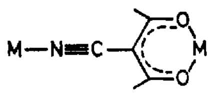
Bis(3-cyanopentane-2,4-dionato)dihalogenotin(IV) Complexes

By **Frank S. Delk** and **David W. Thompson**,* Department of Chemistry, College of William and Mary, Williamsburg, Virginia 23185, U.S.A.

Bis(3-cyanopentane-2,4-dionato)dihalogenotin(IV) complexes, $SnX_2(cpd)_2$ (X = Cl, Br, or I), have been prepared. While the 3-cyanopentane-2,4-dionate anion is a trifunctional ligand, spectral data are consistent with the $SnX_2(cpd)_2$ complexes being six-co-ordinate having oxygen-chelated β-diketonate ligands; evidence does not suggest a metal–cyanide interaction.

THE 3-cyanopentane-2,4-dionate anion (cpd) is a ligand of potential interest because of its planar structure and the presence of two oxygen and one nitrogen donor atoms. This trifunctional character within the planar framework gives rise to the possibility of an uncommon metal–ligand bridging interaction of the type (I). Indeed, we have found evidence for this bridging structure in a few cpd complexes of tin(IV), titanium(IV), and zirconium(IV).[1] Other cpd complexes have been reported[2] including those for iron(III), manganese(III), copper(II), chromium(III), aluminium(III), and zinc(II) for which no unusual properties or trifunctional bridge bonding was reported.



(I)

In this paper we report the synthesis and characterisation of $SnX_2(cpd)_2$ (X = Cl, Br, or I) complexes.

EXPERIMENTAL

Reagents.—Pentane-2,4-dione and thallium ethoxide were purchased from Aldrich and Ventron-Alfa, respectively, and used without further purification. 3-Cyanopentane-2,4-dione was synthesised as previously reported[1b, 3, 4] and purified by vacuum sublimation at 40 °C. Tin tetrachloride was obtained from Fischer and distilled prior to use; tin tetrabromide and tetraiodide were obtained from Ventron-Alfa and used without further purification. All solvents were distilled under nitrogen from either calcium hydride or phosphorus pentaoxide and stored over 4A molecular sieves.

Preparation of Tl(cpd).—3-Cyanopentane-2,4-dione (4.9 g, 39 mmol) dissolved in benzene (20 cm^3) was added dropwise with stirring to a solution of thallium ethoxide (9.7 g, 39 mmol) in benzene (30 cm^3) held at 0 °C. Upon addition of the ligand solution a dense white precipitate formed. The reaction mixture was stirred for 4 h. The product was filtered off, washed with benzene, and dried under vacuum at 22 °C. I.r., $\nu_{max.}$ (Nujol): 2 192s, 1 610vs, br, 1 542m, 1 370s, 1 346s, 1 168w, 1 031m, 1 018m, 984m, 903m, 673w, 650m, 600m, 549w, 541w, 511s, and 399m cm^{-1}.

Preparation of $SnCl_2(cpd)_2$.—All manipulations were carried out under an atmosphere of dry nitrogen or *in vacuo* in modified Schlenk-type glassware.[5] Solvents and reagents were transferred under nitrogen using syringe techniques and a Vacuum Atmospheres Dri-Lab.

Tin tetrachloride (1.06 cm^3, 9.00 mmol), dissolved in CH_2Cl_2 (25 cm^3), was added dropwise to a slurry of Tl(cpd) (6.0 g, 18 mmol) in CH_2Cl_2 (40 cm^3). The resulting cream coloured solution was heated at reflux for 12 h. TlCl was filtered from the hot solution. Addition of hexane (80 cm^3) and standing overnight at 5 °C yielded a crystalline yellow product in high yield, m.p. 207—209 °C (decomp.) [Found: C, 32.6; H, 2.70. $SnCl_2(C_6H_6O_2N)_2$ requires C, 32.9; H, 2.75%]. I.r., $\nu_{max.}$ (Nujol): 2 228 slight splitting, 1 575vs, vbr, 1 418s, 1 375s, 1 340s, 1 297m, 1 199m, 1 178w, 1 043w, 1 018m, br, 937s, 717m, 660m, 633m, 563w, 535m, 452s, and 410m cm^{-1}.

Preparation of $SnBr_2(cpd)_2$.—This compound was prepared in the same way as the dichloro-analogue using $SnBr_4$ (8.2 mmol) and Tl(cpd) (16.5 mmol). A light orange solid product was isolated, m.p. 205—207 °C (decomp.) [Found: C, 27.45; H, 2.15. $SnBr_2(C_6H_6O_2N)_2$ requires C, 27.35; H, 2.30]. I.r., $\nu_{max.}$ (Nujol): 2 228 slight splitting, 1 572vs, br, 1 419s, 1 375s, 1 340s, 1 296m, 1 199m, 1 177w, 1 042w, 1 021m, br, 937s, 716m, 661m, 631m, 563w, 534m, 448s, and 410m cm^{-1}.

Preparation of $SnI_2(cpd)_2$.—Using the procedures described above, SnI_4 (9.6 mmol) and Tl(cpd) (19.2 mmol) were allowed to react. A yellow product was isolated, m.p. 232—234 °C with some prior decomposition beginning at 224 °C [Found: C, 23.3; H, 1.95. $SnI_2(C_6H_6O_2N)_2$ requires C, 23.35; H, 1.95]. I.r., $\nu_{max.}$ (Nujol): 2 227 slight splitting, 1 578 vs, br, 1 412m, 1 368s, 1 341s, 1 297m, 1 196m, 1 173m, 1 040w, 1 017m, 933s, 712m, 656m, 637m, 560w, 534m, 443s, and 409m cm^{-1}.

