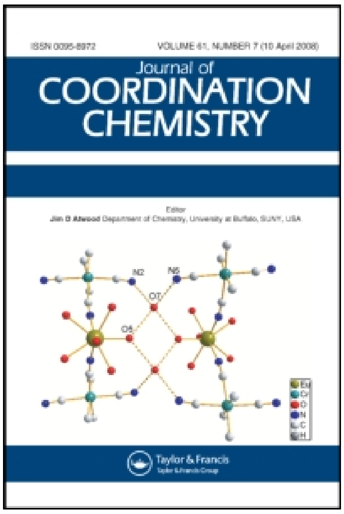

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DIRECT ELECTROCHEMICAL SYNTHESIS OF SOME METAL CHELATE COMPLEXES

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transition elements, complexes of

A convenient electrochemical synthesis of various ML_2, ML_3, ML_4 and MOL_2 complexes (M = Ti,Zr,Hf,V,Cr,Mn, Fe,Co,Ni,Cu,In; L = acetylacetonate anion, 3-hydroxy-2-methyl-4-pyronate anion, 2-acetylpyrrolate anion, and other bidentate ligands) is described. The metal, as the anode of simple cell, is oxidised in the presence of the parent compound of the ligand (HL) in an organic solvent mixture. Gram quantities of complex can be produced in a few hours; other advantages of this method are discussed. Current efficiency measurements serve to identify the reaction mechanism.

INTRODUCTION

The synthesis and structural study of metal chelate compounds is one of the classical themes of coordination chemistry, as evidenced by the extensive literature on the subject (see Refs. 1 and 2 for reviews). Complexes in which the chelating ligand is a singly charged anion, such as acetylacetonate (2,4-pentanedionate), have the especial attraction that the complex ML_n is a neutral species when n = oxidation number of the metal ion in question. Such compounds are often insoluble in water, and various structural problems have made them the focus of considerable attention.[3]

The synthesis of neutral chelate compounds normally has as a starting point an aqueous solution of a suitable salt of the metal in question; addition of the chelating agent is followed by extraction, precipitation, crystallisation, etc., as the system demands. The difficulties which may arise in such work-up procedures have been noted by several authors (e.g. Refs. 4, 5). Since the parent neutral compounds are very weak acids, the direct reaction

$$M + nHL \longrightarrow ML_n + n/2H_2 \qquad (1)$$

is rarely possible except for strongly electropositive metals (alkali and alkaline earth elements), and somewhat surprisingly, lead and copper.[6]

Since metals are often readily available, and are generally cheaper than their compounds, direct synthesis from the metal is an attractive route, and anhydrous metal acetylacetonates have recently been produced by the co-condensation of metal atoms and 2,4-pentanedione.[7] We now report that a wide range of neutral chelates can be produced by the electrochemical oxidation of the metal in the presence of the neutral compound. Particular attention has been paid to the ligands 2,4-pentadionate (acac), 3-hydroxy-2-methyl-4-pyronate (pyrone) and 2-acetyl-pyrrolate ($pyr.COCH_3$), although some reactions have been carried out with other compounds. The aim of the present work has been to explore the usefulness of the method rather than to establish conditions of high yield, and the choice of these ligands was dictated by their general usefulness, by the nature of the synthetic methods presently available and by previous experience in this laboratory. One welcome, if unexpected, result of the work has been to yield methods for the production of both ML_3 and MOL_2 species of titanium and vanadium; possible synthetic applications of this are suggested. While the present work was in progress, Lehmkukl and Eisenbach[8] described cells for the continuous high yield production of iron, cobalt and nickel acetylacetonates, and their techniques could presumably be applied to any of the systems discussed below.

