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Crystal Structure and Polarized Electronic Spectra for Diruthenium Tetraacetate Chloride

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A crystal structure determination of $Ru_2(O_2CCH_3)_4Cl$ indicates an $I2/m$ unit cell, with a:b:c = 8.207 (2):7.440 (2):11.320 (3), β = 95.46 (5)°, and Z = 2. $Ru_2(O_2CCH_3)_4^+$ ions alternate with Cl^- ions to form linear chains with Ru–Ru = 2.287 (2) Å and Ru–Cl = 2.577 (1) Å. Polarized absorption spectra were recorded at 300 and 5 K for a $\bar{1}01$ face of a single crystal which provide exact $\parallel z$ and $\perp z$ molecular polarizations. For $\parallel z$ polarization, the intensity was too high to measure at energies above 19 100 cm^{-1}. However, a shoulder was clearly apparent at 19 000 cm^{-1} in this polarization. For the x,y polarization, the absorption was measurable from 12 000 to 30 000 cm^{-1}. Two bands at 17 900 and 22 500 cm^{-1} are weak, but their temperature dependence indicated dipole-allowed character. Assignments of the transitions are discussed.

Introduction

Stephenson and Wilkinson[1] reported the preparation of dimeric complexes of ruthenium with bridging carboxylate ligands in 1966. The formulas of the compounds indicated mixed +2, +3 oxidation states for the ruthenium, and the high magnetic moments corresponded to three unpaired electrons per dimeric unit. The existence of the bridged dimeric units was proven by the X-ray diffraction crystal structure determination of Cotton et al.[2] for the butyrate compound. They found that the dimeric complexes had chlorides coordinated at terminal positions. Each chloride bridged two dimeric units. Since the Ru–Cl–Ru angle was 125°, the structure was composed of intermeshed zigzag chains of dimers linked by the chlorides. In the meantime, Norman et al.[3] have performed self-consistent-field scattered-wave Xα calculations for the $Ru(O_2CH)_4^+$, $Ru(O_2CH)_4{\cdot}2H_2O^{2+}$, and $Ru(O_2CH)_4Cl_2^-$ species. Stephenson and Wilkinson's procedure yielded a microcrystalline product, $Ru_2(O_2CCH_3)_4Cl$, with acetate bridges. However, very recently Cotton et al.[4] reported procedures for preparation of and crystal structures for five compounds of carboxylate-bridged $Ru^{II,III}$ dimers which included the $Ru_2(O_2CCH_3)_4(H_2O)_2^+$ cation and the $Ru_2(O_2CCH_3)_4Cl_2^-$ anion. Also included was the hydrate, $Ru_2(O_2CCH_3)_4Cl{\cdot}2H_2O$. We have recently modified Stephenson and Wilkinson's procedure to prepare single crystals of the anhydrous $Ru_2(O_2CCH_3)_4{\cdot}Cl$ as highly dichroic thin platelets which were therefore ideal for single-crystal spectroscopy. The present paper reports the crystal structure and the polarized optical spectra of these crystals.

Experimental Section

Preparation of $Ru_2(O_2CCH_3)_4Cl$. $RuCl_3{\cdot}xH_2O$ (0.13 g) was dissolved in a solution of 15 mL of glacial acetic acid and 3 mL of acetic anhydride. *o*-Dichlorobenzene (25 mL) was added, and the solution was allowed to reflux for 1 h under a slow stream of oxygen as the solution turned from dark brown to dark green. A dark brown solid was filtered off and discarded. Refluxing under an oxygen flow was continued for two 5-h periods. After each period the solution was cooled slowly, and a normal microcrystalline preparation of $Ru_2(O_2CCH_3)_4Cl$ was filtered from the solution. After the second filtration, the precipitate was washed with a very limited amount of methanol. The filtrate with the wash solution was set aside for later recovery. Some 3 months later, it was noted that a small quantity of crystals had settled from this solution. The crystals were collected on a filter, washed with a small amount of methanol, and dried immediately. From this batch were selected the crystals for spectroscopy and for X-ray diffraction.

