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THE ELECTRONIC ABSORPTION AND CIRCULAR DICHROISM SPECTRA, AND THE ABSOLUTE STEREOCHEMISTRY OF THE TRIS-CATECHYL-ARSENATE(V) ION

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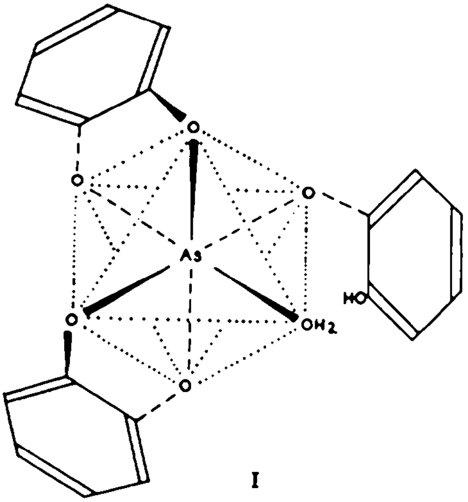
Abstract—The circular dichroism and absorption spectra of the (+)- and (−)-isomers of the tris-catechyl-arsenate(V) ion are reported. The spectra are analysed by means of the coupled dipole model in which the excitation moments of the three catechol chromophores interact to give helical charge displacements responsible for the optical activity of the corresponding absorption bands. The results show that the longer and the shorter wavelength absorption bands of catechol are polarized respectively along the two-fold rotation axis of the chromophore and along the in-plane direction perpendicular to that axis. It is found that tricatechyl arsenic acid and its anion have a tris-chelate structure, and not the bis-chelate structure with a monodentate catechol ligand previously proposed, and that the (+)-isomer of the complex has the stereochemical form of a left-handed three-bladed propellor.

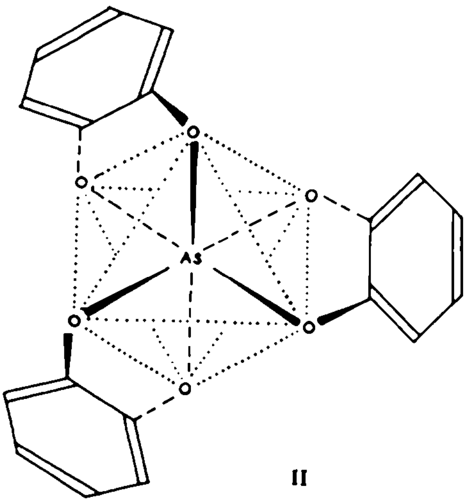
THE complex of arsenic(V), HAs $(C_6H_4O_2)_3 \cdot 5H_2O$, prepared from catechol and arsenic acid,[1] was assigned the bis-chelate structure (I)[2] on the grounds that the pentahydrate of the acid, which is monobasic, loses only four molecules of water on dehydration, and that the coordinated water molecule of the analogous antimony(V) complex is replaceable by a molecule of pyridine. The complex was resolved into its optical enantiomers by Rosenheim and Plato,[3] who proposed the tris-chelate structure II for the anion. However, the structure I[2] would be resolvable if the monodentate catechol ligand and the coordinated water molecule occupied *cis* positions. Recent electrochemical and kinetic studies[4] indicate that the complex is a relatively weak acid with a pK_a value of 2·75, and that the racemization and hydrolysis of the complex acid is rapid in the pH range 1–3, whereas the enantiomers of the anion in neutral solution are optically stable and resistant to aquation. These observations are compatible[4] with the bis-chelate structure (I) proposed[2] for the complex acid, and with the tris-chelate structure (II) suggested[3] for the complex anion.

