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COORDINATION COMPOUNDS OF INDIUM

XXXIX. THE REACTION OF DIMETHYLINDIUM(III) COMPOUNDS WITH DIBASIC ORGANIC ACIDS

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Summary

The reaction between dimethylindium(III) compounds (especially $(CH_3)_2In(OAc)$) and various dibasic organic acids (especially toluene-3,4-dithiol, H_2TDT) can lead to the evolution of 2.0, 1.0, or 0.67 moles of methane per $(CH_3)_2In(OAc)$ unit, depending on solvent conditions. Spectroscopic and molecular weight studies show that an intermediate $[(CH_3)In(OAc)(HTDT)]_2$ is formed in the reaction. The structure of this and similar species are discussed in terms of the relationship to the polymeric parent $(CH_3)_2In(OAc)$, and to its adducts with neutral donor ligands. Possible controlling factors in the stabilisation of the intermediate products are discussed.

Introduction

One of the most useful properties of compounds in which indium or another Group III element is bonded to one or more methyl groups is that the latter will react with proton donors, eliminating methane, and yielding interesting coordination compounds. One such reaction, described in detail in an earlier publication, involves trimethylindium and toluene-3,4-dithiol, in which case the product is an indium(III) complex containing indium bonded to one carbon and two sulphur atoms. Structural studies showed that although the initial reaction product is polymeric, adducts of the monomeric compound with mono- and bidentate organic donors can readily be prepared [1]. An attractive feature of such reactions is that they can often be used to prepare indium complexes which are not readily accessible by other routes.

During work on the chemistry of acetato(dimethyl)indium(III), $(CH_3)_2In(OAc)$, and other dimethylindium species, we found that a variety of decomposition reactions occurred with organic solvents, apparently involving the elimination of methane and the formation of uncharacterized insoluble decomposition products. This suggested that the methyl groups of $(CH_3)_2In(OAc)$, which is itself prepared by the reaction of trimethylindium with acetic acid [2], still retain the reactivity of the parent compound insofar as reactions with proton donors are concerned, and we have therefore investigated in detail the more readily controlled reaction of acetato(dimethyl)indium(III) with toluene-3,4-dithiol (H_2TDT). A striking feature of this system is that the methyl groups may react under different conditions with one or both of the acidic hydrogen atoms of toluene-3,4-dithiol, implying the existence of an unusual intermediate compound in which an indium atom is bonded both to a methyl group and to a monodentate, protonated toluene-3,4-dithiolate ligand (HTDT) whose acidic proton is in some way hindered from further reaction. This intermediate has been isolated and studied. The product from the complete elimination of both methyl groups is acetato(toluene-3,4-dithiolato)indium(III), which is a Lewis acid and forms adducts with monodentate and bidentate nitrogen donors.

Other work reported in the present paper shows that the solvent has a marked effect on the extent of the reaction, and that the stepwise elimination of methane occurs with dimethylindium species other than the acetate, and with dibasic acids other than toluene-3,4-dithiol. A preliminary account of some of this work has already been published [3].

Experimental

Spectroscopic and analytical techniques were as described in earlier publications from this laboratory [4]. Preparative work was carried out in a nitrogen-filled dry box. The volume of gas evolved in reaction was measured in a simple manometric system attached to a standard vacuum line: all volumes quoted are corrected to S.T.P.

The solvents were all dried and distilled in vacuo before use.

Preparative and gas volumetric studies

Acetato(dimethyl)indium(III). Dilute acetic acid (2.5 mmole) in diethylether was added dropwise to trimethylindium (0.406 g, 2.53 mmole) in the same solvent. The volume of gas evolved (53.2 ml, 2.38 mmole) indicated the reaction of only one methyl group. The compound was purified by vacuum sublimation.

