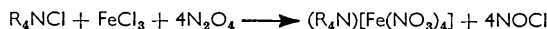


956. *Alkylammonium and Cæsium Tetranitratoferrates*

By C. C. ADDISON, P. M. BOORMAN, and N. LOGAN

SEVERAL anionic tetranitrato-complexes of first-row transition metals have recently been described; these have normally involved metals in +2 oxidation states^{1,2} (e.g., Cu(II), Ni(II), Mn(II), and Co(II)), but Naldini³ has suggested that compounds of empirical formula $\text{FeR}_2(\text{NO}_3)_3$ (where R = Ph_3P or Ph_3As) may have the structure $[\text{FeR}_4(\text{NO}_3)_2]^+[\text{Fe}(\text{NO}_3)_4]^-$. We report here the preparation and some properties of a series of compounds $(\text{R}_4\text{N})[\text{Fe}(\text{NO}_3)_4]$ (where R = Et or H), which are clearly salts of the tetranitratoferrate(III) anion; the isolation of the cæsium salt $\text{Cs}[\text{Fe}(\text{NO}_3)_4]$ has also been of value when considering infrared spectra.

The alkylammonium complexes were prepared by reaction of equimolar mixtures of anhydrous iron(III) chloride and the alkylammonium chloride with liquid dinitrogen tetroxide:



Solvolysis was vigorous at 20°, and reaction was complete within a few minutes. A red-brown crystalline precipitate of the tetraethylammonium salt separated from solution almost immediately; when R_4N^+ was Et_3HN^+ , $\text{Et}_2\text{H}_2\text{N}^+$, or EtH_3N^+ , crystallisation did not occur until most of the solvent had been removed under reduced pressure.

The cæsium salt was prepared by solvolysis of an equimolar mixture of iron(III) chloride and cæsium chloride in an approximately 1 : 2 v/v ethyl acetate-liquid dinitrogen tetroxide mixture. Crystallisation does not occur satisfactorily from this medium; the solvents were therefore removed until the residue became viscous, and an excess of a 1 : 2 v/v methyl cyanide-dinitrogen tetroxide mixture added. This solution was shaken for several days, after which evaporation of solvent gave a yellow-brown crystalline precipitate of $\text{Cs}[\text{Fe}(\text{NO}_3)_4]$.

Experimental.—Analyses. Amine contents of the complexes were determined by distillation from alkaline solutions, and the nitrogen remaining as nitrate was determined by the Kjeldahl method. Cæsium was determined by precipitation as the tetraphenylborate.

TABLE I

(N* = nitrogen present as nitrate)

Compound	Found (%)			Calc. (%)		
	Fe	Amine	N*	Fe	Amine	N*
$\text{EtNH}_3[\text{Fe}(\text{NO}_3)_4]$	15.7	13.1	15.9	16.0	12.9	16.0
$\text{Et}_2\text{NH}_2[\text{Fe}(\text{NO}_3)_4]$	14.7	19.5	14.6	14.8	19.4	14.8
$\text{Et}_3\text{NH}[\text{Fe}(\text{NO}_3)_4]$	14.0	24.2	13.2	13.8	24.9	13.8
	Fe	C	N*	Fe	C	N*
$\text{Et}_4\text{N}[\text{Fe}(\text{NO}_3)_4]$	13.0	21.9	12.7	12.9	22.2	12.9
	Fe	Cs	N	Fe	Cs	N
$\text{Cs}[\text{Fe}(\text{NO}_3)_4]$	13.0	29.1	13.0	12.8	30.3	12.8

Physical properties. All the alkylammonium compounds were stable indefinitely at room temperature in a dry atmosphere, but were hydrolysed readily in moist air. Some properties are listed in Table 2.

The packing behaviour of the ethyl- and diethyl-ammonium salts made them unsuitable for the determination of their magnetic moment by the Gouy method. The moments for the other two (Table 2) are close to the value expected for a high-spin Fe^{3+} ion. The molar conductivities for 0.001M-solutions in nitromethane agree with those found for 1 : 1 electrolytes in this medium.⁴

¹ D. K. Straub, R. S. Drago, and J. T. Donoghue, *Inorg. Chem.*, 1962, **1**, 848.

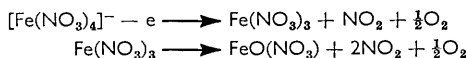
² F. A. Cotton and T. G. Dunne, *J. Amer. Chem. Soc.*, 1962, **84**, 2013; F. A. Cotton and J. G. Bergman, *ibid.*, 1964, **86**, 2941.

