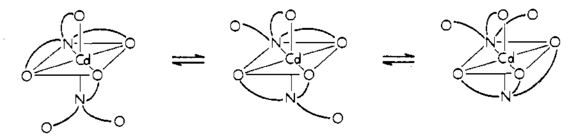
and that the second nta^{3-} of $Cd(nta)^{4-}$ is more than bidentate, as represented by VI and VII, at least part of the time.


V VI VII

$K^{\mathrm{Cd(nta)^-}}{}_{\mathrm{Cd(nta)(X)}}$ is equal to the ratio of the formation (k_f) and dissociation (K_d) rate constants for the reaction described by eq 5. If complexation of ligand X by $Cd(nta)^-$ occurs *via* the dissociative mechanism,[25] K_f for the ligands gly^-, ida^{2-}, and nta^{3-} will decrease as the charge on the ligand increases due to electrostatic effects. k_d has to decrease in this same order for the stability constants to increase in the order

$$K^{\mathrm{Cd(nta)^-}}{}_{\mathrm{Cd(nta)(gly)^{2-}}} < K^{\mathrm{Cd(nta)^-}}{}_{\mathrm{Cd(nta)(ida)^{3-}}} < K^{\mathrm{Cd(nta)^-}}{}_{\mathrm{Cd(nta)_2{}^{4-}}}$$

which is consistent with an increasing degree of coordination by the second ligand. The small change in $K^{\mathrm{Zn(nta)^-}}{}_{\mathrm{Zn(nta)(X)}}$ as the charge on X increases suggests the structures of the gly^-, ida^{2-}, and nta^{3-} complexes of $Zn(nta)^-$ are similar to those proposed above for the Cd(nta)(X) complexes.

Registry No. nta, 139-13-9; tren, 4097-89-6; en, 107-15-3; gly, 56-40-6; ma, 141-82-2; ida, 142-73-4; $Zn(nta)(en)^-$, 36245-45-1; $Cd(nta)(en)^-$, 36191-48-7; $Cd(tren)(en)^{2+}$, 36191-49-8; $Zn(nta)(gly)^{2-}$, 36191-50-1; $Cd(nta)(gly)^{2-}$, 36191-51-2; $Cd(tren)(gly)^+$, 36191-52-3; $Zn(nta)(ida)^{3-}$, 12717-57-6; $Cd(nta)(ida)^{3-}$, 12717-56-5; $Zn(nta)(ma)^{3-}$, 36191-53-4.

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An Improved Synthesis and a Structural Study of Six-Coordinate Tin Tropolonates by Dipole Moments and Kerr Constants in Solution

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Dipole moments and molar Kerr constants determined at 25° for tropolone in cyclohexane and carbon tetrachloride have been used to estimate the optical anisotropy of the tropolonate ligand. A comparison of dipole moments and Kerr constants calculated for the various candidate structures with those obtained from experiment indicates that the tin tropolonates $R_2Sn(trop)_2$ (where R = Cl, CH_3, or C_6H_5) exist preferentially in solution as the cis form. An improved method of synthesis is also described.

The existence of monomeric, neutral, six-coordinate organotin chelate compounds of the type R_2SnCh_2 has been an established fact for a number of years.[1,2] The organic substituent R can be either an alkyl or an aromatic group while the ligand Ch^- can be one of a variety of bidentate types. Because of the possible involvement of tin "d" orbitals and a lingering uncertainty concerning molecular geometries of tin complexes,[3] the structures of these molecules remain the object of considerable interest.

