(Figure 6, region B) and data that are consistent with the sequence of electron-transfer steps shown in Scheme II.

Scheme II

$$(TPP)Co + 2CH_3CN \rightleftharpoons [(TPP)Co^{III}(CH_3CN)_2]^+ + e^-$$

$$[(TPP)Co^{III}(CH_3CN)_2]^+ \rightleftharpoons [(TPP)Co^{III}(CH_3CN)]^{2+} + CH_3CN + e^-$$

$$[(TPP)Co^{III}(CH_3CN)]^{2+} \rightleftharpoons [(TPP)Co^{III}]^{3+} + CH_3CN + e^-$$

The experimental slopes of $E_{1/2}$ vs log [CH_3CN] for reactions 1-3 are -120, 50, and 55 mV, and these values compare favorably with theoretical slopes of -118, 59, and 59 mV for the sequence of steps shown in Scheme II.

Formation constants of $\log \beta_2 = 6.6$ and $\log K_1 = 2.1$ were calculated for the binding of two CH_3CN ligands to [(TPP)Co]$^+$ and one CH_3CN ligand to [(TPP)Co^{III}]$^{2+}$. This latter reaction is given by eq 5 and is the first formation constant ever measured

$$[(TPP)Co^{III}]^{2+} + CH_3CN \overset{K_1}{\rightleftharpoons} [(TPP)Co^{III}(CH_3CN)]^{2+} \quad (5)$$

for axial ligand binding to the doubly oxidized [(TPP)Co^{III}]$^{2+}$. The log β_2 value of 6.6 for CH_3CN binding to [(TPP)Co]$^+$ compares to values of log β_2 between 5.7 and 15.6 for the binding of other neutral ligands to the singly oxidized complex.[33]

The oxidative chemistry of (TPP)Co in the presence of high and low concentrations of CH_3CN was also monitored by thin-layer UV-visible spectroscopy. In CH_2Cl_2 containing less than 10^{-2} M CH_3CN, the oxidized compound is characterized by a Soret band at 432 nm, a major visible band at 545 nm, and a shoulder at 582 nm. This spectrum is similar to the spectrum of [(TPP)Co(CO)]$^+$ under 1 atm of CO, which has a Soret band at 431 nm, a major visible band at 545 nm, and a shoulder at 582 nm (see Table II). The spectrum of the singly oxidized species under these solution conditions is attributed to five-coordinate [(TPP)Co^{III}(CH_3CN)]$^+$.

Different spectra are obtained for electrooxidized (TPP)Co in CH_2Cl_2 containing [CH_3CN] greater than 10^{-2} M. Under these conditions, the UV-visible bands are located at 435, 549, and 585 nm. This 3-4-nm red shift gives a spectral pattern similar to that of [(TPP)Co^{III}(L)$_2$]$^+$ where L = Me_2SO or py, and the spectrum in CH_2Cl_2/CH_3CN mixtures is assigned to the six-coordinate [(TPP)Co^{III}(CH_3CN)$_2$]$^+$.

Conclusion

The combination of cyclic voltammetry with thin-layer UV-visible spectral data of (TPP)Co in methylene chloride and benzene clearly indicates a binding of one CO molecule to the singly oxidized [(TPP)Co]$^+$. This is the first evidence of CO binding to an oxidized cobalt porphyrin under any solution conditions. This bound CO is lost upon further electrooxidation to generate the porphyrin π cation radical. A similar set of rections occur between CH_3CN and electrooxidized [(TPP)Co]$^+$ at low acetonitrile concentrations, and this contrasts with results at high CH_3CN concentrations where the formation of [(TPP)Co^{III}(CH_3CN)$_2$]$^+$ is observed.

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Registry No. [(TPP)Co], 14172-90-8; [(TPP)Co]$^{2+}$, 28132-69-6; [(TPP)Co]$^{3+}$, 60430-19-5; [(TPP)Co(CO)]$^+$, 122189-71-3; [(TPP)Co(CH_3CN)$_2$]$^+$, 122189-73-5; [(TPP)Co(CH_3CN)]$^+$, 122189-72-4; CO, 630-08-0; CH_3CN, 75-05-8; CH_2Cl_2, 75-09-2; benzene, 71-43-2.

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Fluoride-Assisted Stabilization of Manganese(III) in Aqueous Medium. A General Approach to the Synthesis of Mixed-Ligand Fluoro Complexes of Manganese(III)

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The importance of fluoride as a stabilizing ligand for manganese(III), both in aqueous solution as well as in solid complexes, has been emphasized, and a host of new mixed-ligand fluoro complexes have been synthesized from aqueous solutions. While $K_3[MnF_2(C_2O_4)_2]\cdot 3H_2O$ has been synthesized from a redox reaction of $KMnO_4$ with $H_2C_2O_4\cdot 2H_2O$ in the presence of KF at ca. 0 °C, the other mixed-ligand fluoromanganates(III), with EDTA, HPO_4^{2-}, and glycine (glyH) being the coligands, have been synthesized from the reactions of MnO(OH) in 48% HF with the corresponding ligands in water in the presence of alkali-metal fluoride (for EDTA and HPO_4^{2-}) and alkali-metal carbonate (for glyH). Three molecular complexes, $[MnF_3(H_2O)(phen)]\cdot 2H_2O$, $[MnF_3(H_2O)(bpy)]\cdot 2H_2O$, and $[MnF_3(urea)_2]\cdot 3H_2O$ have been prepared also from the reactions of MnO(OH) in 40% HF with the respective ligand solutions. All the compounds, except $K_3[MnF_2(C_2O_4)_2]\cdot 3H_2O$, are stable in the absence of moisture. Their characterization and structural assessment are based on the results of elemental analyzes, chemical determination of oxidation state, IR and electronic spectroscopic studies, magnetic susceptibility measurements, and in a few cases pyrolysis studies. Whereas the room-temperature magnetic moment of $[MnF_3(urea)_2]\cdot 3H_2O$ is 4.3 μ_B, those of the others lie in the range 4.78-5.0 μ_B. A magnetostructural correlationship has been explored by comparing the present empirical magnetic moments with those of the binary fluoromanganates(III). Pyrolysis of $[MnF_3(urea)_2]\cdot 3H_2O$ at ca. 500 °C affords MnF_3, a compound of acknowledged importance.

