The Excited State Absorption Spectrum of

Tris(acetylacetonato)chromium(III)

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The excited state absorption spectrum of $Cr(acac)_3$ dissolved in a methanol-ethanol glass at 100°K has been obtained in the visible region. One absorption band and shoulder is observed and assigned as originating from the ^2E_g state going to doublets of higher energy. Several complexes for which no excited state spectrum could be obtained are discussed.

Recently[1] we reported a study of the excited state absorption spectrum of $K_3Cr(NCS)_6$ in a rigid medium at 100°K. By this means we were able to observe electronic transitions between chromium(III) doublet states and thus observe several doublets. While this technique has been employed with some rare earths[2] and in ruby[3-5] ours was the first report of such a study involving a discrete complex ion. We now wish to report on the excited state absorption spectrum of another complex, tris(2,4-pentanedionato)chromium-(III), $[Cr(acac)_3]$, and the interesting problem of several complexes which failed to exhibit such a spectrum.

EXPERIMENTAL

Reagents. Reagent grade chemicals were used as received; complexes were prepared by standard techniques. Tris(ethylenediamine)chromium(III) acetate was prepared from the chloride by metathesis with silver acetate in methanol, followed by concentration of the cold solution. This salt was very hygroscopic and had to be kept dry to avoid hydrolysis.

Rigid media. All complexes were studied in methanol-ethanol (1:4 by volume) glass at 100°K. At this temperature there was no problem of cracking and the compounds were sufficiently soluble to give at least 10^{-4} M solutions. On cooling below this temperature the glass usually cracked preventing light transmission through the sample.

In order to avoid solvolysis of the compounds fresh solutions were used for each spectrum and cooling was started within ten minutes of mixing.

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Cells. It was found convenient to construct cells by cementing silica windows to 9 cm lengths of 25 mm diameter pyrex tubing using silicone rubber cement. Standard 10 cm spectrophotometer cells were too fragile to withstand the occasional cracking of the alcohol glass.

Apparatus. The apparatus used was the same as employed to obtain the data in our earlier paper. The sample cell is mounted at one focus of an elliptical chamber and a 200 watt sec flash lamp at the other. Cooling is by means of cold nitrogen gas. The sample is excited into the ^2E_g state with the flash lamp and 0.5 msec later a spectroflash is passed through the sample. After the transmitted light passes through a Beckman DU monochromator it is detected with an RCA 7102 photomultiplier and the signal sent to a Hewlett Packard storage oscilloscope. The spectroflash is fired at approximately six second intervals. The exciting flash is fired only with alternate spectroflashes. In this fashion a difference in absorbance between the excited and unexcited sample is observed as a difference in amount of light transmitted on the two separate spectroflashes. It is then possible to calculate the absorbance for the excited state from the relationship

$$\text{absorbance} = \log \ (I_0/I)$$

where I_0 is the observed unexcited spectroflash intensity and I is the observed spectroflash intensity following the exciting flash.

Using 10^{-3} M solutions and a slit width of 0.05 mm, sufficient transmitted light intensity could be obtained.

Samples were scanned from 9000 cm^{-1} to 26 000 cm^{-1}.

For the non-excited state absorption spectrum a styrofoam container was constructed to fit in the cell compartment of a Cary 14 spectrophotometer. This had double lucite windows and was maintained at 100°K by means of cold nitrogen gas. In this fashion it was possible to obtain the Cr(acac)$_3$ absorption spectrum under conditions identical to those employed in the flash studies.

RESULTS

The excited state absorption spectrum of Cr(acac)$_3$ in methanol-ethanol glass at 100°K shows one asymmetric band and a shoulder (Fig. 1). No spectral features were observed between 9000 and 17 000 cm^{-1}; data could not be obtained much above 22 000 cm^{-1}. In this glass at 100°K the unexcited absorption spectrum shows a peak at 18 700 cm^{-1} and a very strong absorption (possibly of charge transfer origin) starting near 22 000 cm^{-1}. It is the onset of this latter band which limits the range of our spectrum; insufficient light is transmitted
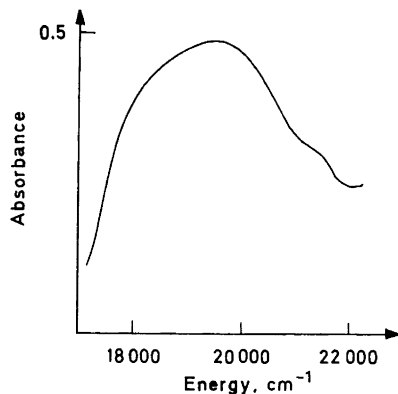

Fig. 1. The excited state absorption spectrum of Cr(acac)$_3$ in methanol-ethanol glass at 100°K.

for us to make any observations above this energy region. In our earlier report on $K_3Cr(NCS)_6$ the spectral range studied was somewhat greater since the first charge transfer band begins at considerably higher energy and does not interfere.

To compute a molar extinction coefficient for the principle band in the excited state spectrum it is necessary to assume an excited state concentration at the time of observing the spectroflash. Assuming half the molecules to be in the excited state we calculate a value of 130 for the molar extinction coefficient. This is in the range one commonly observes for spin-allowed transitions in chromium(III) complexes and is, therefore, very reasonable.

