Co-ordination Compounds of Indium. Part 47.[1] Indium(I) and Thallium(I) Derivatives of Alkanedithiols

Corrado Geloso, Hassan E. Mabrouk, and Dennis G. Tuck
Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario N9B 3P4, Canada

The electrochemical oxidation of anodic indium in non-aqueous solutions of a series of alkanedithiols $R(SH)_2$ (R = 1,2-C_2H_4, 1,2-C_3H_6, 1,3-C_3H_6, 1,4-C_4H_8, 2,3-C_4H_8, 1,5-C_5H_{10}, or 1,6-C_6H_{12}) gives the unusual indium(I) compounds In[SR(SH)], containing the alkanethiol(thiolato) ligand. These compounds can be deprotonated by either NEt_3 or $NBu^n{}_4OH$ to form salts of the $[In^I(S_2R)]^-$ anion; this anionic complex can be oxidized by I_2 to the corresponding indium(III) species $[In^{III}I_2(S_2R)]^-$, which can also be produced by successive I_2 oxidation and deprotonation of $In^I[SR(SH)]$. Reaction with the *o*-quinones *o*-$X_4C_6O_2$ gives the catecholato derivatives $[In^{III}\{SR(SH)\}(O_2C_6X_4\text{-}o)]$ (X = Cl or Br). Carbon disulphide insertion occurs at only one In–S bond. With thallium, the products of electrochemical oxidation are $Tl_2(S_2R)$ in all the cases studied.

The lower oxidation states of indium still represent a relatively unexplored area of Group 3 chemistry,[2] and one obvious hindrance to progress is the lack of readily available starting materials for synthetic work. As far as indium(I) is concerned, the solubility of cyclopentadienylindium(I), $[In(C_5H_5)]$, has lead to the synthesis of anionic[3] or neutral[4] indium(I) compounds, and in view of the results discussed below it is relevant that the reaction between $[In(C_5H_5)]$ and 2-mercaptopentan-3-one or 2-mercaptocyclohexanone (HL) gives the corresponding InL species, the only indium(I) thiolates reported to date. Non-aqueous solutions of indium(I) halides have also proven useful in synthesis,[5] and in terms of the present result it is important that both $[In(C_5H_5)]$ and InX (X = Cl, Br, or I) readily undergo oxidation with mild reagents such as iodine,[6] diphenyl disulphide[7] (or selenide),[7] and substituted *o*-benzoquinones.[8]

The electrochemical oxidation of sacrificial anodes as a route to both inorganic and organometallic compounds has been extensively studied in this laboratory,[9] and one of the several useful features of this method is the tendency to form products in which the metal is in a low oxidation state. A recent relevant example is the synthesis of catecholatotin(II) and related compounds.[10] We now report that the oxidation of indium in solutions of alkanedithiols $R(SH)_2$ gives the unusual indium(I) species In[SR(SH)] in good yield, by work which is an extension of previous syntheses of zinc and cadmium $M(S_2R)$ compounds.[11] The oxidation of these indium(I) compounds has been studied. In contrast, the use of thallium anodes leads to the more conventional $Tl_2(S_2R)$ compounds.

Experimental

Indium and thallium metals (Alfa Inorganics) were in the form of rods, 0.6 cm in diameter. Acetonitrile (Reagent Grade) was distilled before use, and stored over phosphorus pentoxide. Dithiols and other reagents were used as supplied (Aldrich).

Inorganic halogen analysis was by the Volhard method,[12] and metal analysis by atomic absorption spectrophotometry, using an IL 250 instrument. Elemental analyses were by Guelph Chemical Laboratories Ltd.

Infrared spectra were recorded with a Nicolet 5DX instrument, using KBr discs. Molar conductivities were measured in a standard platinum electrode cell, standardized with 1 mol dm^{-3} aqueous KNO_3, using a YSI model 31 conductivity bridge.

Preparative Electrochemistry.—The electrochemical methods used were those in general use in this laboratory. The cell consisted of a tall-form beaker (100 cm^3), and the solution phase was a mixture of the appropriate dithiol (0.1—0.2 g) dissolved in acetonitrile (50 cm^3) containing tetraethylammonium perchlorate (*ca.* 30 mg). The anode (area *ca.* 2 cm^2) was supported on a platinum wire, and a second coiled platinum wire (*ca.* 1 mm in diameter, 5 cm long) formed the cathode. The high applied voltage required to drive ions through the low dielectric solution phase was supplied by a Coutant LQ 50/50 power supply, capable of delivering up to 200 mA at 50 V. The composition of the solution phase, the electrochemical conditions, and other experimental details are given in Tables 1 and 2. All experiments were conducted at room temperature in an atmosphere of dry nitrogen, which was bubbled slowly through the cell and so served to agitate the contents of the solution gently during the electrolysis.