Introduction

Manganese can adopt a wide spectrum of oxidation states, and this ability is reflected in its redox functions in biological systems.[1] The tripositive state of the metal is important in this context and requires a special attention not only because it is difficult to stabilize in aqueous medium[2] and many of its complexes demonstrate unusual magnetic and structural features[3-7] but also because it has biochemical relevance in diverse redox functions, including water splitting by photosynthetic enzymes,[8] dispro-

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portionation of H_2O_2 in microorganisms,[9] and reduction of ribo- to deoxyribonucleotides in coryneform bacteria.[10] Solid manganese(III) compounds are still considered scarce since they are difficult to obtain. It is believed, however, that complex formation[11,12] leads to lowering of redox potential of the manganese(III)/manganese(II) couple and results in enhancement of stability of manganese(III). Accordingly, appropriate complexing agents for and suitable routes to the synthesis of stable manganese(III) complexes from aqueous solutions turn out to be the essential prerequisites for further studies.

There have been indications[2] in regard to the capability of F^-, SO_4^{2-}, $C_2O_4^{2-}$, PO_4^{3-}, $P_2O_7^{4-}$, and EDTA to stabilize manganese(III) in solution. Recent results of its chemistry[4,6,13-19a] led us to anticipate that a strong acidic ligand like F^- has a pronounced stabilizing effect on manganese(III) both in solution as well as in the solid. In addition, coordination of F^- also brings about antiferromagnetism in fluoromanganates(III).[3,4,7] Thus the chemistry of mixed-ligand fluoromanganates(III) would be interesting and significant since the concept of ligand additivity predicts[19b] their properties to be different from those of the corresponding binary complexes. In fact, a notable reduction of antiferromanganetism[13,17] in $[MnF_3(SO_4)]^{2-}$ and $[MnF_3(C_2O_4)]^{2-}$ in contrast to that of $[MnF_5]^{2-}$, and a remarkable hike in stability of $[MnF_3(C_2O_4)]^{2-}$ as opposed to that of $[Mn(C_2O_4)_3]^{3-}$ support the above prediction. As a case in point, therefore, it is necessary to obtain more knowledge in the field of manganese(III) chemistry.

The change in properties in going from $[Mn(C_2O_4)_3]^{3-}$ to $[MnF_3(C_2O_4)]^{2-}$ was demonstrated in an earlier paper;[17] however, the effect of substitution of one $C_2O_4^{2-}$ by two F^- ligands was not dealt with. Like $[Mn(C_2O_4)_3]^{3-}$, the EDTA–manganese(III) system has been reported to be unstable[20a] with respect to heat and light. It was expected that an introduction of F^- as a coligand might result in stable fluoro–EDTA complexes of manganese(III). Further, in view of an increasing interest[21] in metal–amino acid systems owing to their potentials as biomimetic models, it was considered worthwhile to synthesize hitherto unreported mixed-ligand fluoro–(glycine) complexes of manganese(III). Moreover, hydrogen orthophosphate complexes of manganese(III) are reported[22] to exist only in solution although $MnPO_4 \cdot H_2O$ is well characterized.[23] In line with our strategy it was anticipated that fluoride would be able to contribute significantly in stabilizing hydrogen orthophosphate–manganese(III) systems leading to an access to fluoro(hydrogen orthophosphato)manganates(III). Besides these, the only molecular mixed-ligand fluoromanganese(III) complex known[18] to our knowledge is $[MnF_3(H_2O)(phen)] \cdot 2H_2O$ although a few molecular mixed-ligand chloro complexes have been reported.[18,24] Our interest in molecular mixed-ligand fluoromanganese(III) complexes was not only to provide some novel examples but also to obtain prospective candidates for studies of oxidation reactions.

As a sequel to our continued endeavor to detail the chemistry of mixed-ligand fluorometalates,[4,13-17,25-27] we report herein the synthesis, characterization, and assessment of structure of a good number of mixed-ligand fluoromanganates(III) of the types $K_3[MnF_2(C_2O_4)_2] \cdot 3H_2O$, $K[MnF_4(EDTA)] \cdot 3H_2O$, $A[MnF_4(glyH)_2] \cdot 3H_2O$ (A = Na, K, NH_4), $A_3[MnF_2(HPO_4)_2] \cdot 3H_2O$ (A = Na, K, NH_4), and molecular mixed-ligand fluoro complexes of the types $[MnF_3(H_2O)(phen)] \cdot 2H_2O$, $[MnF_3(H_2O)(bpy)] \cdot 2H_2O$, and $[MnF_3(urea)_2] \cdot 3H_2O$ (phen = 1,10-phenanthroline and bpy = 2,2′-bipyridine). Also incorporated in this paper is a set of internally consistent data to highlight the effect of coligands on the magnetic and structural properties of fluoromanganates(III).

Experimental Section

The chemicals used were all reagent grade products. The compound MnO(OH) was prepared by the oxidation of $Mn(OH)_2$ with H_2O_2.[28] Infrared spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer. Electronic spectra were recorded on a Cary Model 2380 spectrophotometer. The reflectance spectra of solids were recorded against MgO by using a Carl-Zeis Jena VSU 2-P instrument. The Gouy method was used to measure the magnetic susceptibility of the complexes with $Hg[Co(NCS)_4]$ as the standard. The pH values were measured with a Systronic Type 335 digital pH meter and also with pH indicator (BDH) paper.

