The Absorption and the Circular Dichroism Spectra and the

Absolute Configuration of the Tris Acetylacetonato

Silicon(IV) Ion

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The electronic absorption and circular dichroism spectra of the *laevo* tris acetylacetonato silicon(IV) ion, l-Si(acac)$_3^+$, have been measured. The results show that there is little, if any, delocalisation of π-electrons from one ligand to another or to the silicon atom in this complex. It is found that the $\pi \rightarrow \pi^*$ transition of lowest energy in the acetylacetonate ion is polarized parallel to the oxygen-oxygen direction of the anion, and that the dipole moments of this excitation in the three ligands of l-Si(acac)$_3^+$ couple to give resultant transitions with A_2 and E symmetry in the group D_3 of the complex ion. The absorption and circular dichroism bands of l-Si(acac)$_3^+$ due to these resultant transitions are identified by means of their relative frequencies and intensities. From the assignment of the transitions responsible for the observed circular dichroism bands it is shown that the absolute stereochemical configuration of the complex l-Si-(acac)$_3^+$ has the form of a right-handed three-bladed propellor.

U se has previously been made of the internal ligand transitions in dihedral transition metal complexes for non-empirical assignments of the symmetries of the electronic transitions as well as the absolute configuration of the complex.[1,2] However, the electronic absorption spectra of transition metal complexes in the region of the internal ligand transitions are extremely complex as the electronic transitions of the ligands and of the metal ion either mix with or are overlaid by charge transfer transitions between ligand and metal. The corresponding coordination compounds of non-transitional elements are free from this complication, and thus give simpler spectra. In the present work we report the measurement and the analysis of the absorption and the circular dichroism spectra of the *laevo*-trisacetylacetonato silicon(IV) ion, l-Si-

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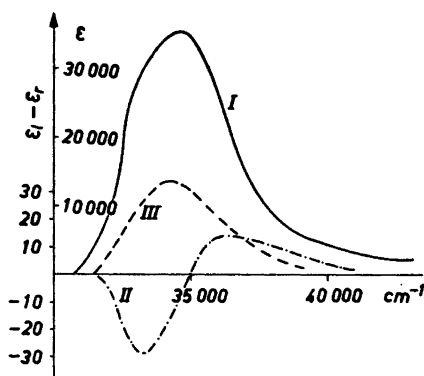
Fig. 1. I, Molar absorption of d,l-Si(acac)$_3$-ClO$_4$ and II, Molar circular dichroism of l-Si(acac)$_3$ClO$_4$ in water, both extrapolated back to instant of mixing. III, Molar absorption of Kacac in 1 M KOH.
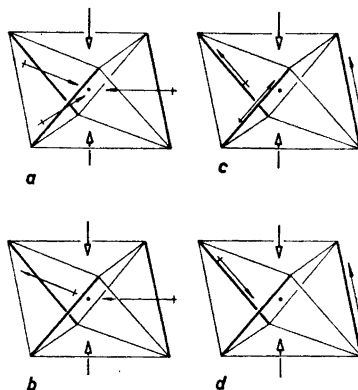

Fig. 2. Coupling of the possible $\pi \to \pi^*$ transitions of acac$^-$ in a dihedral complex (see text).

(acac)$_3{}^+$. The accessible spectrum of this ion consists (Fig. 1) of a single absorption band with nearly the same frequency and with three times the intensity of that of the acetylacetonate anion, acac$^-$, indicating that the silicon-ligand interactions are very small. The absorption band of l-Si(acac)$_3{}^+$ consists of two components, a moderate-intensity shoulder at 33 500 cm^{-1} and the main high-intensity peak at 34 700 cm^{-1}, corresponding to the two bands observed (Fig. 1) in the circular dichroism spectrum.