In a typical experiment, the electrochemical oxidation of an indium anode in a solution phase of acetonitrile (50 cm^3), ethane-1,2-dithiol (0.12 cm^3, 0.13 g, 1.4 mmol), and tetraethylammonium perchlorate (30 mg) was carried out for 2 h at 10 V and 20 mA. As the electrolysis proceeded, hydrogen gas evolved at the cathode, and a yellow product formed at the anode; this material, which deposited in the cell during the experiment, was subsequently collected and washed several times with acetonitrile, dried *in vacuo*, yield 0.24 g (1.15 mmol, 83% on the basis of 160 mg of indium metal dissolved), and identified as $In(SC_2H_4SH)$. Essentially identical procedures gave $In(SC_nH_{2n}SH)$ (*n* = 3—6) in yields ranging between 75 and 88%, while with thallium anodes the products were identified as $Tl_2(S_2C_nH_{2n})$.

Characterization of these products depended on elemental analysis and i.r. spectroscopy to confirm the presence of the ligand, since the insolubility prevented the use of n.m.r. spectroscopy. Analytical results are given in Tables 3 and 4.

Deprotonation of $In(SC_nH_{2n}SH)$.—(*i*) The compound $In(SC_6H_{12}SH\text{-}1,6)$ (0.40 g, 1.52 mmol) was added to a solution of NEt_3 (0.21 cm^3, 0.15 g, 1.51 mmol) in acetonitrile, (20 cm^3), and the mixture stirred for 6 h. The yellow colour of the suspended solid disappeared, and the colourless product was collected, washed with acetonitrile, dried *in vacuo*, and identified as $[NEt_3H][In(S_2C_6H_{12}\text{-}1,6)]$; yield 0.44 g, 80%. Similar procedures with $In(SC_4H_8SH\text{-}1,4)$ and NEt_3 yielded $[NEt_3H][In(S_2C_4H_8\text{-}1,4)]$.

(*ii*) The compound $In(SC_4H_8SH\text{-}1,4)$ (0.70 g, 3.0 mmol),

Table 1. Experimental conditions for the electrochemical synthesis of In[S(CH$_2$)$_n$SH] compounds

Dithiol	Time of electrolysis (h)	Voltage[a] (V)	Metal consumed (mg)	Mass of product (g)	Yield[b] (%)	E_F (mol F^{-1})
1,2-C$_2$H$_4$(SH)$_2$	2	10	165	0.24	83	0.97
1,2-C$_3$H$_6$(SH)$_2$	2	10	160	0.23	75	0.94
1,3-C$_3$H$_6$(SH)$_2$	2	10	168	0.23	72	0.98
1,4-C$_4$H$_8$(SH)$_2$	2	20	170	0.31	90	0.99
2,3-C$_4$H$_8$(SH)$_2$	0.5	30	39	0.06	75	0.90
1,5-C$_5$H$_{10}$(SH)$_2$	0.5	30	36	0.08	85	0.85
1,6-C$_6$H$_{12}$(SH)$_2$	2	10	180	0.36	88	1.05

[a] Voltage to give an initial current of 20 mA. [b] Based on quantity of metal consumed.

Table 2. Experimental conditions for the electrochemical synthesis of Tl$_2$[S$_2$(CH$_2$)$_n$] compounds *

Dithiol	Voltage (V)	Time of electrolysis (h)	Metal consumed (mg)	Mass of product (mg)	Yield (%)	E_F (mol F^{-1})
1,2-C$_2$H$_4$(SH)$_2$	30	1.75	280	263	77	1.05
1,2-C$_3$H$_6$(SH)$_2$	35	0.5	106	119	89	—
1,3-C$_3$H$_6$(SH)$_2$	35	0.5	82	101	98	1.07
1,4-C$_4$H$_8$(SH)$_2$	35	0.5	79	—	—	1.03
2,3-C$_4$H$_8$(SH)$_2$	25	0.6	106	119	87	1.10
1,5-C$_5$H$_{10}$(SH)$_2$	20	0.5	79	102	97	1.03
1,6-C$_6$H$_{12}$(SH)$_2$	30	0.5	57	64	83	0.74

* Footnotes as in Table 1.

