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Preparation and Electrochemical Behaviour of Tris Dithiocarbamato Complexes $[Bu_4N]M(Et_2dtc)_3$ with M = Ba, Zn, Cd, and Hg

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The compounds $[Bu_4N]M(R_2dtc)_3$ (M = Ba, Zn, Cd and Hg; R = Me, Et) have been prepared. Conductivity measurements and an electrochemical oxidation study with pulse polarographic and cyclic voltammetric techniques show that in acetone solutions the barium tris anion, $Ba(Et_2dtc)_3^-$, is completely dissociated into the bis complex, $Ba(Et_2dtc)_2$ and a ligand ion, Et_2dtc^-; the zinc and mercury tris anions are not completely dissociated and the cadmium anion only to a minor extent.

Introduction

The dithiocarbamate ligand ($R_2NCS_2^-$) stabilizes high (formal) oxidation states of transition metals. A number of dithiocarbamato complexes can be oxidized both by halogens and in an electrochemical way, resulting in compounds in which the metal is oxidized [1, 2]. The complexes $M(R_2dtc)_2$ with M = Zn, Cd, and Hg are, however, oxidized by halogens to the thiuramdisulfide complexes, $M(R_4tds)X_2$ [3, 4]. Recently it has been found [5] that $Zn(R_2dtc)_2$ reacts with $[Bu_4N]R_2dtc$ giving a tris dithiocarbamato complex, $[Bu_4N]Zn(R_2dtc)_3$, the crystal and molecular structure of which has been determined [6]. This paper describes the synthesis, characterisation, and electrochemical oxidation behaviour of the bis complexes $M(Et_2dtc)_2$ as well as tris complexes $[R_4N]M(Et_2dtc)_3$ with M = Ba, Zn, Cd, and Hg.

Results and Discussion

Synthesis

The bis complexes, $M(R_2dtc)_2$, M = Zn, Cd, Hg; R = Me, Et, were prepared using procedures normal for the synthesis of dithiocarbamates [1, 7]. $Ba(Et_2dtc)_2$ could only be prepared by refluxing in acetone stoichiometric amounts of $BaCl_2 \cdot 3H_2O$ and $NaEt_2dtc \cdot 3H_2O$. However, neither $Ba(Me_2dtc)_2$, insoluble in acetone, nor dithiocarbamates derived from Mg, Ca, and Sr could be obtained in this way.

The tris complexes $[R_4N]M(Et_2dtc)_3$ (M = Ba, Zn, Cd, and Hg) can be prepared by reacting equimolar

TABLE I. Analytical Data.[a]

Complex	%C	%H	%N
$Zn(Me_2dtc)_2$	23.57(23.57)	3.87(3.96)	9.38(9.16)
$Cd(Me_2dtc)_2$	20.30(20.43)	3.41(3.43)	7.96(7.94)
$Hg(Me_2dtc)_2$	16.06(16.34)	2.60(2.74)	6.16(6.35)
$Ba(Me_2dtc)_2$	19.12(19.08)	3.17(3.20)	7.47(7.40)
$Zn(Et_2dtc)_2$	33.11(33.19)	5.62(5.57)	7.85(7.74)
$Cd(Et_2dtc)_2$	29.22(29.37)	4.90(4.93)	6.82(6.85)
$Hg(Et_2dtc)_2$	23.92(24.16)	3.98(4.06)	5.58(5.64)
$Ba(Et_2dtc)_2$	27.41(27.68)	4.65(4.65)	6.33(6.46)
$[Bu_4N]Zn(Et_2dtc)_3$	49.27(49.47)	8.91(8.84)	7.46(7.44)
$[Bu_4N]Cd(Et_2dtc)_3$	46.30(46.56)	8.29(8.32)	6.98(7.01)
$[Bu_4N]Hg(Et_2dtc)_3$	41.98(41.94)	7.47(7.49)	6.29(6.31)
$[Bu_4N]Ba(Et_2dtc)_3$	44.98(45.15)	8.17(8.07)	6.68(6.79)

[a] Theoretical values in parentheses.

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TABLE II. Infrared Data (cm^{-1}) of the Complexes in the Solid State (KBr).

