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COORDINATION COMPOUNDS OF INDIUM

XX*. THE REACTION OF 1,2-BIS(TRIFLUOROMETHYL)DITHIETE WITH CYCLOPENTADIENYLINDIUM(I)

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SUMMARY

Cyclopentadienylindium(I) reacts readily with 1,2-bis(trifluoromethyl)dithiete (L) to yield the solid compound CpInL. The 1/1 adducts with 2,2′-bipyridine and 1,10-phenanthroline are monomeric, five coordinate neutral species. Spectroscopic and chemical analogies with the previously reported InLX ($X=Cl$, Br, I) compounds and their derivatives leads to the formulation of the present compounds as dithiolato complexes of indium(III). The cyclopentadienyl ligand is in the σ-bonded diene (*monohapto*) form.

INTRODUCTION

The compound 1,2-bis(trifluoromethyl)dithiete[1] (L) reacts with a variety of transition metal complexes to give complexes in which the metal is bonded to the two sulphur atoms. In a recent paper from this laboratory[2], it was shown that indium(I) halides also react with L by an oxidative insertion reaction to yield indium(III) compounds which contain a C_2S_2In ring. The relevant properties of these species were found to be very similar to those of anionic indium(III) dithiolates previously prepared[3] by more conventional methods. Crystal structure studies[4] confirmed the existence of a planar C_2S_2In ring in a salt of the $[In(MNT)_3]^{3-}$ anion (MNT= maleonitriledithiolate anion = 1,2-dicyanoethylene-1,2-dithiolate anion).

Organometallic compounds of indium(I) are presently only two in number, namely cyclopentadienylindium(I) (CpIn), first prepared by Fischer[5], and the analogue with methylcyclopentadiene[6]. Cyclopentadienylindium(I) is a stable and easily handled substance, and as such is an attractive starting point for the preparation of other organoindium compounds. We may note here that tricyclopentadienylindium(III) is also known, and that in this molecule the indium atom exhibits the acceptor properties characteristic of other indium(III) species[6].

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We have now studied the reaction of cyclopentadienylindium(I) with 1,2-bis(trifluoromethyl)dithiete and find that, as with the indium monohalides, the product is a polymeric species which forms adducts with neutral bidentate organic donors. The reaction is more easily carried out than with the indium(I) halides, since both CpIn and the dithiete are soluble in chloroform. The structure of the reaction product and its derivatives have been studied spectroscopically, and we conclude that these are indium(III) species, with the cyclopentadienyl ligand in the σ-bonded diene (*monohapto*) form.

EXPERIMENTAL

General

Preparative, spectroscopic, polarographic and analytical techniques were as in earlier work[2,6]. Cyclopentadienylindium(I)[5] and 1,2-bis(trifluoromethyl)dithiete[1] were prepared by methods described in the literature. Acetone for polarographic work was Reagent Grade, and was refluxed with, and distilled from, anhydrous calcium sulphate before use.

Preparative methods

Cyclopentadienyl[1,2-bis(trifluoromethyl)dithiolato]indium(III). Cyclopentadienylindium(I) (0.5 g, 2.8 mmoles) was dissolved in freshly distilled spectroscopic grade chloroform which had been previously treated with conc. sulphuric acid and distilled water to remove any ethanol stabilizer. The dropwise addition of a solution of an equimolar quantity of freshly distilled dithiete (L) (0.63 g) gave an immediate yellow precipitate, and further precipitation resulted when petroleum ether was added to the final reaction mixture. The solid, CpInL, was washed with petroleum ether and dried *in vacuo*. (Found: C, 26.4; H, 1.2; In, 28.1. $C_9H_5S_2F_6In$ calcd.: C, 26.6; H, 1.2; In, 28.3%.) The compound is soluble in acetone, ether and methanol, slightly soluble in benzene and chloroform, and insoluble in carbon tetrachloride. At 170° CpInL decomposes violently, even under nitrogen; the decomposition products were not identified.

