ELECTROSYNTHESIS OF TRANSITION METAL FLUORO COMPLEXES BY THE DISSOLUTION OF A SACRIFICIAL METAL ANODE

M. C. CHAKRAVORTI,* GAMPA. V. B. SUBRAHMANYAM and D. BANDYOPADHYAY

Department of Chemistry, Indian Institute of Technology, Kharagpur-721 302, India

(Received 15 June 1990; accepted 28 June 1991)

Abstract—A general method for the electrosynthesis of anionic fluoro complexes of transition metals has been developed by the oxidation of sacrificial metal anodes in 20% HF medium at room temperature and at an applied potential of 2–8 V. Some mixed-valent complexes, e.g. $Fe_2F_5 \cdot 2H_2O$ and $Fe_2F_5 \cdot 7H_2O$, have also been obtained by the same method. $K_2[MnF_5] \cdot H_2O$ was obtained by subsequent electrolytic oxidation of the Mn(II) fluoro complex obtained *in situ* in the first step. The method is rapid and gives a good yield with high purity.

Electrochemical synthesis in which a sacrificial metal anode is dissolved in the presence of an electrolyte containing an appropriate ligand is an established way for the electrolytic synthesis of a variety of metal complexes¹ in a single step. The process uses the metals directly, and thus contamination of the product by the anions, which is often encountered in chemical methods using the metal salts, is absent. The method is rapid and highly selective. Thiocyanato complexes of a large number of metals have been prepared by the dissolution of metal anodes in a solution containing HSCN.^{2,3} The chloro complex, $[CoCl_4]^{2-}$ has been prepared⁴ by using a cobalt anode in the presence of hydrochloric acid. We have also reported⁵ a very convenient electrosynthesis of $K_2[MoOF_5]$ using a molybdenum anode. We have now extended our studies with various transition metals and demonstrated that the procedure can be used as a general method for the preparation of a wide variety of fluoro complexes of different metals in various oxidation states from aqueous medium. The results are presented in this communication. Some complexes in higher oxidation state, e.g. K₂[MnF₅]·H₂O, can be prepared by a two step electrolysis-the first step resulting in the formation in situ of the complex in the normal oxidation state by the dissolution of the sacrificial metal anode, followed by electrolytic oxidation of the complex using inert platinum electrodes. The fluoro complexes reported in this communication are already known. Some of these are remarkable in having a variety of structures and physical properties. Many of these were prepared earlier from a non-aqueous medium or by reactions in the solid state at high temperature. The present method uses an aqueous medium at room temperature. Pure metals which are not strongly electropositive dissolve in aqueous hydrofluoric acid slowly even at higher temperature, but the application of an electrical potential increases the rate of dissolution at room temperature.

EXPERIMENTAL

The metals were in the form of rods, lumps, chips or foils and were mostly 99.8% pure. Titanium powder was pressed to make pellets. A few metals (e.g. chromium and manganese) were first deposited on a platinum foil by the electrolysis of their salt solutions and these were subsequently used as the anode. Other chemicals were of AR/GR quality from reputable manufacturers.

The electric power was supplied by a dc power supply (Aplab, India). A milliammeter was connected into the circuit in cases where the current was very feeble. The electrolytic cell was a tall form of polythene beaker (100 cm^3) fitted with a rubber

^{*} Author to whom correspondence should be addressed.

stopper through which four holes were made. The appropriate metal rods which formed the anode were inserted through a hole. In cases where metal lumps, foils or pellets were used, these were fused onto a platinum wire which was inserted through the hole. Chromium and manganese were previously deposited onto a platinum foil sealed to a platinum wire which served as the anode. In all cases a platinum foil (about $1 \times 1 \times 0.15$ cm) connected to a platinum wire served as the cathode and was introduced through the second hole. Two polythene tubes were introduced through the other two holes. These allowed input and exit of nitrogen where it was necessary to carry out electrolysis in the absence of air.

Fluorine was analysed by titration with $Th(NO_3)_4$ after fusing the complex with sodium hydroxide, or steam distillation of fluorosilicic acid.⁶ Potassium and caesium were determined by atomic absorption using a Pye Unicom instrument (SP-2900). Other metals were analysed by standard titrimetric or gravimetric methods. Reflectance spectra were recorded using a Shimadzu UV spectrophotometer (No. 3100) against barium sulphate.

Infrared spectra were recorded in CsI pellets using a Perkin–Elmer instrument (No. 883). Magnetic susceptibility was measured by the Gouy method using Hg[Co(NCS)₄] as calibrant. Diamagnetic corrections were taken from a standard source.⁷ X-ray powder diffraction patterns were obtained with a Philip's diffractometer (PW 1729) employing nickel filtered Cu- K_{α} radiation.

