Complex Fluoroberyllates. Synthesis and Physicochemical Characterization of Mixed-Fluoro Complexes of Beryllium Containing Hydrogenoxalate ($HC_2O_4^-$), Glycinate, and Dihydrogenphosphate ($H_2PO_4^-$) as Co-Ligands

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Synthesis of novel mixed complex fluoroberyllates of the types $M_2[BeF_3(HC_2O_4)]\cdot H_2O$ (M=NH_4 or Na), $K_2[BeF_3(HC_2O_4)]$, $M_2[BeF_3(NH_2CH_2COO)]\cdot H_2O$ (M=NH_4 or Na), and $M_2[BeF_2(H_2PO_4)_2]$ (M=NH_4 or K) has been achieved from the reaction of $Be(OH)_2$ with MF and the corresponding co-ligands viz., oxalic acid, glycine, and orthophosphoric acid, at pH ca. 2. Vibrational spectroscopic evidences have been provided in respect of coordinated F^- and the ligands $HC_2O_4^-$, $NH_2CH_2COO^-$, or $H_2PO_4^-$. IR spectra of ammonium salt of the complexes demonstrate the presence of hydrogen bonding.

The chemistry of fluoroberyllium compounds is gaining fast momentum probably due to many unusual properties which make some of them highly useful industrially.[1] Notable applications are, for instance, in the manufacture of glass,[1,2] as coating materials, and in nuclear technology.[1] Biological implications of beryllium fluorocomplex are also documented in literature.[3] Significantly some fluoroberyllates are known to be ferroelectric.[4,5] Unfortunately, however, there is only a very limited accessibility of such compounds, especially mixed fluoroberyllates.

For a number of years, we have been trying our hands in the field of fluoro and mixed fluoro metal compounds for a variety of reasons.[6] The interesting properties and applications of fluoroberyllium species[1–5,7] prompted us to undertake studies on fluoro chemistry of the metal.

The main concerns were to identify appropriate coligands, improvise practical routes to newer mixed fluoroberyllates, and isolate and characterize the compounds. We considered this to be important to provide new materials amenable to physical studies. Another important aim was to demonstrate the new synthesis directly from $Be(OH)_2$. This would reduce the extra steps involved in the preparation of BeF_2, a commonly used starting material for fluoroberyllates.[1] The coligands have been drawn from the anions of a dicarboxylic acid, $HC_2O_4^-$, an aminocarboxylic acid, $NH_2CH_2COO^-$, and a tribasic acid, $H_2PO_4^-$, such that target species are obtained.

The synthesis of new compounds of the types $M_2[BeF_3(HC_2O_4)]\cdot H_2O$ (M=NH_4, Na, or K), $M_2[BeF_3(NH_2CH_2COO)]\cdot H_2O$ (M=NH_4 or Na), and $M_2[BeF_2(H_2PO_4)_2]$ (M=NH_4 or K), and the results of some physicochemical studies on them constitute the subject matter of the present report.

Experimental

The chemicals used were all reagent grade products. Infrared spectra were recorded on a Perkin Elmer Model 983 spectrophotometer and Laser Raman (LR) spectra on an instrument described earlier.[8] The pH values of the reaction solutions were measured with an Elico model LI 120 pH meter and also with indicator paper (BDH).

Synthesis. Ammonium and Sodium Trifluoro(hydrogenoxalato)beryllate Monohydrate, $M_2[BeF_3(HC_2O_4)]\cdot H_2O$ (M=NH_4 or Na) and Potassium Trifluoro(hydrogenoxalato)beryllate, $K_2[BeF_3(HC_2O_4)]$: To a slution of $BeSO_4\cdot 4H_2O$ (1.0 g, 5.65 mmol) in water (150 cm^3), dilute NaOH solution was added slowly with continuous stirring. The precipitate of $Be(OH)_2$, was filtered and washed 5 to 6 times with water. $Be(OH)_2$ was transferred into a polyethylene beaker. To it were added water (10 cm^3) and 16.95 mmol each of solid MF(M=NH_4, Na, or K) and $H_2C_2O_4\cdot 2H_2O$ with stirring.

The mixture was heated on a steam bath for ca. 20 min to obtain a clear solution. The pH of the solution was recorded to be 2. The reaction solution was allowed to cool and to this ethanol was added to precipitate the product. The product was filtered and washed 3 to 4 times with ethanol and dried in vacuo over concd H_2SO_4. Yield 1 g (85%) for $(NH_4)_2[BeF_3(HC_2O_4)]\cdot H_2O$, 1.1 g (88.7%) for $Na_2[BeF_3(HC_2O_4)]\cdot H_2O$ and 1.25 g (95%) for $K_2[BeF_3(HC_2O_4)]$.