One significant difference in experimental conditions between the previous studies with indium(I) halides[2] and the present work is worth recording. In the former the presence of trace amounts of ethanol proved essential for reaction to occur; in the homogeneous reaction with CpIn, the presence of ethanol resulted in an immediate dark brown precipitate, which did not analyse satisfactorily, and pure CpInL was only obtained when the chloroform was purified in the manner described above.

The preparation was also attempted in purified dichloromethane. With a 1/1 ratio of CpIn and dithiete, a red solution was initially formed, and the addition of inert solvents (benzene, petroleum ether) resulted in the formation of a brown precipitate. With excess dithiete, the colour of the solution changed from yellow (initially) through red to a final purple; the precipitate produced by adding inert solvent remained blue even after repeated washing with petroleum ether. In neither case were satisfactory analyses obtained for the products.

Cyclopentadienyl(2,2′-bipyridine)[1,2-bis(trifluoromethyl)dithiolato]indium(III). Freshly prepared CpInL (0.4 g) was dissolved in dry ether, and an equimolar quantity of 2,2′-bipyridine in the same solvent, were mixed. An immediate yellow precipitate formed; the amount of precipitate increased during a 2 h period of stirring. The solid was washed with petroleum ether and dried. (Found: C, 40.4; H, 2.5; In, 19.4; N, 5.0. $C_{19}H_{13}N_2S_2F_6In$ calcd.: C, 40.6; H, 2.3; N, 20.5; In, 5.0%.) This adduct, which begins to decompose at 160° and turns black at 185°, is soluble in nitromethane, benzene, dimethylsulphoxide, and acetone, slightly soluble in chloroform, and insoluble in methanol and ether.

Analogous procedures with anhydrous 1,10-phenanthroline gave rise to *cyclopentadienyl*(1,10-*phenanthroline*)[1,2-*bis*(*trifluoromethyl*)*dithiolato*]*indium*(*III*), which has similar properties to the 2,2′-bipyridine adduct, decomposing at approx. 200°. (Found: C, 42.9; H, 2.4; In, 19.8; N, 4.8. $C_{21}H_{13}N_2S_2F_6In$ calcd.: C, 43.0; H, 2.2; In, 19.6; N, 4.8%.) When 1,10-phenanthroline monohydrate was used, the product was a yellow solid, decomposing above 250°, slightly soluble in donor solvents such as dimethylsulphoxide, but insoluble in most organic solvents, and analysing as the 1,10-phenanthroline monohydrate adduct. (Found: C, 41.5; H, 2.4; In, 19.2; N, 5.0. $C_{21}H_{15}N_2OS_2F_6In$ calcd.: C, 41.7; H, 2.5; In, 19.0; N, 4.6%.)

DISCUSSION

The reaction product CpInL

A characteristic feature of the $In^{III}LX$ compounds (X=Cl, Br or I)[2] and of methyl(toluene-3,4-dithiolato)indium(III)[8], all of which contain C_2S_2In–X (or CH_3) moieties, is that the coordinative unsaturation associated with formally three-coordinate indium(III) results in extensive polymerisation in the solid state. One consequence of this is that the compounds in question are insoluble in all except donor solvents, which in favourable circumstances can give rise to addition compounds. In contrast, CpInL is soluble in polar solvents, but decomposes rapidly in strong donors. Previous studies showed that the halogen compounds InLX are unstable in pyridine, but dissolve in dimethylsulphoxide (DMSO) to form the salts $[InL(DMSO)_4]X$, in which the halide ion is no longer bonded to indium[2]. An analogous reaction with CpInL would obviously result in the formation of the reactive cyclopentadienide anion, so that the decomposition which occurs in such solvents can be ascribed to reactions initiated by ionic species of this type. Conductivity measurements demonstrated the presence of ionic species in a freshly prepared m*M* solution of CpInL in nitromethane (under nitrogen). The molar conductivity was 9.4 $ohm^{-1} \cdot cm^2$ (about 10% of that for 1/1 electrolytes in this solvent), but here again the solute species formed are unstable, since the solution throws down a precipitate after some minutes.