In the present work the electronic absorption and CD spectra of the optical isomers of the tris-catechyl-arsenate ion have been measured (Fig. 1, Table) with the object of determining the stereochemistry of the enantiomers, and of investigating the polarization directions of the electronic transitions in the catechol chromophore. The accessible spectrum of the complex anion in the quartz UV region consists (Fig. 1) of two bands with nearly the same frequency as the corresponding bands of catechol in the neutral form, and with absorption intensities approximately three times as large. A weak positive CD absorption is associated with the longer wavelength band system of the (+)-isomer of the complex ion, and in the region of the

[1] R. F. Weinland and J. Heinzler, *Chem. Ber.* **52**, 1316 (1919).
[2] H. Reihlen, A. Sapper and G. A. Kall, *Z. Anorg. Chem.* **144**, 218 (1925).
[3] A. Rosenheim and W. Plato, *Chem. Ber.* **58**, 2000 (1925).
[4] J. H. Craddock and M. M. Jones, *J. Am. Chem. Soc.* **83**, 2839 (1961).



I



II

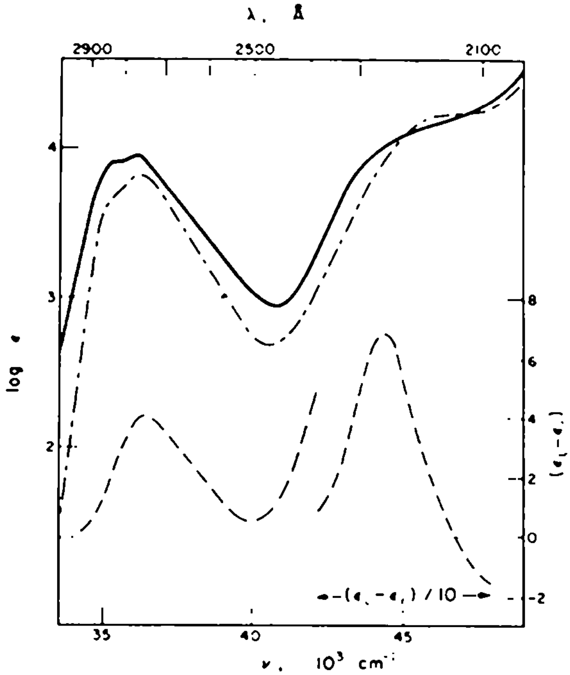


Fig. 1. The absorption spectrum ———, and the circular dichroism · ···· —, of the (+)-tris-catechyl arsenate (V) ion in water and the absorption spectrum — · — · —, of catechol at pH 7·0 with the intensity scale multiplied by a factor of three.

shorter wavelength band system a strong positive CD and the beginnings of a negative dichroism band are observed (Fig. 1).

The optical activity of the enantiomers of the tris-catechylarsenate ion derives largely from interactions between the transition moments of the three non-coplanar catechol chromophores. In general the charge displacements resulting from these transitions have a helical form, and the motion of the electron promoted by the absorption of radiation has both a linear and a rotatory component, which are associated with an electric and magnetic dipole transition moment, respectively. The scalar product of the electric and the magnetic moment represents the rotational strength of the electronic transition in the complex ion, and a comparison of the experimental rotational strength obtained from the CD spectrum of the complex with the values calculated for the two optical isomers gives the absolute stereochemistry of the enantiomer studied.

The calculation of the rotational strengths of the complex ion II requires a knowledge of the energy, dipole strength and the polarization direction of the electronic transition of the free ligand, and of the stereochemical relations between the three ligands in the complex, apart from absolute configuration. As indicated,[3] the optical activity of the complex ion suggests that the six oxygen atoms are bound octahedrally to the arsenic atom, and that the three catechol ligands are related by one three-fold and three two-fold axes of rotation, the complex belonging to the point group, D_3. The energy and the dipole strength of the electronic transitions of catechol are readily obtained from the frequency and the area, respectively, of the corresponding absorption bands of the molecule, but the polarization directions of the transitions are known as yet only from theoretical studies.

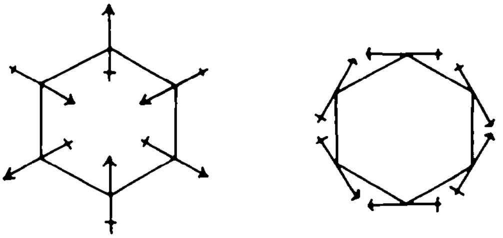


FIG. 2. The component dipole moments of the transitions giving (a) the α-band (^1L_b) and (b) the p-band (^1L_a) of benzene.