(i) Synthesis of Potassium Difluorobis(oxalato)manganate(III) Trihydrate, $K_3[MnF_2(C_2O_4)_2] \cdot 3H_2O$. To an aqueous solution (20 cm^3) of 1 g (6.33 mmol) of $KMnO_4$, kept in an ice bath in the dark, was added an aqueous solution of 3.2 g (25.38 mmol) of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$). The resulting solution was stirred in an ice bath for ca. 20 min followed by rapid filtration to remove any undissolved residue. To the cherry red filtrate was added 0.74 g (12.74 mmol) of solid KF, and the mixture was stirred for a further period of ca. 20 min. An equal volume of precooled (~0 °C) ethanol was added with continuous stirring. A very light pink microcrystalline product that precipitated out at this stage was filtered off. To the cherry red filtrate, again an excess of precooled ethanol (twice the volume of filtrate) was added to obtain the cherry red microcrystalline $K_3[MnF_2(C_2O_4)_2] \cdot 3H_2O$. The compound was then isolated by quick filtration, washed twice with precooled ethanol, and finally dried in vacuo over concentrated H_2SO_4 in the dark. The yield of $K_3[MnF_2(C_2O_4)_2] \cdot 3H_2O$ was 1.7 g (61%). IR: 1730 m and 1680 s (ν_{as}(C═O)), 1435 s (ν(C—O) + ν(C—C)), 1315 s (ν(C—O) + δ(O—C—O)), 780 m (δ(O—C—O)), 460 m (ring def + δ(O—C—O)), 490 m (ν(Mn—F)), 3460 m (ν(O—H)), 1640 s cm^{-1} (δ(H—O—H)).

(ii) Synthesis of Potassium Tetrafluoro(ethylenediaminetetraacetic acid)manganate(III) Trihyrate, $K[MnF_4(EDTA)] \cdot 3H_2O$. Freshly prepared MnO(OH) was dissolved in 48% HF (2.5 cm^3, 60.0 mmol of HF/0.89 g, 10.11 mmol of MnO(OH)) and stirred for ca. 10 min. The mixture was placed in an ice bath, and to it was added an aqueous solution of 2.96 g (10.11 mmol) of ethylenediaminetetraacetic acid (EDTA) slowly with continuous stirring (EDTA was dissolved in water containing 2–3 drops of 10% KOH solution). To the resulting deep pink solution was added 2.35 g (40.45 mmol) of solid KF (Mn:KF = 1:4), and the solution thus obtained was stirred for a further period of ca. 30 min in an ice bath. The pH of the solution at that stage was found to be ca. 2. The solution was filtered followed by the addition of an equal volume of diethylether to the filtrate with stirring. The organic layer became red-pink in color with the aqueous layer being practically colorless. To the above was added an equal volume of a mixture of ethanol and acetone (1/1, v/v) and the whole was kept in a freezer for *ca.* 3 h. A deep pink

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Table I. Analytical Data of Mixed-Ligand Fluoro Complexes of Manganese(III)

	% found (% calcd)						
compd (color)	A or N	Mn	F	C_2O_4 or PO_4	C	H	N
$K_3[MnF_2(C_2O_4)_2]\cdot 3H_2O$	26.75	12.51	8.82	39.65[a]	10.87	1.38	
(cherry red)	(26.64)	(12.48)	(8.63)	(39.98)[a]	(10.91)	(1.36)	
$K[MnF_4(EDTA)]\cdot 3H_2O$	7.73	10.77	14.81		23.29	4.23	5.46
(pink)	(7.57)	(10.64)	(14.72)		(23.26)	(4.26)	(5.42)
$(NH_4)[MnF_4(glyH)_2]\cdot 3H_2O$		15.73	21.41		13.67	5.68	11.78
(pink)		(15.56)	(21.52)		(13.61)	(5.66)	(11.89)
$Na[MnF_4(glyH)_2]\cdot 3H_2O$	6.53	15.21	21.54		13.61	4.53	7.84
(pink)	(6.42)	(15.34)	(21.22)		(13.42)	(4.47)	(7.82)
$K[MnF_4(glyH)_2]\cdot 3H_2O$	10.6	14.82	20.62		12.88	4.32	7.46
(pink)	(10.45)	(14.68)	(20.31)		(12.84)	(4.28)	(7.48)
$(NH_4)_3[MnF_2(HPO_4)_2]\cdot 3H_2O$	10.72	14.22	9.87	48.7[b]			
(pink-brown)	(10.69)	(13.98)	(9.67)	(48.35)[b]			
$Na_3[MnF_2(HPO_4)_2]\cdot 3H_2O$	17.21	13.68	9.44	46.8[b]			
(pink-brown)	(16.91)	(13.47)	(9.32)	(46.57)[b]			
$K_3[MnF_2(HPO_4)_2]\cdot 3H_2O$	25.56	12.22	8.58	41.5[b]			
(pink-brown)	(25.71)	(12.04)	(8.33)	(41.64)[b]			
$[MnF_3(H_2O)(phen)]\cdot 2H_2O$		15.77	16.81		41.54	(4.11)	8.12
(dull orange)		(15.87)	(16.47)		(41.63)	(4.04)	(8.09)
$[MnF_3(H_2O)(bpy)]\cdot 2H_2O$		17.51	17.62		37.32	4.37	8.82
(dull orange)		(17.06)	(17.69)		(37.28)	(4.35)	(8.69)
$[MnF_3(urea)_2]\cdot 3H_2O$		18.92	19.81		8.43	4.85	19.64
(chocolate)		(19.21)	(19.93)		(8.39)	(4.89)	(19.6)

[a] C_2O_4. [b] PO_4.

oily mass was formed, which was separated by decantation. This was treated three to four times with acetone and finally dried in vacuo to obtain the pink solid $K[MnF_4(EDTA)]\cdot 3H_2O$. Starting from 0.89 g of MnO(OH) yielded 1.35 g of $K[MnF_4(EDTA)]\cdot 3H_2O$ (25.8%). IR: 1738 and 1723 (ν_{as}(O–C–O)), 440 and 390 (ν(Mn–N)), 298 and 245 (δ(N–Mn–N)), 494 (ν(Mn–F)), 3450 (ν(O–H)), 1660 cm^{-1} (δ(H–O–H)).