Indium(III) complexes with bidentate disulphur donor ligands show an interesting series of one-electron polarographic reduction steps[2,3,8], corresponding formally to $In^{III} \rightarrow In^{II} \rightarrow In^{I} \rightarrow In^0$. Attempts to study CpInL polarographically in acetonitrile solution were unsuccessful, in that no well-defined reduction processes could be detected. This may simply be a result of the instability of the compound in a basic solvent. The polarogram of a solution of the 2,2′-bipyridine adduct in acetone (m*M* concn., carrier electrolyte 0.1 *M* tetraethylammonium perchlorate) showed a sharp one-electron reduction wave at +0.58 V, and less well-defined steps at approx. −0.05 and −1.61 V; all these reductions were polarographically irreversible. The solution was fairly unstable, so that typically no reduction waves could be detected

30 min after the preparation of the solution. A comparison of these results with those for related species[2,3] seems pointless in view of this instability.

The mass spectrum of CpInL showed no molecular ion peak, and the only identifiable species were the decomposition products of InCp and L. The compounds InLX were found to be too involatile for mass spectrometric investigation[2].

Adducts of CpInL

Although CpInL is unstable in the presence of strong monodentate donors (*e.g.* pyridine, DMSO), it was possible to form stable addition compounds with the bidentate nitrogen donors 2,2′-bipyridine (Bipy) and 1,10-phenanthroline (Phen). The molecular weights of these 1/1 adducts in acetone were 555 and 569 respectively (calcd. for CpInL·Bipy 562, for CpInL·Phen 586), and the molar conductivities of m*M* solutions in nitromethane 0.7 and 4.8 ohm^{-1}·cm^{2}. These two compounds are therefore formulated as monomeric five-coordinate species (InCS$_2$N$_2$), similar to the adducts formed by these ligands with methyl(toluene-3,4-dithiolato)indium(III)[8]. These similarities persist in the case of the adduct of CpInL [or CH$_3$In(TDT)] with monohydrate of 1,10-phenanthroline, since in both cases the adduct has very different solubility properties from (say) CpInL·Phen. It is believed that in both cases the hydrated product is polymeric in the solid state.

Nuclear magnetic resonance studies

The ambient temperature (40°) ^{1}H and ^{19}F NMR spectra of CpInL and its addition compounds are shown in Table 1. The ^{19}F resonances of the bipyridine and phenanthroline adducts are almost identical to those found for [InL(DMSO)$_4$]$^+$ cations in DMSO solution ($\nu = -2.908 \pm 0.002$ kHz)[2] and confirms that the dithiete moiety is in a very similar environment in these species, and in CpInL.

The proton resonances of the cyclopentadienyl group appear as a sharp singlet, implying either that the cyclopentadienyl group is in a *pentahapto* environment (*i.e.* π-symmetry), as in the solid state of CpIn itself[9], or that it is undergoing fluxional rotation. The latter situation holds for Cp$_3$In and its adducts in solution[6], although the crystal structure[10] of Cp$_3$In shows that two of the cyclopentadienyl ligands are σ-bonded dienes (following the terminology of Fritz[11]), or *monohapto*.

TABLE 1

^{1}H AND ^{19}F NMR SPECTRA OF CpInL AND ITS ADDUCTS AT APPROX. 40°

	^{1}H (in Hz)[a]		*^{19}F (in kHz)*[b]	
	CDCl$_3$	*DMSO-d$_6$*	*CDCl$_3$*	*DMSO-d$_6$*
L			−3.526	−3.613 (neat)
CpIn	366			
CpInL	370	345	−3.032	
CpInL·Bipy[c]		380		−2.893
CpInL·Phen[c]		383		−2.898

[a] Relative to external TMS, at 60 MHz. [b] Relative to external CFCl$_3$, at 56.4 MHz. [c] Bipy = 2,2′-bipyridyl, Phen = 1,10-phenanthroline. Proton resonances from these ligands were also observed.

The frequency difference between CpIn and Cp_3In is small (≈10 Hz)[6], and is unreliable as a diagnostic test of the stereochemistry of the cyclopentadienyl group, especially since change of solvent, or coordination of donor ligands, produce similar or larger changes in the ^1H frequency. The proton spectrum of CpInL · Bipy in acetone was run over a series of temperatures down to −75°, but no change was detected in the singlet of the cyclopentadienyl group.