Complexes	$\nu(\mathrm{C{\cdots}N})$	Other Main Bands between 1400 and 1000 cm^{-1}							ν(C–S)	ν(C–S) + δ(S–C–S)
Bu_4NMe_2dtc	1488	1335		1258		1100	1054	1033	980	578
$KMe_2dtc \cdot 3H_2O$[a]	1498	1361		1257		1125	1049		966	583
$NaMe_2dtc \cdot 2H_2O$	1490	1365		1250		1120	1045		965	575
$Ba(Me_2dtc)_2$	1486	1367		1258		1128	1047	1036	981	582
$Zn(Me_2dtc)_2$	1520	1394		1245		1150	1052	1016	975	565
$Cd(Me_2dtc)_2$	1512	1384		1244		1143	1045	1014	958	565
$Hg(Me_2dtc)_2$	1502	1382		1246		1145	1046	1015	967	567
Bu_4NEt_2dtc	1485		1302	1245	1214	1105			989	572
$NaEt_2dtc \cdot 3H_2O$	1475		1295	1265	1200	1125			990	
$Ba(Et_2dtc)_2$	1484		1307	1270	1208	1145			992	612, 565
$Zn(Et_2dtc)_2$	1501		1299	1273	1208 1203	1146			994	611, 564
$Cd(Et_2dtc)_2$	1499		1301	1273	1207	1149			991	612, 562
$Hg(Et_2dtc)_2$	1495		1309	1271	1207	1147			988	606, 560
$[Bu_4N]Ba(Et_2dtc)_3$	1482		1305	1256	1216	1123			1001	570
$[Bu_4N]Zn(Et_2dtc)_3$	1492 sh 1479		1305	1265	1215	1133			999	603, 567
$[Bu_4N]Cd(Et_2dtc)_3$	1483		1307	1272	1216	1143			1000	605, 565
$[Bu_4N]Hg(Et_2dtc)_3$	1480		1304	1269	1213	1137			990	600, 564

amounts of the bis dithiocarbamato complex and $[Bu_4N][Et_2dtc]$ in acetone solutions. The analytical data of the newly synthesized complexes are in agreement with their proposed compositions (Table I).

All compounds are white except those of mercury, which are light yellow. The dimethyl derivatives are hardly soluble in any solvent, those of barium can be dissolved in water. The diethyl derivatives are reasonably soluble in acetone and chloroform though the barium complex is insoluble in the latter solvent. The tris complexes dissolve well in all common organic solvents, in nitrobenzene, but not in other aprotic ones.

Infrared Study

The values found for $\nu(\mathrm{C{\cdots}N})$ in $Ba(R_2dtc)_2$ are close to the frequencies of the not co-ordinated ligand (in Bu_4Ndtc). The values for $M(R_2dtc)_2$, M = Zn, Cd and Hg, are at least 10 cm^{-1} higher. Coordination of a third ligand to the bis complexes lowers $\nu(\mathrm{C{\cdots}N})$ of the formed tris compounds to the value of the free Et_2dtc^- ion. The infrared data show that for the methyl derivatives absorption bands around 1335 cm^{-1} and 1100 cm^{-1} are shifted to higher frequencies going from the free dimethyldithiocarbamate ion (in Bu_4NMe_2dtc) through the potassium and barium salt to group IIB metal ions. These frequencies assigned by Jensen [8] to vibrations of the methyl groups are thus clearly affected by the nature of the coordinated metal.

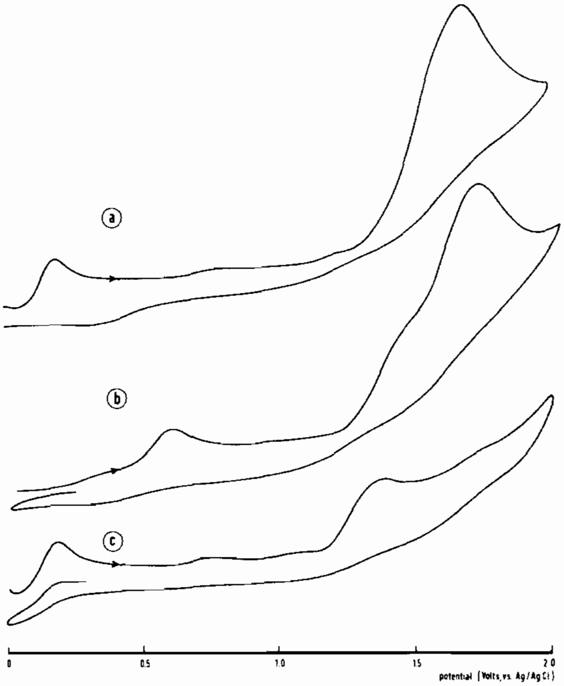

Fig 1. Cyclic voltammetric curves of 5.10^{-3} mole/l solutions of $[Bu_4N]_2M(Et_2dtc)_3$ in acetone, with M = (a) Zn, (b) Cd and (c) Hg.