(iii) Synthesis of Alkali-Metal and Ammonium Tetrafluorobis(glycine)manganate(III) Trihydrates, $A[MnF_4(glyH)_2]\cdot 3H_2O$ (A = Na, K, NH_4). An amount of 0.89 g (10.11 mmol) of freshly prepared MnO(OH) was dissolved in 2.0 cm^3 (40.0 mmol) of 40% HF. The molar ratio between MnO(OH) and HF was held at 1:4. The solution was stirred for ca. 10 min followed by the addition of 1.52 g (20.2 mmol) of glycine, keeping the MnO(OH):glycine ratio at 1:2, and the resulting solution was stirred for a period of ca. 15 min. To this was added a specific amount of A_2CO_3 (A = Na, K, NH_4) [MnO(OH):A_2CO_3 = 1:0.5] with stirring. The whole was then concentrated over a steam bath followed by a slow addition of acetone, whereupon pink microcrystalline $A[MnF_4(glyH)_2]\cdot 3H_2O$ (A = Na, K, NH_4) was precipitated out. The compound was isolated by centrifugation, washed three times with acetone, and then dried in vacuo over concentrated H_2SO_4. The yields of $Na[MnF_4(glyH)_2]\cdot 3H_2O$, $K[MnF_4(glyH)_2]\cdot 3H_2O$, and $(NH_4)[MnF_4(glyH)_2]\cdot 3H_2O$ were 3.2 g (87%), 3.5 g (92%), and 3 g (85%), respectively. IR of $(NH_4)[MnF_4(glyH)_2]\cdot 3H_2O$ (a typical example of the series): 1715 (ν_{as}(COOH)), 1596 ($\delta(NH_2)$), 1445 ($\delta(CH_2)$), 1411 (ν(C—O)), 1335 ($\rho_w(CH_2)$), 1256 ($\rho_t(NH_2)$), 1130 ($\rho_r(NH_2)$), 1027 ($\rho_w(NH_2)$), 913 ($\rho_r(CH_2)$), 888 and 871 (ν(CCN)), 740 (δ(C═O)), 606 (π(C═O)), 505 br (ν(Mn–N) + ν(Mn–F)), 355 (δ(N–Mn–N)), 3445 (ν(O—H)), 1640 cm^{-1} (δ(H—O—H)).

(iv) Synthesis of Alkali-Metal and Ammonium Difluorobis(hydrogen orthophosphato)manganate(III) Trihydrates, $A_3[MnF_2(HPO_4)_2]\cdot 3H_2O$ (A = Na, K, NH_4). To an aqueous suspension (25 cm^3) of 0.89 g (10.11 mmol) of MnO(OH) was added alkali-metal or ammonium fluoride, AF (A = Na, K, NH_4), with maintenance of the MnO(OH):AF ratio at 1:3, and the resulting mixture was stirred for ca. 5 min. To it was added 8 cm^3 (142.9 mmol) of orthophosphoric acid, H_3PO_4 (88–93%; weight/cm^3 at 20 °C = 1.75 g) slowly with continuous stirring to obtain a violet solution. Stirring was continued for a further period of ca. 10 min. To the violet solution, obtained as above, an equal volume (in each case equal to that of the violet solution) of ethanol–acetone (1/1, v/v) was added with constant stirring. This resulted in the precipitation of pink-brown microcrystalline $A_3[MnF_2(HPO_4)_2]\cdot 3H_2O$ (A = Na, K, NH_4). The compound was separated by filtration, purified by washing three to four times with acetone, and finally dried in vacuo over concentrated H_2SO_4. The yields of $Na_3[MnF_2(HPO_4)_2]\cdot 3H_2O$, $K_3[MnF_2(HPO_4)_2]\cdot 3H_2O$, and $(NH_4)_3[MnF_2(HPO_4)_2]\cdot 3H_2O$ were 2.2 (50%), 2.4 (52%), and 2.1 g (53%), respectively.

(v) Synthesis of Trifluoroaquo(1,10-phenanthroline)manganese(III) Dihydrate, $[MnF_3(H_2O)(phen)]\cdot 2H_2O$. An aqueous suspension (20 cm^3) of freshly prepared MnO(OH) (0.89 g, 10.11 mmole was dissolved in 3 cm^3 (72 mmol) of 48% HF. To the clear solution was slowly added an ethanolic solution of 1,10-phenanthroline (2.0 g, 10.11 mmol), maintaining a Mn:phen ratio of 1:1. The solution was stirred for ca. 20 min, whereupon a dull orange compound started appearing. Stirring was continued for a further period of ca. 10 min followed by the addition of about 10 cm^3 of ethanol. The compound was filtered, washed three to four times with ethanol, and then dried in vacuo over concentrated H_2SO_4. Yield of $[MnF_3(H_2O)(phen)]\cdot 2H_2O$ was 2.5 g (71.4%).

(vi) Synthesis of Trifluoroaquo(2,2′-bipyridine)manganese(III) Dihydrate, $[MnF_3(H_2O)(bpy)]\cdot 2H_2O$. Freshly prepared MnO(OH) (0.89 g, 10.11 mmol) was dissolved in 3 cm^3 (72 mmol) of 48% HF with stirring to obtain a clear solution. To the above solution was added a concentrated ethanolic solution of 1.58 g (10.11 mmol) of 2,2′-bipyridine and the whole was stirred for ca. 10 min to obtain a red-brown solution. This was then concentrated over a steam bath to nearly half of its original volume. Acetone was added slowly to the concentrated solution, which precipitated out dull orange $[MnF_3(H_2O)(bpy)]\cdot 2H_2O$. The compound was isolated by filtration, followed by washing with acetone (two to three times) and finally dried in vacuo over concentrated H_2SO_4. Yield of $[MnF_3(H_2O)(bpy)]\cdot 2H_2O$ was 2 g (61.4%).

(vii) Synthesis of Trifluorobis(urea)manganese(III) Trihydrate, $[MnF_3(urea)_2]\cdot 3H_2O$. An aqueous suspension of 0.89 g (10.11 mmol) of freshly prepared MnO(OH) was dissolved by a slow addition of 3 cm^3 (72 mmol) of 48% HF with continuous stirring. To the clear reaction solution was added 1.82 g (30.34 mmol) of solid urea slowly with maintenance of the Mn:urea ratio at 1:3. Stirring was continued for a further period of ca. 20 min. The resultant red-brown solution was concentrated over a steam bath, and to it acetone was slowly added until chocolate-colored microcrystalline $[MnF_3(urea)_2]\cdot 3H_2O$ precipitated out. The product was filtered, and purified by washing two to three times with acetone. The compound was dried in vacuo over concentrated H_2SO_4. Yield of $[MnF_3(urea)_2]\cdot 3H_2O$ was found to be 1.2 g (41.5%). IR: 1535 (ν(C═O)), 3424 ($\nu(NH_2)$), 1480 (ν_{as}(CN)), 1152 (NH_2 rocking), 1030 (ν_s(CN)), 610 (δ(NCO)), 532 (δ(NCN)), 453 (ν(Mn—F)), 3445 (ν(O—H)), 1645 cm^{-1} (δ(H—O—H)).