The absorption band of the acetylacetonate ion at 34 300 cm^{-1} is due to a $\pi \to \pi^*$ transition which has a moment in the plane of the anion (I) orientated along either the oxygen-oxygen direction (y) or the two-fold rotation axis (x). (The shown geometry of the molecule is supposed to be fixed in solution by means of a solvent molecule hydrogen bonded to the two oxygen atoms [3]). If the transition is x-polarized, the three ligand transition moments in the D_3 complex l-Si(acac)$_3{}^+$ couple to give a resultant transition with A_1 symmetry (Fig. 2a) and a doubly-degenerate transition with E symmetry (Fig. 2b). Neither of these two resultant transitions of the D_3 complex are optically-active, since neither the one nor the other involves a helical displacement of charge. The A_1 transition is symmetry-forbidden, but the E transition is allowed and it should have a dipole strength, which governs the intensity of the unpolarized absorption, three times as large as that of a single acac$^-$ ligand. Since the 34 700 cm^{-1} band of l-Si(acac)$_3{}^+$ is optically-active and is split into two components (Fig. 1) the 34 300 cm^{-1} transition of the acetylacetonate ion (I) cannot be x-polarized.

If the acac$^-$ transition is y-polarized, the three ligand transition moments in l-Si(acac)$_3{}^+$ couple to give a resultant transition with A_2 symmetry (Fig. 2c) in the group D_3 of the complex and a doubly degenerate transition with E symmetry (Fig. 2d). Both the A_2 and the E transition have a non-zero rotation-

I
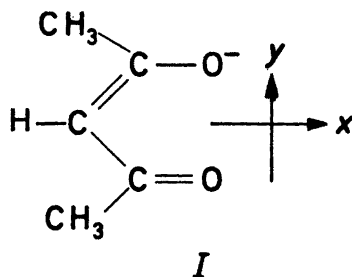
al strength R and dipole strength D, these quantities being measured experimentally by the band areas of the circular dichroism and the unpolarized absorption, respectively. [4] The A_2 transition (Fig. 2c) involves a helical charge-displacement along and about the three-fold rotation axis of the complex (II),

II
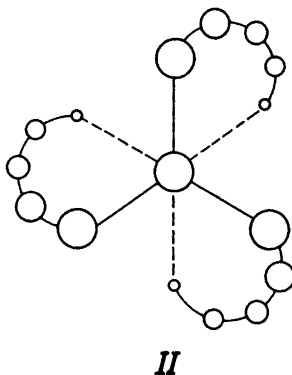
and the two components of the E transition involve similar charge-displacements along and about two mutually orthogonal directions both perpendicular to the C_3 axis, *e.g.* one of the three two-fold axes (Fig. 2 d). It follows from the geometry of the octahedron and from the definition of the rotational strength as the product of the magnetic dipole (μ) and the electric dipole (ϱ) transition moments (eqn. 3) that the dipole and the rational strengths of the A_2 and the E transitions are related by

$$D(A_2) \; = \; 2 \; D(E) \; = \; 2 \; D_{acac} \qquad\qquad (1)$$
$$R(A_2) \; = \; - \; R(E) \qquad\qquad\qquad\qquad (2)$$
$$R_{ba} \quad\;\; = \; \bar{\varrho}_{ab} \; \bar{\mu}_{ba} \qquad\qquad\qquad\qquad (3)$$

where D_{acac} is the dipole strength of the absorption band given by the free acetylacetonate ion.

These expectations are supported by the measured spectra of *l*-Si(acac)$_3$$^+$ (Fig. 1) which show two circular dichroism bands of nearly equal areas and opposed signs, and an unpolarized absorption band with a moderate and a high-inten-

sity component. The intensity relation suggests that the low-frequency shoulder in the unpolarized absorption and the low-frequency circular dichroism band are due to the E transition (Fig. 2d) of the complex, and the high-frequency dichroism band and unpolarized absorption maximum to the A_2 transition (Fig. 2c). The energy of the A_2 transition would intuitively be estimated to be higher than that of the E transition, and this supports the band assignments made on the basis of the intensities.