Recent solution- and crystal-state investigations have strongly supported the assignment of cis-type structures. Electric polarization studies[3-6] have clearly shown that such configurations are favored for a wide variety of β-keto enolates. An X-ray analysis[7] of dimethyltin bis(8-hydroxyquinolinolate) has indicated a distorted octahedral structure with a C-Sn-C bond angle of 111°. Mossbauer spectra[8-11] of solids tend to be interpreted in terms of similar cis structures, although crystalline bis(2,4-pentanedionato)-dimethyltin(IV) has been assigned a trans configuration on the basis of quadrupole splitting. The nmr spectra of analogous tropolonates have also been interpreted in terms of a favored cis arrangement.[12,13]

β-Keto enolates have frequently been used in structural studies because of their stability and the relative ease of interpretation of their spectra. However, it has been suggested[14,15] that in solution the β-keto enolate groups may be nonrigid and for that reason structural information derived from spectral and dielectric measurements may be

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suspect.[6] The use of tropolonates in such studies ensures that the ligand is more rigidly planar[16,17] and this should result in a more confident interpretation of dipole moment and Kerr constant data for compounds of the type R_2SnCh_2 In addition the anticipated large optical anisotropy of the tropolonate ligand itself should lead to theoretical values of the Kerr constants for candidate structures of R_2SnCh_2 which will be large and distinctively different.

Experimental Section

Reagents. The solvents benzene, carbon tetrachloride, and cyclohexane were fractionated and then stored over sodium wire (C_6H_6, C_6H_{12}) or anhydrous calcium chloride (CCl_4). Tropolone obtained from Aldrich Chemical Co. was analyzed and found to be pure. Thallous ethoxide from the same source was used as supplied.

Analyses. These were performed by the Australian Microanalytical Service, C.S.I.R.O., Parkville, Victoria 3052, Australia.

Molecular Weights. All molecular weights were determined by means of a Mechrolab Model 301A vapor pressure osmometer. Solutions were 0.5–1.0% by weight.

Refractive Indices. These were measured by means of a Phoenix differential refractometer.

Kerr Constants and Dipole Moments. The standard techniques of measurement are described elsewhere.[18-21] The electric birefringence measurements were made using light of wavelength 589 nm.

Preparation of Complexes. Below are reported the first successful syntheses of organometallic tropolonates *via* the thallous salt route. Thallous tropolonate has been synthesized and caused to react with organotin halides under very mild conditions to produce the corresponding organotin tropolonates in good yield. This procedure should prove highly effective as a general means of producing organometallic tropolonates since reactions studied proceed rapidly under conditions mild enough to avoid metal–carbon bond cleavage. Reactions were generally carried out in 50-ml portions of benzene unless otherwise indicated.

Thallous Tropolonate. Thallous ethoxide (1.409 g, 5.65 mmol) was mixed with tropolone (0.690 g, 5.65 mmol). The very slightly soluble product precipitated immediately and quantitatively. A portion used for chemical analysis and melting point determinations was recrystallized from benzene; mp 278–279°. *Anal.* Calcd for $C_7H_5O_2Tl$: C, 25.83; H, 1.55. Found: C, 25.95; H, 1.39.

Bis(tropolonato)diphenyltin(IV). Thallous tropolonate (1.068 g, 3.28 mmol) and dichlorodiphenyltin(IV) (0.565 g, 1.64 mmol) were mixed with stirring. Lumps of the slightly soluble thallous tropolonate were crushed to ensure the completion of the reaction. Insoluble thallous chloride was removed by filtration. The volume was reduced to *ca.* 10 ml by means of an evaporator, 20 ml of petroleum ether was added, and the solution was allowed to stand overnight in a stoppered flask. Large yellow crystals were collected in 50% yield. Addition of larger amounts of petroleum ether increased the yield. The compound prepared in this manner is quite pure without further recrystallization if washed in petroleum ether and dried overnight in a vacuum desiccator; mp 233–234°. *Anal.* Calcd for $C_{26}H_{20}O_4Sn$: C, 60.62; H, 3.91. Found: C, 60.24; H, 3.92. Mol wt: calcd, 515; found (benzene), 538.