Structure Determination. A small irregular platelet (0.32 × 0.15 × 0.02 mm) was mounted on a four-circle diffractometer interfaced with a PDP-15 computer.[5] Rotation photographs indicated that the crystal was of satisfactory quality. The local program ALICE prepared by Jacobson[5] was used to index automatically all reflections and select a monoclinic set of axes. Graphite-monochromated Mo Kα X radiation (λ = 0.710 02 Å, determined by calibration with NaCl) was used for data collection. A scan rate of 0.5 s/step of 0.01° in ω was employed with the scan range dependent on peak width. Stationary-crystal, stationary-background counts were taken at the beginning and end of each scan. All data within $2\theta < 50°$ in four octants were collected. Data were collected for 1428 points with no restrictions on hkl. Since no significant intensity had been recorded for a reflection $h + k + l = 2n + 1$, the remaining 741 reflections were measured with the constraint $h + k + l = 2n$. The unit cell dimensions were obtained from a least-squares fit of 13 strong lines with $25° < 2\theta < 37°$. The condition $h + k + l = 2n$ implies the existence of a body-centered cell. However, a change of axes will give a C-centered cell so the possible space groups were indicated to be $C2$, $C2/c$, and $C2/m$. The condition $l = 2n$ for $h0l$, required for $C2/c$, was not observed. A refinement of the structure was therefore performed under $C2/m$ with a higher symmetry than $C2$. The refinement was actually performed under the equivalent $I2/m$ space group for comparison with the structure of the dihydrate reported by Cotton et al.[4] For the body-centered cell, a:b:c = 8.207 (2):7.440 (2):11.320 (3)Å, β = 95.46 (5)°, V = 688.1 Å^3, Z = 2, and d(calcd) = 2.286 g/cm^3. Lorentz and polarization corrections were applied to the intensities, but absorption corrections were omitted. All the atom positions except hydrogen could be obtained from a three-dimensional Patterson function. The anisotropic refinement without inclusion of hydrogens converged to very satisfactory final residuals, R = 0.037, where $R = (\sum||F_o| - |F_c||)/\sum|F_o|$, and R_w = 0.048, where $R_w = [\sum w(|F_o| - |F_c|)^2/\sum F_o^2]^{1/2}$. No significant peaks remained on a final electron density map.

Spectral Measurements. The crystal spectra were recorded by a Cary spectrophotometer, Model 14, according to procedures that have been described previously.[6] For low temperatures an Andonian Associates liquid-helium Dewar equipped with platinum and germanium resistance thermometers was employed. An R928 photomultiplier tube in the Cary spectrophotometer permitted spectral measurements out as far as 800 nm. The thickness of a crystal platelet was measured to be 12 μ by means of a scale in a microscope eyepiece. Molar absorptivities, ϵ, were calculated by dividing the measured absorbances by the product of the crystal thickness times the molar concentration in the crystal (4.83 M). The faces of platelets were identified upon the four-circle diffractometer. It was found that the instructions to call the $\bar{1}01$ reflection into diffraction would bring the

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Table I. Positional and Thermal Parameters[a] and Their Standard Deviations for $Ru_2(O_2CCH_3)_4Cl$

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{22}
Ru	0.0	0.1537 (1)	0.0	94 (1)	31 (2)	40.1 (7)	0	5.6 (7)	0
Cl	0.0	0.5	0.0	145 (7)	75 (7)	57 (3)		48 (4)	0
O(1)	0.2344 (6)	0.1493 (8)	0.0727 (4)	106 (8)	63 (9)	62 (5)	−18 (8)	2 (5)	1 (6)
O(2)	0.0735 (6)	0.1475 (8)	−0.1646 (4)	112 (8)	64 (9)	54 (4)	−1 (8)	19 (4)	14 (6)
C(1)	0.3037 (14)	0.0	0.0969 (10)	104 (18)	54 (20)	52 (9)	0	10 (10)	0
C(2)	0.0906 (13)	0.0	−0.2163 (9)	89 (17)	73 (20)	48 (9)	0	1 (10)	0
C(3)	0.4729 (14)	0.0	0.1593 (12)	93 (19)	135 (26)	84 (13)	0	−24 (12)	0
C(4)	0.1281 (19)	0.0	−0.3439 (10)	262.31	108 (25)	39 (10)	0	39 (14)	0

[a] Anisotropic thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \times 10^{-4}]$.

