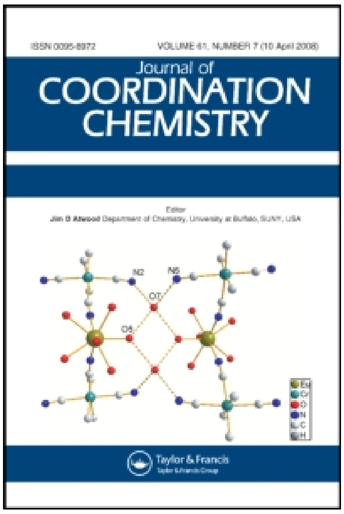

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Allan T. Casey[a]; Angelica M. Vecchio[a]
[a] Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria, Australia

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THE ELECTROCHEMICAL SYNTHESIS OF ETHYLXANTHATE AND DIMETHYLDITHIOCARBAMATE COMPLEXES OF IRON, COBALT, NICKEL AND COPPER

ALLAN T. CASEY* and ANGELICA M. VECCHIO

Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia

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An electrochemical synthetic method has been developed to effect the one-step preparation of transition metal xanthates and dithiocarbamates by oxidation of the metal in an acetone solution of ethyl dixanthogen or tetramethylthiuram disulphide. Results are presented for *O*-ethylxanthate and *N*,*N*′-dimethyldithiocarbamate complexes of iron(III), cobalt(III), nickel(II) and copper(I, II).

Keywords: electrochemical synthesis, *O*-ethylxanthate, *N*,*N*′-dimethyldithiocarbamate, transition metal complexes

INTRODUCTION

While electrolytic synthetic procedures have been common in organic chemistry for many years, their application to the preparation of metal complexes has been more pronounced in the last decade. Tuck[1] has described the general principles, and other papers from his laboratory[2-5] have described the preparation of anhydrous metal halides, anionic halide complexes and organometallic complexes by the electrochemical oxidation of a metal in the presence of an organic solution of the appropriate ligands. It was also found[6] that the oxidation of a metal into a non-aqueous solution of a thiol or disulphide is a convenient and direct route to the neutral thiolato complexes of such elements as zinc, cadmium, mercury, tin, lead, gallium, indium and thallium. One of the most interesting feature of the disulphides, especially the thiuram disulphides (absent in other dithiones[7]), is their ability to be reduced at the disulphide linkage to the corresponding anion. Since there is considerable interest in thiolate chemistry in this department[8] and as a further extension[9] of previous reports on the direct electrochemical synthesis of *N*,*N*′-dimethyldithiocarbamate and *O*-ethylxanthate complexes of various metals, we now present results on the direct synthesis of dithiolate complexes of iron, cobalt, nickel and copper.

EXPERIMENTAL

General

Metals were conveniently handled as wires or rods and were mostly 99.9% pure (JMC Puratronic Grade 1, or Alfa Products). A stout platinum sheet (4 mm × 80 mm) formed the inert cathode.

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* Author for correspondence

Acetone was dried by refluxing over magnesium sulphate and nitromethane was dried over phosphorus pentoxide. Petroleum ether (40–60°C; A.R. grade) was used as supplied. All other organic reagents were A.R. grade and used as supplied Tetramethylthiuram disulphide (Fluka) was commercially available. Ethyl dixanthogen was made by oxidizing potassium ethylxanthate with iodine[10].

The metal content of the products was determined by atomic absorption spectrophotometry. Standard AAS solutions and solutions of free metal ions were made up using Millipore-Q water. Cupric chloride ($CuCl_2$ BDH standard solution for AAS; 1 cm^3 = 1.00 mmg Cu), cobalt chloride ($CoCl_2$; 1 cm^3 = 0.99 mg Co), ferric chloride ($FeCl_3$ BDH standard solution for AAS; 1 cm^3 = 1.00 mg Fe) and nickel chloride ($NiCl_2$; 1 cm^3 = 1.00 mg Ni) were used as the metal standards. Analyses were obtained with a Techtron Model A 100 spectrophotometer using Phototron Fe and Co lamps, an S and J Juniper and Company Ni lamp and a Techtron Cu lamp. Microanalytical data were from the Analytical Laboratories, Engelskirchen, Germany.

