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COORDINATION COMPOUNDS OF INDIUM

XVI*. THE REACTION OF TRIMETHYLINDIUM WITH TOLUENE-3,4-DITHIOL

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SUMMARY

Trimethylindium reacts with toluene-3,4-dithiol in ether to yield methylindium toluene-3,4-dithiolate, which is apparently polymeric in the solid state. Reaction of this compound with monodentate and bidentate donors gives dimeric or monomeric adducts. The relationships between these species are discussed in the light of NMR and other spectroscopic studies.

INTRODUCTION

Previous work in this laboratory has shown that complexes of indium(III) with bidentate sulphur donor ligands can be readily prepared[1,2]. For example, indium(III) chloride reacts smoothly with the toluene-3,4-dithiolate (TDT) anion in ethanol to give the anion $[\mathrm{In(TDT)_2}]^-$, which can be crystallised as the tetraethylammonium salt. Adducts with such neutral bidentate donors as 2,2′-bipyridine (Bipy) can also be obtained as the six-coordinate anion $[\mathrm{In(TDT)_2Bipy}]^-$. Evidence has been obtained for the existence of $[\mathrm{In(TDT)_3}]^{3-}$ in solution, but solid compounds could not be isolated in this case. These compounds, and the analogous complexes with 1,2-dicyanoethylene-1,2-dithiolate and 1,1-dicyanoethylene-2,2-dithiolate, form an interesting series of four-, five- and six-coordinate indium species. In this group of compounds, as with other indium(III) complexes, changes in coordination number are brought about relatively easily.

We have now investigated a different route to indium(III)–dithiolate complexes, using the reaction of trimethylindium with the parent compound toluene-3,4-dithiol. The reactions of trimethyl compounds of Group IIIA elements with organic bases has been widely investigated by a number of authors[3]. Trimethylindium is an electron pair acceptor, and with donors containing an acidic hydrogen, elimination of methane from an adduct can take place if the basic molecule has a hydrogen atom attached to the donor atom. The reaction with toluene-3,4-dithiol apparently follows

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* For Part XV, see ref. 8.
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this pattern, in that an unstable adduct, which we were not able to isolate, loses two molecules of methane almost immediately and we have confirmed this reaction stoichiometry:

$$In(CH_3)_3 + CH_3C_6H_3(SH)_2 \rightarrow (CH_3C_6H_3S_2)InCH_3 + 2\,CH_4 \qquad (1)$$

Three-coordinate indium(III) monomeric species are coordinatively unsaturated, and as a result the compound CH_3InTDT has Lewis acid properties. The initial reaction product is apparently polymeric, but adducts of $CH_3In(TDT)$ and of the dimer have been obtained with mono- and bidentate organic donors. Spectroscopic and molecular weight studies have been carried out on these compounds. The results are in keeping with earlier studies of indium(III) dithiolate complexes[2,4].

EXPERIMENTAL

Spectroscopic and analytical techniques were as described in earlier publications[2,5]. All results refer to experiments performed under nitrogen.

Preparative methods

Trimethylindium. A threefold excess of methyllithium in ether was carefully added to a slurry of indium trichloride (4.52 g) in the same solvent, the reaction vessel being cooled in ice. Distillation at 100° following the addition of all the methyllithium gave an apparently quantitative yield of trimethylindium.

Methylindium(III) toluene-3,4-dithiolate

Toluene-3,4-dithiol (3.2 g) in ether was slowly added, with stirring, to a fresh solution of trimethylindium. After addition of the first drops of the TDT solution, a white solid precipitated and gas was evolved; volumetric and mass-spectral evidence showed that over the whole reaction two molar equivalents of methane were released for each mole of trimethylindium used. The white precipitate was collected, washed twice with ether and dried *in vacuo*. Analysis showed that this substance was methylindium(III) toluene-3,4-dithiolate $[CH_3In(TDT)]$, which is insoluble in all but donor organic solvents, and which decomposes without melting at ~300°. Extended vacuum sublimation (16 h, 150°) yielded a small quantity of sublimate, which was shown mass spectrometrically to be the $CH_3In(TDT)$ monomer. Analytical results for the parent substance, and for the other compounds prepared, are given in Table 1.