In the quartz UV region catechol gives absorption bands at 2770 and 2150 Å which are termed the α- and the p-band, respectively, in the classification of Clar,[5] or the ^1L_b and the ^1L_a bands, respectively, according to the nomenclature of Platt.[6] The corresponding bands of benzene are forbidden, as the component transition dipoles mutually cancel (Fig. 2). In substituted benzenes the component transition dipole at the position of substitution is changed in magnitude, however, giving a non-zero resultant moment.[7] For disubstituted benzenes the resultant moment is the vector sum of the two component transition dipoles induced by the substituents, and absorption intensities predicted by this method show good agreement with experiment.[7] Vector addition of the two component dipoles induced by the two hydroxy groups gives a resultant moment orientated along the two-fold rotation axis *a* of catechol(III) for the longer wavelength α-band (Fig. 3a), and along the in-plane direction *b* perpendicular to that axis III for the shorter wavelength p-band. The corresponding transition moment directions predicted for the α- and the p-bands

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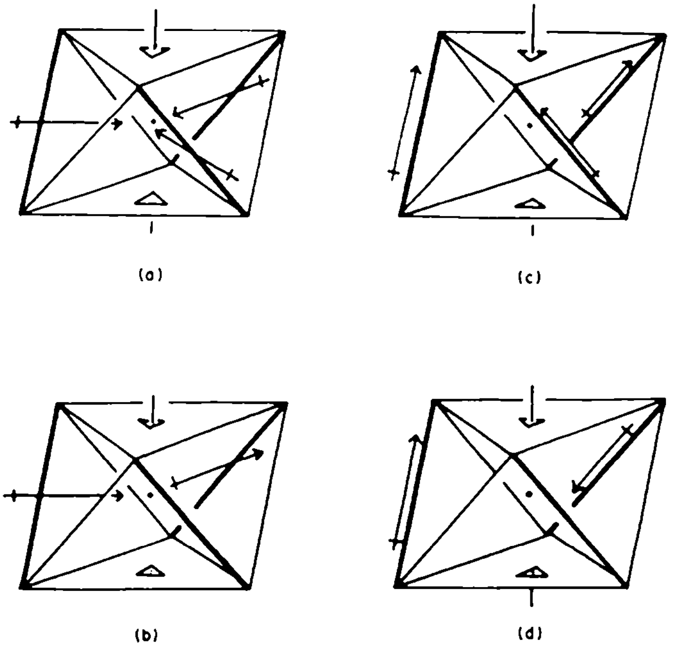
[5] E. Clar, *Chem. Ber.* **69**, 607 (1936); *Polycyclic Hydrocarbons*. Springer, Berlin, Academic Press, London (1964).

[6] J. R. Platt, *J. Chem. Phys.* **17**, 484 (1949).

[7] J. R. Platt, *J. Chem. Phys.* **19**, 263 (1951).

of 1,4-dimethoxybenzene have been verified by a study of the polarized crystal spectrum of the molecule.[8]

To a zero order approximation, a given electronic transition of the catechol chromophore is triply degenerate in the complex ion II, but the degeneracy is split by Coulombic interactions between the transition charge densities of the three chromophores. In general two resultant transitions are the product of the interaction, one non-degenerate with A_1 or A_2 symmetry, and the other doubly degenerate with E symmetry in the group D_3 (Fig. 3). The two-fold axis *a* of the catechol chromophore III becomes one of the two-fold axes of the complex ion II, and if a transition moment of the free ligand is orientated along this axis the resultant non-degenerate transition in the complex ion has A_1 symmetry, and it is forbidden as the component dipoles mutually cancel (Fig. 3a).


(a) (c)

(b) (d)

FIG. 3. The component dipole moments of the excitations of catechol, polarized (*a* and *b*) along the two-fold axis of the chromophore and (*c* and *d*) along the in-plane direction perpendicular to that axis, giving resultant transitions in the tris-catechyl arsenate (V) complex with (a) A_1, (b) E_a (c) A_2, and (d) E_b symmetry in the group D_3.