Bis(tropolonato)dimethyltin(IV). Thallous tropolonate (3.124 g, 9.31 mmol) and dichlorodimethyltin(IV) (1.000 g, 4.55 mmol) were mixed in benzene and allowed to react completely as indicated by the disappearance of the yellow solid, thallous tropolonate. The solution was filtered to remove thallous chloride then evaporated to dryness. The light yellow crystalline product was dissolved in a minimal amount of hot benzene (5–8 ml). Yellow crystals came down in *ca.* 80% yield when 50 ml of petroleum ether was added slowly with stirring to the cool solution; mp 186–187°. *Anal.* Calcd for $C_{16}H_{16}O_4Sn$: C, 49.15; H, 4.12. Found: C, 49.45; H, 4.13. Mol wt: calcd, 391; found (benzene), 396.

Table I. Solvent Constants at 25°

Solvent	ϵ_1	d_1	$(n_1)_D{}^a$	$10^7(B_1)_D{}^a$	$10^{14}({}_sK_1)_D{}^a$
C_6H_6	2.2725	0.87378	1.4973	0.410	7.56
CCl_4	2.2270	1.58454	1.4575	0.083	0.894
C_6H_{12}	2.0199	0.77389	1.4235	0.054	1.33

[a] Measurements made with sodium D light.

Dichlorobis(tropolonato)tin(IV). The method of preparation has been described before;[22] mp 368–370°. *Anal.* Calcd for $C_{14}H_{10}O_4Cl_2Sn$: C, 38.94; H, 2.33; Cl, 16.42. Found: C, 38.92; H, 2.48; Cl, 17.1.

Physical Constants. The constants which appear in Table I apply to the solvents at 25°. Standard notation has been used.[21]

Measurements. Incremental changes in the dielectric constants, densities, refractive indices, and Kerr constants ($\Delta\epsilon$, Δd, Δn, and ΔB, respectively) were measured for solutions having solute weight fractions w_2. The coefficients $\alpha\epsilon_1$, β, γ, and δ were derived using the relations $\alpha\epsilon_1 = \Sigma\Delta\epsilon/\Sigma w_2$, $\beta = \Sigma\Delta d/d_1\Sigma w_2$, $\gamma = \Sigma\Delta n/n_1\Sigma w_1$, and $\delta = \Sigma\Delta B/B_1\Sigma w_2$. From these data are derived[19,21] the solute dipole moments and molar Kerr constants shown in Table II. The term ${}_\infty({}_mK_2)$ which refers to the solute molar Kerr constant at infinite dilution is obtained as

$$
{}_\infty({}_mK_2) = {}_sK_1(1 - \beta + \gamma + \delta - H\gamma - J\alpha\epsilon_1)M_2 \tag{1}
$$

where ${}_sK_1$ (the specific Kerr constant of the solvent), H, and J are solvent constants;[21] M_2 is the solute molecular weight.

Discussion

Dipole Moments. Dielectric polarization measurements made on the tropolonates in benzene indicate that the complexes are highly polar. A comparison with the moments of corresponding acetylacetonates[3,4] shows very similar trends—see Table III. In general the tropolonates appear to be more polar and somewhat less soluble in benzene; the solubility of $Cl_2Sn(trop)_2$ is especially low.

Structures of the tropolonates, analogous to those considered earlier[3] for the acetylacetonates, are represented in Figures 1-3. The large moments observed for each of the complexes examined clearly indicate that the preferred solution-state configuration is, in each case, a cis-type form rather than the centrosymmetric trans configuration I which would be nonpolar. Dielectric loss measurements performed by others to be reported elsewhere[23] confirm that for each of these substances in benzene the major component of the "static" total polarization is that due to orientation effects of permanent electric dipoles.

