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The Electrochemical Synthesis of *O*-Ethylxanthato and *N,N'*-Dimethyldithiocarbamato Complexes of Indium(III), Tin(IV), Lead(II), Bismuth(III) and Tellurium(IV)

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Abstract

The *O*-ethylxanthato and *N,N'*-dimethyldithiocarbamato main group metal complexes were produced by the one-step electrochemical oxidation of the metal (M = In, Sn, Pb, Bi, Te) in the presence of an acetone solution of ethyl dixanthogen or tetramethylthiuram disulphide.

Introduction

The direct electrochemical synthesis of inorganic and organometallic halides of a number of main group metals can be achieved by the anodic oxidation of the metal in a simple non-aqueous cell [1]. Tuck and co-workers [2] have shown that neutral thiolato complexes of tin(IV) can be prepared by this method using solutions of the appropriate thiol in acetonitrile. Similarly, oxidation in the presence of thiols or disulphides is a convenient, direct route to neutral and anionic thiolato complexes of such elements as gallium, indium and thallium [3].

Since the chemistry of lead–thiolato complexes is well established [4] and metathetical preparations of indium, tin, bismuth, lead and tellurium xanthates have been reported in the literature [5–11], the electrochemical method has suggested a possible pathway to the preparation of metal xanthates and dithiocarbamates by oxidation of the metal in the presence of dixanthogen or thiuram disulphide. In continuing our study of the electrochemical synthesis of metal xanthates and dithiocarbamates [12, 13], we now present a new general synthetic route to the *O*-ethylxanthato and *N,N'*-dimethyldithiocarbamato complexes of indium, tin, lead, bismuth and tellurium.

Experimental

General

Metals were in the form of rods or lumps and were mostly 99.9% pure (JMC Puratronics:Grade 1; Alfa Products). A stout platinum sheet (4 mm X 80 mm) formed the inert cathode.

Acetone was dried over magnesium sulphate and distilled. Petroleum ether (40–60 °C; A.R. grade) was used as supplied. All other reagents were used as supplied.

Tetramethylthiuram disulphide (Fluka) was commercially available. Ethyl dixanthogen was made by the oxidation of potassium ethylxanthate with iodine [14] and was recrystallized from dichloromethane. Electrolytic solutions were continuously flushed with argon during the course of the experiments.

Electrochemical Syntheses

The metal to be oxidized was housed in a 100 cm^3 glass cell used in preparations reported previously [12, 13]. An acetone solution of ethyl dixanthogen or tetramethylthiuram disulphide formed the organic phase with the addition of tetraethylammonium perchlorate (*ca.* 20 mg) as the electrolyte. A sufficient current flow was achieved by the application of a d.c. voltage of 50 V.

In all cases except for the bismuth complexes, a solid precipitated during electrolysis. This was subsequently collected, washed several times with petroleum ether and dried. For the bismuth experiments, reduction of solvent *in vacuo* followed by the addition of petroleum ether yielded the desired products. These compounds were then thoroughly dried *in vacuo*. Total yields were in the range 30–86% based upon the quantity of metal dissolved. Experimental conditions for the electrochemical synthesis of metal xanthates and dithiocarbamates are listed in Table I.

Instrumentation

Voltages were supplied from a Bang and Olufsen SN15 power supply delivering up to 50 V (d.c.) and 1 A.

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TABLE I. Experimental Conditions for the Electrochemical Preparation of Metal Xanthates and Dithiocarbamates

System/oxidized form of ligand	Metal	Solution composition		Initial voltage (V)	Initial current (mA)	Time (min)	Metal dissolved (mg)	Yield		Complex
		Ligand (mg)	Acetone[a] (cm^3)					(mg)	(%)	
Ethyl dixanthogen $[EtOCS_2]_2$	In	200	40	50	15	63	60	90	35	$In(exa)_3$
	Sn	100	40	50	46	41	82	200	56	$[Sn(exa)_2S]_2$
	Pb	200	30	50	27	47	140	160	60	$Pb(exa)_2$
	Bi	100	25	50	8	150	63	80	47	$Bi(exa)_3$
Tetramethylthiuram disulphide $[Me_2NCS_2]_2$	In	200	40	50	21	74	110	130	28	$In(Me_2dtc)_3$
	Sn	200	40	50	32	50	80	310	77	$Sn(Me_2dtc)_4$
	Pb	100	30	50	22	54	120	180	69	$Pb(Me_2dtc)_2$
	Bi	100	25	50	14	50	80	160	73	$Bi(Me_2dtc)_3$
	Te	200	30	50	24	109	30	120	86	$Te(Me_2dtc)_4$

[a]Plus 20 mg of $(C_2H_5)_4NClO_4$ in each case.

