Electronic Spectra of cis and trans Disubstituted Octahedral Chromium(III) Complexes

An Advanced Inorganic Chemistry Experiment

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Electronic spectroscopy is a valuable tool used routinely in coordination chemistry research laboratories. For a long time it has been one of the most classical and powerful techniques available to elucidate the fine details of coordination compound stereochemistry. It is well known that the understanding of the stereochemistry of amine complexes of chromium(III), cobalt(III), or ruthenium(II) was almost entirely based on their electronic spectra.

A. B. P. Lever (1) says

> Whilst many physical techniques play their part in the elucidation of the geometric and electronic structure of a metal complex, a study of the electronic spectra can often provide the most detailed information. In the spectrum we see a map of the energy bands within the molecule—the trick is to learn how to read this map.

Since visible and UV spectrophotometers are now very common in teaching laboratories, in our opinion it is very interesting to let the students learn about the large analytical and structural elucidation powers of this technique.

Among the most dramatic examples that show the power of electronic spectra to elucidate stereochemistry are the spectra of cis and trans disubstituted octahedral complexes of Cr(III) or Co(III), which display well-known patterns. Use of these also shows the power of the group theory in quantum mechanics. At present, elementary group theory is part of the inorganic chemistry curricula of most universities.

In our department the students spend part of their laboratory time in synthesizing of *cis*- and *trans*-[CrF$_2$(en)$_2$]Cl, recording their spectra, and interpreting them. By doing this they get first-hand knowledge about cis/trans isomeric chemistry, learn about electronic spectra, and study the intricate differences between cis and trans electronic spectra, which are currently neglected in almost all textbooks. Usually, only trans isomers are explained, apparently because they fit elementary group predictions and the cis isomer spectra do not.

Furthermore, we think the preparation of *trans*- and *cis*-[CrF$_2$(en)$_2$]Cl complexes is also interesting from the synthesis point of view since they are both formed during the reaction and their separation is easily achieved because of their different solubilities. It is not clear, at present, whether both isomers really are formed simultaneously or one of the isomers is being isomerized to the other during the reaction. The easiness of trans–cis isomerization in this kind of complex is well known. On the other hand their electronic spectra are very typical, showing all the details expected for them. The cation *trans*-CrF$_2$(en)$_2$$^+$ is of particular interest because of the large splitting of the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ bands (2).

Experimental

trans-[CrF$_2$(en)$_2$] Cl (3)

A solution of 30 g (0.11 mol) of chromium(III) chloride hexahydrate in 100 mL of water was placed in a 400-mL polyethylene beaker and diluted with 24 g (0.6 mol) of a 48% solution of hydrofluoric acid. The beaker was packed in ice and 100 g (1.58 mol) of aqueous 95% ethylenediamine was added dropwise over 1 h. After the addition of the ethylenediamine was completed, the dark red-purple solution was heated for 2 h on a steam bath to complete the reaction. The solution, which had darkened in color during the heating, was transferred to an evaporating dish, and the excess water was removed by heating for an additional 2 h at 90–95 °C. During this time a crust was formed on the surface of the liquid, and this was broken up frequently during the late stages of the evaporation. At the end of the 2 hours the reaction mixture was cooled to 10 °C in an ice bath and filtered.

Caution: All work should be done in a hood. The manipulation of 95% ethylenediamine or 48% HF solutions is potentially dangerous; the latter can seriously damage the skin.

The crystals that had precipitated were collected, washed with 100 mL of EtOH followed by 100 mL of acetone, and air-dried. The above procedure yielded 15.5 g (56%) of reddish orange crystals.

cis-[CrF$_2$(en)$_2$] Cl (4)

To the mother liquor from the synthesis of trans isomer (150 mL) were added, in order, dry MeOH (300 mL), Me$_2$CO (300 mL), and Et$_2$O (200 mL) with vigorous stirring, whereupon a pink solid slowly began to precipitate. **Caution:** All procedures involving ether are hazardous. Occasionally, the precipitation had to be started by scratching the beaker's walls. In order to assure complete precipitation, the mixture was kept at low temperature (freezer) for 2 h. The solid was filtered and washed with dry Me$_2$CO and Et$_2$O and dried in a dry air stream to avoid the formation of resins or gums.

Electronic Spectra

It is convenient to record the electronic spectra in aqueous solution and to record the spectra of both isomers superimposed at the same molar concentration to show their similarities and differences in band positions and molar absorptivities. Also it would be instructional to record the spectrum of the initial solution since it displays a cis pattern, although cis and trans species are present in the solution.

Theory

Octahedral chromium(III) complexes exhibit three spin-allowed transitions (5) from the ground state $^4A_{2g}$ to the excited states $^4T_{2g}(F)$, $^4T_{1g}(F)$, $^4T_{1g}(P)$. It is well known that only the first two transitions are generally displayed in the spectrum because the highest in energy is in fact overlapped by charge-transfer bands. The cis and trans octahedral disubstituted complexes belong to C_{2v} and D_{4h} symmetry point groups, respectively, but, from the view of the electronic environment around the metal ion, both symmetry groups are in practice the tetragonal one, D_{4h}. This fact is not generally recognized and is neglected in almost all textbooks, but it is well explained in Ballhausen's classic *Introduction to Ligand Field Theory* (6).

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The electrostatic potential, V, at the point (x,y,z) due to two point charges, q_1 and q_2, placed on the x axis at a distance $\pm a$ from the center of the coordinate system, is given by

$$V = \frac{1}{a}(q_1 + q_2)\left[1 + \left(\frac{r}{a}\right)^2 P_2(x) + \left(\frac{r}{a}\right)^4 P_4(x)\right]$$

In this expression $P_2(x)$ and $P_4(x)$ are the first two even Legendre functions and r the radius vector of the point (x,y,z). Notice that only the sum of q_1 and q_2 is of importance for the crystalline field potential. In other words the crystalline potential for an octahedron can be written as the sum of three contributions, each of them containing the sum of the axial electronic charges.