A more quantitative estimate of the energy separation between the A_2 and the E transitions in the complex l-Si(acac)$_3{}^+$ may be obtained from the self-consistent field molecular orbitals of the acetylacetonate ion, which have been calculated recently by Forster.[5] If the π-electron orbitals of acac$^-$ are numbered in the order of their decreasing binding energy, $\psi_1 \rightarrow \psi_5$, the $\pi \rightarrow \pi^*$ transition of lowest energy is $\psi_3 \rightarrow \psi_4$. This transition in the anion (I) should be y-polarized,[5] as is found here experimentally. The dipole strength D_{acac} of the transition $\psi_3 \rightarrow \psi_4$ in the anion (I) is given by the expression,

$$D_{acac} = (e \sum_s C_{s3} \ C_{s4} \ \bar{r}_s)^2 \tag{4}$$

where e is the electronic charge, C_{sj} is the atomic orbital coefficient of the atom s in the molecular π-orbital ψ_j, and $\bar{r}_s$ is a vector defining the position of the atom s. The S.C.F. atomic orbital coefficients[6] give, through eqn. (4), a theoretical dipole strength of 28.7×10^{-36} c.g.s. for the transition $\psi_3 \rightarrow \psi_4$, compared with the experimental value of 14×10^{-36} c.g.s. obtained from the area of the absorption band of acac$^-$ at 34 300 cm^{-1}. Thus the S.C.F. orbitals overestimate the magnitude of the transition monopoles, $C_{s3} \ C_{s4}$, by a factor of $\sim \sqrt{2}$, which has been used as an empirical correction factor in the subsequent calculation of the electrostatic interaction between the transition monopoles of the three ligands in l-Si(acac)$_3{}^+$.

The electronic states of the complex l-Si(acac)$_3{}^+$ belong to the representation A_1, A_2, or E of the Group D_3. The ground state is totally symmetric (A_1) and the upper states resulting from the excitation $\psi_3 \rightarrow \psi_4$ in the three ligands have the forms,

$$\Phi (A_2) = (1/\sqrt{3}) \ (\chi_a{}'\chi_b\chi_c + \chi_a\chi_b{}'\chi_c + \chi_a\chi_b\chi_c{}') \tag{5}$$

and

$$\Phi (E) = (1/\sqrt{2}) \ (\chi_a{}'\chi_b\chi_c - \chi_a\chi_b{}'\chi_c) \tag{6}$$

where χ refers to the ground state and χ' to the excited configuration of a particular ligand, the three ligands being distinguished by the subscripts a, b, and c. The second component of the doubly-degenerate upper state of l-Si-(acac)$_3{}^+$ with E symmetry has a form orthogonal to those expressed in eqns. (5) and (6).

Electrostatic interactions between the transition monopoles of different ligands in a given complex ion give the transitions to the A_2 and to the E upper states different energies. If it is assumed that there is no electron exchange between the ligands of a particular complex ion, the energy difference is,

$$\nu (A_2) - \nu (E) = 3 \ N \ \sum_{s(a)} \sum_{t(b)} \ (C_{s3} \ C_{s4})_a \ (C_{t3} \ C_{t4})_b \ \gamma_{st} \tag{7}$$

where γ_{st} is the repulsion integral between electrons on the atoms s and t, the sums being taken over all of the atoms s of the ligand a and all of the atoms t of the ligand b in a given complex ion. Since the S.C.F. atomic orbital coefficients overestimate the magnitude of the transition monopoles (C_{s_2} C_{s_4}), the empirical correction factor $N = 1/2$ is introduced into eqn. (7), the factor being the ratio of the experimental to the theoretical dipole strength of the 34 300 cm^{-1} absorption of the acetylacetonate ion. With this correction factor, the S.C.F. coefficients and the repulsion integrals reported by Forster,[5,6] give (eqn. 7) the frequency separation between the A_2 and the E transition of l-Si(acac)$_3{}^+$ as 1500 cm^{-1}, compared with the experimental value from the absorption spectrum of 1200 cm^{-1}.

The relative intensities of the two components of the unpolarized absorption band (eqn. 1), and the molecular orbital calculation (eqn. 7) of the energy interval between the A_2 and the E transition of l-Si(acac)$_3{}^+$, indicate that these two transitions have the higher and the lower frequency, respectively. Thus the circular dichroism band of l-Si (acac)$_3{}^+$ at 36 300 cm^{-1} can be assigned with confidence to the A_2 transition and the band at 33 200 cm^{-1} to the E transition.

