Direct Electrochemical Synthesis of Cationic Complexes

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The electrochemical oxidation of both transition and main-group metals in the presence of dimethyl sulphoxide (dmso) or acetonitrile plus tetrafluoroboric acid gives rise to salts of the type $[ML_6][BF_4]_n$ [M = V, Cr, Mn, Fe, Co, Ni, Zn, Cd, or In; L = dmso or CH_3CN (not all combinations); n = 2 or 3, depending on M]. The electrochemical conditions described give gram quantities of product from 5—25 h electrolyses with simple apparatus.

THE direct electrochemical synthesis of inorganic or organometallic compounds depends on the electrolytic oxidation of a metal in the presence of a suitable ligand, or ligand precursor.[1] Recent work from this laboratory has utilized the advantages of non-aqueous solvents as electrochemical reaction media, and a number of anhydrous inorganic halides,[2-4] anionic halide complexes,[3,5] and neutral complexes with chelating ligands [6] have been successfully prepared in one-step syntheses under such conditions.

We now describe the applications of similar methods to the direct synthesis of cationic complexes of both transition elements and main-group metals. The experimental work has been concerned with dimethyl sulphoxide (dmso) and acetonitrile complexes, systems which were chosen because of the compatibility of these solvents with tetrafluoroboric acid: this was itself used as the source of a convenient and stable counter ion for salt formation. In an earlier report,[7] the use of solutions of dmso in perchloric acid was briefly described, but considerations of personal safety persuaded us of the advantages of dmso–HBF_4 and CH_3CN–HBF_4. One readily available commercial source of HBF_4 is as a 48% aqueous solution, and we have used both this and a solution in anhydrous diethyl ether as the starting material. A short report of this work has already been published.[8]

The syntheses are simple and straightforward, but we should draw attention here to the interesting fact that, while most of the reactions are indeed electrochemical, in at least two, or possibly three, cases there is a spontaneous chemical reaction between dmso–HBF_4 and the metal.

EXPERIMENTAL

Preparations.—The electrochemical procedure was essentially the same as that described in earlier work, except that a tall-form Polythene beaker (200 cm^3) was used for the cell. The solution phase was typically prepared by mixing equal volumes of 48% HBF_4 aqueous solution (Alfa Inorganics), or a solution of HBF_4 in diethyl ether (Aldrich), with purified dmso at 0 °C. Electrolytic oxidation of a number of transition and main-group metals was achieved with voltages in the 0.5—3.0 V range, giving currents of 0.1—0.3 A. Over a period of 10—20 h at room temperature, typically 1—2 g of metal dissolved, giving 5—10 g of product. In many cases the products precipitated as electrolysis proceeded (dmso + V, Cr, Fe, Ni, Zn, or In; acetonitrile + Ti); in other systems, reduction in volume *in vacuo* (dmso + Co, CH_3CN + In or Cr) or heating followed by the addition of diethyl ether (dmso + Mn or Cd) yielded solid material.

The electrical conditions for these electrochemical oxidation reactions are listed in Tables 1 and 2. Some typical reaction procedures are described below, along with one example of the use of the final electrolyte solution as the starting point for the synthesis of a related cationic complex.

Analyses.—Metal and boron analyses were by atomic absorption spectrophotometry. Microanalyses of selected samples were carried out by Spang Microanalytical Laboratory, Michigan, or Guelph Chemical Laboratories Ltd. In addition, the presence of co-ordinated ligand and of the BF_4^- anion were confirmed by i.r. spectroscopy,[9-11] using a Beckman IR-12 instrument. Analytical results are given in Table 3.