Between the spectra of the several diethyl derivatives no remarkable differences exist, only the free diethyl dithiocarbamate ion (in Bu_4NEt_2dtc) shows

TABLE III. Voltammetric Data for the Oxidation of the Complexes.[a]

Complex	Oxidation of the Free dtc$^-$ Ligand					Oxidation of M(dtc)$_3^-$ Complexes				
	Pulse Polarography			Cyclic Voltammetry		Pulse Polarography			Cyclic Voltammetry	
	$E_{1/2}$ (V)	$E_{3/4} - E_{1/4}$ (mV)	i_1/c (mA l mol^{-1})	$E_p^{an.}$ (V)	$\frac{i_p}{cV^{1/2}}$ $\frac{mA\ l\ sec^{1/2}}{mol^{-1}\ V^{1/2}}$	$E_{1/2}$ (V)	$E_{3/4} - E_{1/4}$ (mV)	i_1/c (mA l mol^{-1})	$E_p^{an.}$ (V)	$\frac{i_p}{cV^{1/2}}$ $\frac{mA\ l\ sec^{1/2}}{mol\ V^{1/2}}$
Na(Et$_2$dtc)	0.13	49	151	0.19	8.3					
Ba(Et$_2$dtc)$_2$	0.21	81	170	0.32	10.5					
[Bu$_4$N]Ba(Et$_2$dtc)$_3$	0.16	101	237	0.31	13.4					
[Bu$_4$N]Zn(Et$_2$dtc)$_3$	0.13	48	115	0.20	6.0	0.74	80	22	0.82	0.6
[Bu$_4$N]Cd(Et$_2$dtc)$_3$	0.15	34	2.1	0.32	0.5	0.50	53	69	0.59	5.2
[Bu$_4$N]Hg(Et$_2$dtc)$_3$	0.16	52	95	0.24	5.3	0.74	72	31	0.78	0.9

[a] In acetone (0.1 M Bu$_4$NClO$_4$) *vs.* a Ag/AgCl electrode (0.1 M LiCl–acetone).

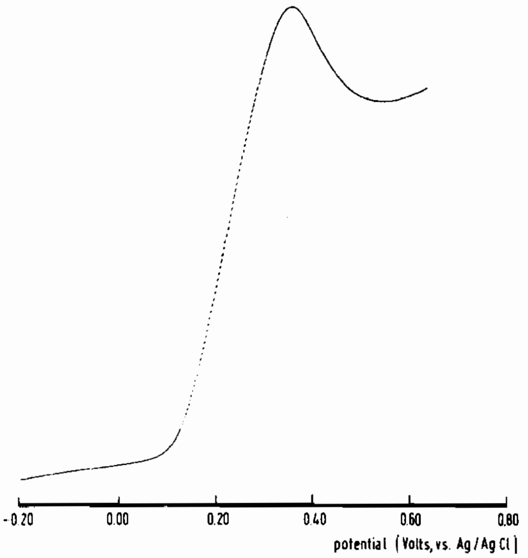

Fig. 2. Pulse polarogram of the oxidation of Et$_2$dtc$^-$ in acetone 10^{-3} mole/l Ba(Et$_2$dtc)$_2$.

deviations from the values found in the complexes for the frequencies around 1270 cm^{-1} and 1140 cm^{-1} (Table II).

Voltammetry

Cyclic voltammograms in the potential range 0 to 2 Volt of 2 mM solutions of [Bu$_4$N]M(Et$_2$dtc)$_3$, showed that these compounds exhibit three distinct irreversible oxidation reactions in the ranges 0.20–0.32, 0.59–0.82 and 1.40–1.60 V (see Fig. 1).

The oxidation waves of the bis complexes, M(dtc)$_2$ M = Ba, Zn, Cd, and Hg, were also found in the last range. The data of the electrochemical measurements are given in Tables III and IV.

