

Direct Synthesis of Alkali Trifluorocobaltate(II) Monohydrates, $A[\text{CoF}_3] \cdot \text{H}_2\text{O}$ ($A = \text{NH}_4, \text{Na}, \text{or K}$). First Synthesis and Structural Assessment of Mixed-ligand Fluoro Complexes of Cobalt(II), $[\text{Co}(\text{NH}_3)_4\text{F}_2]$ and $A[\text{CoF}(\text{SO}_4)(\text{H}_2\text{O})_2]$ ($A = \text{NH}_4, \text{Na}, \text{or K}$)

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Alkali trifluorocobaltate(II) monohydrates, $A[\text{CoF}_3] \cdot \text{H}_2\text{O}$ ($A = \text{NH}_4, \text{Na}, \text{or K}$), have been synthesised directly from the reaction of $\text{Co}(\text{OH})_2$ and alkali fluorides in 40% HF followed by precipitation with ethanol at $\text{pH} < 3$. While a higher pH (5–6), maintained by the addition of AOH, contaminates the product for $A = \text{Na}$ or K , a molecular complex $[\text{Co}(\text{NH}_3)_4\text{F}_2]$ is formed in the case where aqueous ammonia is used to raise the pH . The synthesis of mixed fluorocobaltates(II) of the type $A[\text{CoF}(\text{SO}_4)(\text{H}_2\text{O})_2]$ ($A = \text{NH}_4, \text{Na}, \text{or K}$) has been achieved by reacting $\text{Co}(\text{OH})_2$ with AF and A_2SO_4 , in the ratio 1:2:1, in the presence of a very small amount of 40% HF at a steam-bath temperature. The compounds were isolated by the addition of ethanol. The compounds have been characterised from the results of elemental analyses, pyrolysis at 120°C , magnetic susceptibility measurements, i.r., laser Raman, and electronic spectroscopic studies. While the magnetic moments and electronic spectra of $[\text{Co}(\text{NH}_3)_4\text{F}_2]$ and $[\text{CoF}(\text{SO}_4)(\text{H}_2\text{O})_2]^-$ suggest an octahedral or a distorted-octahedral environment for cobalt(II), i.r. and laser Raman spectra provide evidence for the occurrence of a bridging bidentate sulphate ligand in the latter.

Interest in the fluoro complexes of Co^{II} with perovskite or related structures^{1–3} owes its origin mainly to their unusual magnetic behaviour.^{4,5} The properties of such compounds depend upon their genesis, and contamination affects their magnetic properties rather seriously.⁶ A limited accessibility to fluorometalates, however, is an impediment; for instance, $\text{K}[\text{CoF}_3] \cdot \text{H}_2\text{O}$ has been known for some time⁷ but the existence of the corresponding NH_4^+ or Na^+ salts has not been reported. Similarly, information concerning mixed-ligand fluorocobaltates(II) is very scanty. Such mixed-ligand complexes of transition metals enable a comparison of their properties with those of the corresponding binary fluoro complexes in addition to exhibiting some other interesting properties as reported recently.^{8–10}

As a continuation of our endeavour in this field,^{8,9,11–13} we have extended our studies to cobalt chemistry. This paper reports a general synthesis of $A[\text{CoF}_3] \cdot \text{H}_2\text{O}$ ($A = \text{NH}_4, \text{Na}, \text{or K}$), synthesis and structural assessment of the hitherto unknown mixed-ligand fluorocobaltates(II) $[\text{Co}(\text{NH}_3)_4\text{F}_2]$ and $A[\text{CoF}(\text{SO}_4)(\text{H}_2\text{O})_2]$ ($A = \text{NH}_4, \text{Na}, \text{or K}$), and highlights the changes in magnetic properties on going from $A[\text{CoF}_3] \cdot \text{H}_2\text{O}$ to the mixed-ligand fluorocobaltates(II).

Experimental

The chemicals used were of reagent-grade quality. I.r. spectra were recorded on a Perkin-Elmer 983 spectrophotometer. The laser Raman spectra were recorded on a SPEX Ramalog model 1403 spectrometer. The 5145-Å laser line from a Spectra-Physics model 165 argon laser was used as the excitation source. The scattered light at 90° was detected with the help of a cooled RCA 31034 photomultiplier tube and a photon-count processing system. The spectra were recorded at ambient temperature by making pressed pellets of the compounds. Magnetic susceptibility measurements were made by the Guoy method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant. Electronic spectra ($11\,750\text{--}50\,000\text{ cm}^{-1}$) were recorded on a Cary model

2300 spectrophotometer. The pH of the reaction solutions was measured with a Systronics type 335 digital pH meter and also with pH indicator (BDH) paper.