The corresponding doubly-degenerate resultant transition of the complex ion with E symmetry involves a non-helical charge displacement (Fig. 3b) the direction of the linear motion of the electron and the axis of the rotatory motion being orthogonal, so that the scalar product of the electric and the magnetic dipole transition moments vanishes. The rotational strength of this resultant transition, denoted E_a to distinguish it from other transitions of the same symmetry, is zero, but the dipole strength is three times as large as that of the parent transition of the free ligand, to a first approximation.

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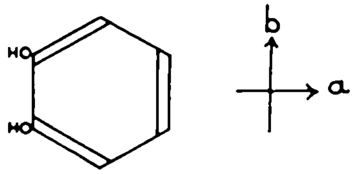
[8] A. C. Albrecht and W. T. Simpson, *J. Chem. Phys.* 23, 1480 (1955).

If the transition moment of the free ligand is directed along the *b* axis of the catechol chromophore III, the corresponding dipoles in the complex ion II are orientated parallel to the octahedral edge spanned by the chelate rings. The resultant non-degenerate transition of the complex ion has A_2 symmetry, and it involves a helical charge displacement along and about the three-fold axis C_3 of the complex (Fig. 3c). The corresponding doubly-degenerate resultant transition, termed E_b, has two components which involve helical charge displacements around mutually perpendicular directions orthogonal to the C_3 axis of the complex (Fig. 3d).



III

The electric moment ρ of a resultant transition of the complex ion II is the vector sum of the corresponding transition dipoles of the three ligands, and the magnetic moment μ is proportional to the vector product of each component dipole and the radial vector from the coordinated atom to the position of the dipole in the ligand. The resultant moments are readily evaluated if it is assumed that a transition moment of the catechol chromophore is a point dipole located at the centre of the benzene ring. The electric dipole moment ρ_L of a *b*-polarized transition of the catechol chromophore III is resolvable into a component $\rho_L \cos\theta$, parallel to the C_3 axis of the complex ion, and a component $\rho_L \sin\theta$, orientated perpendicular to the C_3 axis and to the radius vector of length *d* from the arsenic atom to the centre of the benzene ring (Fig. 4), where θ is the angle (35° 16′) between the plane of the chelate ring and the three-fold axis of the complex. For the resultant transition of the complex ion with A_2 symmetry the electric moment is given by,

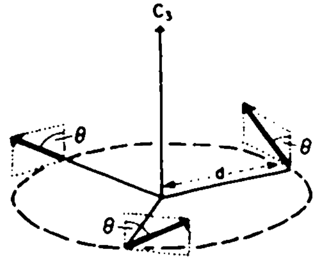


FIG. 4. The mutual stereochemical relations of the three catechol excitation dipoles giving a resultant transition with A_2 symmetry in the tris-catechyl-arsenate (V) complex where *d* is the distance between the arsenic atom and the centre of each benzene ring, and θ is the angle between the plane of each benzene ring and the three-fold rotation axis C_3 of the complex.

$$\rho(A_2) = (1/\sqrt{3})(\rho_L + \rho_{L'} + \rho_{L''})\cos\theta \tag{1}$$

and the magnetic moment is,

$$\mu(A_2) = (1/\sqrt{3})\pi\bar{\nu}\, d(\rho_L + \rho_{L'} + \rho_{L''})\sin\theta \tag{2}$$

where $\bar{\nu}$ is the frequency in wave numbers of the chromophore transition. Analogous expressions are obtained for the moments of the resultant E_b transition.

The rotational strengths, $R = (\rho \cdot \mu)$, obtained for the $P(C_3)$ configuration[9] of the complex ion, in which the three chelate rings present the appearance of a right-handed (plus) three-bladed propellor when viewed along the direction of the principal axis, are given by,

$$R(A_2) = -R(E_b) = \sqrt{2}\, \pi \bar{\nu}\, d D_L \tag{3}$$

where D_L is the dipole strength ρ_L^2 of the ligand transition. For the enantiomeric $M(C_3)$ configuration[9] the rotational strengths have the same magnitude but the signs are reversed, and for both configurations the dipole strengths are,

$$D(A_2) = 2D(E_b) = 2D_L \tag{4}$$

The A_2 and the E_b transitions deriving from a given *b*-polarized excitation of the catechol chromophore III have different energies, and the frequency interval between them in the point-dipole approximation is given by,

$$\bar{\nu}(A_2) - \bar{\nu}(E_b) = \sqrt{3} D_L/(12hc\, d^3) \tag{5}$$

where *h* is Planck's constant and *c* is the velocity of light.