A well resolved wave (pulse voltammetry) was observed at 0.15 V (*vs.* Ag/AgCl electrode, 0.1 M LiCl–acetone) for all the tris compounds and Ba(Et$_2$dtc)$_2$. All these waves show the same shape (Fig. 2), characteristic of the irreversible voltammetric oxidation of the free Et$_2$dtc$^-$ ligand, liberated from these complexes. The formed radical R$_2$dtc$^\bullet$, rapidly dimerises to the thiuram disulfide [9]. Such irreversible system leads to a depletion of the oxidized species at the electrode resulting in a significant decrease of the limiting current [10]. Surprisingly a further irreversible oxidation wave was observed for the tris compounds, at 0.50 V for [Bu$_4$N]Cd(Et$_2$dtc)$_2$ and at 0.70 V for [Bu$_4$N]M(Et$_2$dtc)$_3$, M = Zn and Hg. This indicates that the tris complexes are oxidized as such. It is well established [3, 4] that the chemical oxidation of M(R$_2$dtc)$_2$, M = Zn, Cd, and Hg, with the halogens leads to the thiuram disulfide compounds M(R$_4$tds)X$_2$. So it is very well possible that at these potentials the tris complexes are oxidized to analogous products

TABLE IV. Voltammetric Data for the Oxidation of the Complexes.[a]

Oxidation of the $M(Et_2dtc)_2$ Complexes

Complex	Pulse Polarography			Cyclic Voltammetry	
	$E_{1/2}$ (V)	$E_{3/4} - E_{1/4}$ (mV)	i_l/c (mA l mol^{-1})	$E_p^{an.}$ (V)	$\frac{i_p}{cv^{1/2}}$ $\frac{mA\ l\ sec^{1/2}}{mol\ V^{1/2}}$
$Ba(Et_2dtc)_2$	1.39	127	267	1.59	7.4
$[Bu_4N]Ba(Et_2dtc)_3$	1.46	142	473	1.60	8.1
$Zn(Et_2dtc)_2$	1.46	113	465	1.60	21.5
$[Bu_4N]Zn(Et_2dtc)_3$	1.51	137	619	1.62	23.0
$Cd(Et_2dtc)_2$	1.48	51	b	1.51	b
$[Bu_4N]Cd(Et_2dtc)_3$	1.62	71	196	1.64	12.2
$Hg(Et_2dtc)_2$	1.29	110	b	1.40	b
$[Bu_4N]Hg(Et_2dtc)_3$	1.32	85	149	1.40	6.2

[a] In acetone (0.1 *M* Bu_4NClO_4) *vs.* a Ag/AgCl electrode (0.1 *M* LiCl–acetone). [b] Saturated solutions, no reliable data obtained.

TABLE V. Estimation of the Degree of Dissociation for $M(R_2dtc)_3^-$.

Compound	Pulse Polarography				Cyclic Voltammetry			
	i_l/conc. (mA l mol^{-1})				i_p/conc. $v^{1/2}$ (mA l s$^{1/2}$ mol^{-1} V$^{-1/2}$)			
	at ~0.15 V	at ~0.50 V	Sum	α	at ~0.15 V	at ~0.50 V	Sum	α
$Zn(Et_2dtc)_3^-$	115	22	137	0.84	6.0	0.6	6.6	0.41
$Cd(Et_2dtc)_3^-$	2.1	69	71	0.03	0.5	5.2	5.7	0.09
$Hg(Et_2dtc)_3^-$	95	31	126	0.75	5.3	0.9	6.2	0.83

$$M(Et_2dtc)_3^- \rightarrow M(Et_4tds)(Et_2dtc)^+ + 2e \qquad (1)$$

M = Zn, Cd, Hg

Comparison of the current functions (i_l/conc. for pulse voltammetry and i_p/conc. $v^{1/2}$ for cyclic voltammetry) show that the cadmium tris complex is present in a much larger concentration than the zinc and mercury complexes. Considering these current functions for both the first and second wave in more detail, an indication can be obtained of the degree of dissociation (Table V). Both applied techniques show, in a good agreement between them, that $Cd(Et_2dtc)_3^-$ is dissociated only to a minor extent, while $Zn(Et_2dtc)_3^-$ and $Hg(Et_2dtc)_3^-$ are nearly completely dissociated.