Table 3. Analytical results for In[S(CH$_2$)$_n$SH] compounds and derivatives

		In (%)		I (%)	
Compound	Colour	Found	Calc.	Found	Calc.
In(SC$_2$H$_4$SH-1,2)	Yellow	55.5	55.6	—	—
In(SC$_3$H$_6$SH-1,2)	Yellow	51.5	51.8	—	—
In(SC$_3$H$_6$SH-1,3)	Yellow	51.8	51.7	—	—
In(SC$_4$H$_8$SH-1,4)[a]	Yellow	48.9	48.6	—	—
In(SC$_4$H$_8$SH-2,3)	Yellow	48.8	48.6		
In(SC$_5$H$_{10}$SH-1,5)	Orange	46.4	46.2		
In(SC$_6$H$_{12}$SH-1,6)[b]	Yellow	43.6	43.5	—	—
InI$_2$(SC$_2$H$_4$SH-1,2)	Colourless	25.0	24.9	54.9	54.9
InI$_2$(SC$_3$H$_6$SH-1,2)	Pale yellow	24.2	24.1	53.8	53.3
InI$_2$(SC$_3$H$_6$SH-1,3)	Cream	24.4	24.1	53.2	53.3
InI$_2$(SC$_4$H$_8$SH-1,4)	Cream	23.7	23.5	51.7	51.8
InI$_2$(SC$_6$H$_{12}$SH-1,6)	Yellow-green	22.2	22.4	49.0	49.0
[NEt$_3$H][In(S$_2$C$_6$H$_{12}$-1,6)][c]	Colourless	31.8	31.5	—	—
[NEt$_3$H][InI$_2$(S$_2$C$_4$H$_8$-1,4)]	Cream	19.3	19.5	43.1	43.0
[NEt$_3$H][InI$_2$(S$_2$C$_6$H$_{12}$-1,6)]	Cream	18.6	18.6	41.2	41.0
[NBu$_4$][In(S$_2$C$_4$H$_8$-1,4)]	Colourless	23.1	23.3	—	—
[NBu$_4$][In(S$_2$C$_6$H$_{12}$-1,6)]	Colourless	22.0	22.0	—	—
[NBu$_4$][InI$_2$(S$_2$C$_4$H$_8$-1,4)]	Colourless	15.2	15.4	34.0	34.0
[NBu$_4$][InI$_2$(S$_2$C$_6$H$_{12}$-1,6)]	Colourless	14.9	14.8	32.9	32.8
[In(SC$_2$H$_4$SH-1,2)(O$_2$C$_6$Br$_4$-*o*)]	Yellow	18.1	18.2	—	—
[In(SC$_2$H$_4$SH-1,2)(O$_2$C$_6$Br$_4$-*o*)]·2py	Pale yellow	14.7	14.5	—	—
[In(SC$_2$H$_4$SH-1,2)(O$_2$C$_6$Cl$_4$-*o*)]	Yellow	25.4	25.3	—	—
[In(SC$_2$H$_4$SH-1,2)(O$_2$C$_6$Cl$_4$-*o*)]·2py	Deep yellow	18.7	18.8	—	—
In(SC$_4$H$_8$SH-1,4)·CS$_2$	Deep yellow	36.8	36.9	—	—
In(SC$_6$H$_{12}$SH-1,6)·CS$_2$	Yellow-orange	33.6	33.7	—	—

[a] Found: C, 19.5; H, 3.6; S, 26.2. Calc.: C, 20.4; H, 3.85; S, 27.2%. [b] Found: C, 28.0; H, 4.75. Calc.: C, 27.3; H, 4.95%. [c] Found: C, 38.7; H, 7.70. Calc.: C, 39.5; H, 7.9%.

suspended in acetonitrile (20 cm^3), was treated with 40% NBu$^n_4$OH (1 cm^3, 3.9 mmol) and stirred overnight. The colourless insoluble solid was collected, washed with acetonitrile, and dried *in vacuo*. This product was identified as [NBu$^n_4$][In(S$_2$C$_4$H$_8$-1,4)] (1.28 g, 74% yield).

Oxidation of In(SC$_n$H$_{2n}$SH)].—(*i*) The compound In(SC$_4$H$_8$SH-1,4) (0.45 g, 1.91 mmol) was suspended in acetonitrile (10 cm^3) and a solution of iodine (0.49 g, 1.93 mmol as I$_2$) in the same solvent (10 cm^3) added dropwise over 1 h with stirring. After this period the solution phase was almost colourless; stirring was continued for another hour, and the resultant cream solid collected, washed with acetonitrile, and dried *in vacuo*; yield of InI$_2$(SC$_4$H$_8$SH-1,4) 0.78 g (83%).

Table 4. Analytical results for $Tl_2(S_2C_nH_{2n})$ compounds

Compound	Colour	Tl (%) Found	Tl (%) Calc.
$Tl_2(S_2C_2H_4$-1,2)	Orange	81.8	81.6
$Tl_2(S_2C_3H_6$-1,2)*	Orange	79.8	79.4
$Tl_2(S_2C_3H_6$-1,3)	Orange	80.0	79.4
$Tl_2(S_2C_4H_8$-1,4)	Yellow-orange	77.7	77.3
$Tl_2(S_2C_4H_8$-2,3)	Orange	76.7	77.3
$Tl_2(S_2C_5H_{10}$-1,5)	Yellow	76.3	75.3
$Tl_2(S_2C_6H_{12}$-1,6)	Yellow	73.1	73.4

* Found: C, 6.60; H, 1.05. Calc.: C, 7.00; H, 1.15%.