Estimates of the group dipole moment associated with the tropolonate moiety can be extracted from the measured moments of the three tin tropolonates if it is assumed that the complexes have a regular octahedral structure and using the following component moments derived by Lorberth and Noth:[24] $\mu(\mathrm{Sn}\overrightarrow{-}\mathrm{Cl}) = 4.2$ D in tin dichloride groupings; $\mu(\mathrm{Sn}\overrightarrow{-}\mathrm{CH_3}) = 0.6$ D; $\mu(\mathrm{Sn}\overrightarrow{-}\mathrm{C_6H_5}) = 1.1$ D. The tin–tropolonate group moment follows as 2.9 D from $Cl_2Sn(trop)_2$, 2.8 D from $(CH_3)_2Sn(trop)_2$, and 3.0 D from $(C_6H_5)_2$-$Sn(trop)_2$. The values so derived are internally relatively consistent especially since small deviations from component group moment additivity must occur because of the effects of intramolecular electromeric interactions and mutual induction. Such considerations are fully in accord with the designation of a cis configuration for the complexes but the data as such are not sufficiently precise to be used to

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Table II. Dipole Moments and Molar Kerr Constants (from Observations on Solutions at 25°)

Solute[a]	Solvent	$\alpha\epsilon_1$	β	γ	δ	μ^b	$10^{12}{}_\infty({}_\mathrm{m}K_2)$	Concn range, $w_2 \times 10^5$
Tropolone	C_6H_{12}	8.39	0.297	0.14	608	3.38 ± 0.03	982 ± 20	39.1-295.5
Tropolone	CCl_4	19.4	−0.199	0.14	968	3.47 ± 0.03	1048 ± 20	29.7-189.2
$(CH_3)_2Sn(trop)_2$	C_6H_6	4.23	0.435	0.16	−143	3.65 ± 0.03	−4270 ± 200	17.5-110.1
$Cl_2Sn(trop)_2$	C_6H_6	20.0	0.481	0.14	−206	8.8 ± 0.1	−6990 ± 500	1.60-7.05
$(C_6H_5)_2Sn(trop)_2$[c]	C_6H_6	5.02	0.478	0.16		4.6 ± 0.1		82.0-313

[a] trop ≡ tropolonate. [b] Dipole moments were obtained by the "refractivity method" neglecting atomic polarization contributions greater than those implicit in the D-line molecular refractions.[19] [c] High-voltage discharge occurred in the Kerr cell and Kerr constant measurements were not made with this solute.

Table III. Comparison of Dipole Moments of Tropolonate and Acetylacetonate Complexes

Compd	μ	μ(tropolonate) − μ(corresponding acetylacetonate)
$Cl_2Sn(acac)_2$	6.77	
$Cl_2Sn(trop)_2$	8.80	2.03
$(C_6H_5)_2Sn(acac)_2$	3.78	
$(C_6H_5)_2Sn(trop)_2$	4.60	0.82
$(CH_3)_2Sn(acac)_2$	2.95	
$(CH_3)_2Sn(trop)_2$	3.65	0.70

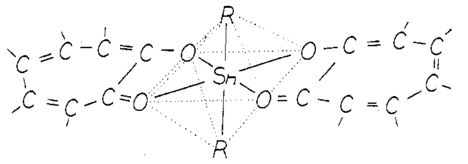

Figure 1. The trans structure.

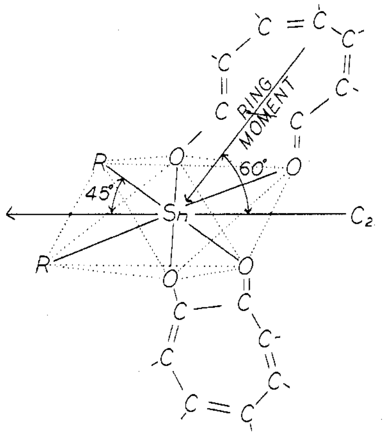

Figure 2. The C_2 cis structure.

ascertain degrees of distortion from the regular octahedral structure.