Preparation of the complexes

 $M_2[TiF_6]$, $M_2[VOF_4]$, $K_3[CrF_6]$, $K[MnF_3]$, $M_3[FeF_6]$, $M[CoF_3]$, $M[NiF_3]$, $Cs_2[NbOF_5]$ and $K_2[TaF_7]$ where M = K or Cs. Each electrolysis was carried out using 10 cm³ hydrofluoric acid (20%). The details of the experimental conditions are given in Table 1. After electrolysis, the solution was filtered to free it from any disintegrated metal particles (when an iron anode was used, a yellow deposit was also obtained from which $Fe_2F_5 \cdot 7H_2O$ and $Fe_2F_5 \cdot 2H_2O$ could be prepared). The potassium and the caesium salts were precipitated by adding concentrated solutions of KF and CsF in HF (20%). The complexes were separated by fil-

Compound	Initial voltage (V)	Initial current (A)	Time of electrolysis (h)	Amount of metal oxidized (g)	Yie (g)	ld (%)	$E_{\rm F}$ (mol ${\rm F}^{-1}$)
K₂[TiF ₆]	5	0.50	2.0	0.400	1.5*	75	0.22
Cs ₂ [TiF ₆]	5	0.50	2.0	0.400	2.9 ^b	81	0.22
K₂[VOF₄]	3	0.35	2.0	0.306	1.0 ^b	74	0.23
Cs ₂ [VOF ₄]	3	0.35	2.0	0.306	1.9*	74	0.23
K ₃ [CrF ₆]	2	0.04	3.0	0.085	0.3	65	0.36
K[MnF ₃]	2	0.05	2.0	0.100	0.2	55	0.49
$K_{3}[FeF_{6}]$	8	0.45	2.0	0.600^{a}	1.1		
$Fe_2F_5 \cdot 7H_2O$					1.5		
$Fe_2F_5 \cdot 2H_2O$					1.0		
K[CoF ₃]	5	0.30	3.0	0.780	1.3	63	0.39
Cs[CoF ₃]	5	0.31	3.0	0.800	2.7	82	0.39
K[NiF ₃]	4	0.05	2.5	0.180	0.3	63	0.65
Cs[NiF ₃]	4	0.05	2.5	0.180	0.5	66	0.65
$K_2[NbOF_5] \cdot H_2O$	5	0.40	2.0	0.555	1.3	74	0.20
$K_2[TaF_7]$	3	0.20	2.0	0.540	1.0 ^b	82	0.19
$K_{2}[MnF_{5}] \cdot H_{2}O$	2(20) ^c	0.05(1.0) ^e	$2.0(3.0)^{\circ}$	0.100	0.3	68	

Table 1. Experimental conditions for the electrochemical synthesis of the complexes

^a Total amount of iron oxidized in one experiment, out of which the yields of K_3 [FeF₆], Fe₂F₅·7H₂O and Fe₂F₅·2H₂O are recorded separately.

^b The compounds were precipitated immediately on the addition of MF. In other cases the compounds were crystallized out on evaporation in a desiccator over concentrated H_2SO_4 .

^c Values in parentheses refer to the subsequent electrolytic oxidation of the initially formed M(II) complex.

tering under suction and dried by pressing between the folds of filter paper and then keeping in a desiccator over KOH. For the calculation of electrochemical efficiency (number of moles of metal dissolved per faraday of electricity passed) the anodes were weighed before and after the electrolysis.

 $Fe_2F_5 \cdot 7H_2O$ and $Fe_2F_5 \cdot 2H_2O$. The residue which was obtained during the electrolysis using an iron anode, was digested with 10 cm³ HF (20%) on a steam bath until it dissolved almost completely. The hot solution was quickly filtered and the filtrate was divided into two parts. One part gave a deposit of $Fe_2F_5 \cdot 7H_2O$ on cooling, while the other gave a precipitate of $Fe_2F_5 \cdot 2H_2O$ on evaporation over a steam bath until the volume was reduced to half. These were separated and dried as described above.

 $K_2[MnF_5] \cdot H_2O$. After 2 h of electrolysis, the manganese anode was replaced by a platinum foil electrode and electrolysis was continued for a further 2 h. Finally, the potassium salt was obtained by the addition of a concentrated solution of KF in HF (20%).