Acetato(toluene-3,4-dithiolato)indium(III). A slight excess of neat toluene-3,4-dithiol (H_2TDT) was added dropwise to a solution of acetato(dimethyl)indium(III) (0.206 g, 2.03 mmoles) in dry ethanol (approx. 1 ml). Gas was evolved (44.9 ml, 2.01 mmole), and a white precipitate of acetato(methyl) (toluene-4-thiol-3-thiolato)indium(III), $(CH_3)In(OAc)(HTDT)$, thrown down. This material (I) was washed with ethanol, and with ether, and dried in vacuo (Found: C, 35.2; H, 3.9; In 32.9. $CH_3In(C_2H_3O_2)(C_7H_7S_2)$ calcd.: C, 34.8; H, 3.7; In, 33.4%.) The compound dissolved sufficiently in ethanol after long equilibration for us to be able to measure the molecular weight on a Hewlett-Packard 302B vapor pressure osmometer; the experimental value of 678 indicates that the species in solution at 26°C is the dimer $[(CH_3)In(OAc)(HTDT)]_2$ (calc. 688).

When the compound I was heated to 40°C with dimethylsulphoxide, a further evolution of gas occurred; 0.63 g of I (0.91 mmole, calculated for the monomer) gave 18.2 ml of gas (0.82 mmole). Similarly when acetato(dimethyl)-indium(III) (0.225 g, 1.05 mmole) reacted with excess toluene-3,4-dithiol in an ethanol/dimethylsulphoxide mixture (1/5), 46.1 ml of gas (2.06 mmole) was produced, showing that under these conditions both methyl groups of $(CH_3)_2$In-(OAc) react to yield acetato(toluene-3,4-dithiolato)indium(III), which was isolated from the reaction mixture. (Found: C, 33.6; H, 2.7; In, 35.5%. $In(C_2H_3O_2)\cdot(C_7H_6S_2)$ calcd.: C, 32.9; H, 2.7; In, 35.1%.) The molecular weight of In(OAc)-(TDT) in DMSO at 43.4°C is 337 (calcd.: 328).

Finally, the reaction between $(CH_3)_2In(OAc)$ and H_2TDT was carried out in the polar solvent hexamethylphosphoramide (HMPA). The gas evolution from 0.86 mmoles of $(CH_3)_2In(OAc)$ and excess H_2TDT in 20 ml HMPA was 12.6 ml, or 66% of theoretical (19.2 ml); a second experiment with 0.75 mmoles gave 10.4 ml of gas (62% theoretical). No precipitate was observed under these conditions; removal of HMPA in vacuo gave an oil which could not be made to solidify by the standard methods. The volume of gas did not increase on heating the reaction mixture to 45°C. With higher (3-fold) concentrations of reactants, a white powder was thrown down after approx. 30 min; this material was collected, washed with diethylether and dried in vacuo. Elemental analysis gave C, 37.9; H, 6.98; N, 13.4; In, 21.9%. We return to these results later.

Other dibasic acids

In Table 1 we summarize the results of experiments with $(CH_3)_2In(OAc)$ and the dibasic acids 1,2-ethanedithiol, 1,3-propanedithiol, salicylic acid, and phthalic acid. In each case, the reaction yielded one mole of methane per mole of $(CH_3)_2In(OAc)$, independent of the solvent (ethanol or DMSO). No further evolution of gas occurred on adding DMSO to a reaction mixture in ethanol after the completion of the initial reaction. The values in Table 1 are for 22°C, but in fact no additional gas formation was detected on heating the reaction mixtures to 45°C.

In the case of the two dithiols, a precipitate formed during gas evolution; analysis for indium confirms that these products are $(CH_3)In(OAc)(C_2H_4S_2H)$ and $(CH_3)In(OAc)(C_3H_7S_2H)$ respectively. With salicylic acid a solid product

TABLE 1

GAS EVOLUTION AND PRODUCT COMPOSITION IN THE REACTION OF $(CH_3)_2In(OAc)$ WITH SOME DIBASIC ACIDS

Reactant	Wt. taken (mmoles)	Vol. of gas (mmoles)		Composition of solid In found (calcd.)[a] (%)
		EtOH	DMSO	
$C_2H_4(SH)_2$	0.89	0.91	—	40.3 (40.7)
	1.05	—	1.04	
$C_3H_6(SH)_2$	0.99	0.99	—	38.2 (38.9)
	0.68	—	0.71	
Salicylic Acid	0.73	0.74	—	35.1 (35.7)
Phthalic Acid	0.69	0.70	—	32.2 (32.8)

[a] Calculated for $CH_3In(OAc)(C_2H_4S_2H)$, etc.

was only obtained by cooling the reaction mixture, but a better route involved removing most of the solvent in vacuo, and for phthalic acid this technique was essential since no solid precipitated from the reaction mixture even on cooling. Again these solids analyse satisfactorily for the appropriate monomethylindium derivative (see Table 1).