The values for the currents of $Ba(Et_2dtc)_3^-$ can be understood assuming a complete dissociation of this complex in acetone solution. Controlled potential electrolysis experiments were carried out with the tris complexes at 0.25 V in order to confirm the one electron oxidation of the liberated Et_2dtc^- ligand to Et_4tds. Somewhat lower n-values than one were found (0.9–1.0). Continuing the electrolysis at a potential up to 250 mV beyond the half wave potential of the second wave a total n-value of 1.1 to 1.2 was obtained.

Bis Complexes

Of the bis complexes only the barium compound showed a free ligand wave at 0.21 V. This somewhat retardive oxidation of the ligand can be ascribed to the very small degree of dissociation of this complex in solution, complete dissociation seems only to be achieved at the electrode during the oxidation reaction.

For these bis complexes as well as the tris compounds a less well resolved wave is observed in the potential range 1.39–1.62 V. This wave could be caused by the oxidation of the bis complexes, because the same $E_{1/2}$ and E_p values are found for both the bis and tris compounds.

For the cadmium complexes prewaves are observed for the bis as well as the tris compounds.

TABLE VI. Molar and Single Ion Conductivities.

Compound	Solvent	Λ_o cm^2 ohm^{-1} mol^{-1}	λ_o^- cm^2 ohm^{-1} eq^{-1}
$[Bu_4N]Ba(Et_2dtc)_3$	Nitrobenzene	23.9	12.3
$[Bu_4N]Zn(Et_2dtc)_3$	″	24.5	12.9
$[Bu_4N]Cd(Et_2dtc)_3$	″	20.3	8.7
$[Bu_4N]Hg(Et_2dtc)_3$	″	23.2	11.6
$[Mo(Et_2dtc)_4][Et_2dtc]$[a]	″	21.6	12.8
$Ba(Et_2dtc)_2$	Acetone	6.0[b]	
$[Bu_4N]Ba(Et_2dtc)_3$	″	145.6	
$[Bu_4N]Zn(Et_2dtc)_3$	″	147.3	
$[Bu_4N]Cd(Et_2dtc)_3$	″	128.2	
$[Bu_4N]Hg(Et_2dtc)_3$	″	142.2	

[a] From ref. 16, assuming $\lambda^o_{Mo(Et_2dtc)_4^+} = 8.8$. [b] At a concentration of 0.001 *M*. A curved line for Λ *vs.* $c^{1/2}$ was obtained in the concentration range 5×10^{-4}–10^{-3} *M*.

For $Cd(Et_2dtc)_3^-$ a reasonably large wave was observed at $E_{1/2} = 1.30$ V (i_l/conc. = 115) and for $Cd(Et_2dtc)_2$ only a small prewave at the same potential. For mercury only the tris compound $Hg(Et_2dtc)_3^-$ showed a prewave at $E_{1/2} = 1.04$ V ($i_l/c = 15.5$). Although we found no indication of what kind of products have been formed in the potential range 1.00–1.60 V the various reports concerning the chemical oxidation reactions carried out on the bis complexes point to the formation of the thiuram disulfide complexes, $M(R_4tds)X_2$ [3, 4, 11]. But also some of the Et_4bitt^{2+} cation may be formed. Solutions of Et_4tds show long drawn-out oxidation waves, while cyclic voltammograms gave $E_p = 1.20$ V. Recently it has been reported [12] that in acetonitrile this compound is oxidized to Et_4bitt^{2+} in an ECE mechanism at 0.80 V *vs.* SCE.