Several other compounds were investigated and found to give no excited state spectrum under these experimental conditions. The complexes examined were tris(ethylenediamine)chromium(III) acetate [Cr(en)$_3$(OAc)$_3$], tris(diethyl-dithiocarbamato)chromium(III) [Cr(dtc)$_3$], and tris(ethylxanthato)chromium-(III) [Cr(exan)$_3$].

DISCUSSION

There are two factors which support our results being an excited state spectrum rather than a spectrum of transitions from the quartet ground state. The first is the experimental method employed; by alternately measuring the light transmitted through the "pumped" and then the "unpumped" glass it is possible to see the difference. At an excited absorption peak the ratio I_0/I (transmitted light of the unexcited glass: excited) was in excess of 3.0. In a transparent region of the excited state spectrum both I_0 and I are well within 1 % of each other.

The second factor supporting the actuality of this spectrum is its temperature dependence. On warming the glass to 125°K the ratio I_0/I diminishes to less than half its value at 100°K. Since the population of excited states (populated by optical pumping) diminishes with increasing temperature (as evidenced by decreasing phosphorescence on warming [6]) this is excellent confirmation of the origin of the observed spectrum.

We have assumed that the state populated on optical pumping is the ^2E_g. Kushida has shown [3] that the only excited states populated by excitation in ruby are the ^2E_g and the $^2T_{1g}$, so our assumption is warranted. For the location of the ^2E_g we rely on the value reported by Porter and Schläfer.[6] They find the ^2E_g to be 12 700 cm^{-1} above the $^4A_{2g}$ ground state. Since the ^2E_g to $^4A_{2g}$ spacing is nearly independent of the value of Dq [7] the location of the ^2E_g state in any O_h chromium(III) complex should be independent of the matrix in which the compound is situated. Thus, this is the value we use for Cr(acac)$_3$ in the glass employed.

The broad band observed in this work has a peak at 19 600 cm^{-1} and a shoulder at 21 400 cm^{-1}. It is entirely possible that the asymmetric shape of this band indicates several components to lie within it. Of considerable importance is the fact that the region from ca. 17 000 cm^{-1} down to 9000 cm^{-1} is transparent. This indicates that the $^2E_g \rightarrow {}^2A_{1g}$ must lie within the observed broad band. Reference to Liehr's energy level diagram [7] predicts this transition to occur

near 17 000 cm^{-1}. If $^2E_g \rightarrow ^2A_{1g}$ were at that location it should appear as a separate peak; we conclude it must be somewhat higher energy.

The transition responsible for the peak at 19 600 cm^{-1} is probably the $^2E_g \rightarrow ^2T_{2g}$, $^2T_{1g}$. And the shoulder at 21 400 is probably the $^2E_g \rightarrow ^2E_g$. Liehr's energy level diagram predicts these transitions at 19 000 cm^{-1} and 21 000 cm^{-1}, respectively. These assignments must be used cautiously, however, because of the unlocated $^2E_g \rightarrow ^2A_{2g}$ transition.

Both Cr(acac)$_3$ and K$_3$Cr(NCS)$_6$ have very similar Dq values (1870 cm^{-1} and 1887 cm^{-1}). In both excited state spectra the first bands are similar, with a little more resolution apparent in the case of the former compound.

Table 1. Complete assignment of the Cr(acac)$_3$ spectrum.

Energy	Assignment	
12 700 cm^{-1}	$^4A_{2}g \rightarrow ^2E_g$	(a)
18 700	$\rightarrow ^4T_{2g}$	(b)
32 300	$\rightarrow ^2T_{2g}$, $^2T_{1g}$	(c)
34 100	$\rightarrow ^2E_g$	(c)

(a) From Ref. 6.
(b) This work.
(c) This work, excited state study.

In Table 1 we have listed the observed spectral bands for Cr(acac)$_3$ converting all excited state absorptions found in this work to their distance from the $^4A_{2g}$ ground state. Our excited state bands agree remarkably well with those observed in ruby by Kushida. The assignments (discussed above) are also those made by Kushida.

Our inability to obtain excited state spectra for the three chromium(III) complexes Cr(en)$_3^{3+}$, Cr(dtc)$_3$, and Cr(exan)$_3$ was to us surprising. We had developed the hypothesis that if a compound can be caused to populate an excited state, as evidenced by its luminescence, one should be able to observe an excited state absorption spectrum. These complexes are all known to luminesce; Cancellieri, Cervone, Furlani and Sartori [8] have investigated the luminescence behavior of a number of sulfur-containing chromium(III) chelates, including Cr(dtc)$_3$ and Cr(exan)$_3$. Both of these complexes were observed to phosphoresce in rigid media at liquid nitrogen temperature. Porter and Schläfer [6] observed Cr(en)$_3^{3+}$ to phosphoresce under similar conditions. While we were forced to work at a slightly higher temperature we still expect some population of the ^2E_g level on optical pumping. But we were not able to observe an excited state spectrum. A study of the temperature dependence of the luminescent behavior of these compounds might prove helpful in answering this question.

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