The signs of the Cotton effects of the two transitions express that the electric and magnetic transition moments are parallel for the A_2 transition but antiparallel for the E transition (eqn. 3). Therefore the complex l-Si-(acac)$_3{}^+$ has the absolute configuration shown (II).

EXPERIMENTAL

$Si(acac)_3Cl, HCl.$ This was prepared by Dilthey's method,[7] the crude product being bright yellow. Five recrystallisations from chloroform by precipitation with ether failed to remove completely the yellow colour, which intensified on storage.

$Si(acac)_3ClO_4.$ Excess of a concentrated sodium perchlorate solution was added to a freshly prepared aqueous solution of the above chloride (twice recrystallised), from which a little brown oil was removed by centrifuging. The white product which separated immediately was centrifuged off and washed with a little cold water. It was dissolved while still wet in chloroform, and after removal of the aqueous layer the product was precipitated with ether. After two recrystallisations the perchlorate was dried at 50° under vacuum. The compound remained colourless after 2 weeks. (Found: C 42.3; H 5.06. Si(C$_5$H$_7$O$_2$)$_3$ClO$_4$ requires C 42.3; H 4.97).

l-$Si(acac)_3$-(R,R)-$dibenzoyl$-$tartrate.$ Resolution of the chloride was effected by a method similar to that previously described.[8] To an aqueous solution of disodium-(R,R)-dibenzoyl-tartrate (1 g) was added an aqueous solution of Si(acac)$_3$Cl, HCl (2 g) and the diastereo-isomer l-Si(acac)$_3$-(R,R)·HC$_{18}$H$_{12}$O$_8$ which separated on cooling was centrifuged off, washed with water, ethanol, and ether, and air-dried. To ensure high optical purity the yield was restricted (0.84 g = 50 % of one optical isomer).

l-$Si(acac)_3ClO_4.$ The above diastereoisomer was ground under chloroform with excess sodium perchlorate in a mortar (5 min). The precipitated disodium-(R,R)-dibenzoyl-tartrate and excess sodium perchlorate were removed from the chloroform solution by centrifuging and filtration. Further product was extracted by grinding with additional chloroform, and from the combined extracts l-Si(acac)$_3$ClO$_4$ was precipitated with ether and centrifuged off. After it had been ascertained that the active form is less soluble than the racemate, the product was purified by three recrystallisations from chloroform and ether.

$Spectral measurements.$ Absorption spectra were recorded on a Unicam SP 700 spectrophotometer. Circular dichroisms were measured with a Roussel-Jouan Dichrographe and optical rotations on a Bellingham and Stanley spectropolarimeter (1 dm cell).

For rotation measurements, a 6.5×10^{-4} M aqueous solution of l-Si(acac)$_3$ClO$_4$ was made up quickly, and this solution was diluted to 2.5×10^{-5} M for measurements of the absorption and circular dichroism. The measured rate of hydrolysis of l-Si(acac)$_3$-ClO$_4$, $k = 1.26 \times 10^{-4}$ sec^{-1} at 20°, (spectrophotometric at 34.5 kk), which agrees with that calculated from the earlier reported data [8] ($k = 1.24 \times 10^{-4}$ sec^{-1}), was found identical with the first-order rate of loss of circular dichroism. From extrapolations back (5 min) to the instant of mixing at various wavelengths, the spectra of Fig. 1 were drawn.

The linear plot of log $(-\alpha_D)$ *versus* time was extrapolated back from the first reading ($\alpha_D = -0.326°$ at 5 min) to give at the instant of mixing $\alpha_D^{25} = -0.347°$, whence $[\alpha]_D^{25} = -1260°$, $[M]_D = -5360°$. This is only slightly higher than that reported for the active chloride which was previously obtained only in solution, so that the diastereoisomer obtained in the resolution is probably essentially optically pure.

Similar values for absorption, circular dichroism and rotation were obtained in chloroform solution. Ethanol was not useful as a solvent as the solvolysis is very rapid, solutions becoming completely inactive in one hour. The logarithmic plots of absorption and circular dichroism versus time were not linear for ethanol solutions.

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