(*ii*) Similar reactions between $In(SC_nH_{2n}SH)$ (n = 2, 3, or 6) and an equimolar quantity (1.25 mmol) of I_2 in acetonitrile gave $InI_2(SC_nH_{2n}SH)$ in yields of the order of 80%.

Preparation of $[NEt_3H][InI_2(S_2C_6H_{12}$-1,6)].—The compound $In(SC_6H_{12}SH$-1,6) (0.74 g, 2.80 mmol) was suspended in acetonitrile (20 cm^3) and iodine (0.72 g, 2.82 mmol) in acetonitrile (10 cm^3) added dropwise with stirring over 2 h, during which time the colour of iodine discharged and a greenish yellow product formed. To this mixture was added NEt_3 (0.39 cm^3, 0.28 g, 2.81 mmol) with stirring. An immediate change of colour to cream was observed, and after a further 2 h the solid was collected, washed, and dried *in vacuo*. The product was identified as $[NEt_3H][InI_2(S_2C_6H_{12}$-1,6)] (1.25 g, 72%). Analogous experiments gave $[NEt_3H][InI_2(S_2C_4H_8$-1,4)] from the reaction of $In(SC_4H_8SH$-1,4) with I_2 in the presence of NEt_3.

Formation of $[NBu^n_4][InI_2(S_2C_4H_8$-1,4)].—The preparation of this compound can be carried out by either of the following methods.

(*i*) The reaction of $In(SC_4H_8SH$-1,4) (0.54 g, 2.32 mmol) with NBu^n_4OH (2.50 mmol) to form $[NBu^n_4][In(S_2C_4H_8$-1,4)] was carried out in acetonitrile as described above. Iodine (I_2, 0.59 g, 2.32 mmol) in the same solvent was added, and the mixture stirred for 2 h, after which the colourless insoluble product was collected, washed with acetonitrile, and dried *in vacuo*. This product was identified as $[NBu^n_4][InI_2(S_2C_4H_8$-1,4)] (1.23 g, 73%).

(*ii*) The compound $In(SC_4H_8SH$-1,4) (0.40 g, 1.70 mmol) was suspended in acetonitrile (25 cm^3), iodine (0.44 g, 1.72 mmol) in MeCN added dropwise over 1 h, and the mixture stirred until the colour of iodine discharged, after which 40% NBu^n_4OH (0.45 cm^3, 1.72 mmol) was added with stirring over 3 h. The colourless solid product was collected, washed with acetonitrile, and dried *in vacuo*. The product was identified as $[NBu^n_4][InI_2(S_2C_4H_8$-1,4)] (0.94 g, 75% yield). Essentially identical procedures with $In(SC_6H_{12}SH$-1,6) gave $[NBu^n_4][InI_2(S_2C_6H_{12}$-1,6)] by either method (*i*) or (*ii*).

Reaction of $In(SC_2H_4SH$-1,2) *with* $X_4C_6O_2$-*o* (X = Cl *or* Br).—(*i*) The compound $In(SC_2H_4SH$-1,2) (0.21 g, 1.0 mmol) was suspended in acetonitrile (20 cm^3), and a solution of *o*-$Cl_4C_6O_2$ (0.25 g, 1.02 mmol) in the same solvent added. During a period of 4 h, the deep brown colour of the quinone disappeared; at the end of this period the resultant insoluble yellow product was collected, washed, and dried *in vacuo*. The substance was identified as the oxidative-addition product $[In(SC_2H_4SH$-1,2)$(O_2C_6Cl_4)]$; yield 0.39 g, 83%.

(*ii*) The compound $In(SC_2H_4SH$-1,2) (0.21 g, 1.00 mmol) was suspended in acetonitrile (20 cm^3) and pyridine (0.16 cm^3, 0.17 g, 2.13 mmol) added, followed by *o*-$Cl_4C_6O_2$ (0.25 g, 1.02 mmol) in acetonitrile. After stirring for 4 h, during which the brown colour disappeared, the solid product was collected, washed, and dried *in vacuo*. This product is the bis(pyridine) adduct $[In(SC_2H_4SH$-1,2)$(O_2C_6Cl_4$-*o*)]·2py; yield 0.51 g, 82%.

(*iii*) This same oxidative-addition reaction was also identified when $In(SC_2H_4SH$-1,2) was treated with tetrabromo-*o*-quinone in the presence or absence of pyridine.

Reaction with Carbon Disulphide.—(*i*) The compound $In(SC_6H_{12}SH$-1,6) (0.35 g, 1.33 mmol), prepared electrochemically, was suspended in acetone (20 cm^3) and carbon disulphide (0.1 cm^3, 0.13 g, 1.66 mmol) added. An immediate change of colour to yellow-orange was observed; after agitation for 2 h, the solid was collected, washed with acetone, and dried *in vacuo*. The product was identified as $In(SC_6H_{12}SH$-1,6)·CS_2 (0.38 g, 84%). Essentially identical procedures with $In(SC_4H_8SH$-1,4) gave the corresponding 1:1 CS_2 addition compound.