$[Cr(dmso)_6][BF_4]_3$.—A portion (*ca.* 10 cm^3) of the dark green solution resulting from electrolysis was warmed on a hot plate to about 50 °C with continuous stirring. After *ca.*

TABLE 1

Experimental conditions for electrochemical preparation of some cationic complexes

Element	Product	Solution phase composition (cm^3)		Initial		Time of electrolysis (h)	Amount of metal dissolved (g)
		dmso	HBF_4 (40%)	Voltage (V)	Current (mA)		
V	$[V(dmso)_6][BF_4]_2$	50	50	2	100	16	0.4
Cr	$[Cr(dmso)_6][BF_4]_3$	[a] 30	30	3.5	100	20	1.3
		20	5 [b]	6	50	7	0.7
Mn	$[Mn(dmso)_6][BF_4]_2$	30	30	[c]			
Fe	$[Fe(dmso)_6][BF_4]_3$	[a] 30	30	2	210	22	1.9
		20	5 [b]	4	40	7.5	0.6
Co	$[Co(dmso)_6][BF_4]_2$	50	50	2	100	16	1.1
Ni	$[Ni(dmso)_6][BF_4]_2$	40	40	2	100	16	1.6
Cu	[d]	30	30	2	200	23.5	2.4
Zn	$[Zn(dmso)_6][BF_4]_2$	40	40	2	100	56	3.0
Cd	$[Cd(dmso)_6][BF_4]_2$	30	30	1	80	22	3.0
In	$[In(dmso)_6][BF_4]_3$	40	40	1	50	62	0.9

[a] Same product obtained in each case. [b] HBF_4 in diethyl ether. [c] Spontaneous reaction (see text). [d] No identifiable product could be isolated from this reaction.

30 min, a thick, dark green solid precipitated. This was filtered off and thoroughly washed with diethyl ether to yield a light green fine powder which was dried *in vacuo*; yield 17.8 g (91%, based on 1.3 g Cr dissolved). The same compound was obtained when aqueous HBF_4 was replaced by HBF_4 in diethyl ether, and the isolation procedure was essentially the same in both cases.

$[Mn(dmso)_6][BF_4]_2$.—The reaction in this case was spontaneous, so that no electrolysis was necessary. When the metal was immersed in a mixture of dmso (30 cm³) and HBF_4 (30 cm³) an immediate reaction was detected as the colourless solution gradually changed to pink. At the end of the reaction period (10 h), 5.2 g Mn had dissolved. A portion (10 cm³) of the resulting solution was warmed to 50 °C with continuous stirring; the pink oil which settled out was decanted and on treatment with diethyl ether gave a fine pink powder which was collected, washed with ether, and dried *in vacuo*.

TABLE 2

Experimental conditions for electrochemical preparation of some cationic acetonitrile complexes

Element	Product	Solution phase composition (cm³) CH_3CN	Solution phase composition (cm³) HBF_4 (40%)	Initial Voltage (V)	Initial Current (mA)	Time of electrolysis (h)	Amount of metal dissolved (g)
Ti	$[Ti(NCCH_3)_6][BF_4]_3$	20	20	*a*			
Cr	$[Cr(NCCH_3)_6][BF_4]_2$	20	20	3	100	24	2.6
Cr	$[Cr(NCCH_3)_4][BF_4]_2$	40	5 [b]	2	50	12	0.5
In	$[In(NCCH_3)_6][BF_4]_3$	20	20	1	100	17	2.4

[a] Spontaneous reaction (see text). [b] HBF_4 in diethyl ether.