Methyl(dimethyl sulphoxide)indium(III) toluene-3,4-dithiolate

Methylindium toluene-3,4-dithiolate (0.4 g) was dissolved in dimethyl sulphoxide, the solution filtered, and excess solvent removed under vacuum to leave a light brown oil. After being washed with ether and petroleum ether, the oil was crystallized to yield off-white crystals of methyl(dimethyl sulphoxide)indium toluene-3,4-dithiolate, which is only slightly soluble in acetone and chloroform, but soluble in donor solvents. The solid decomposes rapidly without melting at 170°, under nitrogen.

Methyl(pyridine)indium(III) toluene-3,4-dithiolate

The procedure described above, using pyridine in place of dimethyl sulphoxide,

TABLE 1

ELEMENTAL ANALYSIS, MOLECULAR WEIGHTS AND MOLAR CONDUCTIVITIES OF METHYLINDIUM(III) TOLUENE-3,4-DITHIOLATE AND DERIVATIVES

Compound	*Analysis found (calcd.)(%)*				*Mol. wt.*	*Molar conductivity in CH_3NO_2 ($ohm^{-1} \cdot cm^2$)*
	C	*H*	*N*	*In*	*Found*[a] *(calcd. for monomer)*	
$CH_3In(TDT)$	34.1	3.3		40.3	284	[d]
	(33.8)	(3.2)		(40.4)	568[b]	
					(284)	
$CH_3In(TDT)\cdot Py$	42.8	4.1	3.5	31.8	739	2.8
	(43.0)	(3.9)	(3.9)	(31.6)	(363)	
$CH_3In(TDT)\cdot DMSO$	33.8	3.9		32.2	710	4.0
	(33.1)	(4.1)		(31.7)	(362)	
$CH_3In(TDT)\cdot(CH_3)_3N$	38.7	5.3	4.1	33.2	350[c]	1.9
	(38.5)	(5.3)	(4.1)	(33.5)	(343)	
$[CH_3In(TDT)]_2\cdot(CH_3)_3N$	35.9	4.2	2.2	37.2	359	[d]
	(36.3)	(4.3)	(2.2)	(36.6)	(314)	
$CH_3In(TDT)\cdot Bipy$	49.3	4.1	6.3	25.5	424	0.6
	(49.1)	(3.9)	(6.4)	(26.1)	(440)	
$CH_3In(TDT)\cdot Phen\cdot H_2O$	49.1	3.5	6.0	23.4	[d]	[d]
	(49.7)	(3.9)	(5.8)	(23.8)	(482)	
$CH_3In(TDT)\cdot Phen$	51.5	3.7	5.9	24.1	456	0.3
	(51.7)	(3.7)	(6.0)	(24.7)	(464)	

[a] In acetone solution unless otherwise stated. [b] Mass-spectrometrically; required values for ^{115}In species. [c] The value in *N,N'*-dimethylacetamide was 685. [d] Insufficiently soluble.

gave white crystals of the pyridine adduct. This substance is only slightly soluble in acetone and ethanol, soluble in donor solvents, and decomposes without melting at 170°.

Methyl(trimethylamine)indium(III) toluene-3,4-dithiolate

A saturated solution of trimethylamine in ether was added to a slurry of methylindium toluene-3,4-dithiolate in the same solvent until the suspended material dissolved to give a clear solution (5 min). Addition of petroleum ether precipitated white crystals of the 1/1 adduct $CH_3In(TDT)\cdot N(CH_3)_3$, which was dried at room temperature (m.p. ~170°, with decomposition). This substance is soluble in donor solvents (*e.g.* DMSO, pyridine, tetrahydrofuran), slightly soluble in acetone, ether, ethanol and dichloromethane, but insoluble in chloroform. In *N,N'*-dimethylacetamide, the 1/1 adduct is a dimer (see Table 1), but the fraction which dissolved in acetone had a molecular weight in solution corresponding to the monomer.

When a solution of $CH_3In(TDT)$ and trimethylamine was evaporated *in vacuo* at room temperature, a white solid of stoichiometry $CH_3In(TDT)\cdot 0.5\ N(CH_3)_3$ was obtained. The solubilities and thermal stability of this material are similar to those of the 1/1 adduct. The molecular weight of the acetone-soluble fraction was that of the monomer of $CH_3In(TDT)\cdot N(CH_3)_3$; similarly, integration of the NMR spectrum of the fraction soluble in dichloromethane showed that the species in solution was the 1/1 adduct.