In the region of the p-band system of the complex ion II, 2500–2100 Å, two CD absorptions with opposed signs are observed (Fig. 1) although the area of only the longer-wavelength dichroism band is accessible. These dichroism bands must originate from a *b*-polarized excitation of the catechol chromophore III, and the theoretically-derived[7] direction of the transition moment responsible for the p-band of catechol at 2150 Å is confirmed. The higher and the lower frequency dichroism bands in the region of the p-band absorption are due to the A_2 and the E_b transitions of the complex ion, respectively (Eq. 5), and since these dichroism bands have a negative and a positive sign, respectively, for the (+)-isomer of the complex (Fig. 1), this enantiomer has the $M(C_3)$ configuration in which the chelate rings have the form of a left-handed (minus) three-bladed propellor II. The observed rotational strength of the positive CD band at 44,300 cm^{-1} is only one-quarter of the theoretical value (Table), as the frequency interval (50 cm^{-1}) between the A_2 and the E_b transitions is small, and the overlap of the two CD bands with opposed signs results in a substantial mutual cancellation of band area.

In the region of the α-band system of the complex ion II, 3000–2500 Å, a single positive dichroism band is observed (Fig. 1) with a rotational strength smaller by an order of magnitude than that of the positive dichroism band associated with the p-band system. The dipole moments of the transitions responsible fof the α- and p-bands of catechol are orthogonal III and they do not mix, but in the complex ion II the resultant transitions of the same symmetry deriving from different catechol excitations interact, and rotational and dipole strength is redistributed to some degree. In particular the E_a and E_b excited states of the complex ion II are mixed, and the wave function of the former is represented by,

$$\psi(E_a) = \psi^{\circ}(E_a) + c\psi^{\circ}(E_b) \tag{6}$$

where the mixing coefficient *c* has the value ~0·1 from the observed rotational

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[9] R. S. Cahn, C. K. Ingold and V. Prelog, *Angew. Chem.* Int. Ed., 5, 385 (1966).

TABLE. THE ABSORPTION SPECTRA OF CATECHOL AND OF THE TRIS-CATECHYL-ARSENATE(V) ION, AND THE CD OF THE (+)-ISOMER OF THE COMPLEX ION IN AQUEOUS SOLUTION AT pH 7·0. THE EXPERIMENTAL DIPOLE AND ROTATIONAL STRENGTHS FROM THE OBSERVED BAND AREAS AND THE CALCULATED ROTATIONAL STRENGTHS (EQ. 3) AND FREQUENCY INTERVAL (EQ. 5) FOR $d = 4·0$ Å

Compound	ν_{abs} (cm^{-1})	ε_{max} (M^{-1} cm^{-1})	D (10^{-36} cgs)	ν_{CD} (cm^{-1})	$(\varepsilon_l - \varepsilon_r)_{max}$ (M^{-1} cm^{-1})	R expt (10^{-40} cgs)	R theor (10^{-40} cgs)	$\nu(A_2) - \nu(E_b)$ (cm^{-1})
(+) - [As(cat)$_3$]	36,200	8800	6·3	36,200	+4·0	+7·9	0	---
				44,300	+68	+88	+360	
	45,500	15,000	12·1					50
				>48,000	−ve	ve	−360	
Catechol	36,100	2300	1·5					
	46,500	5700	4·5					

strengths or ~0·02 from the experimental value for R(E_a) and the theoretical value for R(E_b) (Table). Since the CD associated with the α-band system of the complex ion (II) is small and consists of a single band, which is accounted for by configurational interaction between the E_a and the E_b transitions, it is concluded that the α-band of catechol arises from a transition polarized along the *a* axis of the chromophore III, as theoretical considerations suggest.[7]

The observed intensities of the α- and the p-band systems of the complex ion II are larger and smaller, respectively, than those of the corresponding bands of three neutral catechol ligands, although the frequencies of the bands are not appreciably changed (Fig. 1, Table). The effect is not due primarily to the partly changed state of the catechol ligands in the complex ion II, as both the α- and the p-bands of the catechol anion lie at lower frequencies and have larger intensities than those of the neutral molecule. The intensity changes in the band systems of the complex ion II arise largely from configurational interaction between excited states with E symmetry in the complex, resulting in the donation of dipole strength to the α-band system from the p- and higher-energy band systems.