TABLE I
Electrochemical synthesis of 2,4-pentanedionate (= L) complexes

Compound	Voltage (V)	Initial current (mA)	Time of electrolysis (h)	Wt. of metal dissolved (g)	Colour of product	% metal found	% metal calcd.	Mol. wt. (a)
TiL_3	>50	20	3.5	0.03	deep blue	13.8	13.9	(b)
$TiOL_2$	(c)				yellow	18.2	18.3	(b)
ZrL_4	38	45	7	1.14	colourless	18.5	18.7	(b)
HfL_4	46	40	7	0.83	colourless	30.6	31.1	(b)
VL_3	40	50	11	0.12	olive green	14.5	14.7	348
VOL_2	50	8	12	0.15	brown	19.2	19.2	265
CrL_3	>50	50	2	0.71	red-brown	15.0	14.9	(b)
MnL_2	20	50	5.5	0.96	tan	21.7	21.7	253
FeL_3	15	50	5.5	0.30	deep red	15.9	15.8	353
CoL_2	45	30	4.5	0.16	pink	22.9	22.9	257
NiL_2	25	80	4.5	0.40	green	22.5	22.8	(b)
CuL_2	50	8	18	0.20	pale blue	24.2	24.4	261
ZnL_2	22	50	16	0.84	colourless	24.9	24.8	262

[a] From most intense molecular ion peak in mass spectrum; values correspond to calculated mol. wt. in each case

[b] Not recorded.

[c] Sample produced by aerial oxidation of $Ti(acac)_3$.

TABLE II
Electrochemical synthesis of 3-hydroxy-2-methyl-4-pyronate complexes

Compound	Voltage (V)	Initial current (mA)	Time of electrolysis (h)	Wt. of metal dissolved (g)	Colour of product	% metal found	% metal calcd.	M Mol. wt. (a)
VOL_2	50	15	12	0.12	brown	16.1	16.2	(b)
FeL_3	50	10	16	0.11	rust-red	12.9	12.9	431
CoL_2	50	50	4	0.12	deep red	18.9	18.9	309
NiL_2	50	30	5	0.13	green	18.8	18.9	308
CuL_2	50	30	5	0.13	green	20.1	20.1	313
InL_3	100	40	2	0.15	colourless	23.5	23.6	490

[a] See Footnote (a), Table 1.

[b] Not recorded.

TABLE III
Electrochemical synthesis of 2-acetylpyrrolate complexes

Compound	Voltage (V)	Initial current (mA)	Time of electrolysis (h)	Wt. of metal dissolved (g)	Colour of product	% metal found	% metal calcd.	Mol. wt. (a)
CrL_3	50	20	4	0.06 (b)	dark red	11.6	11.5	(c)
CoL_2	100	20	1	0.06 (b)	red-brown	21.4	21.4	275
NiL_2	50	20	160	0.10 (b)	green	18.1	18.1	274
CuL_2	100	>50	2	0.2	green	21.2	21.5	279
InL_3 (d)	50	40	2	0.74	colourless	28.8	29.0	(c)

[a] See Footnote (a), Table 1.

[b] Synthesis carried out in cells containing only 3 cm^3 of solution.

[c] Not recorded.

[d] L = 2-formylpyrrole.

EXPERIMENTAL

Materials

Metals were obtained from Alfa Inorganics, and could be conveniently handled as wire, rod or sheet; powders cannot be used. Purity was 99.9% or better. Organic solvents (Reagent Grade) were dried and distilled before use. The compounds 2,4-pentanedione, 3-hydroxy-2-methyl-4-pyrone ("maltol"), and others (see Table 4) were used as supplied (Fisher, Aldrich); 2-formyl- and 2-acetylpyrrole were prepared by the methods used in earlier work.[9]

Analytical and Spectroscopic Methods

Metal analysis was generally by atomic absorption spectrometry, and we are indebted to Dr. C. Riddle (Department of Geology, University of Windsor) for assistance in this aspect of the work. Titanium, zirconium and hafnium were analyzed titrimetrically by addition of excess EDTA, followed by back-titration with bismuth(III) nitrate.[10] Vanadium was determined colorimetrically, using the absorptivity at 450 nm of the brown solution formed on addition of hydrogen peroxide.[11] Analytical results are given in Tables I–IV.

Infrared spectra were recorded with a Beckman IR–12 spectrometer over the range 4000–200 cm^{-1}. Mass spectra were obtained with a Varian CH5 instrument operating at low resolution in the electron impact mode. The ion source temperature was typically 250–300°C and the probe temperature 25–75°C, although temperatures of 300°C were used in some cases.