It is clear from these results that the $CH_3In(TDT)/N(CH_3)_3$ system gives rise to a complex set of equilibria involving the monomer and dimer of the 1/1 adduct, and species such as $[CH_3In(TDT)]_2 \cdot N(CH_3)_3$. The nature of these equilibria has not been investigated further.

Methyl(2,2'-bipyridine)indium(III) toluene-3,4-dithiolate

Dropwise addition of a dichloromethane solution of (excess) 2,2'-bipyridine to a slurry of methylindium(III) toluene-3,4-dithiolate in the same solvent caused the latter to dissolve. Crystallisation produced yellow crystals; occluded solvent was removed by grinding the solid and exposing it in a nitrogen atmosphere for 48 h. The solid is soluble in acetone and dimethyl sulphoxide, and melts with decomposition at 220°.

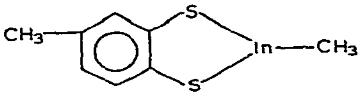
Similar procedures, starting with 1,10-phenanthroline monohydrate, gave yellow crystals of methyl(1,10-phenanthroline)indium(III) toluene-3,4-dithiolate monohydrate, which is stable up to approx. 300°. With anhydrous 1,10-phenanthroline, obtained by heating the monohydrate to 110° *in vacuo* for 6 h, the yellow crystalline product was methyl(1,10-phenanthroline)indium(III) toluene-3,4-dithiolate, m.p. 210° (dec.).

DISCUSSION

Methylindium(III) toluene-3,4-dithiolate and its adducts

The physical properties of the initial reaction product, $CH_3In(TDT)$, are similar to those of the monohalogeno[1,2-bis(trifluoromethyl)ethylene-1,2-dithiolato]indium(III) compounds described earlier[4], namely low volatility, insolubility in inert organic solvents, and air- and water-sensitivity. We believe that in both cases the solid is polymeric, due to intermolecular indium–sulphur bonding, which allows indium to increase its coordination number beyond three. The mass spectra (sample temp. 160°) showed a line at *m/e* 284, corresponding to the molecular ion of the monomer $CH_3{}^{115}In(TDT)$, but in addition a peak at *m/e* 568 indicated the presence of dimer species in the vapor phase, so that the solid polymer breaks down in some stepwise manner on heating *in vacuo*. In this respect, the intermolecular forces are apparently weaker than in the dithieten derivative, for which no mass spectrum could be obtained[4].

The monomer unit is identified as the methylindiumdithiolate;



following the earlier practice[2,4], the term "dithiolate" is used without the prejudice as to the detailed electronic structure of the C_2S_2In moiety. In agreement with this formulation, the infrared spectrum of the reaction product shows a single $In–CH_3$ stretching vibration at 515 cm^{-1} (s), together with a broad strong band at 720 cm^{-1}, assigned to the $In–CH_3$ rocking mode. These values are very similar to those reported for other $In–CH_3$ compounds[5,6]. (See below.)

Two series of addition compounds can be obtained from $CH_3In(TDT)$.

Reaction with the bidentate donors 2,2'-bipyridine or 1,10-phenanthroline gave 1/1 adducts which are monomeric in solution (See Table 1 for molecular weights in acetone). Conductivity measurements show that all the adducts are neutral species, so that these two compounds can be formulated as members of the increasingly large group of five-coordinate indium(III) complexes, with the primary coordination $S_2In(CH_3)N_2$. The nature of the hydrated phenanthroline adduct could not be elucidated, but the marked change in solubility compared with the anhydrous compound suggests that the former may be polymeric.

The three monodentate donors pyridine, dimethyl sulphoxide and trimethylamine each give rise to dimeric, neutral 1/1 adducts with $CH_3In(TDT)$. Dimeric structures have been established for a number of $[M(S_2C_2R_2)_2]_2$ species, where M is a transition metal ion. (See ref. 7 for a review of such structures). The idealised structure involves intermolecular bonding to give two five-coordinate metal atoms in an essentially square-pyramidal $M{-}S_5$ symmetry, with each pyramid sharing a common edge. We believe that in the present systems, the dimerisation involves similar In–S interactions to those in the transition metal complexes, with the penta-coordination completed by the methyl group and the neutral donor ligand. This postulated penta-coordination, which we discuss below in terms of the NMR studies, is analogous to that proposed above for the neutral 1/1 adducts of $CH_3In(TDT)$ with 2,2'-bipyridine and 1,10-phenanthroline. The polymeric structure of the product of the initial reaction can be understood on a similar argument.