Other dimethylindium(III) compounds

The reactions of toluene-3,4-dithiol with dimethylindium(III) compounds were extended to include $(CH_3)_2In(tfac)$ (tfac = 1,1,1-trifluoro-2,4-pentanedionate anion) and $(CH_3)_2In(pyr \cdot CHO)$ ($pyr \cdot CHO$ = 2-formylpyrrolate anion), prepared for other work in this laboratory [5,6]. With $(CH_3)_2In(tfac)$, 0.39 g of solid (1.31 mmole) in ethanol produced 1.34 mmole of gas on reaction with excess toluene-3,4-dithiol at 22°C, and the precipitate which formed had: In, 38.6. $(CH_3)In(tfac)(HTDT)$ calcd.: In, 38.9%. Similarly, 0.128 g $(CH_3)_2In(pyr \cdot CHO)$ (0.54 mmoles) yielded 0.56 mmoles methane, and a precipitate. (Found: In, 48.6. $(CH_3)In(pyr \cdot CHO)(HTDT)$ calcd.: In, 48.3%.) Neither heating to 45° C, nor the addition of dimethylsulphoxide, caused further evolution of gas from these systems.

Adducts of acetato(toluene-3,4-dithiolato)indium(III)

It was possible to obtain 1/1 adducts of In(OAc)(TDT) with 2,2-bipyridyl (bipy) or 1,10-phenanthroline (phen) by two alternative routes. The more obvious of these involved mixing solutions of In(OAc)(TDT) and the ligand in ethanol, when a brown-yellow precipitate of (say) [In(OAc)(TDT)(phen)] formed immediately. Alternatively, when a solution of the ligand was added to $(CH_3)In(OAc)(HTDT)$, gas was evolved, and the 1/1 adduct again obtained. Analysis confirmed the 1/1 stoichiometry (Bipy: found: C, 47.3; H, 3.7; N, 6.1; In, 23,4. $In(C_2H_3O_2)(C_7H_8S_2)(C_{10}H_8N_2)$ calcd.: C, 47.2; H, 3.5; N, 5.8; In, 23.8%). (Phen: found: C, 50.5; H, 3.6; N, 5.7; In, 22.7. $In(C_2H_3O_2)(C_7H_8S_2)(C_{12}H_8N_2)$ calcd.: C, 50.1; H, 3.4; N, 5.5; In, 28.3%.)

When pyridine (py) was used in the reaction with In(OAc)(TDT), a yellow solution resulted, and yellow crystals were obtained when the solution was kept at 0°C overnight, or on the addition of petroleum ether to the solution. The freshly prepared solid analysed satisfactorily as the 1/1 pyridine adduct [In(OAc)(TDT)(py)] (Found: In, 28.5; OAc, 14.5. Calcd.: In, 28.2; OAc, 14.5%), but the compound lost pyridine on standing at room temperature to yield a residue of In(OAc)(TDT) (e.g. after two days, the acetate content rose to 16.3%).

Similar behaviour was observed in the case of dimethylsulphoxide. Acetato(toluene-3,4-dithiolato)indium(III) dissolves in DMSO on heating and the compound obtained by the addition of petroleum ether, or on cooling, analysed for [In(OAc)(TDT)(DMSO)] (Found: In, 29.5. Calcd.: In, 28.5%) but here again the neutral ligand is lost from the solid on standing at room temperature (e.g. after 2 days, In, 31.2%; cf. In(OAc)(TDT) In, 35.1%).

Results and discussion

The experiments described show clearly that $Me_2In(OAc)$ and similar compounds react with dibasic organic acids to eliminate one or two molecules of methane depending on both the reagents and the conditions. Further evidence as to the nature of these reactions is now reviewed.