Elimination of CS_2.—A suspension of $In(SC_6H_{12}SH$-1,6)·CS_2 (0.4 g, 1.18 mmol) in toluene (30 cm^3) was refluxed for 4 h. The colour of the solid changed from yellow-orange to yellow. The suspended product was collected, washed with toluene, dried *in vacuo*, and subsequently identified as $In(SC_6H_{12}SH$-1,6) (0.29 g, 94% yield). Infrared spectroscopy (see below) confirmed the absence of CS_2. A similar result was obtained when $In(SC_4H_8SH$-1,4)·CS_2 was the starting material.

Results and Discussion

Electrochemical Synthesis.—As with other systems involving the formation of metal derivatives of weak acids reported from this laboratory, the present work shows that the electrochemical oxidation of either indium or thallium in solutions of alkanediols is a simple, one-step, efficient route to either $In(SC_nH_{2n}SH)$ or $Tl_2(S_2C_nH_{2n})$. The formation of these two compounds of different stoicheiometry must reflect differing metal–ligand interactions, rather than different electrochemical reactions. Following our standard procedures, we have measured the electrochemical efficiency, E_F, defined as the moles of metal dissolved from the sacrificial anode per Faraday of charge, for both indium and thallium systems (see Tables 1 and 2). The average E_F values are 0.95 ± 0.05 and 1.06 ± 0.03 mol F^{-1}, respectively, so that we can assume an overall value of unity for all the systems studied, independent of the metal or dithiol used.

We have commented elsewhere[10,11] on the interpretation of electrochemical efficiencies for diprotic solutes. In essence, one can write two sequences, involving either the dianion [equations (1) and (2)] or the monoanion [equations (3) and (4)]. At first

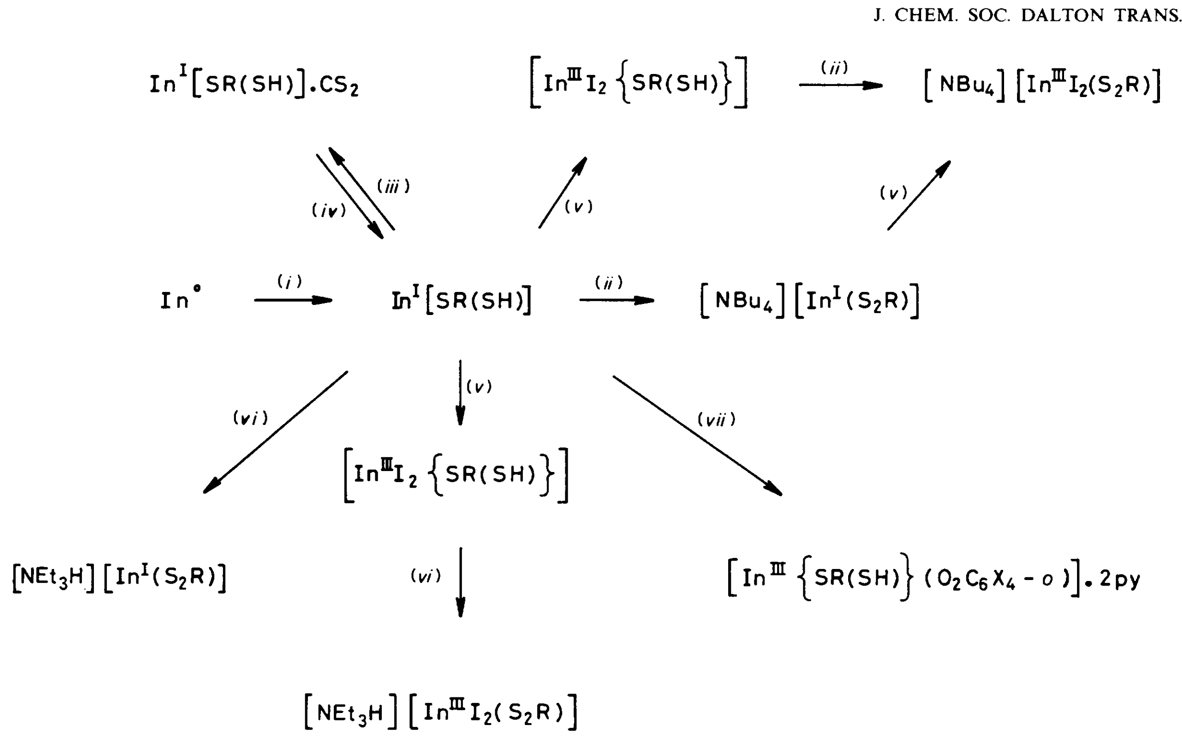
$$\text{cathode: } R(SH)_2 + 2e \longrightarrow RS_2^{2-} + H_2(g) \qquad (1)$$