The ability of 2,2'-bipyridine and 1,10-phenanthroline to disrupt this polymerisation to form a monomeric adduct, in contrast to the behaviour of pyridine, is presumably in part a consequence of the extra stabilisation involved in the formation of the $In{-}N_2C_2$ chelate ring. In addition, this may reflect the preference of indium(III) for penta-coordination in these complexes, since a dimeric species $[CH_3In(TDT)\cdot Phen]_2$ would require hexa-coordinate indium.

Vibrational spectroscopy

Table 2 lists parts of the infrared and Raman spectra of the compounds with special reference to the $In{-}CH_3$ rock, $\nu(In{-}C)$, $\nu(In{-}S)$ and $\nu(In{-}N)$ modes.

As noted earlier, the infrared bands at 720 and 515 cm^{-1} in $CH_3In(TDT)$ are readily assigned, taking published results for other organoindium compounds. Bands at similar frequencies are found in the spectra of the addition compounds. The vibrations assigned to $\nu(In{-}S)$ and $\nu(In{-}N)$ listed in Table 2 are similar to those observed in the infrared spectrum[2] of $[In(TDT)_2]^-$ and $[In(TDT)_2Bipy]^-$. In view of the large number of bands in both Raman and infrared spectra, no detailed analysis was attempted.

NMR spectroscopy

Table 3 shows the results of proton NMR studies with a number of different solvent systems. Because of solubility problems, it was not possible to dissolve (say) $CH_3In(TDT)\cdot DMSO$ in some inert solvent in sufficient quantities to give good NMR spectra. We were therefore forced to use essentially a solution of $CH_3In(TDT)\cdot DMSO$ in DMSO, which means that a detailed comparison of the spectra is difficult.

In addition to the lines listed in Table 3, each spectrum showed a complex series of resonances in the region between 450 and 350 Hz (downfield from TMS), and

TABLE 2

VIBRATIONAL SPECTRA (IN cm^{-1}) OF METHYLINDIUM(III) TOLUENE-3,4-DITHIOLATE AND DERIVATIVES IN THE In–C, In–S AND In–N REGIONS

Compound	In–CH_3 rock (IR+R)	ν(In–C)		ν(In–S)		ν(In–N)	
		IR	R	IR	R	IR	S
$CH_3In(TDT)$	724 s (br)	510 m	509 s	378 w 349 m (br)	378 w 340 m 325 m		
$CH_3In(TDT)\cdot Py$	720 (sh)	507 s	509 vs	383 vw 339 mw	381 m 333 s 324 w	280 mw 270 mw	274 s 255 w
$CH_3In(TDT)\cdot DMSO$	722 s (br)	507 m	[a]	[b]	[a]		
$CH_3In(TDT)\cdot (CH_3)_3N$	727 s (br)	520 s	[a]	378 (sh) 369 m 326 m	[a]	279 w	[a]
$CH_3In(TDT)\cdot Phen$	[b]	508 s	505 m	352 m 381 m	373 w 357 m 345 s	279 w	278 w
$CH_3In(TDT)\cdot Bipy$	[b]	505 m	505 s	372 vw	349 s	301 w	242 w?

[a] Not recorded. [b] Region obscured by absorptions in donor ligand.

TABLE 3

NMR OF METHYLINDIUM(III) TOLUENE-3,4-DITHIOLATE AND DERIVATIVES AT 35° [a]

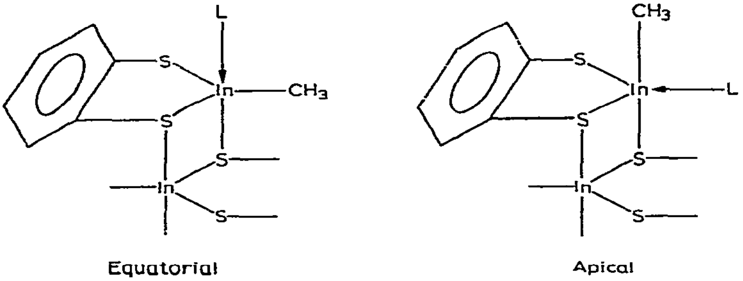
	Solvent	Aromatic CH_3	In–CH_3 [b]	Others
TDT	Neat	112		205+212 (SH)
$CH_3IN(TDT)$	DMSO-d_6	127	+2 (0.4), −13 (0.6)	
$CH_3In(TDT)$	Pyridine-d_5	86(0.8), 78(0.2)	−7 (0.65), −20 (0.35)	
$CH_3In(TDT)\cdot (CH_3)_3N$	CH_2Cl_2	129	+19	138 (N–CH_3)
$CH_3In(TDT)\cdot Phen$	DMSO-d_6	121	−3.5(0.6), −16 (0.4)	
$CH_3In(TDT)\cdot Bipy$	DMSO-d_6	123	−3 (0.4), −15 (0.6)	