TABLE 3

Analytical results for cationic complexes prepared electrochemically

Complex cation [a]	Colour	M (%) Found	M (%) Calc.	B (%) Found	B (%) Calc.
(*a*) L = dmso					
$[VL_6]^{2+}$	Blue-green	7.3	7.4		
$[CrL_6]^{3+}$	Light green	6.6	6.7	4.1	4.2 [b]
$[MnL_6]^{2+}$	Pink	8.0	7.9	3.3	3.2
$[FeL_6]^{3+}$	Lime-green	7.0	7.1	4.1	4.2
$[CoL_6]^{2+}$	Pink	7.5	8.4		*c*
$[NiL_6]^{2+}$	Light green	8.4	8.4		
$[ZnL_6]^{2+}$	Colourless	9.2	9.2		
$[CdL_6]^{2+}$	Colourless	14.8	14.9		
$[InL_6]^{3+}$	Colourless	13.6	13.6	3.8	3.9
(*b*) L = $NCCH_3$					
$[TiL_6]^{3+}$	Violet	8.9	8.6		
$[CrL_6]^{2+}$	Navy-blue	12.4	12.4		
$[CrL_4]^{2+}$	Pink	13.0	13.3		*d*
$[InL_6]^{3+}$	Colourless	18.8	18.2		

[a] As BF_4^- salt. [b] Found: C, 18.4; H, 4.5; S, 24.4. Calc.: C, 18.4; H, 4.7; S, 24.6%. [c] Found: C, 20.5; H, 5.3. Calc.: C, 20.5; H, 5.2%. [d] Found: C, 24.3; H, 3.1; N, 13.5. Calc.: C, 24.6; H, 3.1; N, 14.3%.

$[Fe(dmso)_6][BF_4]_3$ *and* $[Fe(en)_3][BF_4]_3$.—The volume of the final yellow-green electrolyte solution was slowly reduced *in vacuo* at room temperature, whereupon a lime-green solid deposited. The solid was collected, washed thoroughly with diethyl ether, and dried *in vacuo*; yield 24.5 g (92.1% based on metal dissolved). When ethylenediamine(en) was added dropwise to a portion of the original Fe–dmso solution a yellow-brown solid precipitated; this was filtered off dried *in vacuo*, and identified as $[Fe(en)_3][BF_4]_3$ (Found: Fe, 11.2. Calc. for $C_6H_{24}B_3F_{12}FeN_6$: Fe, 11.3%). Infrared spectra confirmed the presence of ethylenediamine and BF_4^-.

$[Ti(NCCH_3)_6][BF_4]_3$.—As with Mn–dmso–HBF_4, the reaction is spontaneous and therefore requires no current flow. The initially colourless solution progressively became light violet, and a solid of this same colour deposited. At the end of the reaction (20 h), when 1.23 g Ti had dissolved, the solid was collected and dried *in vacuo*.

$[Cr(NCCH_3)_6][BF_4]_2$ *and* $[Cr(NCCH_3)_4][BF_4]_2$.—The blue solution resulting from electrolysis with CH_3CN–HBF_4 (aq) was evaporated *in vacuo*. The resultant navy-blue solid was washed with diethyl ether, collected, and dried *in vacuo*, and identified as $[Cr(NCCH_3)_6][BF_4]_2$.

In a second experiment, electrolysis was carried out using a CH_3CN–HBF_4 mixture in diethyl ether. The initially colourless solution gradually became pink as the reaction proceeded. At the end of the electrolysis the volume of the solution was reduced *in vacuo*; a pink solid deposited which was collected, dried *in vacuo*, and characterized as $[Cr(NCCH_3)_4][BF_4]_2$. This substance dissolves in acetonitrile, changing colour to blue-green, and is slightly soluble in methanol with the same colour change.

RESULTS AND DISCUSSION

The methods described appear to be of general application, and could presumably be used to prepare complexes of ligands other than dmso or acetonitrile. Alternatively, the electrochemically prepared solutions can be used as the starting point for the synthesis of other complexes, as exemplified by the ethylenediamine case described above. The chemical yields, based on the quantity of metal dissolved, are high, typically in the 80—90% range. The advantages of the method are those advanced previously, namely the simplicity of the procedure, the cheapness of the apparatus, high yield, and ready availability of stable starting materials. In this context it is instructive to compare the present methods with those in the literature for, for example, $[In(dmso)_6]^{3+}$ or $[Cr(dmso)_6]^{3+}$ complexes.[9,12]