Electrochemical Synthesis

The electrochemical procedures have been described previously.[9] The metal to be oxidized formed the anode of the cell, housed in a 200 cm^3 glass container with a bottom outlet. An acetone solution of the oxidized form of the ligands was used (neutral ethyl dixanthogen or tetramethylthiuram disulphide) with tetraethylammonium perchlorate (*ca* 20 mg) being added to enhance the conductivity in the experiments (insufficient current flows in the absence of electrolyte). The applied voltage of 50V(DC) produced a sufficient current to allow smooth dissolution of metal. A stream of argon served to degas the solutions during electrolysis. Actual electrochemical conditions for the preparation of the complexes appear in Table I. Complexes were isolated by one of two methods:

i) Those which precipitated during electrolysis were washed with acetone and recrystallized from the appropriate solvent (as indicated in Table I) and dried *in vacuo*.

ii) for those compounds which were soluble in acetone, the solution was concentrated by rotary evaporation; the product precipitated upon addition of petroleum ether and was recrystallized from the solvent as indicated in the Table.

Copper(I) ethylxanthate could not be recrystallized since it is insoluble in most solvents and as the divalent copper dithiocarbamate precipitated as lustrous brown-black crystals, no further manipulations were performed. These purification methods removed the possibility of contamination by the electrolyte since the latter is very soluble in acetone and the amount employed should not lead to an impurity in the products. Total yields were in the range 43–98% based upon the quantity of metal dissolved.

Analytical Results:

Anal: calc. for $Fe(exa)_3$: Fe, 13.32. Found 13.53; calc. $Co(exa)_3$: Co, 13.95. Found 13.61; calc. $Ni(exa)_2$: Ni, 19.50; C, 23.93; H, 3.34; S, 42.59. Found Ni, 19.65; C, 23.68; H, 3.28; S, 42.46; calc. Cu(exa): Cu, 34.39. Found 34.67; calc. $Fe(Me_2dtc)_3$: Fe, 13.41. Found 13.59; calc. $Co(Me_2dtc)_3$: Co, 14.05. Found 14.07; calc. $Ni(Me_2dtc)_2$; Ni, 19.63. Found 19.94; calc. $Cu(Me_2dtc)_2$: Cu, 20.90. Found 20.43%.

TABLE I

Experimental conditions for the electrochemical preparation of metal xanthates and dithiocarbamates

System		Solution Composition			Initial				Yield Complex		
oxidized form of ligand	Metal	ligand (mg)	acetone[a] (cm^3)	Method of Isolation[b] (solvent)	Voltage (V)	Current (mA)	Time (min)	Metal Dissolved (mg)	(mg)	%	Complex
ethyl dixanthogen $(EtOCS_2)_2$	Fe	200	60	$CHCL_3/EtOH^{ii}$	40	31	53	30	170	67	$Fe(exa)_3$
	Co	500	50	$CHCl_3/EtOH^{ii}$	50	30	61	50	270	77	$Co(exa)_3$
	Ni	300	60	$EtOH^{i}$	50	53	53	30	90	87	$Ni(exa)_2$
	Cu	200	40	^{i}	40	51	10	35	61	60	$Cu(exa)$
tetramethyl-thiuram disulphide $(Me_2NCS_2)_2$	Fe	200	60	$CH_2Cl_2EtOH^{i}$	40	22	55	26	110	43	$Fe(Me_2dtc)_3$
	Co	500	50	$CHCl_3/EtOH^{ii}$	50	90	40	50	270	77	$Co(Me_2dtc)_3$
	Ni	300	60	$EtOH^{i}$	50	16	120	20	100	98	$Ni(Me_2dtc)_2$
	Cu	200	40	^{i}	40	13	28	12	52	85	$Cu(Me_2dtc)_2$

[i] plus 20 mg tetraethylammonium perchlorate. [ii] for explanation see Experimental Section.

Instrumentation

The electrolysis was controlled by a Bang and Olufsen SN15 power supply delivering up to 50V(DC) and 1A.

Infrared spectra in the range 4400 to 330 cm^{-1} were recorded on a Jasco A 302 spectrophotometer calibrated with polystyrene film. For the range 800–250 cm^{-1} a Perkin-Elmer 457 spectrophotometer was used. Samples were in the form of KBr discs.

Room temperature magnetic susceptibility measurements were made on a magnetobalance using the standard Gouy method. The field was calibrated at ambient temperature using trisethylenediaminenickel(II) thiosulphate.[11] Ligand susceptibilities were calculated using Pascal's constants.

Solution optical spectra were recorded between 190 and 850 nm at 25°C on a Hitachi Model 150:20 double-beam spectrophotometer.

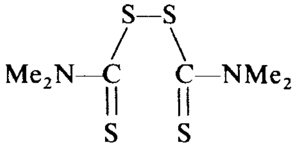
^{1}H and ^{13}C NMR spectra were recorded at 22°C on a Jeol FX-100 spectrometer using an internal deuterium lock referenced against TMS. Samples were recorded in $CDCl_3$.