RESULTS AND DISCUSSION

Our studies show that fluorides of many transition metals can be easily prepared from aqueous HF at room temperature. The applied voltage is low

Compound	μ _{eff} at 300 K, BM	Bands in electronic spectra (cm ⁻¹)	X-ray powder diffraction data, ^a d (Å)	Bands in IR spectra (cm ⁻¹)
K ₂ [TiF ₆]	diamag		2.3(100), 3.31(90), 4.58(80), 9.15(60), 2.17(60), 2.10(40), 2.85(30), 1.70(30)	580
K ₃ [CrF ₆]	4.10	15,000, 15,900, 16,400, 23,400, 36,300	3.00(100), 4.95(80), 4.31(80), 2.51(60), 2.18(60), 2.14(60), 1.76(60)	544, 500, 296
K[MnF ₃]	5.87	19,000, 22,900, 25,000, 29,800, 32,900	2.89(100), 2.09(65), 1.70(30), 4.14(25), 2.41(14)	426, 300
K ₃ [FeF ₆]	5.73	14,200, 19,700, 25,400, 28,800, 30,200	3.00(100), 2.15(40), 4.96(30), 1.76(30), 4.30(20), 1.52(10). 2.50(10), 1.66(10)	580. 484, 310, 275
K[CoF ₃]	3.90	16,400, 19.420	3.90(100), 2.00(70), 1.66(35), 4.08(25), 2.35(14), 1.30(12), 1.82(12), 1.09(10)	485, 384, 276
K[NiF ₃]	2.36	15,200, 21,400, 25,000	2.85(100), 2.00(65), 4.00(30), 1.65(30), 1.41(25), 2.32(12), 1.80(12), 12.70(10)	485, 450, 255
Cs ₂ [VOF₄]	1.90	15,800, 23,800		990.486
Cs ₂ [NbOF ₅]	diamag		3.65(100), 3.52(90), 3.59(90), 2.52(30), 4.00(25), 4.25(18), 2.38(16)	980, 460
K ₂ [TaF ₇]	diamag		5.10(100), 3.45(45), 4.29(40), 3.35(40), 3.19(40), 4.51(30), 2.00(18), 2.11(14), 2.56(10)	530
$Fe_2F_5 \cdot 7H_2O$	7.89	9500, 11,000, 21,700	4.72(100), 4.23(100), 3.83(80), 3.48(80), 3.28(80), 2.74(80), 2.50(80), 2.43(80), 1.86(80)	470, 303, 280, 260
$Fe_2F_5 \cdot 2H_2O$	7.35	7900, 9600, 15,000, 20,500, 25,500	5.65(100), 3.20(80), 5.00(60), 3.65(60), 3.20(60), 3.10(60), 2.85(60), 1.85(60)	500, 336, 300
K ₂ [MnF ₅]·H ₂ O	3.41	12,500, 18,200, 21,200	5.8(100), 5.91(60), 2.96(25), 2.90(25), 3.30(10), 2.21(10), 2.6(8), 2.38(8)	580, 417, 290

Table 2. Physicochemical data for the complexes

^a Values in parentheses are the intensities.

(2-8 V) and the yield is very good (about 60-85% based on the amount of metal oxidized). The main reactions taking place at the electrodes are :

$$2H^+ + 2e \longrightarrow H_2$$
 (at cathode)
 $M - ne \longrightarrow M^{+n}$ (at anode)

which is evident from the observed electrochemical efficiency. A slight deviation of the electrochemical efficiency (Table 1) from the theoretical value of 1/n is ascribed to some disintegration of the metal anode and slight fluctuation of the current during electrolysis.

Anodic dissolution of the metals was also studied in a stream of nitrogen. The products however, were identical with those obtained in air using metal anodes. With titanium, a purple solution was initially obtained, which ultimately gave the same Ti(IV) compound. It appears that a Ti(III) fluoro complex is initially formed, which was subsequently oxidized during the working up.

All the compounds gave satisfactory analytical results of alkali metal, fluoride and the respective transition metals. The oxidation number of Mn in $K_{2}[MnF_{5}] \cdot H_{2}O$ determined iodometrically was +3.0. The observed magnetic moments of the compounds (see Table 2) were in agreement with those reported in the literature.⁸⁻¹¹ The X-ray powder diffraction data of many of the compounds are available in the X-ray powder diffraction file. Our data (Table 2) for these compounds were in excellent agreement with the recorded values. The band positions in the electronic spectra of the complexes are given in Table 2. These also compare well with the literature values.^{8,11,12} The IR spectral data of only a few of the compounds were reported earlier.^{8,13,14} The positions of the important IR spectral bands of the compounds are recorded in Table 2. The M-F stretching frequency occurs around 500 cm^{-1} for all the compounds of the type $[MF_6]^{n-}$ and also for $[TaF_7]^{2-}$, $[VOF_4]^{2-}$, $[NbOF_5]^{2-}$ and $K_2[MnF_5] \cdot H_2O$. A comparison of the vibrational spectra of these diverse types of species is very difficult. However, some characteristic features may be noted. The increase in the position of v_3 in $[CrF_6]^{3-}$ compared to $[FeF_6]^{3-}$ is in keeping with the trend generally found among the hexafluoro complexes. The higher value of the v_3 in $[TiF_6]^{2-}$ compared to that in $[CrF_6]^{3-}$ is again in agreeement with the expected trend. The relatively lower Ta-F band position in the spectra of $[TaF_7]^{2-}$ is attributed to an increased coordination number of the metal. The spectra of $[NiF_3]^-$ and $[CoF_3]^-$ are very similar. In these two complexes and also in $[MnF_3]^-$ the M—F vibration occurs