Attempts were made in the present work to obtain the CD and absorption spectra of the conjugate acid of the complex ion II by extrapolating measurements made at pH 1·0 to zero time in order to allow for the racemization and hydrolysis of the complex. On the basis of the reported[4] pK_a value of 2·75, the complex ion is 98% protonated at pH 1·0, where the dissociation reaction has a half life ~25 min at 20°. The absorption and CD spectra of the complex acid obtained by extrapolation were found to be identical with those of the complex ion II, within experimental error, suggesting either that the complex ion II is not appreciably protonated at pH 1·0 or that the complex acid has a tris-chelate structure similar to that of the anion II.

If the complex acid has the structure I, the electronic transitions giving rise to the α-band system of the acid would be optically-active, without configurational interaction, for all conformations of the unidentate catechol ligand, save that in which it approximated to the chelating position adopted in the anion II. In the latter conformation the excitation dipoles of the three catechol chromophores are coplanar for the α-band system (Fig. 3a and 3b) and are optically-inactive, but this conformation would be the least favoured, owing to steric hindrance between the coordinated water molecule and the unidentate catechol ligand. Thus a relatively large CD, consisting of two or three dichroism bands with alternating signs, would be expected in the α-band region for the complex acid (I) and the conjugate base containing a unidentate catechol ligand.

These conclusions are supported by the PMR spectrum of the complex acid in dimethylsulphoxide, and of the acid and the anion II in deuterium oxide. Only two lines are observed in each of the spectra at 60 Mcs, one due to the aromatic protons and the other due to those of the water molecule or hydroxonium ion. The single absorption of the aromatic protons, which consists of a singlet at 3·25 τ in DMSO or a closely-spaced doublet at 2·95 τ in deuterium oxide, might arise from a rapid exchange of the mono- and bidentate coordination of the catechol ligands to the arsenic atom in the complex acid I. However, the denticity exchange would probably involve the interchange of the coordination positions of the ligands, which is not consistent with the relatively slow rate of racemization of the complex acid.

EXPERIMENTAL

Materials. Tricatechyl arsenic acid was prepared by slow crystallization from an aqueous soln (100 ml) containing arsenic acid (40 g) and catechol (100 g), and was transformed asymmetrically into the (−)-isomer using cinchonine, following the method of Mann and Watson.[10] A similar asymmetric transformation, using quinine,[4] afforded the (+)-isomer. Both enantiomers were converted into and stored as the Ba salt, (+)- and (−)-$Ba[As(C_6H_4O_2)_3]_2 \cdot 2H_2O$; $[\alpha]_D^{20} = \pm 419°$.

Spectra. These were measured with a Jouan Dichrograph (CD), a Unicam SP 700 (isotropic electronic absorption), and a Perkin-Elmer R10 (PMR). The CD spectra of the (+)- and (−)-isomers of the complex ion were mirror image in form. The experimental rotational R and dipole strengths D (Table) were obtained in c.g.s. units from the appropriate band areas through the expressions,[11]

$$R = 22{\cdot}9 \times 10^{-40} \int [(\varepsilon_l - \varepsilon_r)/\bar{\nu}]\, d\bar{\nu}$$

and

$$D = \rho^2 = 91{\cdot}8 \times 10^{-40} \int (\varepsilon/\bar{\nu})\, d\bar{\nu}$$

where the frequency $\bar{\nu}$ is in cm^{-1} and the decadic molar extinction coefficient ϵ is in $M^{-1}\ cm^{-1}$.

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[10] F. G. Mann and J. Watson, *J. Chem. Soc.* 505 (1947).

[11] S. F. Mason, *Quart. Revs* **17**, 20 (1963).