Co-ordination Compounds of Indium. Part XXVIII.[1] Preparation and Oxidation of Indium(I) Derivatives of Bidentate Organic Bases

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Simple compounds of indium(I), InX, with the anions of bidentate monoprotic organic ligands have been prepared for the first time by the reaction of the parent acid with cyclopentadienylindium(I) in organic solvents [X = 4,4,4-trifluoro-1-(thien-2′-yl)butane-1,3-dionate, 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate, quinoline-8-olate, and the anions of 2-mercapto-pentan-3-one and -cyclohexanone]. Studies with one such compound, indium(I) quinoline-8-olate, show that reaction with mild oxidising agents or weak acids gives indium(III) species; this offers a useful synthetic route to unusual co-ordination compounds of In^{III}.

THE present lack of information on the preparation and reactions of indium(I) compounds has been commented upon previously in this series.[2] Relatively few simple salts have been described and the four monohalides, together with the oxide (In_2O) and sulphide (In_2S), constitute the list in standard textbooks. It therefore seemed worthwhile to explore both the possible routes to such compounds and their reactions.

Indium(I) species can be prepared in aqueous solution, and their reducing reactions with a number of reagents have been studied by Taylor and Sykes,[3] but the ready conversion into indium(III) makes this route unattractive for preparative work. The only In^I compound which is soluble in organic solvents is cyclopentadienylindium(I), and the properties of this substance make it a suitable starting point for exchange reactions of the type (1).

$$In(cp) + HX \longrightarrow InX + C_5H_6 \qquad (1)$$

We now report the preparation of In^I compounds of a variety of bidentate organic ligands by this route. The compounds are similar to those described by Lee[4] for thallium(I), although in the latter case the starting material was thallium(I) hydroxide. Because of the limitations imposed by the organic solvent, we have not been able as yet to obtain the analogous In^I compounds of inorganic acids.

RESULTS AND DISCUSSION

We have obtained indium compounds of some typical monobasic bidentate ligands in which the donor atoms are oxygen–oxygen [4,4,4-trifluoro-1-(thien-2′-yl)butane-1,3-dionate (ttbd) and 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate (hdod)], oxygen–nitrogen [quinoline-8-olate (qno)], and oxygen–sulphur (2-mercaptopentan-3-one and 2-mercaptocyclohexanone anions). The compounds (see Table) are all extremely hygroscopic, and the one criterion which must be respected in their preparation is the complete absence of water. There seems to be no reason to doubt that the methods described, based on reaction (1), could also be used to prepare analogous In^I derivatives of organic bases.

One failure of the method should be noted. The reaction of equimolar quantities of In(cp) and acetic acid in benzene–ethanol gave not indium(I) acetate but the previously reported[5] indium diacetate. We suggested previously that this compound is in fact a lattice of $In^{III}[O_2CMe]_3 + In^I[O_2CMe]$ in the solid state, so that reaction (1) (X = O_2CMe) is apparently followed either by disproportionation or by reaction with $MeCO_2H$ to give $In[O_2CMe]_3$ (see below) and thence $In[O_2CMe]_2$. The production of the diacetate in reaction (1) is further evidence of the stability of this unusual substance in the solid state. Attempts to produce $In^I[O_2CMe]$ by altering the stoicheiometry of the reaction mixture did not meet with success.

Analytical results (%) for the indium(I) compounds and derivatives

	Found			Calc.		
	C	H	In	C	H	In
In[ttbd]	30.6	1.6	34.0	28.7	1.5	34.1
In[hdod]	29.3	2.4	24.8	29.4	2.2	24.9
$In[O_2CMe]$	20.3	2.6	49.1	20.6	2.6	49.4
$In[SOC_5H_8]$			49.1			49.6
$In[SOC_6H_8]$ [b]			46.9			47.3
	In		qno	In		qno
$In^I[qno]$	44.9		54.9	44.4		55.5
$In[qno]_3$	21.3		79.7	21.0		78.9
$[In(qno)I_2]$	22.2		28.6	22.4		29.0
$[In(qno)I_2(bipy)]$	17.8		37.7	17.5		38.6
$[In(qno)(pd)_2]$	25.2		30.9	25.2		31.5
[In(qno)(tdt)]	27.5		34.1	27.9		34.9

[a] C_5H_8SO = 2-Mercaptopentan-3-one anion. [b] SOC_6H_8 = 2-Mercaptocyclohexanone anion.