Synthesis of Alkali Trifluorocobaltate(II) Monohydrates, $A[\text{CoF}_3] \cdot \text{H}_2\text{O}$ ($A = \text{NH}_4, \text{Na}$ or K).—Cobalt(II) hydroxide was prepared from an aqueous solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ by precipitation with a 10% solution of NaOH . The precipitate was centrifuged and washed free from alkali and chloride.

To an aqueous suspension of freshly prepared cobalt(II) hydroxide, as obtained above, a concentrated solution of the respective alkali fluoride was added, maintaining the molar ratio of $\text{Co}:\text{AF}$ at 1:3. A small volume of 40% HF ($2.0\text{ cm}^3\text{ g}^{-1}$ of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) was added with stirring. The pink solution, thus obtained, was filtered to remove any traces of undissolved material, and an additional amount of 40% HF (1 cm^3) was added to the filtrate. The pH of the solution was found to lie below 3. The solution was stirred magnetically for *ca.* 10 min. Ice-cold ethanol was added with stirring until precipitation began and the whole was then kept in a freezer for *ca.* 30 min, whereupon pink microcrystalline $A[\text{CoF}_3] \cdot \text{H}_2\text{O}$ was obtained. The product was separated by centrifugation, washed twice with ethanol, and finally dried *in vacuo* over P_4O_{10} .

The yields of $\text{NH}_4[\text{CoF}_3] \cdot \text{H}_2\text{O}$ and $\text{K}[\text{CoF}_3] \cdot \text{H}_2\text{O}$ were 0.7 g (84%) and 0.8 g (84%), respectively, obtained in each case from 1.3 g (5.44 mmol) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, while that of $\text{Na}[\text{CoF}_3] \cdot \text{H}_2\text{O}$ was 0.5 g (76%) obtained from 1.0 g (4.2 mmol) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$.

Synthesis of Tetra-amminedifluorocobalt(II), $[\text{Co}(\text{NH}_3)_4\text{F}_2]$.—Freshly prepared cobalt(II) hydroxide [obtained from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2 g, 8.4 mmol)] was mixed with a concentrated solution of ammonium fluoride (0.95 g, 25.6 mmol) ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}:\text{NH}_4\text{F}$ molar ratio 1:3), and then dissolved in 40% HF (2.5 cm^3). The solution was filtered. The pH of the solution was slowly raised to 5.5–6.0 by dropwise addition of aqueous ammonia with constant stirring and while maintaining the temperature of the solution at *ca.* 0°C . An equal volume of ice-cold ethanol was then added with stirring to obtain pink microcrystalline $[\text{Co}(\text{NH}_3)_4\text{F}_2]$. The reaction container was

allowed to cool in an ice-bath for *ca.* 10 min. The compound was isolated by centrifugation, washed with ethanol, and dried *in vacuo* over P_4O_{10} . Yield: 1.2 g (87%).

Synthesis of Alkali Diaqua(fluoro)sulphatocobaltates(II), $A[CoF(SO_4)(H_2O)_2]$ ($A = NH_4, Na$ or K).—An aqueous suspension of freshly prepared cobalt(II) hydroxide was mixed with concentrated solutions of alkali fluoride and the corresponding alkali sulphate in a $Co:AF:A_2SO_4$ molar ratio of 1:2:1. The mixture was warmed on a steam-bath and 40% HF added dropwise to bring about complete dissolution ($1.0\text{ cm}^3\text{ g}^{-1}$ of $CoCl_2 \cdot 6H_2O$). An excess of HF should not be added, unlike in the synthesis of $A[CoF_3] \cdot H_2O$. The pink solution thus obtained was cooled to room temperature and filtered. The filtrate was stirred magnetically for *ca.* 10 min, followed by addition of ice-cold ethanol until precipitation occurred. The solution was then kept in a freezer for *ca.* 30 min for complete precipitation of pink microcrystalline $A[CoF(SO_4)(H_2O)_2]$ ($A = NH_4, Na$, or K). The compounds were isolated by centrifugation, washed with ethanol, and dried *in vacuo* over P_4O_{10} .