Kerr Effect Data. The molar Kerr constant may be directly related to the principal molecular optical polarizabilities, b_1, b_2, and b_3, by the Langevin-Born theory which leads[21] to

$$
{}_\mathrm{m}K = (2\pi N/405kT)[({}_\mathrm{D}P/{}_\mathrm{E}P)[(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2] + (1/kT)[(\mu_1{}^2 - \mu_2{}^2)(b_1 - b_2) + (\mu_2{}^2 - \mu_3{}^2)(b_2 - b_3) + (\mu_3{}^2 - \mu_1{}^2)(b_3 - b_1)]] \tag{2}
$$

where μ_1, μ_2, and μ_3 are the resolved parts of the permanent electric moment along the principal axes corresponding, in turn, to b_1, b_2, and b_3; ${}_\mathrm{D}P/{}_\mathrm{E}P$ is the ratio distortion polarization to electron polarization (taken as 1.1 in the subsequent calculations); N is Avogadro's number, k is the Boltzmann constant, and T is the absolute temperature. The calculations are simplified if, in the case of tropolone, the assumption is made that the in-plane polarizabilities are equal, *i.e.*, $b_1 = b_2 \neq b_3$ where b_3 is the molecular polarizability perpendicular to the plane of the molecule. Equation 2 now simplifies to

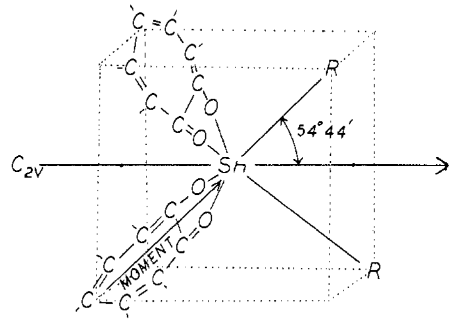

Figure 3. The C_{2v} cis structure.

Table IV. Bond and Group Polarizability Anisotropies $(b_1 - b_3)$[a]

Bond or group	$10^{24}(b_1 - b_3)$, cm^3
Tropolone	14.2
Sn-Cl	5.5
$Sn-CH_3$	5.3
Sn-O	3.5
Sn(trop)	17.7

[a] Values of $(b_1 - b_3)$ have been obtained for bonds and freely rotating groups by calculation: E. R. Lippincott and J. M. Stutman, *J. Phys. Chem.*, 68, 2926 (1964). The anisotropy of the tin tropolonate moiety was obtained by adding the measured value for tropolone to the calculated anisotropy estimates of the two Sn-O bonds (assuming that the Sn-O bonds belonging to a given tropolonate are located at 90° angles to each other).

$$
{}_\mathrm{m}K = (2\pi N/405kT)[2({}_\mathrm{D}P/{}_\mathrm{E}P)(b_1 - b_3)^2 + (1/kT)\mu_{\mathrm{obsd}}{}^2(b_1 - b_3)] \tag{3}
$$

In this way the polarizability anisotropy $(b_1 - b_3)$ of tropolone can be determined from the measured ${}_\infty({}_\mathrm{m}K_2)$ in cyclohexane and in carbon tetrachloride. The values $(b_1 - b_3)$ so obtained are respectively 14.1×10^{-24} cm^3 and 14.2×10^{-24} cm^3. A value of 14.2×10^{-24} cm^3 has been used in all subsequent calculations.

Since the main purpose of this study is the determination of the structures of tin tropolonates in solution, molecular polarizability anisotropies have been calculated for the various candidate structures (Figures 1-3) and these are used to obtain theoretical molar Kerr constants which are then compared with those actually measured. The bond and group polarizability data used in the calculations are given in Table IV. The calculations are summarized in Table V.

The Kerr effect data quite unambiguously point to a preferred cis-type structure for $Cl_2Sn(trop)_2$ and $(CH_3)_2Sn(trop)_2$. For each case the magnitude of the effect is algebraically opposite in sign to that predicted for the trans configuration. With the dimethyltropolonate derivative, distortions toward a basically "tetrahedral" structure C_{2v} (represented by Figure 3) are indicated. The interpre-

Table V. Comparison of Calculated and Measured Molar Kerr Constants for Tin Tropolonates