Characterisation.—Infrared spectra were determined with a Perkin-Elmer model 457 spectrophotometer; the instrument was calibrated with atmospheric CO_2. All products were examined as mulls in Nujol between KBr plates. Hydrogen-1 n.m.r. spectra were obtained with Hitachi–Perkin-Elmer R-20B and Varian FT-80A spectrometers. Samples for physical measurements were prepared in a Vacuum Atmospheres Dri-Lab under nitrogen.

RESULTS AND DISCUSSION

The reaction of $SnCl_4$ with pentane-2,4-dione under reflux in benzene or chloroform leads readily and only to *cis*-dichlorobis(pentane-2,4-dionato)tin(IV), $SnCl_2(pd)_2$;[6] no evidence has been reported for a tri- or mono-substituted pentane-2,4-dionate product, *e.g.* $SnCl(pd)_3$ or $SnCl_3(pd)$. Thus we were surprised that the reaction of $SnCl_4$ with 3-cyanopentane-2,4-dione in a 1 : 2.5 mol ratio in refluxing benzene gave only $SnCl_3$-

(cpd);[1a] this product is stabilised presumably by trifunctional bridge-bonding of the organic ligand. The desired $SnX_2(cpd)_2$ complexes were prepared in a straightforward manner by the reaction of Tl(cpd) with the appropriate tin tetrahalide in a 1 : 2 mol ratio.

The i.r. spectra of the title complexes unambiguously established the presence of oxygen-chelated β-diketonate ligands with very strong characteristic bands $\nu(C\overset{\cdots}{-}O)$ and $\nu(C\overset{\cdots}{-}C)$ in the 1 550—1 600 cm^{-1} region. The complexes also show ν(Sn–O) frequencies at 451, 448, and 441 cm^{-1} which are to be compared with bands at 461, 458, and 448 cm^{-1} in the $SnX_2(pd)_2$ series. The ν(Sn–O) shifts suggest that the presence of the electron-withdrawing cyano-group weakens slightly the Sn–O bonds.[6a, 7]

The three $SnX_2(cpd)_2$ complexes exhibit bands in the ν(C≡N) region at 2 228, 2 228, and 2 226 cm^{-1}, respectively. Each band is split by *ca.* 5 cm^{-1}; this splitting was also observed for $TiCl_2(cpd)_2$.[1a] In free 3-cyanopentane-2,4-dione we observe ν(C≡N) to be at 2 219 cm^{-1} (Nujol) which agrees with other observed values of 2 220.4 ($CHCl_3$) and 2 218.9 (KBr).[2a] In the $SnX_2(cpd)_2$ complexes in the solid state Δν(C≡N) is 6—8 cm^{-1} toward higher energy relative to the free nitrile. While the direction of the shift on co-ordination is in the direction expected for a metal–nitrile interaction, we do not favour CN co-ordination in these complexes because the solution i.r. spectra ($CHCl_2CHCl_2$) show CN stretching bands at virtually identical positions to those in the solid state, and the ^1H n.m.r. spectra (see below) are clearly consistent with the $SnX_2(cpd)_2$ complexes having monomeric six-co-ordinate structures in solution.

Hydrogen-1 n.m.r. data for $SnX_2(cpd)_2$ complexes

Complex	$\delta(CH_3)$[a,b]		T_c[c]/K
$SnCl_2(cpd)_2$	2.07	2.58	328
$SnBr_2(cpd)_2$	2.46	2.56	327
$SnI_2(cpd)_2$	2.41	2.52	309
$SnCl_2(pd)_2$	2.11	2.20	355
$SnBr_2(pd)_2$	2.10	2.19	351
$SnI_2(pd)_2$	2.07	2.17	334

[a] Slow exchange limit. For $SnX_2(cpd)_2$ complexes the solvent is 1,1,2,2-tetrachloroethane; for $SnX_2(pd)_2$ complexes the solvent is deuteriated chloroform. Chemical shifts are relative to $SiMe_4$. [b] Data for $SnX_2(pd)_2$ complexes are taken from reference 6*b*. [c] Coalescence temperature. For $SnX_2(pd)_2$ complexes coalescence temperatures are from reference 6*a*.

Hydrogen-1 n.m.r. data for the title complexes are presented in the Table along with data for the $SnX_2(pd)_2$ complexes for comparison. The ^1H methyl group resonances are about 0.35 p.p.m. downfield relative to the pd analogues, consistent with the electron-withdrawing cyano-group. This is the same trend which was observed for the $Zr(cpd)_4$ and $Zr(pd)_4$ complexes. The methyl region of the spectrum for the $SnX_2(cpd)_2$ complexes shows marked temperature dependence;[6a] at low temperatures two methyl resonances are observed which coalesce to a single peak at higher temperatures. This behaviour is virtually identical to that observed in the $SnX_2(pd)_2$ series; the observance of the two resonances arises from the *cis* stereochemistry of the neutral, monomeric complexes which has two symmetry non-equivalent pairs of pentane-2,4-dionate methyl groups. It is also known that $SnCl_2(pd)_2$ adopts the *cis* configuration in the solid state.[8] Thus the observation of two methyl resonances for the $SnX_2(cpd)_2$ complexes confirms the presence of the *cis* isomers in solution. For the $SnX_2(cpd)_2$ complexes the coalescence temperatures are about 25 °C less than those for the corresponding $SnX_2(pd)_2$ compounds. This may be a result of relatively weaker Sn–O bonds due to the electron-withdrawing CN group *versus* an H, and is consistent with the lower $SnX_2(cpd)_2$ ν(Sn–O) frequencies discussed earlier. It is thought that the $SnX_2(pd)_2$ complexes undergo configurational rearrangement by a mechanism involving intramolecular Sn–O bond-breaking.

The authors thank the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

[0/1338 *Received, 27th August*, 1980]

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