$$\text{anode: } RS_2^{2-} + M \longrightarrow M_2(S_2R) + 2e \qquad (2)$$

$$\text{cathode: } R(SH)_2 + e \longrightarrow RS_2H^- + \tfrac{1}{2}H_2(g) \qquad (3)$$

$$\text{anode: } RS_2H^- + M \longrightarrow M(SRSH) + e \qquad (4)$$

sight, sequence (1) + (2) explains the formation of $Tl_2(S_2R)$ compounds, and (3) + (4) leads to In[SR(SH)], but given the close similarity of the experimental conditions there is no reason to suppose that two different anions are in fact involved. There is also a variant of (3) + (4), included here only for the sake of completeness,[11] in which the migrating anion is hydrogen bonded to a neutral dithiol to give a dimer of the type $[(HS)RSHSR(SH)]^-$. Parallel identical experiments with indium and thallium anodes in cells containing the same solution of HSC_3H_6SH (0.15 cm^3) in MeCN (50 cm^3) showed



Scheme. (*i*) $R(SH)_2$; (*ii*) NBu_4OH; (*iii*) CS_2; (*iv*) heat; (*v*) I_2; (*vi*) NEt_3; (*vii*) (*a*) *o*-$X_4C_6O_2$ (X = Cl or Br), (*b*) py

Table 5. Conductivity results for salts of anionic derivatives of $In(SC_nH_{2n}SH)$

Salt	Solvent[a]	Molar conductivity[b]/ ohm^{-1} cm^2 mol^{-1}
$[NEt_3H][In(S_2C_6H_{12}\text{-}1,6)]$	$MeNO_2$	78
$[NEt_3H][InI_2(S_2C_4H_8\text{-}1,4)]$	$MeNO_2$	81
$[NEt_3H][InI_2(S_2C_6H_{12}\text{-}1,6)]$	$MeNO_2$	75
$[NBu_4][In(S_2C_4H_8\text{-}1,4)]$	Me_2SO	57
$[NBu_4][In(S_2C_6H_{12}\text{-}1,6)]$	Me_2SO	52
$[NBu_4][InI_2(S_2C_4H_8\text{-}1,4)]$	Me_2SO	48
$[NBu_4][InI_2(S_2C_6H_{12}\text{-}1,6)]$	Me_2SO	42

[a] Solute concentration 10^{-3} mol l^{-1}. [b] Standard values for 1:1 electrolytes in these solvents are in the range 60—115 ohm^{-1} cm^2 mol^{-1} for $MeNO_2$, and 50—70 ohm^{-1} cm^2 mol^{-1} for Me_2SO (W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81).

only one qualitative difference; the indium product was brown when first precipitated and became pale yellow over about 20 min, whereas the thallium product was yellow throughout. This suggests that the primary product is $M_2(S_2C_3H_6)$ in both cases and that, in the case of indium, precipitation is followed by a relatively slow protonation process whose stoicheiometry is as in equation (5). Quantitative studes of this problem are planned.

$$In_2(S_2C_3H_6)\,(s) + HSC_3H_6SH \longrightarrow 2\,In(SC_3H_6SH)\,(s) \qquad (5)$$

The products were characterized analytically (Tables 3 and 4), by i.r. spectroscopy, and by conductivity measurements; these results are discussed below. In terms of the general behaviour, these compounds are stable to atmospheric exposure, do not melt below *ca.* 300 °C, are insoluble in common organic solvents, and do not form adducts with neutral donor ligands.

Structural Relationships.—Thallium(I) is a very weakly co-ordinating cation, and many of its solid-state derivatives do not apparently involve donation from ligands present in the lattice. Relevant examples in which the unco-ordinated Tl^+ ion exists are $Tl_2(mnt)$ (mnt = 1,1-dicyanoethylene-2,2-dithiolate anion),[13] and adducts of thiourea(L) and various thallium(I) salts;[14] in the case of TlX·4L (X = NO_3 or ClO_4) the Tl ··· S distance of 3.41(1) Å is greater than the sum of the ionic radii,[15] and a similar condition[16] applies in $Tl(H_2PO_4)$·4L and $Tl(O_2CPh)$·4L. It seems reasonable to conclude that the present $Tl_2(S_2R)$ compounds are also essentially ionic in the solid state.