Elemental Analyses. Manganese was estimated volumetrically by complexometric titration with EDTA[29a] using Erio T as the indicator. The fluoride contents of the compounds were determined by Volhard's method.[29b] Sodium, potassium were determined by the method reported in our earlier paper.[26] Carbon, hydrogen, and nitrogen were estimated by microanalytical methods (The results of analyses were obtained from Amdel Australian Micro Analytical Service, Port Melbourne, Victoria 3207, Australia, and RSIC, NEHU, Shillong, India). The results of elemental analyses are given in Table I.

Chemical Determination of the Oxidation State of Manganese. The oxidation state of manganese was determined iodometrically by treating a freshly prepared ice-cold potassium iodide solution, acidified with dilute sulfuric acid, with the compound followed by titration of the liberated

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Table II. Magnetic Moment Values and Electronic Spectral Data for the Complexes

compd	magnetic moment at 300 K, μ_B	electronic spectral band positions, cm^{-1}		
		$^5B_{1g} \rightarrow {}^5A_{1g}$	$^5B_{1g} \rightarrow {}^5B_{2g}$	$^5B_{1g} \rightarrow {}^5E_g$
$K_3[MnF_2(C_2O_4)_2]\cdot 3H_2O$		11 950	19 800	22 220[a]
$K[MnF_4(EDTA)]\cdot 3H_2O$	4.92	11 800	19 800	22 220[a]
$A[MnF_4(glyH)_2]\cdot 3H_2O$	4.78–4.8	12 000	19 800	21 300[b]
$A_3[MnF_2(HPO_4)_2]\cdot 3H_2O$ (A = Na, K, NH_4)	4.8–4.9	11 000	18 200	20 800[b]
$[MnF_3(H_2O)(phen)]\cdot 2H_2O$	5.0	13 750	19 000	23 250[c]
$[MnF_3(H_2O)(bpy)]\cdot 2H_2O$	4.9	13 750	19 000	23 250[c]
$[MnF_3(urea)_2]\cdot 3H_2O$	4.3	10 810	17 240	20 620[d]

[a] Spectra recorded in aqueous solution. [b] Reflectance spectra. [c] Spectra recorded in DMSO solution. [d] Spectra recorded in methanol solution.

iodine against a standard sodium thiosulfate solution. The iodometry experiment was done in under ice-cold conditions.

Results and Discussion

The problem encountered in the synthesis of manganese(III) compounds from aqueous solutions is largely owing to an ease with which it disproportionates to manganese(IV) and manganese(II).[11,12] In cognizance of the recent experience, it was anticipated that this problem could be overcome by conducting reactions in the presence of F^- ions in an acidic medium. It was also expected that this strategy would lead to the synthesis of a host of mixed-ligand fluoro complexes of manganese(III). An important issue in this context is the selection of an appropriate source of the metal, and for this a knowledge of redox properties of the coligands is necessary. Thus, if a ligand is capable of reducing manganese(VII), $KMnO_4$ may be a good starting material, whereas for ligands having no such properties a manganese(III) species, e.g. MnO(OH), may be suitable.

Oxalic acid reduces $KMnO_4$ to manganese(II) on warming. It was quite rational to think that such a reaction at a low temperature (ca. 0 °C) in the presence of a limited amount of fluoride and an excess of oxalic acid might afford fluoro(oxalato)manganates(III). Accordingly, a reaction of $KMnO_4$ with potassium fluoride and oxalic acid in the ratio 1:2:4 at ca. 0 °C in the dark followed by the addition of ethanol led to the successful synthesis of potassium difluorobis(oxalato)manganate(III) trihydrate, $K_3[MnF_2(C_2O_4)_2]\cdot 3H_2O$:

$$KMnO_4 + 4H_2C_2O_4 + 2KF \rightarrow K_3[MnF_2(C_2O_4)_2] + 4CO_2 + 4H_2O$$

An excess of fluoride should be avoided in this reaction in order to supress the formation of $[MnF_3(C_2O_4)]^{2-}$ and $[MnF_5]^{2-}$. The role of ethanol was to bring about precipitation of the desired product. An alternative route involving a reaction among MnO(OH), F^-, and $C_2O_4^{2-}$ was not suitable since this gave rise to a known species[17] $K_2[MnF_3(C_2O_4)]$ instead of the compound looked for.

In order to overcome the problems encountered[20a] in stabilizing the manganese(III)–EDTA system, it was expected that fluoride might assist in bringing about the stability. A redox reaction between $KMnO_4$ and ethylenediaminetetraacetic acid (EDTA) in the presence of F^- was considered not to be a viable method. Thus a reaction of MnO(OH) in 40% HF with a solution of EDTA containing a very small amount of KOH and KF in the concentration ratio Mn:EDTA:KF = 1:1:4 was carried out, which provided pink microcrystalline $K[MnF_4(EDTA)]\cdot 3H_2O$. Similar reactions carried out at higher pH (≥ 7) were found to be inappropriate as the products obtained were impure. As in the previous case, here also a judicious amount of fluoride is to be used so that the formation of $[MnF_5]^{2-}$ is prevented.

For the synthesis of mixed-ligand fluoromanganates(III) containing glycine (glyH) as the coligand, freshly prepared MnO(OH) was allowed to react with 40% HF and glyH with the ratio Mn:F:glyH being maintained at 1:4:2. Alkali-metal or ammonium carbonate, in lieu of the corresponding fluoride, was used as the source of countercations. This also helped inhibit formation of $[MnF_5]^{2-}$. The compounds synthesized in this way were found to be pink $A[MnF_4(glyH)_2]\cdot 3H_2O$ (A = Na, K, NH_4). It is thus evident that fluoride assisted in stabilizing the manganese(III)–glycine system as anticipated.