Candidate structure	Symmetry	$10^{24}(b_1 - b_2)$, cm^3	$10^{24}(b_1 - b_3)$, cm^3	$10^{12}{}_{\mathrm{m}}K$(calcd)	$10^{12}{}_{\mathrm{m}}K$(obsd)
trans-$(CH_3)_2Sn(trop)_2$	D_{2h}	24.5	24.5	+279	
cis-$(CH_3)_2Sn(trop)_2$	C_2	−12.2	0	−827	
cis-$(CH_3)_2Sn(trop)_2$	C_{2v}	−11.7	−23.5	−2414	−4270
cis-$Cl_2Sn(trop)_2$	C_2	−12.2	0	−5129	−6990
cis-$Cl_2Sn(trop)_2$	C_{2v}	−11.7	−23.5	−15,856	
trans-$Cl_2Sn(trop)_2$	D_{2h}	24.1	24.1	+273	

tation cannot be taken too far, however, since the highly polar tin complexes may be interacting with benzene molecules to form transient collision complexes through stereospecific associations of the benzene π systems with electron deficient sites in the complexes. Such associations would, for solute molecules of this geometry, tend to lead to apparent molar Kerr constants more negative than those of the "isolated" solute.[25]

Registry No. Tl(trop), 36487-20-4; $(C_6H_5)_2Sn(trop)_2$, 36487-15-7; $(CH_3)_2Sn(trop)_2$, 21844-38-2; $Cl_2Sn(trop)_2$, 36544-14-6; Htrop, 533-75-5.

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Circular Dichroism of Chromium(III) Complexes. III.[1] Preparation, Optical Resolution, and Ultraviolet Circular Dichroism Spectra of Mixed Complexes Containing α-Diimines or Ethylenediamine and Acetylacetonate or Its 3-Halogeno Derivatives

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Nine new optically active chromium(II) complexes have been characterized by elemental analysis, infrared spectra, and visible and ultraviolet absorption and circular dichroism (CD) spectra; these are $(-)_{589}[(dip)(phen)Cr(OH)_2Cr(dip)(phen)]^{4+}$, $(-)_{589}[Cr(ox)(dip)(phen)]^+$, $(+)_{546}[Cr(acac)(en)_2]^{2+}$, $(+)_{546}[Cr(acac)_2(en)]^+$, and the corresponding 3-chloro- or 3-bromoacetylacetonato complexes (dip = 2,2′-dipyridyl, phen = 1,10-phenanthroline, acac = acetylacetonate). The mixed α-diimine complexes show the theoretically anticipated exciton CD splitting in their long-axis-polarized $\pi-\pi^*$ transition region. From the comparison of the ultraviolet absorption and CD spectra for the acetylacetonato and 3-halogenoacetylacetonato complexes, the assignment for six CD bands in the ultraviolet region of the bis-acetylacetonato complex has been attempted. The absolute configuration determined on the basis of the exciton CD bands of the present complexes coincided with that based on the dominant CD component in the first d–d absorption band region.

Introduction

There have been a number of studies on transition metal complexes with the ligands containing unsaturated π-electron systems such as α-diimines[2] or β-diketones.[3] The correlations between the circular dichroism (CD) spectra and the absolute configurations of such complexes have been intensively pursued from a stereochemical and spectroscopical viewpoint.[4-8] The coupling between three or two of the same ligands having a long-axis-polarized π-π^* transition, in a dihedral complex, gives rise to a helical charge displacement and causes zeroth-order intrinsic rotational strengths.[4] On the basis of the exciton model dealing with such dipole–dipole coupling, the absolute configurations of the complexes have been nonempirically determined from the CD splitting in the intraligand π-π^* transition region.[4] The exciton splitting is expected to be observed also in the case of mixed complexes such as $[M(dip)_2(phen)]^{n+}$ or $[M(dip)(phen)_2]^{n+}$ (dip = 2,2′-dipyridyl; phen = 1,10-phenanthroline), because such a dipole–dipole coupling occurs not only between the ligands of one kind but also between the nonidentical ligands.[4,7,8] In fact, the CD spectra of these complexes in the ligand transition

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