The indium(I) species are clearly different in structure, and we have investigated their chemical behaviour in two respects, namely oxidation to the corresponding indium(III) species, and deprotonation. The overall results shown in the Scheme are similar to those for In[OR(OH)] compounds also studied in this laboratory,[17] and the oxidation reactions parallel those for tin(II) aryloxides.[10]

When $In(SC_nH_{2n}SH)$ (*n* = 4 or 6) was treated with NEt_3 or NBu_4OH the products were the corresponding NEt_3H^+ or $NBu_4{}^+$ salts of $[In(S_2C_nH_{2n})]^-$, which are 1:1 electrolytes in nitromethane or dimethyl sulphoxide (Table 5). Like other indium(I) compounds such as $[In(C_5H_5)]$[6] and In(SR),[18] $In(SC_nH_{2n}SH)$ compounds react readily with iodine to yield the corresponding indium(III) compound $InI_2(SC_nH_{2n}SH)$. Equally, indium(I) compounds react with *o*-$X_4C_6O_2$ (X = Cl or Br) in the presence or absence of pyridine to form a product which is either an indium(III) catecholato complex, $[In(SC_nH_{2n}SH)(O_2C_6X_4\text{-}o)]$, or its bis(pyridine) adduct, and such oxidative-addition reactions exactly parallel those of indium(I) halides with the same tetrahalogeno-*o*-quinones,[8] as demonstrated by the spectroscopic evidence discussed below. This confirmation of the oxidation state of the $In(SC_nH_{2n}SH)$ products has also been extended to the deprotonated products, since these can be oxidized by iodine to give salts of the indium(III) anions $[InI_2(S_2C_nH_{2n})]^-$. Equally, the indium(III) compounds $InI_2(SC_nH_{2n}SH)$ can be deprotonated to give the $[InI_2(S_2C_nH_{2n})]^-$ complexes, so that the sequence of oxidation + deprotonation can be applied in either direction (Scheme).

This work then confirms the oxidation state of the metal in these unusual species.

A small number of complexes containing the SH ligand is known, and in each case the metal involved is a transition element in a low oxidation state.[19] A co-ordinated thiol has recently been identified[20] in $[IrH(SC_2H_4PPh_2)(HSC_2H_4PPh_2)(CO)]Cl$, and a more directly comparable species is the molybdenum anion[21] in the salt $[NEt_3H][Mo_2(N_2Ph)(HN_2Ph)(S_2C_2H_4)_3(SC_2H_4SH)]\cdot 0.66H_2NNHPh$. A comparable series of indium(I) complexes of aromatic oxohydroxy ligands has been prepared electrochemically,[17] and the thallium(I) 2′-hydroxy-2-oxidobiphenyl compound $Tl(OC_{12}H_8OH)$ and the thallium(III) analogue $[TlEt_2(OC_{12}H_8OH)]$ are also known.[22] There is clearly insufficient evidence at present on which to identify the conditions which favour the stabilization of such singly deprotonated ligands.

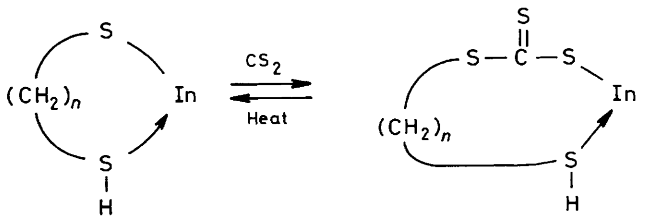
Give the propensity of metal thiolates to form homopolymers in the solid state, it appears that the neutral indium complexes reported here are of this type, with $S \rightarrow In$ cross-linking. The role, if any, of the lone pair on indium(I), and of $S{-}H \cdots S$ hydrogen bonding, in the presumed homopolymerization, has not been studied in the present work.

Infrared Spectroscopy.—The i.r. spectra of the compounds listed in Tables 3 and 4 confirm the presence of the $SC_nH_{2n}SH$ groups. The C–C and C–H bending and stretching modes are essentially unchanged from those in the spectra of the parent dithiols, as shown by comparison with the spectra of the starting materials. The ν(S–H) band, typically at *ca.* 2 550 cm^{-1} for the dithiols, is absent for all the products, and we believe that in the case of the $In(SC_nH_{2n}SH)$ derivatives this mode is lowered and broadened by intermolecular interactions in the solid state (see above); very broad weak bands are observed at *ca.* 2 000 cm^{-1}. The ν(C–S) mode is essentially unaffected by the change from dithiol to complex, being in the region of 640 cm^{-1} in both circumstances.

The NEt_3H^+ salts prepared by the reaction between NEt_3 and $In(SC_nH_{2n}SH)$ (n = 4 or 6) show the typical broad complex absorptions of the cation between 2 480 and 2 760 cm^{-1}, similar to the spectrum[23] of NEt_3HCl. The oxidation of these indium(I) species by $o\text{-}X_4C_6O_2$ (X = Cl or Br) brings about significant changes in the spectrum of the *o*-quinone, since the ν(C=O) mode at *ca.* 1 700 cm^{-1} disappears and is replaced by ν(C–O) vibrations of the $o\text{-}X_4C_6O_2^{2-}$ ligand at 1 240 + 1 430 cm^{-1}. These latter changes are almost identical to those reported in previous work on the reactions of these substituted *o*-quinones with indium(I)[8] and tin(II) halides.[24]