Infrared spectra were recorded as KBr discs on the Jasco A:302 spectrophotometer (4400–330 cm^{-1}). Far infrared were recorded on a Perkin-Elmer 457 calibrated against a polystyrene film.

Solution optical spectra were recorded at 25 °C on a Hitachi Model 150:20 double beam spectrophotometer (190–850 nm),

^{1}H NMR spectra were recorded at 22 °C on the JEOL FX-100 spectrometer using an internal deuterium lock and referenced against tetramethylsilane (TMS). Samples were recorded in $CDCl_3$.

Conductivity measurements were made using a Philips PR9500 conductivity meter with a cell of standard design previously calibrated with a 0.02 M KCl solution. The conductivities of *ca.* 10^{-3} M solutions in nitromethane were measured within five minutes of dissolution. The conductance of tetraethylammonium chloride ($\Lambda_M = 6.7 \times 10^{-3}$ Sm^2 mol^{-1}) was measured in nitromethane for comparative purposes.

TABLE II. Infrared Absorption Frequencies (cm^{-1}) for the Xanthate and Dithiocarbamate Complexes Prepared

Complex	Infrared correlations				Reference
	ν(C–N)	ν(C–O)	ν(C–S)	ν(M–S)	
$In(exa)_3$		1245	1030	400	19
$[Sn(exa)_2S]_2$		1240	1092 1120 1157	450	25, 26
$Pb(exa)_2$		1205	1025	442	21
$Bi(exa)_3$		1220	1030	310	5
$In(Me_2dtc)_3$	1510		980	368	17
$Sn(Me_2dtc)_4$	1530		990	385	27
$Pb(Me_2dtc)_2$	1495		970	442	22
$Bi(Me_2dtc)_3$	1500		970	390 360	17, 24
$Te(Me_2dtc)_4$			970	390 335	22

Results and Discussion

Inspection of Table I shows that good yields of the products as crystalline solids were easily obtained in periods of one to two and one-half hours. This method has also been used successfully for the electrochemical preparation of the analogous compounds of V, Mn, Zn, Ag and Cd [12], and of Fe, Co, Ni, and Cu [13]. The compounds reported here were characterized by melting points, conductance measurements, electronic and infrared spectra and NMR. Since the results obtained agreed well with those in the literature, subsequent recrystallizations were often unnecessary. This method is efficient and avoids the use of the normal aqueous route to metal xanthates and dithiocarbamates.

Conductivity measurements in nitromethane indicated the absence of ionic species; the molar conductances of $\Lambda_M < 10^{-3}$ Sm^2 mol^{-1} supported the formulation of the complexes as covalent compounds. The infrared spectra (values reported in Table II) of the xanthate complexes displayed characteristic absorptions with typical frequencies as follows; ν(C–O) $\simeq$ 1200, ν(C–S) $\simeq$ 1000 and ν(M–S) $\simeq$400 cm^{-1} [15, 16]. For the dithiocarbamates, strong C–N absorptions were observed around 1500 cm^{-1} which are characteristic of the chelated ligand [16–18]. Also observed in the spectra of these complexes was one strong band in the 1000–953 cm^{-1} range, strongly supporting bidentate coordination of the ligand; a doublet being expected in the 1000 ± 70 cm^{-1} range for monodentate behaviour [17, 18].