TABLE IV
Miscellaneous complexes prepared by direct electrochemical oxidation of metal

Compound	% metal found	% metal calcd.	Colour of product
$Ni(dmg)_2$ [a]	20.2	20.2	red
$Co(oxine)_2$ [a]	19.0	19.4	dark blue green
$Co(sal)_2$ [a]	19.5	19.6	orange
$Cu(sal)_2$ [a]	21.0	20.8	blue
Cu(tfacac) [a]	17.4	17.2	turquoise

[a] dmg = dimethylglyoximate; oxine = 8-hydroxyquinolate; sal = salicylaldehyde anion; tfacac = 1,1,1,-trifluoro-2,4-pentanedionate.

Preparative

The experimental techniques were very similar to those described previously.[12] The metal, attached mechanically to a platinum wire lead, formed the anode of cell, with a thick (1 mm) platinum wire as cathode. A voltage of 10–50 V was supplied from a Coutant LQ 50/50 DC power supply; the experimental voltage was that required to produce an initial current in any given cell of the order of 20–50 mA, which corresponded to a sensible rate of dissolution of metal (see Tables I–IV). Electrolysis over 2–10 h, as convenient, normally resulted in approximately 0.5 g of metal dissolving. The cell was tightly sealed, and preparations could be carried out in an atmosphere of dry nitrogen, with mechanical stirring of the solution phase.

The volume of the solution phase was 50–100 cm^3, composed as follows:

Acac complexes other than Ti,V,Cr; 35 mg Et_4NClO_4, 15 cm^3 CH_3OH or acetone, 50 cm^3 Hacac.

Pyrone complexes other than Ti,V; 35 mg Et_4NClO_4, 10 cm^3 CH_3OH, 40 cm^3 benzene, 1.5 g Hpyrone.

Acac, pyrone complexes of Ti,V,Cr; 35 mg Et_4NClO_4, 70 cm_3 Hacac, *or*, 70 cm^3 acetone, 1.5 g Hpyrone, nitrogen atmosphere.

Pyrrole complexes: 10 mg Et_4NClO_4, 0.4 cm^3 Et_3N, 25 cm^3 benzene, 5 cm^3 CH_3OH, 0.4 g 2-acetyl (or 2-formyl) pyrrole, nitrogen atmosphere, cell protected from light.

Other ligands (see Table IV): 60 cm^3 benzene, 15 cm^3 methanol.

The work-up of the final reaction mixture involved either reduction of the total volume in vacuo, or direct addition of hexane or petroleum ether to precipitate the solid complex. Recrystallisation was from acetone, and the final product was washed with dimethyl ether. The compounds were identified by colour (where appropriate), metal analysis, infrared spectra, and molecular weight determined mass-spectrometrically.

Experimental details for the direct electrochemical synthesis of $In(acac)_3$ have been given elsewhere.[13]

RESULTS AND DISCUSSION

In this section, we note any significant spectroscopic information on the compounds prepared, and important preparative points. Since the aim was to establish the applicability of direct electrochemical oxidation of metals in the synthesis of chelate complexes, we have not attempted to establish optimum currents or voltages, or to maximise the yield in the work-up procedure. The methods described in fact normally gave chemical yields of 50–90%, relative to the amount of metal dissolved from the cathode. Mechanical stirring increased the amount of metal oxidised.

2,4-Pentanedionate Complexes

The preparation of these compounds (Table I) was straightforward and presented few problems. The syntheses were carried out in cells open to the air (except for titanium(III) and vanadium(III)), and the products represent conventional oxidation states of the metals concerned. The infrared spectra were essentially identical to those in the literature;[14] the mass spectra, which typically showed prominent ions at ML_n^+, ML_{n-1}^+ and HL^+, aided in the identification of the products. In view of interest in the stereochemistry of cobalt(III) complexes with bidentate ligands, we made a number of attempts to prepare $Co(acac)_3$ by direct electrochemical synthesis in the hope of investigating the stereochemical aspects of the method, but without success. The applied voltage was increased to 450 V, but in each case the product was $Co(acac)_2$. Addition of hydrogen peroxide to the solution phase before electolysis lead to the formation of dark-green crystals of $Co(acac)_3$, but this is almost certainly the result of oxidation of $Co(acac)_2$ *in situ*, and the stereochemical problem was therefore not investigated further. This latter method could however be used for direct synthesis of $Co(acac)_3$ and similar compounds.