Table II. Bond Distances (Å) and Bond Angles (Deg) for $Ru_2(O_2CCH_3)_4Cl$

Distances			
Ru-Ru	2.287 (2)	O(1)-C(1)	1.266 (8)
Ru-Cl	2.577 (1)	O(2)-C(2)	1.258 (8)
Ru-O(1)	2.019 (5)	C(1)-C(3)	1.50 (2)
Ru-O(2)	2.014 (5)	C(2)-C(4)	1.50 (2)
Angles			
Ru-Ru-O(1)	89.1 (2)	Ru-O(1)-C(1)	119.6 (6)
Ru-Ru-O(2)	88.7 (2)	Ru-O(2)-C(2)	120.4 (6)
O(1)-Ru-O(1)	178.1 (3)	O(1)-C(1)-O(1)	122.6 (10)
O(2)-Ru-O(2)	177.4 (3)	O(1)-C(1)-C(3)	118.7 (5)
O(1)-Ru-O(2)	91.1 (2)	O(2)-C(2)-O(2)	121.6 (10)
		O(2)-C(2)-C(4)	119.2 (5)

face of the platelets into the reflecting position. The monoclinic symmetry axis, *b*, lies in this face so the vibrations of the electromagnetic waves traversing the crystal with normal incidence were polarized either parallel to or perpendicular to this *b* axis.

Results and Discussion

Crystal Structure. The atomic positions in the unit cell and the thermal parameters are recorded in Table I. Significant bond distances and angles between bonds are listed in Table II.

The structure is very similar to that of the $Ru_2(O_2CCH_3)_4Cl \cdot 2H_2O$ reported by Cotton et al.[4] in that the dimeric ions alternate with chloride ions along the *b* axis of a monoclinic structure to give linear chains. The *b* axis is 0.041 (3) Å longer than in the hydrate. (The axes of the hydrate are *a*:*b*:*c* = 9.223 (1):7.399 (1):11.143 (1); β = 93.60 (1)°.) Hence the principal difference in the two structures is the longer *a* axis of the hydrate, which permits the water molecules to be packed between the dimer ions. The site symmetry for the dimers is strictly C_{2h}. There are some deviations from the ideal D_{4h} molecular symmetry which are apparently due to packing stresses. Although the planes defined by the two oxygens of a carboxylate and the metal–metal bond form an angle of 91 (1)°, the angle between planes, defined by the carboxylate OCO groups, is 98 (1)°. The Ru–Ru distance is 0.020 Å longer and the Ru–Cl distance is 0.011 Å longer than the corresponding values in the hydrate. These differences are somewhat greater than 3σ and presumably are the consequence of somewhat different packing stresses.

Crystal Spectra. The small platelets with the $\bar{1}01$ face were strongly dichroic, with a deep red color for light polarized $\|b$ and pale violet for light polarized $\perp b$. With the orientation of the dimeric complexes, the light polarized parallel to the *b* axis is also parallel to the molecular *z* axis which lies along the metal–metal bond. If the D_{4h} symmetry were not perturbed, absorption of light polarized perpendicular to the *b* axis would correspond to the molecular *x*,*y* absorption. The energy states will be discussed in terms of the idealized D_{4h} molecular symmetry, but it is recognized that some caution is needed because of the lower crystallographic site symmetry. However, a *z*-polarized transition should strictly have no intensity for the polarization perpendicular to the *b* axis, and an *x*- or *y*-polarized transition should have no intensity for the polarization parallel to the *b* axis. It is possible that the degeneracies of the transitions with *x*,*y* polarization under D_{4h} may be broken.