Oxidation of indium in the presence of ethyl dixanthogen yielded the pale grey indium tris-xanthate. The infrared bands at ν(C–O) 1245, ν(C–S) 1030 and ν(M–S) 400 cm^{-1} were consistent with those reported in the literature [19]. The ^{1}H

NMR spectrum in $CDCl_3$ showed the expected triplet and quartet due to the xanthate ligand protons: $\delta(CH_3)$ 1.50, $\delta(CH_2)$ 4.52 ppm, $^3J(H-H)$ 7.3 Hz. These values agreed well with the literature [19]. The corresponding trivalent dithiocarbamate was produced when indium was electrolyzed in the presence of tetramethylthiuram disulphide. The ^1H NMR spectrum of $[In(Me_2dtc)_3]$ consisted of a singlet at 3.45 ppm as compared to that of 3.65 ppm for tetramethylthiuram disulphide [20]. The ease of this preparation is to be compared with another published method [8] which involved refluxing indium trichloride with potassium ethylxanthate in tetrahydrofuran for three to four hours, followed by extraction and crystallization. The present procedure offers considerable preparative advantages.

When lead was oxidized in the presence of ethyl dixanthogen, fine silver needles of bis(ethylxanthato)-lead(II) began to deposit in the cell as electrolysis proceeded. The melting point of 130 °C was identical to that reported by Kruger *et al.* [21] as were the characteristic infrared absorption bands at $\nu(C-O)$ 1205, $\nu(C-S)$ 1025 and $\nu(M-S)$ 442 cm^{-1}. The high resolution ^1H NMR spectrum of this compound consisted of a triplet at 1.52 ppm (CH_3) and a quartet at 4.71 ppm (CH_2) with $^3J(H-H)$ 7.08 Hz, identical results appearing in the literature [19]. The infrared spectrum of bis(dimethyldithiocarbamato)lead(II) contained a band at 1495 cm^{-1} ($\nu(C-N)$) as expected for a Group IV metal [17, 22]. The ^1H NMR spectrum consisted of a singlet at 3.41 ppm.

Both tris(ethylxanthato)bismuth(III) and tris-(dimethyldithiocarbamato)bismuth(III) were recovered from solutions as yellow–green solids. Their melting points (106 and 135 °C, respectively) [5, 23] and infrared spectral bands (Table II) were consistent with those reported in the literature [5, 17, 24]. The ^1H NMR spectrum of $[Bi(exa)_3]$ consisted of a methyl resonance at 1.43 ppm and a methylene resonance at 4.70 ppm with $^3J(H-H)$ of 6.97 Hz. A single resonance at 3.62 ppm was observed in the NMR spectrum of $[Bi(Me_2dtc)_3]$.

Surprisingly, the oxidation of tellurium in the presence of ethyl dixanthogen did not produce either the bis or tetrakis ethylxanthate species. Application of the electric potential resulted in the solution turning orange but subsequent disproportionation produced a black precipitate identified as elemental tellurium. No tellurium containing xanthate was isolated from the solution. The instability of $[Te(exa)_4]$ has been noted [8] readily decomposing to $[Te(exa)_2]$ and ethyl dixanthogen. Similarly, the dithioselenium(II) complexes, especially the xanthates, are quite unstable in solution where they decompose to elemental selenium and the corresponding disulphide [9]. A different result occurs in the tellurium dithiocarbamate system. An orange, flocculent solid precipitated during electrolysis of the element in the presence of tetramethylthiuram disulphide. The melting point (120 °C) and infrared absorptions identified the compound as $[Te(Me_2dtc)_4]$ in comparison with reported values [22]. Its ^1H NMR spectrum contained a single resonance at 3.62 ppm.

Electrolysis of tin with ethyl dixanthogen produced the unusual pale yellow complex, bis(*o*-ethylxanthato)thiotin(IV), $[Sn(exa)_2S]_2$. The compound produced here was identified by its melting point (d.160 °C) and its infrared absorptions, in good agreement with values reported by Gable *et al.* [25, 26]. Both $[Sn(exa)_2]$ (melting point (m.p.) 47–50 °C) and $[Sn(exa)_4]$ (m.p. 67–69 °C) [6] display quite different infrared absorptions in the C–S region from the compound reported here; the thiotin complex has three bands at 1092, 1120 and 1157 cm^{-1}. This compound was first prepared [26] by reacting potassium ethylxanthate and tin tetrachloride in 1:1 and 3:1 ratios. It was then suggested that the halogeno complex $[Sn(exa)_3Cl]$, rearranged to yield the dimeric thiotin complex. Absorption maxima in the electronic spectrum of the thiotin complex in cyclohexane occurred at 265 and 215 nm (*cf.* $Sn(exa)_4$ 272 and 217 nm; $Sn(exa)_2$ at 306 and 236 nm both in cyclohexane [6]) confirming that the oxidation state of tin in the complex was four.