Finally, in this context, we note that the compound In^I[hdod] was initially obtained as a precipitate when solutions of In(cp) and $Eu[hdod]_3$ were mixed in the course of exploratory experiments on the use of this n.m.r. shift reagent in organoindium chemistry.

Vibrational Spectra.—The i.r. spectrum of Tl^I[qno], as reported by Lee,[4] contains a band at 1 099.5 cm^{-1}, said to be associated with the C=O group, and another at 1 570 cm^{-1}; comparisons with the vibrations of the free ligands, and those of other qno compounds, leads to the conclusion that the qno group is acting as a chelate with Tl^I. The corresponding i.r. frequencies in In^I[qno] are at 1 110 and 1 582 cm^{-1}, and in $In[qno]_3$ at 1 113 and 1 582 cm^{-1}. These values demonstrate that the ligand is in a similar environment in Tl^I[qno], In^I[qno],

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[1] Part XXVII, J. J. Habeeb and D. G. Tuck, *Canad. J. Chem.*, 1974, **52**, 3950.

[2] J. G. Contreras, J. S. Poland, and D. G. Tuck, *J.C.S. Dalton*, 1973, 922 and refs. therein.

[3] R. S. Taylor and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 1628 and refs. therein.

[4] A. G. Lee, *J. Chem. Soc.* (*A*), 1971, 2008.

[5] J. J. Habeeb and D. G. Tuck, *J.C.S. Dalton*, 1973, 243.

and $In^{III}[qno]_3$, namely in a chelating interaction with the metal ion. Similarly, a comparison of the i.r. spectra of $In^{I}[ttbd]$ and $In[ttbd]_3$ shows these spectra to be identical in the $\nu(C=O)$ and $\nu(C=C)$ regions, again establishing that the diketonate is acting as a chelating agent in both molecules in the solid state.

Solution Studies.—None of the In^{I} compounds prepared is sufficiently soluble for n.m.r. studies, and in fact the solubility in organic solvents is extremely low in all cases. For this reason it was not possible to record u.v.–visible spectra (*cf.* ref. 4), but we were able to carry out molecular-weight determinations for $In^{I}[qno]$ in dimethyl sulphoxide at 40 °C, at which temperature the solubility is noticeably enhanced. Three experiments gave values of 814, 829, and 806 respectively calc.: for $In^{I}[qno]$: 259), implying a degree of association of 3.15 under these conditions. Taken in conjunction with the vibrational spectra, these results suggest that the solid $In^{I}[qno]$ consists of a highly associated lattice of metal ion and chelate ligand units. The solid-state stability of this compound and its analogues, in terms of disproportionation to In^{0} and In^{III}, is presumably dependent on this association. The chelation of β-diketonates to Group 1 metals has been reported previously,[6,7] and it appears that the In^{I} compounds are structurally similar to the alkali-metal compounds, except in the matter of the extent of association in the solid.