Ammonium and Sodium Trifluoro(glycinato)beryllate Monohydrate, $M_2[BeF_3(NH_2CH_2COO)]\cdot H_2O$ (M=NH_4 or Na): To an aqueous suspension of $Be(OH)_2$, obtained from $BeSO_4\cdot 4H_2O$ (1.0 g, 5.66 mmol) in a similar way to that described in the preceding synthesis, were added water (10 cm^3) and 16.95 mmol each of MF (M=NH_4 or Na) and glycine with continuous stirring. The mixture was heated over a steam bath for ca 30 min. The pH of the reaction solution was 2—2.5. The solution was cooled to room temperature. Addition of ethanol to this afforded a white microcrystalline product. The compound was separated by filtration, washed 4 to 5 times with ethanol and dried in vacuo over concd H_2SO_4. Yield, 1 g (91%) for $(NH_4)_2[BeF_3(NH_2CH_2COO)]\cdot H_2O$ and 1 g (87%) for $Na_2[BeF_3(NH_2CH_2COO)]\cdot H_2O$.

Ammonium and Potassium Bis(dihydrogenphosphato)difluoroberyllate, $M_2[BeF_2(H_2PO_4)_2]$ (M=NH_4 or K): To an aqueous suspension of $Be(OH)_2$, obtained from $BeSO_4\cdot 4H_2O$ (1.0 g, 5.66 mmol) as mentioned above, was added 16.95 mmol of MF (M=NH_4 or K) and 22.64 mmol of orthophosphoric acid (sp.gr. 1.75 g cm^{-3}) under stirring. The mixture was heated over a steam bath for ca. 20 min and a clear solution was obtained. The pH of the solution was recorded to be 2.

Addition of ethanol to this solution afforded a white microcrystalline product. The compound thus obtained was filtered and washed 3 to 4 times with ethanol and dried in vacuo over concd H_2SO_4. Yield 1.3 g (83%) for $(NH_4)_2$-$[BeF_2(H_2PO_4)_2]$ and 1.5 g (83%) for $K_2[BeF_2(H_2PO_4)_2]$.

Elemental Analysis. Beryllium was estimated gravimetrically.[9a] The fluoride content was determined gravimetrically as lead chlorofluoride.[9b] Oxalate was determined volumetrically with standard $KMnO_4$ solution.[9c] Phosphate estimation was accomplished gravimetrically[9d] and the results checked spectrophotometrically.[9e] Carbon, hydrogen, and nitrogen were determined by micro-analytical methods at the Micro-Analytical Laboratories, North Eastern Hill University, Shillong, India. While sodium content was ascertained by flame photometric method, the potassium was estimated by both flamephotometry as well as atomic absorption spectrophotometry.

Results and Discussion

Synthesis of fluoroberyllate complexes generally uses beryllium fluoride, BeF_2.[1] Its preparation requires high temperature[1,10] and since the compound is hygroscopic, careful handling is recommended. In order to avert these difficulties as well as to demonstrate the efficacy of $Be(OH)_2$ as a source of the metal center, each of the new synthesis was carried out with a freshly prepared beryllium hydroxide sample. Two points were of interest in the present context viz. (i) asymmetry of the metal center, and (ii) the occurrence of hydrogen bonding. While any mixed fluoroberyllate would fulfill the first condition, selection of an appropriate coligand is important to achieve the second point of contention. To reach the destination, the chosen coligands were identified and synthetic reactions conducted at pH values of 2—2.5 of the reaction medium. Thus, under the present reaction conditions $Be(OH)_2$ reacted with MF and oxalic acid to afford $M_2[BeF_3(HC_2O_4)]\cdot H_2O$ ($M=NH_4$ or Na) and $K_2[BeF_3(HC_2O_4)]$, in contrast to $M_2[BeF_2(C_2O_4)]$ (M=Na or K) and $K_2[Be_2F_6(C_2O_4)]\cdot H_2O$ reported in literature.[7] An acidic condition (pH 2) has, seems to us, favored $HC_2O_4^-$ formation which then coordinated to the metal center to produce trifluoro(hydrogenoxalato)beryllate, as obtained. Significant is the rarity, though not unprecedented,[11,12] of hydrogenoxalato as a ligand.