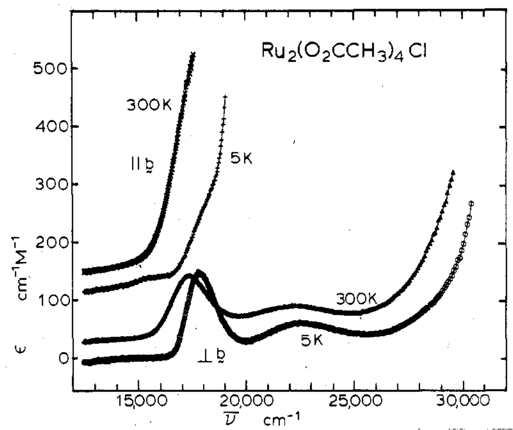

Figure 1. Polarized single-crystal spectra for $Ru_2(O_2CCH_3)_4Cl$. Spectra recorded for a crystal 12 μ thick.

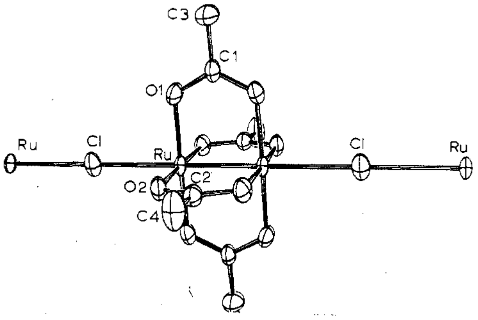

Figure 2. Sketch of the dimeric unit with the terminal chlorides and Ru atoms of adjacent complexes. Unlabeled atoms are related to labeled ones by C_{2h} symmetry.

Spectra for a crystal of $Ru_2(O_2CCH_3)_4Cl$, 12 μ thick, at 300 and 5 K are shown in Figure 1. There is apparently an intense absorption in $\|b,z$ polarization. The molar absorptivity which is very low at 12 500 cm^{-1} rises to above 300 cm^{-1} M^{-1}, the instrumental limit, at 17 000 cm^{-1} at 300 K and 19 000 cm^{-1} at 5 K. For the $\perp b$ polarization the absorption is easily measurable from 12 500 out to 30 000 cm^{-1}. The strongest feature is a band with a maximum of 153 cm^{-1} M^{-1} at 17 800 cm^{-1} for 5 K. The oscillator strength of the band was estimated to be 9 × 10^{-4} by the formula $f = 4.6 \times 10^{-9}\epsilon_{\max}\bar{\nu}_{1/2}$, where $\epsilon_{\max}$ is the maximum molar absorptivity and $\bar{\nu}_{1/2}$ is bandwidth at half-height. There is also a shorter but broader peak with a maximum at 22 500 cm^{-1} with the indicated oscillator strength of 4 × 10^{-4}. It is noted that the bands narrow as the temperature decreases from 300 to 5 K but increase in height so their intensity is virtually unchanged. Thus, although their intensity is comparable to what might be expected for a vibronically excited transition, the lack of a temperature dependence for the intensity indicates they are both dipole-allowed although weak transitions. In the 5 K, $\|b,z$ spectrum there is clearly a shoulder at ca. 18 000 cm^{-1}. This shoulder is on a rapidly rising portion of the spectrum. However, since the intensity is no greater at this point than for the $\perp b$ absorption, the 17 800-cm^{-1} component in x,y polarization must be more intense than that in z polarization.

For the $\perp b$ polarization there was no increase in absorption from 12 500 to 16 000 cm^{-1}, with a molar absorptivity greater than 10 cm^{-1} M^{-1}. For the $\|b$ polarization there is a shoulder at 16 000 cm^{-1}, corresponding to about 20 cm^{-1} M^{-1}. Such a weak absorption is subject to some doubt because of uncertainties in the base lines for small pinholes. For such a component a scan of a thicker crystal would be desirable; however, no crystals with substantially greater thickness of suitable optical quality were available. This shoulder did appear for several crystal mountings and spectral scans.