Oxidation of $In^{I}[qno]$.—The oxidation of In(cp) to give In^{III} compounds by insertion into I–I [8] or S–S [9] bonds has been established in previous papers. We have now shown that the In^{I} compounds described in the present work are also readily oxidised. Some interesting reactions of potential application in the synthesis of In^{III} co-ordination compounds have been explored, specifically in terms of the oxidation of $In^{I}[qno]$. Thus complete reaction with iodine corresponded to addition of an equimolar amount of I_2, and the product was $[In^{III}(qno)I_2]$; this reaction is clearly analogous to that between I_2 and In(cp).[8] The product had the typical reactions of an In^{III} species, in that it formed a 1 : 1 adduct $[In(qno)I_2(bipy)]$ with the neutral bidentate donor 2,2′-bipyridyl. The reaction of $In^{I}[qno]$ with further quantities of Hqno yielded the known compound $In[qno]_3$. Similarly, treatment with pentane-2,4-dione (Hpd) and toluene-3,4-dithiol (H_2tdt) gave $[In^{III}(qno)(pd)_2]$ and $[In^{III}(qno)(tdt)]$ respectively. These reactions of $In^{I}[qno]$ with weak acids are presumably most simply written as (2), a reaction which is

$$In^{I}[qno] + 2HX \longrightarrow [In^{III}(qno)X_2] + H_2 \quad (2)$$

similar to that proposed in an earlier discussion of the reaction of In^{I} halides with Hpd to give dihalogeno(pentane-2,4-dionato)indium(III) compounds.[10,11]

In conclusion, we note that the use of $In^{I}[qno]$ as a starting material gives rise to InO_3N_3, InO_5N, $InONI_2$, $InON_3I_2$, and $InONS_2$ co-ordination kernels; this list could no doubt be extended to provide synthetic routes to a variety of other In^{III} compounds.

EXPERIMENTAL

General.—Preparative and spectroscopic methods were as described in earlier papers.[1,2] Indium analysis was by atomic-absorption spectrophotometry. The first compounds prepared were analysed for In, C, and H; subsequently, only indium analysis was used in view of the similarity of the experimental methods used in the preparative work. For $In^{I}[qno]$ and its derivatives, indium analysis and qno determination served to characterise the compounds. Quinoline-8-olate was brominated with KBr–$K[BrO_3]$, and excess of $K[BrO_3]$ determined by release of I_2 from KI, followed by titration against standard sodium thiosulphate solution.[12] This procedure was checked with known amounts of qno in the presence of indium salts.

Preparation of Indium(I) *Compounds.*—Cyclopentadienylindium was prepared by the method of Fischer and Hofmann.[13] In a typical experiment, solutions of equimolar quantities of In(cp) and quinoline-8-ol (Allied Chemical) in diethyl ether–benzene (1 : 4) were mixed at room temperature. The yellow-green precipitate of *indium*(I) *quinoline-8-olate* which formed after *ca.* 20 min was washed with dry diethyl ether and dried *in vacuo*. Similar methods were successful for the other compounds in the Table. In the case of the reaction of In(cp) and $Eu[hdod]_3$, crystals were detected after a period of *ca.* 16 h at −10 °C.

Oxidation of $In^{I}[qno]$.—When a solution of I_2 in benzene was added dropwise to a freshly prepared solution of In[qno] in diethyl ether–benzene (1 : 4) the colour of the former was discharged immediately. The addition was continued until an orange precipitate of *di-iodo(quinoline-8-olato)indium*(III) was obtained; this was collected, washed, and dried in the usual manner. In a later experiment, $[In^{III}(qno)I_2]$ and 2,2′-bipyridyl were dissolved in benzene–diethyl ether at 40 °C, and the solution placed in a refrigerator; after 2 weeks, yellow-green crystals of *(2,2′-bipyridyl)di-iodo(quinoline-8-olato)indium*(III) were collected.

When a freshly precipitated sample of $In^{I}[qno]$ was heated under reflux with 2 equivalents of Hqno in diethyl ether–benzene for 2 h under nitrogen the solid dissolved. Reduction of the volume of the solution and cooling to 0 °C produced yellow crystals of $In[qno]_3$. A similar procedure using Hpd yielded $[In(qno)(pd)_2]$, while addition of H_2tdt to a freshly prepared solution of $In^{I}[qno]$ produced an immediate yellow precipitate of *(quinoline-8-olato)(toluene-3,4-dithiolato)indium*(III).

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