Electron spin resonance spectra were recorded at ambient and liquid nitrogen temperatures on the Varian V-4500 spectrometer operating at X-band frequencies and calibrated relative to the centre of the hyperfine pattern of diphenylpicrylhydrazyl-(DPPH) ($g = 2.0036$). Samples were dissolved in a 1 : 1 mixture of acetone and toluene.

Conductivity measurements were made using a Philips PR96500 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.

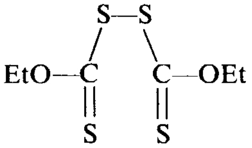
RESULTS AND DISCUSSION

The results of this study show that the preparation of transition metal xanthates and dithiocarbamates can be satisfactorily achieved by the electrochemical synthetic method. Since other transition and main group metal complexes with these ligands have also been prepared in this way,[9] one may say that the method is a general one for these particular syntheses. Attempted preparations in the presence of various dithiocarbamate or xanthate anions failed or produced impure products. However, successful, clean preparations were effected using the oxidized form of the ligand: thiuram disulphide (**I**) for the dithiocarbamate and dixanthogen (**II**) for the xanthate.



(I)

tetramethylthiuram disulphide



(II)

ethyl dixanthogen

The products are generally those of the metals in conventional oxidation states, and have been previously prepared by other workers.[8,12] The current efficiencies were typically 0.1 → 1 mol F^{-1} and non-integral, suggesting that some chain reaction follows the initial electrochemical step. In the simplest view the process occurring is

$$M \rightarrow M^{n+} \quad \text{(anode)} \quad (M = \text{Fe, Co, Ni, Cu})$$

$$(\text{lig})_2 \rightarrow \text{lig}^- \quad \text{(cathode)} \quad (\text{lig} = \text{exa, Me}_2\text{dtc})$$

for an overall reaction,

$$M^{n+} + n(\text{lig}^-) \rightarrow M(\text{lig})_n$$

No attempt was made to further elucidate the mechanism. The products of the synthesis were characterized by comparison of melting point, infrared (values reported in Table II) and optical spectra with data in the literature, together with conductance data, nuclear magnetic resonance spectra and analytical data. Nitromethane solutions of the compounds prepared were found to be non-conducting, the molar conductances being $\Lambda_M < 10^{-3}$ Sm^2mol^{-1}, as compared to 6.7×10^{-3} Sm^2mol^{-1} for tetraethylammonium chloride in nitromethane. This indicated the absence of ionic species and supported the formulation of the complexes as covalent compounds. The analytical results listed confirm the suggested formulation for each of the compounds.

No matter what voltage was applied to the cell, cobalt produced diamagnetic Co(III) derivatives obtained as green, crystalline solids. The conventional synthesis of $Co(exa)_3$ requires peroxide oxidation of the divalent starting materal.[13] Under these conditions the electrochemical method offers a considerable advantage over the standard method yielding highly crystalline trivalent material free from impurities with an infrared spectrum (values in Table II) compatible with that given in the literature.[14] The dithiocarbamate species such as $[Co_2(Me_2dtc)_5]^+$ [15] and $[Co(Me_2dtc)_3]^+$ [16,17] have been produced under oxidizing conditions and are 1:1 electrolytes. The former has a complicated NMR spectrum and the latter is paramagnetic. As the compound produced by this method is a diamagnetic non-electrolyte with a simple NMR spectrum (see below), it can be concluded that neither of these compounds were produced under these conditions. A second recrystallization did not change the observed measurements. Infrared frequencies for $Co(Me_2dtc)_3$ correspond to established values.[18]

With nickel, the brown-green diamagnetic *bis*-dithiocarbamate precipitated during the course of the electrolysis, whereas the *bis*-xanthate was recovered by reducing

TABLE II
Important infrared frequencies (cm^{-1}) for the metal complexes prepared

Complex	ν_{C-O}	ν_{C-N}	ν_{C-S}	ν_{M-S}	Ref.
$Fe(exa)_3$	1230		1040		27,28
$Fe(Me_2dtc)_3$		1510	970	350 390	18
$Co(exa)_3$	1250		1035	350	14
$Co(Me_2dtc)_3$		1525	985	350	18
$Ni(exa)_2$	1265		1030	380	8,14
$Ni(Me_2dtc)_2$		1545	975	380 370	18
Cu(exa)	1195		1038	450	19
$Cu(Me_2dtc)_2$		1520	975	440	12,25

the volume of solvent followed by cooling. In both cases the infrared and electronic spectral data were identical with literature values.[8,14,18] The dithiocarbamate species was too insoluble in deuterated solvents to permit NMR spectra to be obtained.