Our concern for obtaining mixed-ligand fluoromanganates(III) with phosphate as the coligand led us to adopt a slightly different synthetic strategy than the ones enumerated above. Thus, a mixture of MnO(OH) and AF (A = Na, K, NH_4), made in the molar ratio of 1:3, was directly reacted with H_3PO_4. This afforded $A_3[MnF_2(HPO_4)_2]\cdot 3H_2O$, the kind of species sought. While the acidic environment was maintained by H_3PO_4 itself, the alkali-metal fluoride acted as the source of F^- ions, thereby rendering the use of aqueous HF redundant.

In the context of some of our earlier studies, it was suggested[30] that MnO(OH) reacted with 40% HF to produce MnF_3 in solution. Our present interest to develope a route to molecular mixed-ligand fluoromanganese(III) complexes led us to anticipate that a further reaction of MnF_3, generated in situ, with species capable of acting as neutral ligands, e.g. 1,10-phenanthrolene (phen), 2,2′-bipyridine (bpy), and urea, could be a reasonable strategy for synthesis of the desired type of compounds. Accordingly, a solution of MnO(OH) in 48% HF was reacted separately with phen, bpy, and urea to produce $[MnF_3(H_2O)(phen)]\cdot 2H_2O$, $[MnF_3(H_2O)(bpy)]\cdot 2H_2O$, and $[MnF_3(urea)_2]\cdot 3H_2O$, respectively, in high yields (vide Experimental Section). These results provide further support to the notion that MnF_3 is formed in situ from the reaction of MnO(OH) with aqueous HF. The method described is a direct one, and the strategy used herein can be regarded as a pradigm for the synthesis of similar molcular mixed-ligand fluoromanganese(III) compounds.

Characterization and Assessment of Structure. While $K_3[MnF_2(C_2O_4)_2]\cdot 3H_2O$ decomposes quite fast, all the other mixed-ligand fluoro compounds of manganese(III) are stable in the absence of moisture and can be stored for a prolonged period. Their stability can be ascertained by the estimation of manganese and recording of IR spectra periodically. However, the compounds slowly decompose in water. The molecular mixed-ligand fluoromanganese(III) complexes are partially soluble in polar organic solvents.

In view of the anomalous magnetic behavior of many manganese(III) complexes,[4,7] the chemical determination of the oxidation state of the metal is important. The chemically estimated oxidation state of the metal was found to lie in the range 2.9–3.1 in conformity with the presence of manganese(III) in each of the compounds. The instability of $K_3[MnF_2(C_2O_4)_2]\cdot 3H_2O$ precluded a satisfactory magnetic susceptibility measurement on it. While the room temperature (300 K) magnetic moment of $K[MnF_4(EDTA)]\cdot 3H_2O$ was 4.92 μ_B, those of $A_3[MnF_2(HPO_4)_2]\cdot 3H_2O$ and $A[MnF_4(glyH)_2]\cdot 3H_2O$ were found to lie in the range 4.7–4.9 μ_B (Table II). These values are quite normal as expected for a d^4 system. Similarly, the magnetic moments of $[MnF_3(H_2O)(phen)]\cdot 2H_2O$ and $[MnF_3(H_2O)(bpy)]\cdot 2H_2O$ were 5.0 and 4.9 μ_B, respectively. However, the corresponding value for $[MnF_3(urea)_2]\cdot 3H_2O$ was 4.3 μ_B. This suggests that the strong antiferromagnetism encountered[4,7] in the binary $[MnF_5]^{2-}$ complex is largely controlled in $[MnF_3(urea)_2]\cdot 3H_2O$ and is practically absent in the other compounds reported herein. A perusal of our earlier[4,13-17] as well as the present results cause us to state that

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the complex $[MnF_3(urea)_2]$ species may have a polymeric structure through –Mn–F–Mn–F– interactions, while each of the other mixed-ligand fluoro complexes of manganese(III) described in this paper very likely has a monomeric distorted-octahedral structure.

The electronic spectrum of freshly prepared $K_2[MnF_2(C_2O_4)_2]\cdot 3H_2O$, recorded immediately after making a solution containing a very small amount of HF, exhibits bands at 11 950, 19 800, and 22 220 cm^{-1} assigned to $^5B_{1g} \rightarrow {}^5A_{1g}$, $^5B_{1g} \rightarrow {}^5B_{2g}$, and $^5B_{1g} \rightarrow {}^5E_g$ transitions, respectively. The spectral pattern suggests an appreciable splitting of the ^5E_g ground state of manganese(III) leading to a distorted octahedral[31,32] structure of the complex species. The electronic spectra of all the other compounds show absorptions with their positions, patterns, and intensities being similar to those reported above. This therefore adduces support to the notion that each of the complexes has a distorted-octahedral structure with an appreciable splitting of the ^5E_g ground state of the metal.

The IR spectrum of $K_3[MnF_2(C_2O_4)_2]\cdot 3H_2O$ displays a pattern typical of coordinated $C_2O_4^{2-}$ and F^- ligands. For a chelated $C_2O_4^{2-}$, all the C–O vibrations become IR active with the asymmetric (O–C–O) moes shifting to higher frequencies while the symmetric ones are shifted to lower frequencies.[33] The oxalato modes in the present case occur in the region 1680–1750 cm^{-1} and at 1435 cm^{-1}, causing us to state that the $C_2O_4^{2-}$ is bonded to the metal center in a chelated[34] fashion. This situation is different from that of $K_2[MnF_3(C_2O_4)]$[17] in which the $C_2O_4^-$ occurs as a bridging ligand. The band at 490 cm^{-1} has been attributed to ν(Mn–F). The absence of any splitting of this band and appearance of no more bands close to 490 cm^{-1} suggest[25,35] that the two F^- ligands occupy positions trans to one another with the complex $[MnF_2(C_2O_4)_2]^{3-}$ ion most probably having a D_{4h} symmetry. The two additional bands at 3460 and 1640 cm^{-1} owe their origins, respectively, to ν(O–H) and δ(H–O–H) modes of uncoordinated water. One of the notable features of the IR spectrum of $K[MnF_4(EDTA)]\cdot 3H_2O$ is the absence of any band between 1590 and 1650 cm^{-1}. It is therefore apparent that EDTA is present as an un-ionized ligand and its O atoms are not involved[36] in coordination. The appearance of ν_{as}(O–C–O) modes at 1738 and 1723 cm^{-1} arising from the presence of –COOH groups[20] provides further support to the view. Important in this context are the frequencies at 444 and 390 cm^{-1} assigned to ν(Mn–N), and at 298 and 245 cm^{-1} attributed to δ(N–Mn–N) modes that advance strong evidence for the presence of an N-bonded[20,36] EDTA in the complex under discussion. The spectrum also furnishes evidence for coordinated fluoride[35] and lattice water.[4]