Starting from 1.3 g $CoCl_2 \cdot 6H_2O$ in each case the yields of $NH_4[CoF(SO_4)(H_2O)_2]$ and $K[CoF(SO_4)(H_2O)_2]$ were 1 g (80%) and 1.1 g (81%), respectively, while the yield of $Na[CoF(SO_4)(H_2O)_2]$ was 0.7 g (71%) from 1.0 g of $CoCl_2 \cdot 6H_2O$.

Elemental Analysis.—Cobalt was estimated gravimetrically^{14a} and checked by the following method. A known amount of the sample was decomposed by treatment with a 10% solution of NaOH, and then cobalt(II) was oxidised to hydrated cobalt(III) oxide by H_2O_2 . Excess of peroxide was completely removed by boiling, and cobalt was finally estimated iodometrically. The fluoride contents of $A[CoF_3] \cdot H_2O$ and $[Co(NH_3)_4F_2]$ were determined gravimetrically^{14b} as lead chloride fluoride. However, for the mixed fluoro(sulphato) complexes, fluoride was first precipitated as $PbClF$, and chloride was estimated by Volhard's method, from which the fluoride content was calculated.^{14b} Sulphate was estimated gravimetrically^{14c} as $BaSO_4$. Sodium, potassium, and nitrogen were determined by the methods described earlier.¹⁵

Analytical data and room temperature magnetic moments are summarised in the Table.

Results and Discussion

Synthesis.—Cobalt(II) hydroxide is highly soluble in acids and can easily be recovered by the addition of alkali (at $pH > 7$) indicating thereby that an acidic pH should be conducive to the synthesis of cobalt compounds. Fluoride is a potential stabilising ligand for many bivalent transition-metal ions, including cobalt(II). Accordingly reaction of cobalt(II) hydroxide with an alkali fluoride in the presence of 40% HF at pH 1–3, followed by the addition of ethanol led to the synthesis of $A[CoF_3] \cdot H_2O$. The role of ethanol was to bring about precipitation of the desired products. While a pH less than 1 is not required for the synthesis, a pH of 5–6 has been found to be detrimental to the successful synthesis of $A[CoF_3] \cdot H_2O$ with $A = Na$ or K . The products obtained under such conditions were found to be impure with no well defined composition. Interestingly, in the case of the synthesis of $NH_4[CoF_3] \cdot H_2O$, an increase in pH to *ca.* 6, with the addition of aqueous ammonia, produced a new species $[Co(NH_3)_4F_2]$ (see Experimental section), containing co-ordinated ammine and fluoride ligands. It is noteworthy that $K_2[CoF_4]$ and $K[CoF_3]$ were synthesised^{16,17} from the reaction of stoichiometric amounts of CoF_2 and KF , by fusion and crystallisation from an aqueous solution, respectively.

Table. Analytical data and magnetic moments

Compound	$\mu_{\text{eff.}}$ (300 K)	Analysis* (%)			
		A/N	Co	F	SO_4
$NH_4[CoF_3] \cdot H_2O$	4.2	9.25 (9.20)	38.15 (38.75)	36.80 (37.50)	
$Na[CoF_3] \cdot H_2O$	4.17	14.40 (14.65)	37.85 (37.55)	36.80 (36.30)	
$K[CoF_3] \cdot H_2O$	4.21	22.20 (22.60)	33.90 (34.05)	33.10 (32.95)	
$[Co(NH_3)_4F_2]$	5.05	33.80 (33.95)	36.10 (35.70)	23.20 (23.00)	
$NH_4[CoF(SO_4)(H_2O)_2]$	5.2	6.20 (6.15)	26.20 (25.85)	8.50 (8.35)	42.25 (42.10)
$Na[CoF(SO_4)(H_2O)_2]$	5.2	9.60 (9.85)	25.70 (25.30)	8.40 (8.15)	41.35 (41.20)
$K[CoF(SO_4)(H_2O)_2]$	5.1	15.55 (15.70)	23.90 (23.65)	7.80 (7.65)	38.35 (38.55)

* Calculated values are given in parentheses.

