Synthesis of Tetrafluoronickelate(II) and Tetrafluorozincate(II) Complexes from Aqueous Media: A Novel Route to Fluorometalates

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The complexes $A_2[NiF_4]$ (A = NH_4^+, K^+, or Rb^+) and $A_2[ZnF_4]$ (A = NH_4^+, K^+, Rb^+, or Cs^+) have been synthesised, from the corresponding metal acetylacetonates (acac) with 40% HF and AF, in very high yields. The new method also allows the preparation of $[VOF_5]^{2-}$, $[MnF_5]^{2-}$, and $[CrF_5(H_2O)]^{2-}$ from $[VO(acac)_2]$, $[Mn(acac)_3]$, and $[Cr(acac)_3]$ respectively.

Recommended methods[1-3] for the synthesis of $[NiF_4]^{2-}$ or $[ZnF_4]^{2-}$ complexes employ fusion of NiF_2 or ZnF_2 with stoicheiometric amounts of alkali-metal or alkaline-earth-metal fluorides *in vacuo* or in an atmosphere of dry HF. Such methods require not only MF_2 (M = Ni or Zn) but also anhydrous HF which is difficult to handle. Very recently, we described simple syntheses of acetylacetonates of nickel,[4] manganese,[5] chromium,[6] and iron,[7] and as part of a programme aimed at utilising such compounds as precursors, it was envisaged that they would react with aqueous HF and alkali-metal fluorides to provide an easy access to alkali-metal salts of fluorometalates. In this paper we report the synthesis of $[NiF_4]^{2-}$ and $[ZnF_4]^{2-}$ complexes directly from their respective acetylacetonates, and also the scope of the method as a paradigm for other such syntheses.

Experimental

Reagent-grade chemicals were used throughout. $[Zn(acac)_2]\cdot H_2O$[8] (acac = acetylacetonate) and $[VO(acac)_2]$[9] were prepared by the literature methods. $[Ni(acac)_2(H_2O)_2]$,[4] $[Mn(acac)_3]$,[5] and $[Cr(acac)_3]$[6] were prepared by methods developed in these laboratories. Infrared spectra were recorded on a Perkin-Elmer model 125 spectrophotometer. Magnetic susceptibility measurements were made by the Guoy method using $Hg[Co(NCS)_4]$ as calibrant.

Synthesis of $A_2[NiF_4]$ (A = NH_4^+, K^+, *or* Rb^+) *and* $A_2[ZnF_4]$ (A = NH_4^+, K^+, Rb^+, *or* Cs^+).—*A typical procedure.* Freshly prepared $[Ni(acac)_2(H_2O)_2]$ or $[Zn(acac)_2]\cdot H_2O$ was added to an excess of 40% HF (15 $cm^3\ g^{-1}$) followed by the addition of AF, with the molar ratio of metal acetylacetonate and AF being maintained at 1 : 4. The mixture was then heated over a steam-bath with stirring until the metal acetylacetonate dissolved completely (*ca.* 40 min). The solution was filtered, and the filtrate concentrated over a steam-bath until microcrystalline yellow $A_2[NiF_4]$ or white $A_2[ZnF_4]$ started to appear. The reaction container was cooled to room temperature for *ca.* 2 h, and $A_2[NiF_4]$ or $A_2[ZnF_4]$ was separated by centrifugation, dried on a filter paper, and finally dried *in vacuo* over phosphorus pentoxide. Yields varied between 80 and 90%. Analytical data, magnetic moments, and structurally significant i.r. band positions are summarised in the Table.

Reaction of $[M(acac)_n]$ (M = Cr *or* Mn, $n = 3$; M = VO, $n = 2$) *with* NH_4F *and* 40% HF.—The reaction was performed in a manner analogous to that described above. The products obtained were blue $[NH_4]_2[VOF_5]$, green $[NH_4]_2[CrF_5(H_2O)]$, and pink $[NH_4]_2[MnF_5]$ from $[VO(acac)_2]$, $[Cr(acac)_3]$, and $[Mn(acac)_3]$ respectively, with yields lying between 85 and 90%.

Table. Analytical data, magnetic moments, and i.r. bands for $A_2[NiF_4]$ (A = NH_4^+, K^+, or Rb^+) and $A_2[ZnF_4]$ (A = NH_4^+, K^+, Rb^+, or Cs^+)

		Analysis [b]/%				
Compound	$\mu_{eff.}$ [a]/B.M.	A	Ni or Zn	F	I.r./cm^{-1}	Assignment
$[NH_4]_2[NiF_4]$	2.0	16.7 [c]	33.90	44.80	455	ν_{Ni-F}
		(16.4) [c]	(34.35)	(44.50)		
$K_2[NiF_4]$	1.9	36.10	27.85	35.2	455	ν_{Ni-F}
		(36.75)	(27.60)	(35.7)		
$Rb_2[NiF_4]$	2.2		19.55	25.15	460	ν_{Ni-F}
			(19.20)	(24.85)		
$[NH_4]_2[ZnF_4]$	Diamagnetic	15.25 [c]	37.20	42.35	440	ν_{Zn-F}
		(15.80) [c]	(36.85)	(42.80)		
$K_2[ZnF_4]$	Diamagnetic	35.10	30.15	34.20	445	ν_{Zn-F}
		(35.60)	(29.80)	(34.60)		
$Rb_2[ZnF_4]$	Diamagnetic		20.25	24.85	445	ν_{Zn-F}
			(20.95)	(24.35)		
$Cs_2[ZnF_4]$	Diamagnetic		16.75	18.20	440	ν_{Zn-F}
			(16.05)	(18.65)		

[a] $T = 295$ K; 1 B.M. = 9.27×10^{-23} A m^2. [b] Calculated values in parentheses. [c] Analysis for N.

Results and Discussion

$[Ni(acac)_2(H_2O)_2]$ or $[Zn(acac)_2]\cdot H_2O$ undergo a rather facile reaction with hot aqueous HF and alkali-metal fluorides (AF) to afford yellow $A_2[NiF_4]$ ($A = NH_4^+$, K^+, or Rb^+) or white $A_2[ZnF_4]$ ($A = NH_4^+$, K^+, Rb^+, or Cs^+) in a very high yield. The method does not require anhydrous HF or any starting material which is difficult to prepare. The role of AF was not only to increase the F^- ion concentration in the medium but also to provide counter cations, A^+, to enable isolation of the fluorometalates as their alkali-metal salts. In an attempt to explore the scope of the synthetic procedure, similar reactions involving $[VO(acac)_2]$, $[Cr(acac)_3]$, or $[Mn(acac)_3]$ with NH_4F and 40% HF were carried out and the products obtained were identified as $[NH_4]_2[VOF_5]$,[9] $[NH_4]_2[CrF_5(H_2O)]$,[10] and $[NH_4]_2[MnF_5]$[11] respectively, thereby supporting our contention that the method can be used as a paradigm for other such syntheses.

The room-temperature magnetic susceptibility measurements show that while the $A_2[ZnF_4]$ compounds are all diamagnetic, as expected, the magnetic moments of the $A_2[NiF_4]$ compounds lie between 1.9 and 2.2 B.M. in conformity with those reported in the literature.[12] The analytical data and magnetic moments suggest that the compounds are the same as those which have been prepared by other methods and characterized structurally.[13,14] The i.r. spectra of $A_2[NiF_4]$ and $A_2[ZnF_4]$ (Table) also support this view. The spectra do not show any evidence for the presence of alkali-metal difluorides, $A[HF_2]$,[15-17] thus ruling out the possibility of contamination of the end products by $A[HF_2]$.

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