The mode of coordination of glycine (glyH) can be ascertained from a perusal of IR spectra of such complexes. Thus, the COO stretching band appears[37] at ca. 1710 cm^{-1} when the ligand coordinates with a metal center in an un-ionized form, while it falls at ca. 1610 cm^{-1} in the event of glycine's being present in an ionized form. However, when this ligand acts as a chelating ligand, the corresponding absorption[38] occurs at 1640 cm^{-1}. The IR spectra of $A[MnF_4(glyH)_2]\cdot 3H_2O$ (A = Na, K, NH_4) show the aforesaid band at ca. 1715 cm^{-1}, suggesting thereby that the glyH here is un-ionized and coordinated with the metal center through its nitrogen lone-pair electrons. Consequent upon this the corresponding ν(Mn–N) and δ(N–Mn–N) modes have been observed at ca. 505 and ca. 355 cm^{-1}, respectively. This mode of coordination of glycine is not very common, though not unprecedented.[37] The ν(Mn–F) mode could not be identified clearly; however, an increase in intensity and broadening of the band at ca. 505 cm^{-1} suggests an overlap of the ν(Mn–F) with the ν(Mn–N) in the present case. The IR spectra of phosphato–metal complexes are complex[39] because of broadening of peaks and poor resolution. The situation becomes further complicated if the phosphate occurs as a hydrogen phosphate and the compound contains lattice water. The presence of lattice water and hydrogen bonding effect the internal modes of vibrations of phosphate, and ν(O–H) shifts to a lower frequency.[39] The spectra of $A_3[MnF_2(HPO_4)_2]\cdot 3H_2O$ (A = Na, K, NH_4) display strong but broad absorptions in the region 1050–1250 cm^{-1} and broad weak absorptions at 2750–2925 cm^{-1} that are typical of coordinated hydrogen orthophosphate.[39,40] This view is further augmented by the observance of a band at ca. 350 cm^{-1} assigned to the Mn–O stretching mode originating from the O-bonded HPO_4^{2-}. while ν(Mn–F) has been observed at ca. 510 cm^{-1}, the ν(O–H) band of the uncoordinated water has been found to be rather weak and broad owing to the formation of hydrogen bonding as anticipated.

The significant features of IR spectra of $[MnF_3(H_2O)(phen)]\cdot 2H_2O$ and $[MnF_3(H_2O)(bpy)]\cdot 2H_2O$ are the bands due to the coordinated phen and bpy ligands with the corresponding Mn–N stretching modes being at 296 m and 245 s cm^{-1} and 282 s and 233 m cm^{-1}, respectively.[24,41,42] The ν(Mn–F) band for coordinated fluoro ligands[4,43] has been obsrved at ca. 480 cm^{-1}. Another important feature of the spectra of these compounds is the band at ca. 725 cm^{-1}, which has been attributed to the rocking mode of coordinated water. This is particularly important in the present cases as the compounds contain both coordinated as well as lattice water. The characteristic features of the IR spectrum of $[MnF_3(urea)_2]\cdot 3H_2O$ are the absorptions due to coordinated urea and fluoride and lattice water. The important bands of coordinated urea have been observed at 3425 and 1535 cm^{-1}, assignable to $\nu(NH_2)$ and ν(CO) modes, respectively. The unaltered position of $\nu(NH_2)$ and a significant lowering of ν(C=O) band compared to those of free urea[45,46] suggest that the ligand is coordinated with the metal center in an unidentate manner through its oxygen atom. Also important in this context is to note a lowering in position and broadening of the ν(Mn–F) mode, causing us to state that the fluoro ligand is involved also in the formation of bridges among the contiguous Mn centers in the crystal lattice. The bands at 3440 and 1645 cm^{-1} resemble in their shapes and positions those of lattice water encountered in fluoromanganates(III).[4,47]

The results of pyrolytic studies of $K_3[MnF_2(HPO_4)_2]\cdot 3H_2O$ show that the compound loses one molecule of water at 120 °C followed by the loss of two molecules of H_2O at 190–200 °C. The relatively higher temperature required in the latter case points to the involvent of water molecules in hydrogen bonding. The dehydrated material on being heated at 300 °C suffered a loss of two molecules of HF per molecule of the product. The origin of HF in this process lies in the extraction of H^+ from coordinated HPO_4^{2-} by a fluoro ligand. These results further support the formulation of the compounds. Thermogravimetric analysis (TGA) on $[MnF_3(urea)_2]\cdot 3H_2O$ was conducted in the temperature range 40–800 °C. It is evident from the thermogram that the compound starts losing weight at ca. 140 °C, and this continues until 210 °C, giving a horizontal at 210–240 °C. The loss of weight at this stage (19.2%) is commensurate with that of three molecules of water (calculated 18.9%) per formula weight. The intermediate thus formed undergoes sequential weight loses giving

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horizontals at 330–360 °C and 470 °C onward. The corresponding loss of weights have been found to be 40.1% and 62.1%, respectively, due to the expulsion of one urea at each step (calculated 39.9% and 60.8%, respectively). The ultimate product has been found to be MnF_3. No further loss of weight between 470 and 800 °C suggests that MnF_3 once formed in this process does not undergo any change in the range of temperature involved in the present TGA experiment. The information hitherto obtained may be useful for the solid-state synthesis of the intermediates $[MnF_3(urea)_2]$ and $[MnF_3(urea)]$. Further, pyrolysis of $[MnF_3(urea)_2]\cdot 3H_2O$ at ca. 500 °C, under nitrogen, leading to MnF_3 appears to be an useful way of accessing this compound. It may be relevant to add that this route to MnF_3 is simpler than the literature method,[48] and the compound is important as a powerful fluorinating agent.[49]