A glycinium fluoroberyllate, $(NH_2CH_2COOH)_3$-H_2BeF_4 was reported quite some time ago.[13] The compound which is a glycine adduct is very interesting because of its ferroelectric properties. Our interest was to develope glycine coordinated fluoroberyllates. This has been now possible through a direct interaction of $Be(OH)_2$ with alkali fluoride and glyH. It is believed that at pH 2—2.5, a coordinatively unsaturated fluoroberyllate was formed which then accommodated glycinate in its coordination sphere to provide $M_2[BeF_3(NH_2CH_2COO)]\cdot H_2O$ ($M=NH_4$ or Na). Incidentally, the experimental condition was conducive to the formation of glycinate ion enabling it to co-ordinate as an anionic ligand. The sequence of addition of the ligands i.e., MF followed by glycine, is important since a reverse order did not yield the desired compound.

The dissociation of phosphoric acid, H_3PO_4, is highly pH dependent and it has been well established that the acid generates $H_2PO_4^-$ at pH below 4.[14] Based upon this knowledge strategy was worked out and the reaction conducted at pH 2, as described (see Experimental), to obtain $M_2[BeF_2(H_2PO_4)_2]$ ($M=NH_4$ or K). In this way, an access to a number of novel mixed fluoroberyllate complexes could be made to provide materials for further research on their physical properties. The methods are direct and do not require BeF_2, thus offering many advantages.

Characterization and Assessment of Structure. The newly synthesized compounds are white micro-crystalline products, stable for a prolonged period. In contrast to the insolubility of $M_2[BeF_3(HC_2O_4)]$ and $M_2[BeF_2(H_2PO_4)_2]$, the salts of fluoroglycinatoberyllate, $[BeF_3(NH_2CH_2COO)]^{2-}$, are highly soluble and stable in aqueous medium. The stability is attested by molar conductance lying between 232 and 238 $\Omega^{-1}\,cm^2\,mol^{-1}$. The values are also in agreement with a 2 : 1 electrolytic nature of each of them.

The common features of vibrational spectra of the compounds are the presence of two bands, one each at ca. 800s and at 380 m cm^{-1}, which have been assigned to the ν(Be–F) and δ(F–Be–F) modes of coordinated fluoride.[1] Laser Raman signals at ca. 800 and ca. 385 cm^{-1} compliment the assignments. In addition, consequent upon the presence of O-donor ligands in all the three types of complexes, the ν(Be–O) mode has been observed consistently at ca. 920 cm^{-1}. Partinent is to mention that similar observations were made in the spectra of $BeCl_2$ complexes containing O-donor ligands.[1,15] A comparison of this result with that of chlorocompounds of the metal clearly indicates that change of halides does not have a significant effect on the Be–O band positions. Apart from the common features discussed above, each type of the complexes displays a pattern typical of itself. The most significant in the context of vibrational spectra of $M_2[BeF_3(HC_2O_4)]$ is an evidence for the occurrence of $HC_2O_4^-$ as the co-ligand. Though such examples are far less encountered, a strong band at 1630 cm^{-1} seems to be the distinctive feature.[12] The $K_2[BeF_3(HC_2O_4)]$ complex was chosen as a representative example for it did not contain H_2O. Both IR and LR spectra of this compound clearly showed intense signals at 1630 cm^{-1} (Table 1) supporting the contention. Fortunately, this band was also observed in the IR spectra of other two salts of the complex causing it to be a representative feature of the complexes under discussion. In addition, the IR frequencies at ca. 1670 [$\nu_{asym}(COO^-)$] and ca. 1340 [$\nu_{sym}(COO^-)$] were observed due to the coordination of $HC_2O_4^-$ through its carboxylate group, as expected.[16] Thus, the vibrational spectroscopy adduced clean support to the formulation.

Glycine has different ways of coordination with a

Table 1. Analytical Data for the Complexes of Beryllium and Structurally Significant IR Bands of $M_2[BeF_3(HC_2O_4)]\cdot H_2O$ (M=NH_4 or Na), $K_2[BeF_3(HC_2O_4)]$, $M_2[BeF_3(NH_2CH_2COO)]\cdot H_2O$ (M=NH_4 or Na), and $M_2[BeF_2(H_2PO_4)_2]$ (M=NH_4 or K)