If the sum of the charges on the x, y, and z axes are μ_x, μ_y, and μ_z and if $\mu_x = \mu_y = \mu_z$, the complex is said to have a cubic crystalline field. If $\mu_x = \mu_y \neq \mu_z$, the complex is said to have a tetragonal crystalline field. Or if $\mu_x \neq \mu_y \neq \mu_z$, the complex is said to have a rhombic crystalline field. It is possible to define a tetragonal contribution, V_T, to the octahedral crystalline field, $f(x,y,z)$, as:

$$V_T = \left[\frac{\mu_x + \mu_y}{2} - \mu_z\right]f(x,y,z)$$

and

$$\mu_x = \mu_y \neq \mu_z$$

therefore

$$V_T = (\mu_x - \mu_z)f(x,y,z)$$

consequently, for $trans$-MA_4B_2

$$\mu_x = 2q_A$$
$$\mu_y = 2q_A$$
$$\mu_z = 2q_B$$

and for cis-MA_4B_2

$$\mu_x = q_A + q_B$$
$$\mu_y = q_A + q_B$$
$$\mu_z = 2q_A$$

where, q_A and q_B are the point charges due to the ligands A and B. As can be seen, both isomers have equal values for μ_x and μ_y and one different value for μ_z so they belong to the same D_{4h} electronic symmetry point group. Furthermore, for the trans complex

$$\mu_x - \mu_z = 2(q_A - q_B)$$

and for the cis complex

$$\mu_x - \mu_z = -(q_A - q_B)$$

And

$$V_T(trans) = 2(q_A - q_B)f(x,y,z)$$
$$V_T(cis) = -(q_A - q_B)f(x,y,z)$$

From these expressions it may be seen that

$$V_T(cis) = -\tfrac{1}{2}V_T(trans) \qquad (1)$$

Both cis and trans isomers should show the tetragonal splitting of the octahedral transitions, but only the trans isomers exhibit it. The cis isomers have only a half tetrago-

Spectral Data and Assignments

Complex Ion	ν_1 (nm)[a]	ν_2 (nm)[b]	ν_3 (nm)[c]
CrF_6^{3-} [d]	671	441	291
$Cr(en)_3^{3+}$ [d]	458	351	—[e]
cis-$CrF_2(en)_2^+$	517	378	235
$trans$-$CrF_2(en)_2^+$	530[f]	397[g]	248[h]
	465[i]	351[j]	229[k]

[a] $^4A_{2g} \rightarrow {}^4T_{2g}(F)$ (O_h) transition.
[b] $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ (O_h) transition.
[c] $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ (O_h) transition.
[d] Spectral values for CrF_6^{3-} and $Cr(en)_3^{3+}$ from reference 8.
[e] Not observed.
[f] $^4B_{1g} \rightarrow {}^4E_g$ (D_{4h}) component of ν_1.
[g] $^4B_{1g} \rightarrow {}^4E_g$ (D_{4h}) component of ν_2.
[h] $^4B_{1g} \rightarrow {}^4A_{2g}$ (D_{4h}) component of ν_3; calculated from reference 2.
[i] $^4B_{1g} \rightarrow {}^4B_{2g}$ (D_{4h}) component of ν_1.
[j] $^4B_{1g} \rightarrow {}^4A_{2g}$ (D_{4h}) component of ν_2.
[k] $^4B_{1g} \rightarrow {}^4E_g$ (D_{4h}) component of ν_3; calculated from reference 2.

nal contribution with respect to trans isomers and generally the splitting is not observed in the spectrum (eq 1). The minus sign means that the order of splitting in the energy levels would be inverted in both isomers.

Thus, in theory our three-band spectrum of an octahedral d^3 complex, becomes a six-band spectrum, but all six bands are rarely seen. It is generally true that the lowest energy spin-allowed transition is most susceptible to the effects of lower symmetry and the highest energy one is generally overlapped by charge-transfer bands.

Results and Discussion

Reported in the table are the electronic spectra of both cis- and $trans$-$CrF_2(en)_2^+$ isomers ($3,4$) and the band assignments as they are given by Dubicky et al. based on a single-crystal, polarized electronic spectral analysis (2).

The rule of "average environment" (5) relates the pseudo-octahedral mixed complex $CrF_2(en)_2^+$ with CrF_6^{3-} and $Cr(en)_3^{3+}$. By applying this rule we may obtain an approximate value of $10\,Dq$ for cis-$CrF_2(en)_2^{3+}$ and predict its spectrum in this fashion:

$$10\,Dq = \frac{2 \times 14900~\text{cm}^{-1} + 4 \times 21850~\text{cm}^{-1}}{6} = 19500~\text{cm}^{-1}$$

and

$$\Delta E(^4A_{2g} \rightarrow {}^4T_{2g}) = 19500~\text{cm}^{-1}$$

This is in good agreement with the experimental value of 517 nm for the cis-$CrF_2(en)_2^+$ complex.

Using the graphic methods outlined in several textbooks or in reference 5, one can obtain the B value, which is 674 cm^{-1}. Using these B and Dq values for cis-$CrF_2(en)_2^+$, the highest energy transition, $^4A_{2g} \rightarrow {}^4T_{2g}(P)$, is calculated at 235 nm. In this region there are strong charge-transfer bands that overlap and obscure this $d \rightarrow d$ transition.

Literature Cited

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