There has been considerable speculation concerning the electronic configuration of the $Ru_2(O_2CCH_3)_4^+$ complex. The indication of three unpaired electrons, a quartet state, suggested the occupation of three orbitals of approrioximately equal energy. Cotton and co-workers[2] had originally suggested the electronic configuration $\sigma_n\sigma_{n'}\delta^*$ ($a_{1g}a_{2u}b_{1u}$) for the ground state. However, from their recent scattered-wave Xα calculation, Norman et al.[3] concluded that the σ_n and $\sigma_{n'}$ orbitals were of much higher energies but that the Ru–Ru π^* and δ^* orbitals were of comparable energy. They have suggested the configuration would be $(\pi^*)^2\delta^*$ ($e^2{}_g b_{1u}$), which would yield a $^4B_{2u}$ ground state.

A spectrum for a solution of $Ru_2(O_2CCH_3)_4Cl$ in D_2O was reported by Wilson and Taube.[7] This is undoubtedly the spectrum for a hydrated ion. The principal feature was a peak with a maximum of 699 cm^{-1} M^{-1} at 23 500 cm^{-1}. At transition energies below 17 200 cm^{-1}, the molar absorptivity was observed not to fall below 40 cm^{-1} M^{-1}. This general absorption extended from about 7700 to 17 000 cm^{-1}. There was a small peak at about 10 000 cm^{-1} with an ϵ_{max} about 20 cm^{-1} M^{-1} above this general absorption. It was noted that in a KCl pellet containing $Ru_2(O_2CCH_3)_4Cl$ the 10 000-cm^{-1} peak was resolved into two components, one at 10 400 cm^{-1} and the other at 9000 cm^{-1}.

Clark and Franks[8] in an investigation of resonance Raman spectra of the compound included a diffuse-reflectance spectrum of $Ru_2(O_2CCH_3)_4Cl$ which had a maximum at 21 600 cm^{-1} with a shoulder at 17 500 cm^{-1}. This maximum differs by 1900 cm^{-1} from the D_2O solution peak. Clark and Franks noted that the resonance Raman spectrum of the solid, excited by a 19 440-cm^{-1} line, indicated an enhancement of the a_{1g} ruthenium–ruthenium stretching mode with, indeed, a progression based on this vibration in contrast to the normal Raman spectrum. They therefore concluded that the 21 600-cm^{-1} band corresponded to an electric-dipole-allowed transition and proposed that it was the Ru(δ) → Ru(δ^*) ($b_{2g} \rightarrow b_{1u}$) transition. They also favored the $(\pi^*)^2\delta^*$ ground-state configuration.

In their scattered-wave, Xα calculations, Norman et al.[3] treated both the free $Ru_2(O_2CH)_4^+$ and $Ru_2(O_2CH)_4Cl_2^-$ species. Their computations place a $\delta \rightarrow \delta^*$ transition at 8800 cm^{-1}, and accordingly they assign this transition to the 10 400-cm^{-1} component observed by Wilson and Taube[7] in the KCl pellet rather than to the 21 600-cm^{-1} band. Our polarized crystal spectra show that the 21 000-cm^{-1} band clearly has $\|b,z$ polarization. This is the polarization expected for the $\delta \rightarrow \delta^*$ transition. However, we concur with Norman et al.[3] that this is unlikely to be the $\delta \rightarrow \delta^*$ transition. There is strong evidence[9] that the first absorption band observed in $Mo_2(O_2CCH_3)_4$ is the $\delta \rightarrow \delta^*$ transition. This band is considerably less intense in the molybdenum compond than the 21 600-cm^{-1} transition of $Ru_2(O_2CCH_3)_4Cl$. However, the $\delta \rightarrow \delta^*$ transition is expected to be much less intense in the ruthenium dimer, with its 2.287 Å metal–metal bond, than in the molybdenum(II) acetate with its 2.093 Å bond.[10]