The titanium (and vanadium) Hacac systems are especially interesting. Electrolytic oxidation of the metal in the complete absence of oxygen (nitrogen atmosphere, de-gassed solvents) yields an intense blue solution, from which $Ti(acac)_3$ can be obtained. If the electrolysis is done in air, the product is $TiO(acac)_2$, identified by its colour and metal content, and by the characteristic $\nu(Ti = O)$ band in the infrared spectrum[15] at 1080 cm^{-1}. The blue colour of electrolytically prepared $Ti(acac)_3$ is discharged rapidly when oxygen is admitted into the system, and in related work, we have found that this $Ti(III) \rightarrow Ti(IV)$ oxidation can be used in the indirect electrochemical reduction of organic compounds,[16] following the established use of other titanium(III) compounds in such reactions.[17] Finally we note that the electrochemical oxidation of zirconium and hafnium under these conditions gives rise directly to the $M(acac)_4$ species. The contrast between titanium and its heavier congeners in this respect parallels much of the known chemical behaviour of these elements. Given the inertness of these metals to many reagents, the electrochemical techniques described provide a simple and convenient route to these, and other, Group IVA compounds.

The vanadium system behaves similarly to titanium. Electrochemical oxidation in oxygen-free conditions gave rise to a dark-green solution from which $V(acac)_3$ could be precipitated by addition of petroleum ether. In the presence of oxygen, a brown solution was produced, and the product isolated in this case was $VO(acac)_2$, identified analytically and by the characteristic $\nu(V{=}O)$ vibration at 1000 cm^{-1} (c.f. 996 cm^{-1} reported by Selbin, Holmes and McGlynn).[18]

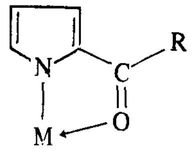
Pyrone Complexes

The preparation of $In(pyrone)_3$ by the reaction between the parent compound and indium trichloride has been reported previously.[19] Since the complexes of this ligand have some structural analogy with dithiolene compounds, it seemed worthwhile to investigate the direct synthesis of transition metal complexes of the ligand in order to establish the oxidation state of the metal in the product. The compounds synthesised directly from the metal are listed in Table II, from which it is clear that the oxidation states are identical to those produced with 2,4-pentanedione.

Identification of the compounds again depended upon metal analysis, mass spectrometric molecular weight and infrared spectroscopy. The mass spectrum of InL_3 was essentially identical to that reported earlier, with peaks corresponding to ML_3^+, ML_2^+, ML^+ and HL^+, and similar spectra were found for the transition metal complexes, except that for VOL_2, only the molecular ion peak and HL were present in significant intensity. For ML_2 compounds, we typically observed ML_2^+, ML^+, and HL^+, except that the ML peak was absent in the case of copper. The infrared spectra all showed a group of intense absorptions between 1610 and 1450 cm^{-1}, corresponding to $\nu(C{=}O)$ and $\nu(C{=}C)$ of the ligand, similar to the vibrations observed for InL_3; no attempt was made to analyse the effect of metal oxidation state or mass upon these vibrations. The compound VOL_2 had a strong band at 970 cm^{-1}, assigned to $\nu(V{=}O)$, in keeping with the observations for the $VO(acac)_2$ complex discussed above.

2-Acetylpyrrole Complexes

Complexes of transition metals with anionic ligands derived from α-substituted pyrroles of the type



have been the subject of a number of preparative and spectroscopic investigations. Complexes of Cu(II),[20, 21] Co(III)[21] and Cr(III),[22] with R = H, CH_3, etc., have been described; in each case the ligand is bidentate, chelating through nitrogen and carbon, and delocalisation of the metal-ligand and ligand-ring orbitals has been suggested.[22] Complexes of indium(III), and of the dimethylindium(III) group, have also been prepared and studied.[9]

The preparative routes to these complexes are not simple, due in large measure to the relative instability of the parent pyrroles, and in the case of the chromium(III) compound the starting material was hexacarbonylchromium(O), which reacts with the parent pyrrole by elimination of hydrogen and carbon monoxide.[22] An investigation of the direct electrochemical synthesis of such complexes was therefore of more than usual interest, and the synthesis of a number of complexes of both transition metal and main group metals has now been achieved. Table III shows that the chromium, cobalt, nickel, copper and indium compounds have been obtained; the indium compound is one that could not be prepared by conventional methods in this laboratory.[9] In order to minimise decomposition of the pyrrole, the experiments were run in the dark, and in an atmosphere of nitrogen. The pyrroles are very weak acids, and the addition of small quantities of triethylamine substantially increased the rate of dissolution of the cathode, presumably by enhancing the concentration of free anion. Even with this addition, the rate of reaction was extremely slow in the case of nickel.