In order to gain access to mixed-ligand fluoro complexes of cobalt(II) containing sulphato groups, the reaction of cobalt(II) hydroxide, dissolved in a minimum volume of 40% HF, with an alkali fluoride and an alkali sulphate in the $Co:AF:A_2SO_4$ ratio of 1:2:1 was carried out which ultimately led to the synthesis of the hitherto unknown complexes of the type $A[CoF(SO_4)(H_2O)_2]$ ($A = NH_4, Na$, or K). Here again, ethanol was used to enable isolation of the compounds in the solid state. Thus under the experimental conditions employed sulphate can compete with fluoride to co-ordinate to the metal centre. It is pertinent to mention here that, although mixed fluoro(sulphato)cobaltate(II) complexes could be synthesised rather easily, our attempts to synthesise similar fluoro(oxalato)cobaltates(II) have not been successful so far. The product was found to be a binary oxalato-cobaltate(II) species containing a chelating oxalate. Thus it is evident that fluoro and mixed fluoro compounds of cobalt(II) of the types $A[CoF_3] \cdot H_2O$, $[Co(NH_3)_4F_2]$, and $A[CoF(SO_4)(H_2O)_2]$ ($A = NH_4, Na$, or K) can be synthesised under suitable experimental conditions.

Characterisation and Assessment of Structure.—The complexes $A[CoF_3] \cdot H_2O$, $[Co(NH_3)_4F_2]$, and $A[CoF(SO_4)(H_2O)_2]$ are all pink microcrystalline products, insoluble in common organic solvents. They slowly decompose in water. The compounds are stable and can be stored in sealed Polythene sample containers; however, they attack glass in the presence of moisture. Their stability can be ascertained by estimation of cobalt contents and recording of i.r. spectra periodically. Chemical determination of the oxidation state of cobalt, by iodometry, showed that the metal occurs in its +2 state in each of the newly synthesised compounds.

While the room temperature (300 K) magnetic moments of $A[CoF_3] \cdot H_2O$ have been found to be *ca.* 4.2, in conformity with that reported by Martin and Nyholm⁷ for $K[CoF_3] \cdot H_2O$, they were found to lie at *ca.* 5.1 for the mixed fluoro complexes $[Co(NH_3)_4F_2]$ and $A[CoF(SO_4)(H_2O)_2]$. These results provide an opportunity for an internal comparison of the observed magnetic moments and suggest that the strong antiferromagnetic exchange interaction operative in the binary fluoro complexes of cobalt(II) is either absent or has been largely controlled in the newly synthesised mixed-ligand fluoro complexes. Similar results have been encountered recently with other metals.^{8,9,13} The normal magnetic moments observed for the mixed fluorocobaltates(II) suggest the presence of high-spin d^7 cobalt(II) species with the complexes having octahedral or

distorted-octahedral structures.^{17,18} The electronic spectra of the compounds, recorded immediately after preparing their aqueous solutions, in the region 11 750–50 000 cm⁻¹, showed bands at 16 000 and 20 000 cm⁻¹ attributed to the transitions ${}^4T_{1g} \rightarrow {}^4A_{2g}$ and ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$, respectively. The positions and intensities of the bands are rather characteristic for a high-spin d^7 cobalt(II) in an octahedral field. This adduces further support to the octahedral or distorted-octahedral environment in each of the compounds. Moreover, the band due to the transition ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ has a shoulder which is typically observed in many cases of octahedral cobalt(II) complexes.¹⁷

The i.r. spectra of $A[\text{CoF}_3] \cdot \text{H}_2\text{O}$ are simple and closely resemble each other. A band at ca. 435 m cm⁻¹, assigned to $\nu(\text{Co-F})$, is a typical feature. Such a band has also been reported for $[\text{CoF}_3]^-$ measured in perovskites.¹⁹ The position and slight broadening of the $\nu(\text{Co-F})$ absorption indicates the possibility of a $-\text{F}-\text{Co}-\text{F}-\text{Co}-\text{F}-$ type of interaction in the complexes. The observed magnetic moments of the compounds also support this view. Two additional bands at ca. 3 440 m br and ca. 1 640 m cm⁻¹ are assigned to $\nu(\text{O-H})$ and $\delta(\text{H-O-H})$ modes of lattice water.²⁰ The broad nature of $\nu(\text{O-H})$ is explained in terms of hydrogen bonding in the molecule.