Spectroscopic studies

The most extensive spectroscopic studies were made on the $Me_2In(OAc)$ + H_2TDT reaction system, with results which completely support the findings of the preparative work described above. The vibrational spectrum of acetato(dimethyl)indium(III) in the ν(In—C) region consists of two bands at 551 (ν_{as}) and 496 (ν_{sym}) cm^{-1}, and a strong broad infrared band at 728 cm^{-1} (In—CH_3 rock) [2,7]. None of these were detected in the spectrum of the final product In(OAc)(TDT), which shows the vibrational modes of coordinated bidentate acetate and toluene-3,4-dithiolate [7,8,9].

The intermediate solid product $(CH_3)In(OAc)(HTDT)$ (I) has bands at 510 m and 720 s(br) cm^{-1}, in keeping with the presence of In—CH_3 groups in the molecule. The Raman spectrum of a solution prepared by dissolving I in DMSO and allowing the gas evolution to go to completion shows no Raman emission at 511 cm^{-1}.

The ^1H NMR spectra confirm that the reaction of H_2TDT and $(CH_3)_2In(OAc)$ in DMSO involves the loss of CH_3 bonded to indium. The spectrum of $(CH_3)_2In(OAc)$ in DMSO has a sharp singlet at +0.05 ppm from external TMS. When H_2TDT was added, two additional resonances of equal intensity, appeared in this region, at +0.18 and +0.37 ppm respectively. After about 1 h at room temperature, the original signal from $(CH_3)_2In(OAc)$ had disappeared but the two new CH_3—In signals were still present, while after two days no resonance could be detected in this region. In all of these spectra, we also observed an acetate CH_3 resonance (+2.27 ppm), and aromatic CH_3 resonance (+2.49 ppm) and a multiplet at +7.5-8.0 ppm due to the benzene ring protons. These remained essentially unchanged in frequency throughout the series of measurements, although weakening in intensity as the reaction proceeds because of the low solubility of In(OAc)(TDT) in DMSO at room temperature. When $CH_3In(OAc)$ (HTDT) (I) was treated with DMSO, the spectrum of the resultant solution was again very weak, but approx. 5 min after the onset of the reaction, two resonances were closely visible in the In—CH_3 region. These disappear almost completely after a reaction time of 2 h at room temperature.

We suggest that the detection of two In—CH_3 resonances, both for a solution of I, and in the $(CH_3)_2In(OAc)/H_2TDT$ reaction mixture discussed above, is evidence for the presence of two species of different molecularity in the solution. Since the soluble fraction of I is a dimer in ethanol, it appears likely that the reaction scheme is:

$$(CH_3)_2In(OAc) \xrightarrow[-CH_4]{H_2TDT} \text{dimer I} \rightarrow \text{solvated monomer} \xrightarrow[-CH_4]{} In(OAc)(TDT)$$

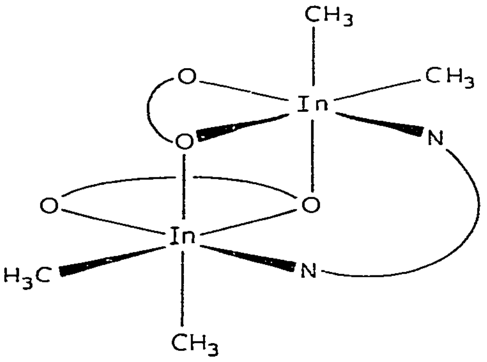
The reaction is then seen as proceeding completely from left to right when DMSO is the reaction medium, but halting with the precipitation of I in the presence of ethanol.

In the case of the bipy and phen adducts of In(OAc)(TDT), the vibrational spectra served to confirm *(a)* the absence of In—CH_3 stretching or rocking modes, and *(b)* the coordination of the bidentate ligand to the metal, using the standard literature criteria. NMR studies were not attempted for these systems.

