

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

Mihir K. Chaudhuri,\* Soumitra K. Ghosh, and Zavei Hiese

Department of Chemistry, North-Eastern Hill University, Shillong 793003, India

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<sup>1-3</sup> for the synthesis of  $[NiF_4]^{2-}$  or  $[ZnF_4]^{2-}$  complexes employ fusion of  $NiF_2$  or  $ZnF_2$  with stoichiometric 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,<sup>4</sup> manganese,<sup>5</sup> chromium,<sup>6</sup> and iron,<sup>7</sup> 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.  $[Zn(acac)_2] \cdot H_2O$ <sup>8</sup> (acac = acetylacetonate) and  $[VO(acac)_2]$ <sup>9</sup> were prepared by the literature methods.  $[Ni(acac)_2(H_2O)_2]$ ,<sup>4</sup>  $[Mn(acac)_3]$ ,<sup>5</sup> and  $[Cr(acac)_3]$ <sup>6</sup> 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 ( $15 \text{ cm}^3 \text{ g}^{-1}$ ) 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  $Cs^+$ )

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

<sup>a</sup>  $T = 295 \text{ K}$ ; 1 B.M. =  $9.27 \times 10^{-23} \text{ A m}^2$ . <sup>b</sup> Calculated values in parentheses. <sup>c</sup> Analysis for N.

### Results and Discussion

[Ni(acac)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] or [Zn(acac)<sub>2</sub>·H<sub>2</sub>O] undergo a rather facile reaction with hot aqueous HF and alkali-metal fluorides (AF) to afford yellow A<sub>2</sub>[NiF<sub>4</sub>] (A = NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, or Rb<sup>+</sup>) or white A<sub>2</sub>[ZnF<sub>4</sub>] (A = NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, or Cs<sup>+</sup>) 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<sup>-</sup> ion concentration in the medium but also to provide counter cations, A<sup>+</sup>, 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)<sub>2</sub>], [Cr(acac)<sub>3</sub>], or [Mn(acac)<sub>3</sub>] with NH<sub>4</sub>F and 40% HF were carried out and the products obtained were identified as [NH<sub>4</sub>]<sub>2</sub>[VOF<sub>5</sub>],<sup>9</sup> [NH<sub>4</sub>]<sub>2</sub>[CrF<sub>5</sub>(H<sub>2</sub>O)],<sup>10</sup> and [NH<sub>4</sub>]<sub>2</sub>[MnF<sub>5</sub>]<sup>11</sup> 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<sub>2</sub>[ZnF<sub>4</sub>] compounds are all diamagnetic, as expected, the magnetic moments of the A<sub>2</sub>[NiF<sub>4</sub>] compounds lie between 1.9 and 2.2 B.M. in conformity with those reported in the literature.<sup>12</sup> 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.<sup>13,14</sup> The i.r. spectra of A<sub>2</sub>[NiF<sub>4</sub>] and A<sub>2</sub>[ZnF<sub>4</sub>] (Table) also support this view. The spectra do not show any evidence for the presence of alkali-metal difluorides, A[HF<sub>2</sub>],<sup>15-17</sup> thus ruling out the possibility of contamination of the end products by A[HF<sub>2</sub>].

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