The compounds prepared electrochemically are identical with those obtained by other routes. In addition to elemental analysis and mass spectrometric molecular weights, the infrared spectra confirm the presence of the acetylpyrrole ligand. The strong $\nu(C{=}O)$ absorption in the parent compound appears at 1549, 1555 and 1540 cm^{-1} respectively in the chromium(III), cobalt(II) and copper(II) complexes, in agreement with earlier work.[20-22] The simple electrochemical preparation of these interesting compounds is a nice illustration of the attraction of this synthetic method.

Miscellaneous Complexes

We have also tested the applicability of the electrochemical method in the synthesis of a number of complexes involving ligands other than those discussed above. Table IV shows that four readily available ligands were successfully used, with nickel, cobalt and copper anodes. In each case the metal content and infrared spectra confirmed the identity of the product. No doubt complexes of these ligands with other transition metals could also be readily produced in this way.

Reaction Mechanism

The present paper is one of a number of investigations of direct electrochemical synthesis currently proceeding in this laboratory. In studies of the electrochemical oxidation of transition metals in the presence of bromine,[23] measurements of the current efficiency, expressed as moles of metal dissolved per Faraday of electricity, have proven extremely helpful in identifying the possible mechanism. In such experiments, and in work on organotin halides,[24] the current efficiencies are of the order of 2–10 mol F^{-1}, values which have been interpreted in terms of a free radical mechanism.

In the present systems, on the other hand, the measured current efficiencies are all significantly less than 1.0 mol F^{-1}. These results are taken as showing that the overall electrode reactions of a metal M and parent acid HL are:

$$\text{cathode} \quad ne^- + n\text{HL} \longrightarrow n\text{L}^- + n/2\text{H}_{2\,(g)} \qquad (2)$$

$$\text{anode} \quad n\text{L}^- + \text{M} \longrightarrow \text{ML}_n + ne^- \qquad (3)$$

for which the current efficiency should be equal to $1/n$. The experimental values are

Ti/acac	$1/n = 0.25$ mol F^{-1}	(theory 0.33)
Ni/acac	$1/n = 0.51$ mol F^{-1}	(theory 0.50)
Co/acac	$1/n = 0.54$ mol F^{-1}	(theory 0.50)
Cu/acac	$1/n = 0.44$ mol F^{-1}	(theory 0.50)
V/pyrone	$1/n = 0.35$ mol F^{-1}	(theory 0.33)†

These results are in good agreement with the mechanism outlined above, as is the production of a gas, identified as hydrogen, at the cathode. The effect of small amounts of base on the rate of formation of pyrrole complexes is also readily explained on this basis. The simplicity of the mechanism, which is clearly different from that observed in the halogen systems, suggests that this electrochemical technique should find general application in the synthesis of metal complexes involving anionic ligands derived from weak acids.

General

The experiments described in this paper show that direct electrochemical synthesis can be used for the rapid production of a wide variety of chelate complexes of various transition and main group metals. The method is rapid and simple, requires neither high temperature nor expensive apparatus, and affords complexes in gram quantities starting from the readily available metals.

The ligands examined in the present work are typical of many of those used in inorganic chemistry, in that they are the conjugate bases of very weak acids. Our experience suggests that the method could be equally well applied to ligands other than those discussed above; we have successfully produced acetates of chromium(III), indium(III), iron(III) and thallium(I) in this way.[25] Some preliminary investigation of solvent conditions and applied voltage is necessary, but such factors are apparently readily explored and should prove no barrier to the rapid synthesis of the compounds required. We believe that such methods should have wide application in coordination chemistry.

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†Product = VOL_2; calculation assumes that VL_3 is the primary product which subsequently undergoes oxidation.

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