Reaction of $In(SC_nH_{2n}SH)$ *with Carbon Disulphide.*—The preparative results show that carbon disulphide reacts easily with $In(SC_nH_{2n}SH)$ (n = 4 or 6), and the products are the result of an *in situ* insertion reaction at the In–S bond. The synthesis of $RSCS_2^-$ complexes by the reaction of CS_2 with RS^- prior to complexation with a metal is well established,[25] but examples of *in situ* insertion into an existing thiolato complex are still relatively rare, especially with Group 3 compounds. In the cases studied in the present work the results show that only one of the two M-S bonds is attacked, as is the case in the reaction of $M[S_2(CH_2)_n]$ (M = Zn or Cd) compounds discussed elsewhere.[12]

The i.r. spectrum of the 1:1 insertion product shows strong vibrations at 916 + 985 cm^{-1}, absent from the spectrum of the parent $In(SC_4H_8SH)$, assigned as ν(C=S). The ν(C–S) mode is hardly changed at *ca.* 640 cm^{-1}. Following earlier arguments,[12,26,27] we conclude that CS_2 attacks at only one M–S bond to give the thioxanthate species. Such attack is apparently favoured by the presence of an alkyl group attached to the M–S bond;[26] the reaction of only one M–S bond is a common feature of such reactions.[12,26,27]



As with the systems studied previously, carbon disulphide is eliminated from the thioxanthate group on heating to give back the original thiolato compound, as shown by the elemental analysis and i.r. spectra.

Acknowledgements

This work was supported by Operating Grants (to D. G. T.) from the Natural Sciences and Engineering Research Council of Canada.

References

1 Part 46, T. A. Annan, D. H. McConville, B. R. McGarvey, A. Ozarowski, and D. G. Tuck, *Inorg. Chem.*, 1989, **28**, 1644.
2 D. G. Tuck, 'Comprehensive Inorganic Chemistry,' eds. G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 3, p. 153.
3 J. J. Habeeb and D. G. Tuck, *J. Chem. Soc., Dalton Trans.*, 1976, 866.
4 J. J. Habeeb and D. G. Tuck, *J. Chem. Soc., Dalton Trans.*, 1975, 1815.
5 C. Peppe, D. G. Tuck, and L. Victoriano, *J. Chem. Soc., Dalton Trans.*, 1982, 2165.
6 J. G. Contreras and D. G. Tuck, *J. Organomet. Chem.*, 1974, **66**, 405.
7 C. Peppe and D. G. Tuck, *Can. J. Chem.*, 1984, **62**, 2798.
8 T. A. Annan and D. G. Tuck, *Can. J. Chem.*, 1988, **66**, 2935.
9 D. G. Tuck, *Pure Appl. Chem.*, 1979, **51**, 2005.
10 H. E. Mabrouk and D. G. Tuck, *J. Chem. Soc., Dalton Trans.*, 1988, 2539.
11 H. E. Mabrouk and D. G. Tuck, *Inorg. Chim. Acta*, 1988, **145**, 237.
12 See D. A. Skoog and D. G. West, 'Fundamentals of Analytical Chemistry,' Saunders, New York, 1982, p. 186.
13 M. Dräger and G. Gattow, *Z. Anorg. Allg. Chem.*, 1972, **387**, 281, 300.
14 G. Pfrepper, *Z. Anorg. Allg. Chem.*, 1966, **347**, 160.
15 J. C. A. Boeyens and F. H. Herbstein, *Inorg. Chem.*, 1967, **6**, 1408.
16 J. C. A. Boeyens, *Acta Crystallogr., Sect. B*, 1970, **26**, 1251.
17 H. E. Mabrouk and D. G. Tuck, *Can. J. Chem.*, 1989, **67**, 746.
18 J. H. Green, R. Kumar, N. Seudeal, and D. G. Tuck, *Inorg. Chem.*, 1989, **28**, 123.
19 H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 322.
20 D. W. Stephan, *Inorg. Chem.*, 1984, **23**, 2207.
21 H. C. Hseih, T. Nicholson, and J. Zubieta, *Inorg. Chem.*, 1988, **27**, 241.
22 O. L. Brady and E. D. Hughes, *J. Chem. Soc.*, 1933, 1227.
23 B. Chenon and C. Sandorfy, *Can. J. Chem.*, 1958, **36**, 1181.
24 T. A. Annan, R. K. Chadha, D. G. Tuck, and K. D. Watson, *Can. J. Chem.*, 1987, **65**, 2670.
25 D. Coucouvanis, *Prog. Inorg. Chem.*, 1979, **26**, 301.
26 S. J. Black, F. W. B. Einstein, R. Kumar, and D. G. Tuck, *Inorg. Chem.*, 1986, **25**, 4181.
27 R. K. Chadha, R. Kumar, and D. G. Tuck, *Polyhedron*, 1988, **7**, 1121.

Received 10*th October* 1988; *Paper* 8/04020F