Compounds	Analysis/%								IR	Assignments
	Be	M	F	C_2O_4	PO_4	C	H	N		
$(NH_4)_2[BeF_3(HC_2O_4)]\cdot H_2O$	4.23		27.38	41.63	—	11.18	5.19	12.95		
	(4.31)		(27.25)	(42.08)		(11.48)	(5.31)	(13.40)	818 s,br	ν(Be–F)
									347 m,br	δ(F–Be–F)
									911 s	ν(Be–O)
									3450 s	ν(O–H)
									1657 s	δ(H–O–H)
									1668 s	$\nu_{asym}(COO^-)$
									1310 m	$\nu_{sym}(COO^-)$
									725 w	$\delta(CO^-_2)$
$Na_2[BeF_3(HC_2O_4)]\cdot H_2O$	4.14	21.12	25.64	39.85		10.85	1.32			
	(4.11)	(21.0)	(26.02)	(40.18)		(10.97)	(1.38)		810 s,br	ν(Be–F)
									345 m,br	δ(F–Be–F)
									920 s	ν(Be–O)
									3445 s	ν(O–H)
									1650 s	δ(H–O–H)
									1670 s	$\nu_{asym}(COO^-)$
									1310 m	$\nu_{sym}(COO^-)$
									720 w	$\delta(CO^-_2)$
$K_2[BeF_3(HC_2O_4)]$	3.86	34.11	24.95	38.19		10.19				
	(3.86)	(33.52)	(24.44)	(37.74)		(10.30)			818 s,br	ν(Be–F)
									396 m,br	δ(F–Be–F)
									911 s	ν(Be–O)
									1672 s	$\nu_{asym}(COO^-)$
									1338 m	$\nu_{sym}(COO^-)$
									719 w	$\delta(CO^-_2)$
$(NH_4)_2[BeF_3(NH_2CH_2COO)]\cdot H_2O$	4.70		29.18			12.89	7.21	20.80		
	(4.64)		(29.35)			(12.37)	(7.28)	(21.64)	802 s,br	ν(Be–F)
									363 m,br	δ(F–Be–F)
									930 s	ν(Be–O)
									1610 s	$\nu(COO^-)$
									3440 s	ν(OH)
									1657 s	δ(H–O–H)
$Na_2[BeF_3(NH_2CH_2COO)]\cdot H_2O$	4.24	23.11	28.14			11.94	2.75	6.81		
	(4.41)	(22.54)	(27.93)			(11.77)	(2.97)	(6.87)	822 s,br	ν(Be–F)
									363 m,br	δ(F–Be–F)
									930 s	ν(Be–O)
									1615 s	$\nu(COO^-)$
									3438 s	ν(O–H)
									1629 s	δ(H–O–H)
$(NH_4)_2[BeF_2(H_2PO_4)_2]$	3.38		13.55		70.15			9.88		
	(3.26)		(13.73)		(68.50)			(10.13)	810 s,br	ν(Be–F)
									372 m,br	δ(F–Be–F)
									922 s	ν(Be–O)
									1104 s br	coord. $H_2PO_4^-$
									2854 w br	
$K_2[BeF_2(H_2PO_4)_2]$	2.78	23.89	11.21		59.24					
	(2.83)	(24.53)	(11.92)		(59.46)				815 s,br	ν(Be–F)
									373 m,br	δ(F–Be–F)
									926 s	ν(Be–O)
									1108 s br	coord. $H_2PO_4^-$
									2922 w br	

metal center and various possible modes of coordination can be ascertained from IR spectroscopic studies.(17) The distinctive features in respect of coordinated glycine ligand in the present case is the consistent appearance of a band at ca. 1610 cm^{-1}, well separated from the δ(H–O–H) mode (1645 cm^{-1}) of lattice water. This observation as well as the absence of any absorption around 1700 cm^{-1} cause us to state that the co-ligand occurs in its ionic form and attaches itself with the beryllium center through its carboxylic oxygen. The band at 1615 cm^{-1} has been assigned to COO^- stretching mode(17) of coordinated glycinate.

The IR spectral pattern of metal phosphato comlexes are in general rather complicated owing the peak broadening and poor resolution. The spectra of $M_2[BeF_2(H_2PO_4)_2]$ complexes exhibited a medium intensity band at ca. 1108 and a broad weak absorption at ca. 2850 cm^{-1} attributable to the presence of phosphates. These bands are rather typical of coordinated hydrogenphosphato ligand[18] and are in conformity with the formulation.

A notable general feature of IR spectra of all the compounds, dealt with in this report, is the broadening of both ν(Be–F) and δ(F–Be–F)modes. This is a clean reflection of a definite possibility of intramolecular hydrogen bonding in each of the compounds.

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