The insoluble $[Sn(Me_2dtc)_4]$ complex precipitated as a highly crystalline, orange solid. Its melting point ($\geqslant$160 °C), infrared spectrum and electronic spectrum (bands at 253, 290 and 425 nm in chloroform) agreed well with those reported [27]. The ^1H NMR spectrum contained a major peak at 3.43 ppm consistent with reported values [20, 28]. The infrared and NMR spectra support *octa*-coordination for the tin(IV) dithiocarbamate [27, 28].

Conclusions

The results presented herein show that the electrolytic method is an excellent route to the dithiolates of these metals.

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References

1 D. G. Tuck, *Pure Appl. Chem., 51,* 2005 (1979).
2 J. L. Hencher, M. Khan, F. F. Said and D. G. Tuck, *Inorg. Nucl. Chem. Lett., 17,* 287 (1981).

3 F. F. Said and D. G. Tuck, *Inorg. Chim. Acta, 59,* 1 (1982).
4 E. W. Abel, in A. F. Trotman-Dickenson (ed.), 'Comprehensive Inorganic Chemistry', Vol. 2, Pergamon, Oxford 1973, p. 143.
5 G. Winter, *Aust. J. Chem., 29,* 559 (1976).
6 C. L. Raston, P. R. Tennant, A. H. White and G. Winter, *Aust. J. Chem., 31,* 1493 (1978).
7 R. W. Gable, B. F. Hoskins, R. J. Sheen and G. Winter, *Inorg. Chim. Acta, 72,* 173 (1983).
8 S. Husebye, *Acta Chem. Scand., 21,* 42 (1967).
9 O. Foss, *Acta Chem. Scand., 7,* 226 (1953).
10 F. Galsbol and C. E. Schaffer, *Inorg. Synth., 10,* 42 (1967).
11 H. Delephine, *Ann. Chem., 6,* 645 (1951).
12 A. T. Casey and A. M. Vecchio, *Transition Met. Chem., 11,* 366 (1986).
13 A. T. Casey and A. M. Vecchio, *J. Coord. Chem.,* submitted for publication.
14 E. E. Reid, 'Organic Chemistry of Bivalent Sulphur', Vol. IV, Chemical Publishing Co, New York, 1962.
15 G. Winter, *Rev. Inorg. Chem., 2,* 253 (1980).
16 D. Coucouvanis, *Prog. Inorg. Chem., 11,* 233 (1970).
17 J. Chatt, L. A. Duncanson and L. M. Venanzi, *Suomen Kemi, B29,* 75 (1956).
18 F. Bonati and R. Ugo, *J. Organomet. Chem., 10,* 257 (1967).
19 B. F. Hoskins, E. R. T. Tiekink, R. Vecchiet and G. Winter, *Inorg. Chim. Acta, 90,* 197 (1984).
20 C. J. Pouchert, 'The Aldrich Library of NMR Spectra', 2nd edn., Aldrich Chemical Co. Inc., U.S.A., 1983.
21 M. R. Hunt, A. G. Kruger, L. Smith and G. Winter, *Aust. J. Chem., 24,* 53 (1971).
22 H. L. M. Van Gaal, J. W. Diesveld, F. W. Pijpers and J. G. M. van der Linden, *Inorg. Chem., 18,* 3251 (1979).
23 L. Bourgeois and J. Bolle, *Mem. Services Chim. Etat. (Paris), 34,* 411 (1948).
24 B. F. Hoskins, E. R. T. Tiekink and G. Winter, *Inorg. Chim. Acta, 105,* 171 (1985).
25 R. W. Gable, *Ph.D. Thesis,* University of Melbourne, to be submitted in 1987.
26 R. W. Gable, C. L. Raston, A. H. White and G. Winter, *J. Chem. Soc., Dalton Trans.,* 1392 (1981).
27 F. Bonati, G. Minghetti and S. Cenini, *Inorg. Chim. Acta, 2,* 375 (1968).
28 D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc. A,* 1152 (1969).