The i.r. spectrum of $[\text{Co}(\text{NH}_3)_4\text{F}_2]$ displays absorptions arising from the presence of co-ordinated NH_3 and fluoride ligands. The frequencies at 3 138 s br, 1 630 m, 1 395 s, and 770 m cm⁻¹ are well precedented in the literature^{21,22} and are assigned to $\nu(\text{NH}_3)$, $\delta_d(\text{NH}_3)$, $\delta_s(\text{NH}_3)$, and $\rho_r(\text{NH}_3)$ modes (d = deformation, s = stretching, r = rocking), respectively, of co-ordinated ammonia. These frequencies appear at relatively lower values than those of free ammonia.²¹ Consequent upon the co-ordination of NH_3 molecules, the $\nu(\text{Co-N})$ and $\delta(\text{N-Co-N})$ bands appear at 350 m and 195 s cm⁻¹, respectively, rendering it certain that the ammine ligands are co-ordinated to the metal centre. The medium intensity band at 434 cm⁻¹ is assigned to $\nu(\text{Co-F})$. The lack of further bands around 434 cm⁻¹ suggests²³ the probability of a D_{4h} symmetry for $[\text{Co}(\text{NH}_3)_4\text{F}_2]$, with the two F^- ligands occupying positions *trans* to each other.

The significant features of the i.r. spectra of $A[\text{CoF}(\text{SO}_4)(\text{H}_2\text{O})_2]$ ($A = \text{NH}_4, \text{Na}, \text{or K}$) are absorptions due to co-ordinated sulphate, fluoride, and H_2O . Bands arising from SO_4^{2-} are observed at ca. 1 150 s, ca. 1 105 s, and ca. 1 060 s cm⁻¹ due to ν_3 , at 980 m cm⁻¹ due to ν_1 , at ca. 630 s, ca. 610 s, and ca. 555 s cm⁻¹ due to ν_4 , and at ca. 450 s br cm⁻¹ due to ν_2 of the co-ordinated sulphate.²⁴ The laser Raman spectra, recorded on solids, exhibited signals at ca. 1 150, ca. 1 100, and ca. 1 050 cm⁻¹ due to ν_3 , at ca. 975 cm⁻¹ due to ν_1 , at ca. 640, ca. 610, and ca. 550 cm⁻¹ due to ν_4 , and at ca. 460 cm⁻¹ due to ν_2 of the SO_4^{2-} ligand. The i.r. and laser Raman spectral pattern, especially the appearance of ν_1 and ν_2 vibrations, as well as the splitting of ν_3 and ν_4 into three bands each clearly points to a lowering of site symmetry of the sulphato group from T_d to C_{2v} which in turn suggests that SO_4^{2-} is present here as a bidentate ligand.²⁴ A bidentate sulphate can, however, occur as either a chelated ligand bound to one metal centre or a bridging ligand bound to two metal centres. A distinction between the two types is made on the basis of the observed ν_3 band positions, since chelating bidentate sulphato complexes have ν_3 vibrations at energies higher than those of bridging sulphato complexes.^{24,25} The observations of ν_3 bands at lower energies compared to those generally observed for chelated sulphato ligands therefore suggests that SO_4^{2-} occurs as a bridging ligand^{24,25} in the compounds under investigation. This leads us to believe that the cobalt(II) centres are intermolecularly bridged through the sulphate ligand in the crystal lattice. The $\nu(\text{Co-F})$ band could not be distinctly identified since the ν_2 mode of the sulphato

ligand appears at the same position. However, an increase in intensity and broadening of the i.r. peak at ca. 450 cm⁻¹ suggest the possibility of overlap between $\nu(\text{Co-F})$ and ν_2 . The other characteristic features of i.r. spectra are bands at ca. 3 350 m, 1 640 w br, and ca. 730 m cm⁻¹ which are assigned to $\nu(\text{O-H})$, $\delta(\text{H-O-H})$, and the rocking mode of water, respectively. The weak nature of $\delta(\text{H-O-H})$ and the presence of a medium band at ca. 730 cm⁻¹ provide evidence for co-ordination of the water molecules to the metal centre.^{26,27} Moreover, pyrolysis of $A[\text{CoF}(\text{SO}_4)(\text{H}_2\text{O})_2]$ at 125–130 °C for 3 h did not show any weight loss, and the i.r. spectra recorded before and after pyrolysis were found to be practically the same, thus rendering further support to the notion that the water molecules are co-ordinated.

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