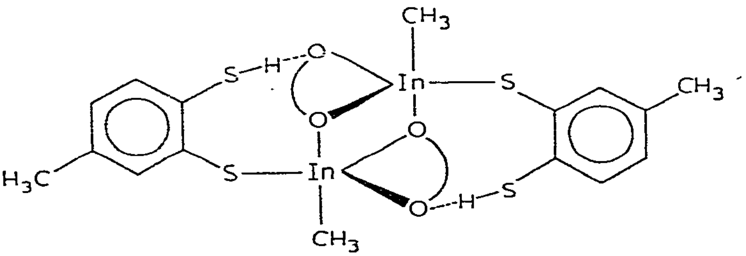
Structural

A monomeric In(OAc)(TDT) molecule would contain a pseudo-tetrahedral InO_2S_2 coordination kernel, but in view of the known [10] polymeric nature of crystalline $(CH_3)_2In(OAc)$, and the tendency of organoindium(III)-dithiolene complexes to associate [1], it seems unlikely that In(OAc)(TDT) would be monomeric in the solid state, despite the molecular weight evidence as to the lack of association in DMSO (see Experimental). The inability of this compound to form stable crystalline adducts with DMSO or pyridine is also in keeping with the analogous behaviour of indium(III) acetate [7], in which solid state polymerisation is again believed to be important. The bipy and phen adducts of In(OAc)(TDT) on the other hand are almost certainly monomeric six-coordinate $InO_2N_2S_2$ species, and we note in passing the usefulness of this preparative route to such unusual mixed-donor atom complexes.

The structure of the unusual intermediate $(CH_3)In(OAc)(HTDT)$ presents an interesting problem bearing in mind the evidence that the stable species in ethanol solution is the dimer. Dimeric species have been identified in adducts of $(CH_3)_2In(OAc)$ with certain bidentate donors [8], and the structure proposed for $[(CH_3)_2In(OAc)]_2$phen is derived from polymeric acetato(dimethyl)indium itself [10], namely:



The partial retention of intermolecular In—acetate bonding in the derivatives of $(CH_3)_2In(OAc)$ with bases is therefore established. The dimer $[(CH_3)In(OAc)$-



(I)

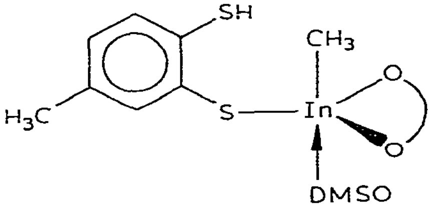
Fig. 1. The proposed structure of the dimer $[(CH_3)In(OAc)(HTDT)]_2$ (I).

$(HTDT)]_2$ is presumed to involve similar intermolecular bonding, but with the additional complication of two stabilised HTDT units. We propose the structure as shown in Fig. 1.

The methyl group on In and the acidic SH are prevented from reacting by *(a)* steric separation, and *(b)* the stabilisation of the SH by hydrogen-bonding to an acetate oxygen. The basic nature of such an oxygen is shown by its ability to bond to a neighbouring indium atom in the parent $(CH_3)_2In(OAc)$ [10]. A useful analogue for the stabilisation of acidic hydrogen atoms is in anions [11,12] such as $[(RCOO)_2H]^-$. Hydrogen bonding by thiols has been demonstrated by the NMR studies of Mathur and Li [13,14]. Evidence of the stabilisation of a potentially bidentate donor as a monodentate ligand to a metal is found in the crystal structure of $[(Meen)_2Cu(hfac)_2]$ (Meen = $(CH_3)_2NC_2H_4NH_2$; hfac = $CF_3 \cdot CO \cdot CH \cdot CO \cdot CF_3^-$), in which a six-coordinate copper atom is bonded to two bidentate diamine ligands and two monodentate hfac whose non-coordinated oxygens are hydrogen-bonded to the NH_2 groups of Meen [15]. The proposed structure for $[(CH_3)In(OAc)(HTDT)]_2$ is therefore in keeping with known structures, and with the spectroscopic and other information in the present paper.

Effect of solvent on the reaction

The effect of using DMSO instead of ethanol as a solvent in the $(CH_3)In(OAc)/H_2TDT$ reaction is to bring about further reaction between the —SH and In—CH_3 groups. We believe this arises in part because the higher solvating power of DMSO relative to ethanol breaks up the dimer I to produce a solvated monomer:



which is similar to the adduct [8] $(CH_3)_2In(OAc) \cdot DMSO$. The steric rigidity inherent in the dimer is now removed, and elimination of methane can readily occur. We have reported in earlier work [8] the ability of DMSO to break down the dimeric adduct $[(CH_3)_2In(OAc)]_2$ phen to produce a derivative of monomeric $(CH_3)_2In(OAc)$. The failure of ethanol to cause decomposition of the dimer I is in keeping with the relative coordinating ability of DMSO and ethanol. Equally, the failure of DMSO to bring about the release of the second mole of methane in the other systems studies is presumed to be evidence of an inherently high stability in the relevant dimer species.