³ L. Naldini, *Gazzetta*, 1960, **90**, 1231.

⁴ R. S. Nyholm and R. V. Parish, *Chem. and Ind.*, 1956, 470.

The full conductivity against concentration curve for nitromethane solutions of the tetraethylammonium salt has been presented elsewhere⁵ for comparison with curves for the nitrosonium and nitronium salts and is typical of weak electrolyte behaviour in this medium.

Electrolysis of solutions. Solutions of the tetraethylammonium salt in nitromethane were electrolysed (20 hr., current 0.3—0.4 mA) in a Hittorf type of cell. For several concentrations, similar results were obtained; the iron content of the cathode compartment decreased, but a flocculent brown precipitate developed at the anode. This is explained by the anode reactions



Attempts to isolate the simple nitrate $\text{Fe}(\text{NO}_3)_3$ have been unsuccessful, and thermogravimetric analysis⁵ of the adduct $\text{Fe}(\text{NO}_3)_3 \cdot \text{N}_2\text{O}_4$ indicates that the simple nitrate readily decomposes to the oxide nitrate $\text{FeO}(\text{NO}_3)$, which we believe to be the precipitate formed. Similar experiments

TABLE 2

Physical properties of alkylammonium tetranitratoferrates $\text{R}_4\text{N}^+[\text{Fe}(\text{NO}_3)_4]^-$

R_4N	M. p. (decomp.)	Λ in nitro- methane ($\text{ohm}^{-1} \text{cm.}^2$) at 25° and 0.001M	μ_{eff} (B.M.) at 20°
EtNH_3	80	81	—
Et_2NH_2	58	76	—
Et_3NH	77	81	5.96
Et_4N	147	82	6.03

with methyl cyanide as the medium again showed a migration of iron-containing species from the cathode but, in this case, no precipitate developed in the anode compartment. The stronger ligand properties of methyl cyanide probably result in the stabilisation of the simple nitrate, as occurs with aluminium nitrate in the adduct⁶ $\text{Al}(\text{NO}_3)_3 \cdot 2\text{MeCN}$.

Infrared spectra. The spectrum of the tetraethylammonium compound is characteristic of the series. By comparison with the spectrum of tetraethylammonium chloride it was possible to assign the nitrate bands; these are compared with the spectrum of the caesium compound in Table 3. All the nitrate groups are covalent, and possibly bidentate (but unsymmetrically so²) as in $[\text{Co}(\text{NO}_3)_4]^{2-}$.

TABLE 3

Infrared spectra of tetranitratoferrates

Assignment ($-\text{ONO}_2$)	$(\text{Et}_4\text{N})[\text{Fe}(\text{NO}_3)_4]$			$\text{Cs}[\text{Fe}(\text{NO}_3)_4]$		
ν_4	1600vs, sp	1560vs, b	1490vs, sp	1590s, sh	1560vs, b	1475vs, sh
ν_1	1295vs, b	1240vs, sp		1270vs, b	1235vs, sh	
ν_2	1020vs, sp			1022s, sp	1005vs, sp	
ν_6	800s, sp			795s, sp	791s, sp	
ν_3 or ν_5	760vs, sp			758vs, sp		

Solution properties. All five compounds showed some solubility in polar organic solvents, but were quite insoluble in non-polar solvents. The electronic spectrum of the tetraethylammonium salt in methyl cyanide⁵ showed intense absorption ($\epsilon = 9390$) at $280 \text{ m}\mu$, which is attributed to electron transfer from nitrate ligand to metal. The possibility of forming a hexanitratoferrate ion has been examined by addition of tetraethylammonium nitrate to a solution of the compound $(\text{Et}_4\text{N})[\text{Fe}(\text{NO}_3)_4]$ in nitromethane. The specific conductivity of the solution varied linearly with added $\text{Et}_4\text{N} \cdot \text{NO}_3$, and no breaks occurred at $\text{Et}_4\text{N} \cdot \text{NO}_3 : (\text{Et}_4\text{N})[\text{Fe}(\text{NO}_3)_4]$ ratios of up to 4 : 1.

The authors are indebted to the D.S.I.R. for a maintenance grant (to P. M. B.).

THE UNIVERSITY, NOTTINGHAM.

[Received, March 11th, 1965.]

⁵ C. C. Addison, P. M. Boorman, and N. Logan, *J.*, 1965, 4978.

⁶ C. C. Addison, P. M. Boorman, and N. Logan, unpublished results.