Norman et al. assigned the 21 600-cm^{-1} band to the transition $e_u \rightarrow \pi^*$ (e_g). There are four excited $e_u \rightarrow e_g$ quartet states, but only one transition is dipole allowed, $^4B_{2u} \rightarrow {}^4B_{1g}$, with z polarization. The e_u orbitals contain mostly an oxygen contribution, but they were calculated to contain 24% of the charge on the Ru atoms; that is, they contain appreciable contribution from the Ru–Ru π-bonding orbitals. The relatively modest intensity of this dipole-allowed transition would be a consequence of this minor involvement of metal atoms in the e_u orbitals, as well as the relatively long metal–metal distance. Such a transition which is dipole allowed in z polarization should be vibronically allowed with x,y polarization by coupling with e_g vibrations. The presence of such a vibronically allowed peak at 21 600 cm^{-1} in this region would be somewhat obscured by the broad band at 22 500 cm^{-1}, and no evidence of a peak at 21 600 cm^{-1} can be discerned.

The weak peak at 17 800 cm^{-1}, dipole allowed in $\perp b$ polarization, is not likely a spin-forbidden transition, because its intensity is so high, although dipole-allowed character would be possible in both z and x,y polarizations as a consequence of spin–orbit coupling for $e_u \rightarrow \pi^*$ (e_g) transitions. Norman et al. placed Cl (e_u) → π^* (e_g) (z polarized) at 13 500 cm^{-1}, Cl (e_g) → δ^* (b_{1u}) (x,y polarized) at 16 000 cm^{-1}, and Cl (a_{2u}) → π^* (e_g) (x,y polarized) at 18 700 cm^{-1}. All of these transitions should be quite weak, because of the long Ru–Cl distance of 2.577 Å. The latter would probably be the most intense of these three transitions and could perhaps account for the 17 800-cm^{-1} band as they assigned it. The somewhat weaker absorption in z polarization at nearly the same energy would then have to be attributed to some other dipole-forbidden transition at about the same energy.

The calculations of Norman et al. placed three transitions, dipole-allowed by x,y polarization, at 23 000, 24 100, and 24 700 cm^{-1}, respectively. The 24 100-cm^{-1} transition was essentially the Ru–Ru π^* (e_g) → Ru–Ru σ^* (a_{2u}) transition with the orbitals primarily on the metals. It seems that such a transition should be much too intense to account for the peak at 22 500 cm^{-1}. From the spectrum recorded for $\perp b$ at 5 K, the π^* (e_g) → σ^* (a_{2u}) transition would therefore have to be above 30 000 cm^{-1}. On the other hand, the other two transitions were indicated to be 0 → π^* (e_g) and should probably be of suitable intensity for the broad 22 500-cm^{-1} band. The presence of these two transitions close together would account for the width of this band.

Some of the spectral results are therefore rationalized reasonably well on the basis of the scattered-wave Xα theory. There is a satisfactory explanation of one moderately intense band with z polarization from 12 500 to 25 000 cm^{-1} as observed. The presence of electric-dipole-allowed but weak absorption bands are also accounted for. The calculation does place what should be an intense x,y-polarized transition at least 7000 cm^{-1} below where it can occur in the observed crystal spectra. Of course, it should be remembered that the calculation treats the finite $Ru_2(O_2CH)_4Cl_2^-$ species, which is a somewhat different situation. Since some of the bands are assigned to Cl–Ru charge-transfer transitions, it would be especially valuable to have spectra of the complex with terminal aquo ligands. Also, it would be desirable to grow the somewhat larger crystals which would be needed to extend the

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absorption measurements further into the near-infrared region.