The products are generally obtained with the metal in a low oxidation state (II or III), which as noted previously [1,4] is one of the interesting features of electrochemical oxidation. With two exceptions, analogous products were obtained for any given metal from both dmso and acetonitrile. The exceptions involve chromium and titanium. In dmso–HBF_4 the product is the chromium(III) complex, whereas in the presence of acetonitrile chromium(II) species were recovered. We believe that this is due to the relatively easy oxidation of Cr^{II} to Cr^{III} in the oxygenated solvent. With titanium, the $[Ti(NCCH_3)_6]^{3+}$ salt was recovered from acetonitrile; in dmso, although significant quantities of metal dissolved, no characterizable products could be recovered. In other work[13] we have shown that electrochemically generated titanium(III) is a good reducing agent for a number of organic molecules, including diphenyl sulphoxide, and the present results are entirely in keeping with this.

Apart from the oxidation state, the complexes are conventional six-co-ordinate species, again with one exception, namely $[Cr(NCCH_3)_4][BF_4]_2$ obtained from CH_3CN-HBF_4–diethyl ether. This compound does not appear to have been reported previously. The i.r. spectrum of the BF_4^- anion shows that there is significant distortion from T_d symmetry, and bridging BF_4^- groups could obviously lead to a six-co-ordinate species with a CrN_4F_2 kernel. Further work on this compound is planned.

Electrochemical Considerations.—The first point to be made in terms of the electrochemical aspect of these syntheses is that the applied voltage needed for reaction is substantially lower than that used in other work (*cf.* Tables 2 and 3). This is due in part to the presence of large quantities of water in many of the solutions, but since the ether systems require similar voltages it is clear that the high concentration of ions derived from HBF_4 is the most important factor in this regard.

As in our earlier studies, we have measured the current efficiency E_F, defined as moles of metal dissolved per Faraday of electricity. The values for some representative systems are given in Table 4, and show Faradaic behaviour in all but three cases, since $E_F = 0.33 \pm 0.03$ for those systems which yield $[ML_6]^{3+}$ cations, and 0.50 ± 0.02 where $[ML_6]^{2+}$ complexes are formed. The most obviously divergent systems are Ti–CH_3CN and Mn–dmso, where the reactions are chemical rather than electrochemical. For Zn–dmso, E_F is greater than 0.5 by an amount which exceeds the experimental error (± 0.05), and this may be evidence of some chemical reaction over and above the electrochemical oxidation. With the exceptions noted, the overall stoicheiometry of the anode reaction is as in the equation. There is at

$$M + m[BF_4]^- + nL \longrightarrow [ML_n][BF_4]_m + me^-$$

present no obvious rationale for the distinction between titanium and manganese and the remaining elements.

TABLE 4

Current efficiencies in the preparation of cationic complexes

Metal	Electrolytic solutions	E_F/mol F^{-1}
Ti	$HBF_4 + H_2O + CH_3CN$	∞
Cr	$HBF_4 + H_2O +$ dmso	0.42
Cr	$HBF_4 + H_2O + CH_3CN$	0.51
Mn	$HBF_4 + H_2O +$ dmso	∞
Co	$HBF_4 + H_2O +$ dmso	0.53
Cd	$HBF_4 + H_2O +$ dmso	0.52
Zn	$HBF_4 + H_2O +$ dmso	0.77
In	$HBF_4 + H_2O +$ dmso	0.34
In	$HBF_4 + H_2O + CH_3CN$	0.35

We should also note that the current efficiency for chromium is the same for both dmso and CH_3CN systems within experimental error, and that the value of 0.47 confirms that chromium(II) is indeed the initial product of the electrochemical oxidation of this metal under these experimental conditions. The oxidation of Cr^{II} to Cr^{III} in dmso, but not acetonitrile, was noted earlier.

This work was supported by Operating Grants from the Natural Sciences and Engineering Research Council of Canada.

[0/572 *Received, 17th April,* 1980]

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