Conductance Study

For the tris complexes the equivalent conductances were measured in nitrobenzene solutions in the concentration range (1–4) × 10^{-3} mol/l. The conductivities are in the range expected for 1:1 electrolytes. From the Onsager equation $\Lambda = \Lambda_0 - A\sqrt{c}$ (with $A = 0.78\ \Lambda_0 + 44.2$) [15] the electric conductivities at infinite dilution could be determined. From these values the single ion conductivities (λ_0^-) for the negative ions were derived, assuming $\lambda^0(Bu_4N^+) = 11.6$ cm^2 ohm^{-1} eq^{-1} [15]. With the exception of the cadmium compounds λ_0 values were found about the reported value of the diethyldithiocarbamate anion, $\lambda^0_{Et_2dtc^-} = 12.8$ [16] (Table VI). This again indicates a dissociation of these tris complexes into their bis complexes and the free ligand ion. Since $Ba(Et_2dtc)_2$ is not soluble in nitrobenzene additional conductivities were determined in acetone solutions in the concentration range (0.2–1) × 10^{-3} mol/l. For $Ba(Et_2dtc)_2$ the conductivity remains very low and plots of Λ *vs.* $c^{1/2}$ resulted in a curved line. This indicates that there is almost no dissociation, increasing somewhat by dilution. The obtained values for the molar conductivities of the tris complexes $[Bu_4N]M(Et_2dtc)_3$ (M = Ba, Zn, Hg) are in agreement with those reported for a 1:1 electrolyte in this solvent [13]. Table VI. Slightly curved lines for Λ *vs.* $c^{1/2}$ indicate that in this concentration range no complete dissocation is achieved. The distinctly lower molar conductivity of the $[Bu_4N]Cd(Et_2dtc)_3$ compound shows that, like in nitrobenzene, the complex is only dissociated to a minor extent in acetone.

Discussion

A crystal and molecular structure determination have been reported [6] for the tris compound $[Bu_4N]Zn(Me_2dtc)_3$. The isolation of pure products (Table I, analytical data) indicates that the tris complexes $[Bu_4N]M(Et_2dtc)_3$, with M = Ba, Cd and Hg, may exist as well in the solid state. However, in solution the compounds behave in a somewhat different way. The barium bis complex is nearly undissociated, thus a relatively strong bond between this metal ion and the ligands is present. The $Ba(dtc)_3^-$ complex is completely dissociated into the bis compound and the free ligand ion. The zinc and mercury tris complexes are nearly totally dissociated, up to about 90%. This is in accord with the known behaviour of these metals. For zinc six coordination will not be achieved for stereochemical reasons, which is indicated in the molecular structure of the tris compound [6]. Two dtc ligands are unidentate coordinated while only one ligand is bidentate bonded to the zinc ion, thus enhancing a rapid dissociation when the compound is dissolved. For mercury the covalent bond formation with sulfur ligands results in stable four coordinated compounds. Cadmium in general behaves much like zinc though more often octahedral coordination occurs and the metal has a greater tendency to form stable compounds with sulfur containing ligands. This general behaviour is also present here, which explains the stability of the cadmium tris compound in solution.

Experimental

Infrared spectra were measured on Perkin-Elmer 257, Perkin-Elmer 283 and Hitachi EPI-L spectrophotometers. Electrochemical measurements were made with a three electrode Bruker E 310 instrument with platinum working and auxiliary electrodes. Measurements were made with *ca.* 2×10^{-3} *M* complex solutions in acetone (0.1 *M* Bu_4NClO_4) with potentials referred to a Ag/AgCl (0.1 *M* LiCl–acetone) reference electrode [17]. Normal pulse voltammograms were obtained at a scan rate of 5 mV/sec from an initial position of zero current through the redox wave with a pulse frequency of 2.0 pulses/sec. Cyclic voltammograms were taken with a scan rate of 200 mV/sec. All values reported in this paper are measured on the first scan voltammogram.

Conductivity measurements were performed as described earlier [14].

Complexes

$Ba(Me_2dtc)_2$ was prepared by addition of a water solution of $(Bu_4N)(Me_2dtc)$ (4 mmol) to a solution of $Ba(ClO_4)_2$ (2 mmol) in water. After filtration of the formed precipitate of Bu_4NClO_4 the compound was isolated by evaporation of the filtrate.

$Ba(Et_2dtc)_2$ could also be prepared with this method or, alternatively, by the following procedure. $BaCl_2 \cdot 2H_2O$ (5 mmol) and $Na(Et_2dtc) \cdot 3H_2O$ were refluxed in 100 ml acetone for six hours. After filtration, the solution was concentrated to 40 ml and cooled to –20 ℃. The white powder was recrystallised from acetone. Yield 80%.

$M(R_2dtc)_2$ (M = Zn, Cd, Hg; R = Me, Et) were prepared from the metal halides and sodium dithiocarbamate salts in water as described in the literature [7].

The compounds with R = Et were recrystallised from acetone or chloroform and acetone mixtures.

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