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Supplementary Material Available: Table of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

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Preparation and Molecular Structure of Bis[2-[(dimethylamino)methyl]phenyl]chloroindium(III), a Five-Coordinate Diorganoindium Complex

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The neutral complex L_2InCl (L = 2-[(dimethylamino)methyl]phenyl) is the only product isolated from the reaction between $InCl_3$ and LiL in diethyl ether. The absolute configuration has been established by a complete three-dimensional X-ray diffraction study. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 9.351$ (1) Å, $b = 10.411$ (2) Å, $c = 19.092$ (4) Å, and $V = 1858.7$ Å^3. Diffraction data were collected with a Syntex $P2_1$ automated diffractometer using graphite-monochromatized Mo Kα radiation. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations; final discrepancy indices are $R_F = 0.015$ and $R_{wF} = 0.022$ for 1729 observed reflections. The crystal structure shows that the molecule has distorted trigonal-bipyramidal stereochemistry with an InC_2Cl equatorial plane (In–Cl = 2.465 (1) Å, In–Cl(1) = 2.144 (3) Å, In–C(21) = 2.154 (3) Å) and apical In–N bonds (In–N(1) = 2.442 (Å) and In–N(2) = 2.482 (2) Å).

Introduction

X-ray crystallographic studies are now providing an increasing amount of information on the stereochemical properties of the coordination compounds of indium(III). Most of the inorganic structures which have been determined have proven to be tetrahedral (e.g., $InCl_4^-$),[1] octahedral ($InCl_6^{3-}$),[2] or substitution derivatives of these stereochemistries such as $[InI_2(Me_2SO)_4]^+$ (Me_2SO = dimethyl sulfoxide),[3] $[InCl_4(H_2O)_2]^-$,[4] or $[InCl_5(H_2O)]^-$.[5] This field was reviewed[6] in 1975, and a discussion of the structural results for neutral and anionic chloro complexes has been given elsewhere.[2] Only two five-coordinate indium(III) compounds have been identified by X-ray methods, although a number of such structures have been proposed on the basis of spectroscopic or other evidence. The neutral adduct $InCl_3{\cdot}2Ph_3P$ has D_{3h} symmetry in the coordination kernel with apical phosphine ligands.[7] The anion $InCl_5^{2-}$ has a square-based pyramidal structure,[8] and while there has been some discussion about the details of this structure,[9] it is clear that the stereochemistry differs markedly from those of the isoelectronic neighbors $CdCl_5^{3-}$ and $SnCl_5^-$, which have D_{3h} symmetry.[10,11]

Distorted trigonal-bipyramidal geometries have been observed by X-ray techniques for a number of triorgano- [$(CH_3)_3In$[12] and $(C_6H_5)_3In$[13]], diorgano- [$(C_2H_5)_2InOSC(CH_3)$[14] and $(CH_3)_2In(ON{=}CHC_5H_4N)$[15]], and organoindium compounds [$(CH_3InCl_2)_2$].[16] For each of these compounds pentacoordination results from intermolecular association. We now report the structure of bis[2-[(dimethylamino)methyl]phenyl]chloroindium(III) as the first example of an organoindium compound which has a trigonal-bipyramidal geometry as a result of intramolecular coordination. The preparation and molecular structure determination of this compound are described below. Other related preparative work and dynamic NMR studies of the solution behavior will be discussed elsewhere.

Experimental Section

Preparative Data. When freshly prepared [2-[(dimethylamino)methyl]phenyl]lithium (0.22 mol) in diethyl ether was added dropwise to a suspension of indium(III) chloride (24.0 g, 0.11 mol) in the same solvent (100 cm^3), an exothermic reaction lasting about 45 min occurred and a brown suspension formed. The reaction mixture was stirred for 24 h at room temperature, after which the suspended solid was collected by filtration. This solid was extracted with 3 × 100 cm^3 of benzene; when the volume of the bulk washings was reduced to 50 cm^3 by distilling off the solvent, a white solid was obtained, which was collected, washed with cold petroleum ether (bp 30–60 °C) and

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