Effect of acidity

It is reasonable to question whether the acidity of the acids studied plays any critical role in the stepwise reactions observed. The dissociation constants for three of the dibasic acids have been measured:

Phthalic acid:	K_1 1.12 × 10^{-3};	K_2 3.91 × 10^{-6}	[16]
Salicylic acid:	K_1 1.76 × 10^{-3};	K_2 4.2 × 10^{-13}	[16]
$C_2H_4(SH)_2$:	K_1 1.1 × 10^{-9};	K_2 3.2 × 10^{-11}	[17]

Propanedithiol is a weaker acid than $C_2H_4(SH)_2$ [18]. It is unfortunate that no values have been reported for H_2TDT, but one can derive some guidance from the known properties of related compounds. The dissociation constants of the benzenethiols are in the order $o\text{-}C_6H_4(SH)_2 > m\text{-}C_6H_4(SH)_2 > p\text{-}C_6H_4(SH)_2 > C_6H_5SH$; K_1 for C_6H_5SH [20] is 3.0 × 10^{-7}, so the K_1 for $o\text{-}C_6H_4(SH)_2$ may well be 10^{-5} (c.f. Sidgwick [21]), and a similar value should apply for H_2TDT; K_2 may be of the order of 10^{-8} (by analogy with K_1 and K_2 for catechol).

It is difficult to see that these figures offer any clear guidance as to the course of the reactions discussed above. With the exception of salicylic acid, K_1 and K_2 do not appear to differ substantially in any of the acids studied. Thus, while acid strength is doubtless one factor involved in the reaction, it does not appear to be the dominant factor.

We may note in this context that the Hammett constants [22,23] show that the CH_3 group in H_2TDT should make the —SH group at the 3-position slightly more reactive than that *para* to CH_3, but only by a factor of approx. 1.25. Thus the identification of the *p*-SH as being that remaining after the elimination of one mole of methane, and hence involved in intramolecular hydrogen-bonding (Fig. 1) is not a random choice, but equally one cannot exclude the possibility of a disordered arrangement of these —S and —SH groups in the solid state.

The reaction of hexamethylphosphoramide

As noted in the Experimental section, the methane yield in the $(CH_3)_2In(OAc)$—H_2TDT reaction in HMPA is only 66% of that calculated for one mole of gas. The simplest stoichiometric reaction would then involve $(CH_3)_2In(OAc)$ reacting as the trimer:

$$[(CH_3)_2In(OAc)]_3 + H_2TDT \rightarrow 2CH_4 + [(CH_3)_4In_3(OAc)_3(TDT)]$$

A number of possible structures can be written for this latter molecule, and an additional complication is that the product could equally well be $[(CH_3)_4In_3(OAc)_3(HTDT)_2]$, implying that each of two molecules of H_2TDT gives rise to one mole of methane. Elemental analysis shows the presence of nitrogen, so that the final product must also contain HMPA. A compound $(CH_3)_4In_3(OAc)_3(HTDT)_2(HMPA)_4$ would have C, 38.0; H, 7.1; N, 11.1; In, 22.8%, in reasonable agreement with the experimental results. The structural formulation of such a molecule, derived from $(CH_3)_2In(OAc)$ and based on six-coordination of all three indium atoms and hydrogen-bonding is not difficult, and a number of structures can be written.

The details of the structure are less important than the fact that analytical and gas evolution results point to the formation of a solvated unit involving three In(OAc) groups. The evidence in this paper shows that molecules based on three, two or one of these In(OAc) units can be prepared from the polymeric $(CH_3)_2$-In(OAc), which can clearly be degraded into oligomeric units of differing molecularity. A similar conclusion was reached from studies of the complexes which $(CH_3)_2$In(OAc) can form with various neutral mono- and bidentate donors [7]. These related phenomena are in part a reflection of the tendency of indium to seek a coordination number greater than four with small electronegative donor atoms.

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