at a lower frequency which is probably due to a -F-M-F-M-F- type of interaction in the complexes.^{8,15,16} The spectrum of $K_2[MnF_5] \cdot H_2O_1$ which contains both bridging and terminal fluoride,¹⁷ gives a number of bands in the region 600 cm^{-1} . The mixed-valent 250 complexes $Fe_2F_5 \cdot 2H_2O$ and $Fe_2F_5 \cdot 7H_2O$ have been widely studied.^{10,11,18,19} While the former contains fluoride bridges, the latter is represented as $[Fe(H_2O)_6]$ $[FeF_5(H_2O)]$. In keeping with these structures their spectra also give a number of bands in the above region. The spectra of the two oxo complexes $[VOF_4]^{2-}$ and $[NbOF_5]^{2-}$ give the characteristic M=O bands in the region 970–1000 cm⁻¹, in addition to M-F bands.

In recent years there has been growing interest in the synthesis of coordination compounds starting directly from metals.²⁰⁻²² Many metals are readily available in more than 99.8% purity. As stated earlier, the metals may also be previously deposited on a platinum foil by electrolysis of their salt solutions. The method, therefore serves as a general one for the electrosynthesis of fluoro complexes from aqueous medium at room temperature.

REFERENCES

- 1. V. A. Konev, V. Yu. Kukushkin and Yu. N. Kukushkin, *Russ. J. Inorg. Chem.* 1986, **31**, 838.
- D. G. Tuck, M. J. Taylor and C. Oldham, *Inorg. Chim. Acta* 1985, 100, L9.
- 3. M. C. Chakravorti and G. V. B. Subrahmanyam, unpublished work.
- C. Oldham and D. G. Tuck, J. Chem. Edn. 1982, 59, 420.
- M. C. Chakravorti and D. Bandyopadhyay, *Polyhedron* 1988, 7, 1135.
- G. Charlot and D. Bezier, English translation by R. C. Murray, *Quantitative Inorganic Analysis*, p. 425. Methuen and Co., London (1957).
- 7. J. Lewis and R. G. Wilkins, *Modern Coordination* Chemistry, p. 403. Interscience, New York (1960).
- R. Colton and J. H. Canterford, *Halides of the First Row Transition Metals*, pp. 194, 237, 242, 245, 295, 370, 469. Wiley, New York (1969).
- R. S. Nyholm and A. G. Sharpe, J. Chem. Soc. 1952, 3579; 1957, 563.
- E. G. Walton, P. J. Corvan, D. B. Brown and P. Day, *Inorg. Chem.* 1976, 15, 1737.
- 11. E. G. Walton, D. B. Brown, H. Wong and W. M. Reiff, *Inorg. Chem.* 1977, 16, 2425.
- A. B. P. Lever, *Inorganic Electronic Spectroscopy*, pp. 419, 481, 508. Elsevier, Amsterdam (1984).
- D. F. Evans and P. A. W. Dean, J. Chem. Soc. A. 1967, 698.
- R. D. Peacock and D. W. A. Sharp, J. Chem. Soc. 1958, 2762.
- 15. M. N. Bhattacharjee, M. K. Chaudhuri, M. Devi

and Y. Khriesavilie, J. Chem. Soc., Dalton Trans. 1987, 1055.

- 16. I. Nawagawa, A. Tsuchida and T. Shimanouchi, J. Chem. Phys. 1967, 47, 982.
- 17. A. J. Edwards, J. Chem. Soc. A 1971, 2654.
- K. J. Gallagher and M. R. Ottaway, J. Chem. Soc., Dalton Trans. 1975, 978.
- 19. W. Hall, S. Kim, J. Zubieta, E. G. Walton and D. B. Brown, *Inorg. Chem.* 1977, 10, 1884.
- 20. P. L. Timmis, Adv. Inorg. Radiochem. 1972, 14, 121.
- 21. G. A. Ozin and A. Vander Volt, Prog. Inorg. Chem. 1975, 19, 105.
- 22. D. G. Tuck, Pure Appl. Chem. 1979, 51, 2005.