Vibrational spectra

Although the many strong infrared absorptions of the dithiete ligand make a detailed interpretation of the infrared spectra of the complexes impossible, the results do provide an insight into the structures involved. Table 2 lists the important features of the infrared spectra, together with the Raman spectra in the ν(In–C) region.

TABLE 2

VIBRATIONAL SPECTRA OF CpInL AND RELATED COMPOUNDS (in cm^{-1})

	ν(C=C) (L) *IR*	$\nu\left(CF_3{-}C{<}^{C}_{S}\right)$ *IR*	*ν(In–C)* *R*	*ν(In–C)* *IR*	*Cp ring deformation* *IR*
L	1620 s	890 w, 835 s			
CpInL	1529 s	893 s, 830 m	337 s	340 s	862 s
CpInL · Bipy	[a]	890 s, 830 s	327 s	325 m	844 m
CpInL · Phen	1520 s	889 s, 829 m	335 s	332 m	868 m
CpInL · Phen · H_2O	1520 ms	890 s, 830 m		330 w	868 s

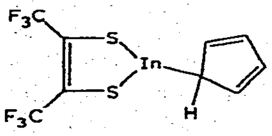
[a] Obscured by vibrations of Bipy.

We first discuss those infrared absorptions associated with dithiete. The strong absorption at 1620 cm^{-1} in the parent molecule, due to ν(C=C) of the four-membered ring, appears as a strong band in the 1530–1520 cm^{-1} region in CpInL and its adducts. The intense ν(C–F) absorption obscures the ν(C–S) region, but it is possible to identify the $CF_3{-}C{<}^{C}_{C}$ stretch, which is found to be between 820 and 900 cm^{-1}. These frequencies are close to the values reported for InLX compounds; as was pointed out earlier[2], such vibrations correspond to ν_1 and ν_3 in the assignments made for complexes of dithiolate ligands and transition metal ions[12].

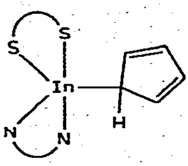
The identification of the mode of bonding of cyclopentadienyl ligand by means of vibrational spectroscopy has been the subject of a number of papers[11,13]. The important regions are the ν(C–H) frequency (≈3000 cm^{-1}), and the ring deformation at 850 cm^{-1}. For CpInL, (in hexachlorobutadiene mull) we find two weak bands in the infrared at 3080 and 2940 cm^{-1}, indicating σ-bonding of the cyclopentadienyl ligand. This criterion could not be applied in the case of the adducts, because of much stronger absorptions in this region by 2,2′-bipyridine and 1,10-phenanthroline. All the compounds examined show strong absorbances at ≈860 cm^{-1}, (Table 2), again indicating σ-bonding of cyclopentadienyl in the diene form. The single ν(In–C) mode is also in keeping with such a structure. The latter frequencies are slightly higher than those reported for Cp_3In and its adducts[6].

General

The chemical and spectroscopic evidence all points to the formulation of monomeric CpIn (I), and its adducts (II) as compounds of indium(III) bonded to both a σ-bonded diene cyclopentadienyl ligand and bidentate 1,2-bis(trifluoromethyl)-1,2-dithiolato anion. As in previous discussions, the term "dithiolate" is not intended to prejudge any future study of the detailed electronic structure of the C_2S_2In ring system. The structural similarities to the InLX compounds have been emphasised a number of times in the present paper. Of equal importance is the nature of the indium–cyclopentadienyl interaction, which appears very similar to that in Cp_3In. The contrast with transition metal–dithiete–cyclopentadienyl complexes is also of interest, since in such molecules the cyclopentadienyl ligand is found to be in the *pentahapto* (π) configuration[14].



(I)



(II)

The reaction of CpIn[1] with L is another of the series of oxidative insertion reactions involving indium(I) species and organic molecules[2,6]. It is hoped to discuss some aspects of such reactions in future papers dealing with mechanistically simpler systems than that described here.

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