Concluding Remarks

Fluoride-assisted stabilization of manganese(III) has been demonstrated by synthesizing a large number of mixed-ligand fluoro compounds of the metal from aqueous solutions. The coligands have been drawn from $C_2O_4^{2-}$, EDTA, HPO_4^{2-}, glycine, 2,2′-bipyridine, 1,10-phenanthroline, and urea, and the importance of the chemical determination of the oxidation state of the metal in such compounds has been emphasized. Each of the newly synthesized complexes has a distorted octahedral structure. An internal comparison of magnetic moments of $[MnF_5]^{2-}$,[4] $[MnF_3(SO_4)]^{2-}$,[13] $[MnF_3(C_2O_4)]^{2-}$,[17] and $[MnF_3(urea)_2]\cdot 3H_2O$ and the other compounds reported herein led to a qualitative magnetostructural correlation. Thus, for a fluoro- or mixed-ligand fluoromanganese(III) species, the magnetic moment appears to be normal when there is no intermolecular fluoro bridge; however, if there is any –Mn–F–Mn–F– interaction in the crystal lattice there exists a finite possibility of antiferromagnetism. Pyrolysis of $[MnF_3(urea)_2]\cdot 3H_2O$ at ca. 500 °C affords MnF_3, a compound of acknowledged importance as a potential fluorinating agent. This route to MnF_3 is simpler than the literature method.[48] The molecular mixed-ligand fluoromanganese(III) complexes are expected to show interesting oxidation reactions.

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Potentiometric and Spectrophotometric Study of the Proton, Cobalt(II), Nickel(II), and Copper(II) Complexes of 2-Amino-*N*,3-dihydroxybutanamide and 2-Amino-*N*-hydroxy-3-phenylpropanamide in Aqueous Solution[†]

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The equilibria and relevant stability constants of species present in aqueous solutions of cobalt(II), nickel(II), and copper(II) with DL-threonyl hydroxamic acid (2-amino-*N*,3-dihydroxybutanamide, adhb) and DL-phenylalanyl hydroxamic acid (2-amino-*N*-hydroxy-3-phenylpropanamide, ahpp) were determined by using both a potentiometric method and a spectrophotometric method in 0.5 mol dm^{-3} KCl solution at 25 °C. The protonation constants of the ligands and the formation constants of several metal complexes were calculated from potentiometric and spectrophotometric data with the aid of the SUPERQUAD and SQUAD programs, respectively. The following cumulative association constants $\beta_{pqr} = [M_pH_qL_r]/[M]^p[H]^q[L]^r$ were obtained: adhb, $\log \beta_{011} = 12.746$ (1), $\log \beta_{021} = 21.614$ (1), $\log \beta_{031} = 28.387$ (3); Co^{II}–adhb, $\log \beta_{101} = 5.787$ (16), $\log \beta_{102} = 10.299$ (16), $\log \beta_{1-12} = 1.429$ (36), $\log \beta_{201} = 8.807$ (36); Ni^{II}–adhb, $\log \beta_{101} = 6.476$ (7), $\log \beta_{102} = 13.300$ (4), $\log \beta_{1-12} = 5.115$ (13); Cu^{II}–adhb, $\log \beta_{102} = 19.507$ (10), $\log \beta_{2-12} = 20.377$ (10), $\log \beta_{1-12} = 9.918$ (28); ahpp, $\log \beta_{011} = 9.013$ (5), $\log \beta_{021} = 15.899$ (7); Cu^{II}–ahpp, $\log \beta_{102} = 19.783$, $\log \beta_{2-12} = 20.750$ (39). The ligands are bound to the metal ions through the N atom of the α-amino group and the deprotonated $-NHO^-$ group in a bidentate manner. The UV–visible studies provide important evidence for the formation of different metal(II) complexes with 2-amino-*N*,3-dihydroxybutanamide, depending on the pH. The experimental curves [$\epsilon = f(\lambda)$], deduced from refinement of absorbance data with the program SQUAD, have been resolved into precisely positioned absorption bands by Gaussian analysis using a nonlinear least-squares computer program NLIN. The resulting data for metal(II)–adhb systems have been used in weak tetragonal (CuL_2) or a square-planar (NiL_2) ligand-field models to calculate as far as possible ligand-field parameters. The solution electronic spectra can be also employed to observe the equilibria between different complexes and to estimate the coordination sphere around the metal ions. Equilibrium constants for their formation and the probable structures of the chelated compounds formed in aqueous solution are the object of discussions in terms of their possible significance to biological reactions, and their stability is compared with that of analogous chelated compounds.

Introduction

There has been a great deal of interest in recent years regarding the chemistry of hydroxamic acid derivatives due to their biological importance and analytical and industrial applications. For example, along with amino acids, hydroxamic acid derivatives have been widely investigated as inhibitors of proteolytic enzymes. Some of these compounds have showed themselves to be potent inhibitors of thermolysin,[1,2] elastase,[3] and aminopeptidases[4,5] as well as growth factors, tumor inhibitors, constituents of antibiotics, and cell division and pigments factors.[6-8] These enzymes are

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[†] Abbreviations: aha = 2-amino-*N*-hydroxyacetamide, ahp = 2-amino-*N*-hydroxypentanamide, hasn = *N*-hydroxy-D-asparagine, ahhe = 2-amino-*N*-hydroxyhexanamide, ahpr = 2-amino-*N*-hydroxypropanamide, ahip = α-amino-*N*-hydroxy-1*H*-imidazole-4-propanamide, ahhpp = 2-amino-*N*-hydroxy-3-(*p*-hydroxyphenyl)propanamide, ahinp = α-amino-*N*-hydroxy-1*H*-indole-3-propanamide, ahpp = 2-amino-*N*-hydroxy-3-phenylpropanamide, adhp = 2-amino-*N*,3-dihydroxypropanamide.

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