In the absence of an electric current, no xanthates were obtained with copper. Electrolysis in the presence of dixanthogen produced an immediate precipitate of the diamagnetic, golden copper(I) compound whose infrared frequencies agreed with those in the literature.[19] Due to its insolubility, no NMR spectra were obtained. Of all the copper xanthates known, only *p*-cresol xanthate gives a paramagnetic species, *i.e.*, copper in the divalent state, which is very unstable towards reduction;[20] thus it is not surprising that a copper(I) xanthate is produced in the preparations described here.

In the presence of the thiuram disulphide on the other hand, highly crystalline, dark brown *bis*(dimethyldithiocarbamate)copper(II) precipitated as electrolysis proceeded. It has been reported[21] that a copper(I) tetramer with dithiocarbamates was produced by the reaction of copper bronze with tetramethylthiuram disulphide over a period of two to ten hours but required several recrystallizations to obtain a pure product. This is equivalent to reacting finely divided metallic copper with the oxidized ligand since it has been shown[22] that metals can be activated by producing a finely divided state. In this work, activation has been produced by the application of electric potential. However, it is evident here that highly crystalline $Cu(Me_2dtc)_2$ is produced without the need for subsequent recrystallization and the short time in which it is obtained is significant. Also, it was not surprising that a Cu(II) dithiocarbamate was produced as compared to the previous case where Cu(exa) was formed, since Akerström[23] reported that an instantaneous reaction occurs when excess tetramethylthiuram disulphide is added to a Cu(I) dithiocarbamate, resulting in the formation of the divalent species. The magnetic moment of 1.63 BM for the $Cu(Me_2dtc)_2$ complex prepared electrochemically confirmed the d^9 state and the solution electron-spin resonance spectrum showed the expected four lines at room temperature with a hyperfine coupling constant of $79.4 \times 10^{-4}\,cm^{-1}$.[24] This value and the infrared absorption frequencies agree well with those found in the literature.[12,25]

As with cobalt, no matter what voltage was applied to iron in the presence of dixanthogen or thiuram disulphide, iron(III) xanthates and dithiocarbamates were produced. The dithiocarbamate complex precipitated as a brown solid during electrolysis. Recrystallization from a CH_2Cl_2/C_2H_5OH mixture gave a pure compound as indicated by metal analysis. The magnetic moment of 2.72BM at 295°K (strongly temperature dependent) confirmed the predominantly low-spin ground state of the iron(III) *tris*-xanthate. Conventional synthetic methods often yield a large proportion of polymeric material from which it is difficult to separate the pure compound. The low yield reported here is probably due to the formation of these polymeric materials but the product recovered proved to be of good purity. The well known *tris*-dithiocarbamate lies at the high-spin-low-spin cross-over.[26] The infrared spectrum of each compound was identical with that already reported.[18,27,28]

Nuclear magnetic resonance spectra (^1H and ^{13}C) were recorded for ethyl dixanthogen, tetramethylthiuram disulphide and for cobalt and nickel xanthates and cobalt dithiocarbamate, and served a two-fold purpose; first, to characterize the species, and secondly as a criterion of purity. The ^1H NMR spectrum of ethyl dixanthogen consisted of a triplet centred at $\delta(CH_3)$ 1.43 ppm and a quartet centred at $\delta(CH_2)$ 4.70 ppm with $^3J(H\text{–}H)$ 7.08 Hz. In $Co(exa)_3$, the resonances were detected at $\delta(CH_3)$ 1.47 ppm, $\delta(CH_2)$ 4.61 ppm, $^3J(H\text{–}H)$ 7.08 Hz. For the nickel species, the values were δ1.46 ppm, 4.56 ppm, $^3J(H\text{–}H)$ 7.07 Hz. The integration of the multiplets agreed well with the proposed stoichiometries of the metal complexes.

The room temperature ^1H NMR spectrum of tetramethylthiuram disulphide consists of a predominant peak at 3.65 ppm.[29] The corresponding resonance in the cobalt dithiocarbamate was observed further upfield at 3.25 ppm.

The proton decoupled ^{13}C NMR spectrum of ethyl dixanthogen consists of three singlets at δ 14.19, 72.75 and 208.20 ppm. The corresponding resonances for the cobalt(III) and nickel(II) xanthates occur at δ 13.81, 67.04, and 201.38 and at 13.79, 68.48 and 231.44 ppm, respectively.

The proton decoupled ^{13}C NMR spectrum of tetramethylthiuram disulphide also consists of three singlets at δ 41.81, 47.34 and 193.13 ppm. The corresponding resonances for the cobalt(III) dimethyldithiocarbamate occur at δ 29.72, 37.67 and 205.27 ppm. These values agree well with values for other metal xanthate and dithiocarbamate complexes reported in the literature.[9,30,31]

The method described herein represents a simple synthesis of metal xanthates and dithiocarbamates directly from the metal in question.

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