is $\approx 3 \times 10^{-6}$. The total relative intensities of the cooperative absorptions, referred to the neighboring transitions (origins plus vibronic sidebands) to the $\Gamma_7(^2T_{2g})$ and $\Gamma_8(^2T_{2g})$ states and evaluated by graphical methods (±10% precision), are identical (≈17%) for K_2ReCl_6 (paramagnetic phase) and K_2TcCl_6. The large line width of the cooperative absorptions, already observed for the pure hexachlororhenates, is explained as the result of the combination of all the broadening mechanisms of the single ion transitions.

All of the six possible simultaneous excitations are observed for K_2TcCl_6, and no cooperative absorption is obscured by overlapping single ion transitions. Conversely, the transition to the $\Gamma_8(^2E_g) + \Gamma_8(^2E_g)$ state cannot be measured for K_2ReCl_6 and Cs_2ReCl_6, as it overlaps with the $\Gamma_8(^4A_{2g}) \rightarrow \Gamma_8(^2T_{2g})$ transition. The intensity of the individual cooperative absorptions goes through a maximum corresponding to the transition to $\Gamma_8(^2E_g) + \Gamma_6(^2T_{1g})$ at 18 470 cm^{-1} (Figure 1). This behavior differs from that observed for K_2ReCl_6 and Cs_2ReCl_6, for which the intensity of the cooperative absorptions decreases rapidly as the transition energy increases, so that the transition to $\Gamma_6(^2T_{1g}) + \Gamma_6(^2T_{1g})$ could not be detected.[2] These differences in the intensity of the individual cooperative absorptions can be explained by the fact that the higher energy cooperative absorptions lie significantly closer to the lowest allowed LMCT transitions, from which intensity can be borrowed, in K_2TcCl_6 than in K_2ReCl_6 and Cs_2ReCl_6.[2,9,11,13]

The difference between the experimental energy of a cooperative absorption and the sum of the single ion transitions is defined as the exciton–exciton interaction energy.[14,15] These interaction energies range from 10 to 30 cm^{-1} for K_2ReCl_6, whereas their values are much more spread (from −65 to 288 cm^{-1}) for K_2TcCl_6, even allowing for the higher uncertainties of the experimental data for the latter compound. Due to the fact that the lattices of K_2ReCl_6 and K_2TcCl_6 are closely similar, as the two crystals are isostructural at room temperature with almost identical lattice parameters (±0.2%), this behavior cannot be ascribed to simple geometrical factors, but must involve differences in the coupling. The reasons for this behavior remain to be elucidated.

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Photochemical Grafting of Triosmium Dodecacarbonyl to Inorganic Metal Oxides

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Introduction

Metal carbonyl cluster compounds have attracted much attention as precursors for the preparation of highly dispersed supported metal catalysts.[1-4] A variety of transition-metal carbonyl clusters have been supported on metal oxides. Traditionally, metal clusters have been attached to supports by means of a thermally induced reaction between the metal carbonyl and surface hydroxyl groups.[5-16] However, thermal excitation often

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