[a] Hz from internal TMS, at 60 MHz. [b] Relative intensities shown in parentheses.

readily assigned to the aromatic protons of the TDT ligand. For the 1,10-phenanthroline and 2,2′-bipyridine complexes, the resonances of the ring protons of the donor ligands were also observed, although some solubility problems encountered with these species resulted in low intensity spectra.

The results in Table 3 merit some detailed discussion. One interesting feature is the anomalous values for the resonance frequency of the toluene-methyl group of $CH_3In(TDT)$ in pyridine-d_5. In view of the much smaller changes in this resonance in the related compounds, it seems unlikely that this can be an intermolecular effect, and the high field shift is therefore attributed to the effect of the diamagnetic anisotropy of the aromatic solvent.

Column four of Table 3 gives the resonance frequencies of the protons of the methyl group bonded to indium. For the 1/1 adducts of DMSO and pyridine, we observe a pair of sharp lines, whose relative intensity at 35° is shown in parentheses. Such a result might arise from a monomer–dimer equilibrium, but the spectrum of the DMSO compound was unchanged between 10 and 90°, so that this can be rejected. We believe that the explanation depends upon the penta-coordination of indium discussed above. For a coordination of three sulphur atoms, one methyl and one neutral donor, two possible stereochemistries exist:



We name these isomers in terms of the position of the methyl group relative to the primary toluene-3,4-dithiolate ring coordinated to the indium atom in question. As would be expected, the energy difference between the two different methyl groups is small, and the populations roughly equal.

For the pyridine complex, the methyl group of the TDT also gives a doublet in the NMR spectrum. This is ascribed to the effect of the pyridine, which will lie above the TDT methyl group when the indium methyl is in the apical position, so that the TDT methyl also has two different environments. It is not clear whether any significance is attached to the slight differences in the integrated relative intensities of the indium–CH_3 and toluene–CH_3 resonances.

For the 1/1 $CH_3In(TDT)\cdot N(CH_3)_3$ adduct, only one indium–methyl resonance is observed. This is in keeping with the dissociation phenomena discussed above (See Experimental). Alternatively, models show that trimethylamine, being a bulkier ligand than DMSO or pyridine, probably cannot form a complex with a methyl group in the apical position because of steric crowding with the adjacent TDT phenyl ring. The single In–CH_3 resonance would then be that of the methyl group uniquely in the equatorial position.

Complexes with the bidentate ligands 2,2′-bipyridine and 1,10-phenanthroline also show two In–CH_3 resonances. The situation here is complicated by the presence of the donor solvent dimethyl sulphoxide. It is clear however that in all the compounds examined the methyl groups attached to indium are chemically similar, and are in environments only slightly different from the methyl groups of tetramethylsilane.

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REFERENCES

1 F. W. B. Einstein, G. Hunter, M. K. Yang and D. G. Tuck, *Chem. Commun.*, (1968) 423.
2 D. G. Tuck and M. K. Yang, *J. Chem. Soc. A*, (1971) 214.
3 G. E. Coates and K. Wade, *Organometallic Compounds*, Vol. I, Methuen, London, 3rd ed., 1967, p. 361.
4 A. F. Berniaz, G. Hunter and D. G. Tuck, *J. Chem. Soc. A*, (1971) 3254.
5 J. S. Poland and D. G. Tuck, *J. Organometal. Chem.*, 42 (1972) 307.
6 H. C. Clark and A. L. Pickard, *J. Organometal. Chem.*, 8 (1967) 427.
7 J. A. McLeverty, *Progr. Inorg. Chem.*, 10 (1968) 49.
8 K. Bowden, G. T. Tanner and D. G. Tuck, *Can. J. Chem.*, in press.