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Hexaminmetal(III)–Pentafluorooxovanadates(IV)

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Fluorocomplexes of VO^{2+} are mainly studied with alkali and ammonium ions [1–5], where the stoichiometries VOF_5^{3-}, VOF_4^{2-}, $VOF_4{\cdot}H_2O^{2-}$ and $V_2O_2F_7^{3-}$ were found. With larger cations only the preparation of $[(C_4H_9)_4N]_3VOF_5{\cdot}6HF$ was reported [6].

The complexes of the general formula $[M(NH_3)_6]$-$[VOF_5]$, (M = Cr, Co, Rh) were prepared by the reaction of VOF_2 with $[M(NH_3)_6]Cl_3$ in 20% HF. The products are insoluble in water and in aqueous HF solution, and were precipitated almost quantitatively. Their X-ray powder patterns (Guinier de-Wolf camera, CuKα radiation), were indexed on the basis of the cubic unit cell and the cell parameters refined by the least-squares method. Crystallographic data, together with analytical results, are given in Table I and Table II respectively.

These complexes are also isostructural to $[Cr(NH_3)_6]MF_6$, (M = Mn, Fe), which crystallize in cubic space group Pa3 with octahedral cations and anions, arranged as Na^+ and Cl^- ions in NaCl lattice [7]. Each fluorine atom forms three hydrogen bonds, causing a considerable deformation of the Cr–NH_3 tetrahedron. These facts were also confirmed by vibrational spectroscopy [8]. For hexaminchromium–hexafluoromanganate(III) the observed equivalence of six Mn–F bonds (S_6 site symmetry) was explained by dynamic Jahn–Teller effect. The high crystal symmetry of our compounds can only be interpreted by the statistical orientation of the VOF_5^{3-} octahedra.

Infrared spectra (Table III), recorded on a Perkin–Elmer 521 instrument, bear a close resemblance to those of $[M(NH_3)_6]M'F_6$ series [8]. Most fundamental frequencies of the hexaminmetal ions are split.

TABLE II. Observed Spacings, Intensities and Indices of Reflections of $[Rh(NH_3)_6][VOF_5]$.

d (Å)	I_{rel}	*h k l*
5.79	5	1 1 1
5.00	10	2 0 0
3.53	8	2 2 0
3.01	5	3 1 1
2.89	6	2 2 2
2.67	5	3 2 1
2.355	4	3 3 0, 4 1 1
2.297	4	3 3 1
2.24	6	4 2 0
2.13	4	3 3 2
2.042	7	4 2 2
1.960	2	5 1 0, 4 3 1
1.922	4	3 3 3
1.763	5	4 4 0
1.665	8	4 4 2, 6 0 0
1.579	7	6 2 0
1.504	8	6 2 2
1.440	2	4 4 4
1.398	2	7 1 1, 5 5 1
1.385	6	6 4 0
1.359	2	7 2 1, 6 3 3, 5 5 2
1.334	5	6 4 2
1.300	1	7 3 1, 5 5 3
1.269	1	6 5 1, 7 3 2
1.248	1	8 0 0
1.210	1	8 2 0
1.117	1	8 2 2, 6 6 0

ν(N–H), however, is also broadened. Additionally, overtones and combination bands appear. This all accounts for the presence of hydrogen bonding between N–H and the anion.

The main feature of IR spectra of all vanadyl complexes is a strong V–O stretching absorption band, which appears at 985 ± 50 cm^{-1} [9]. It was shown that the ν(V–O) frequency primarily depends on the amount of pπ–dπ donation from oxygen to metal. The electron-accepting capacity of the vanadium is considerably striken by the presence of fluoride ions, which delocalize their π-bonding electrons into empty orbitals of vanadium. Two

TABLE I. Analytical and Crystallographic Data.

	Colour	% V*	% NH_3*	% F*	*a* (Å)	D_m (gcm^{-3})	D_c (gcm^{-3})	Z
$[Cr(NH_3)_6][VOF_5]$	Yellow–Green	16.44(16.11)	31.69(32.33)	30.44(30.05)	10.015(3)	2.20	2.091	4
$[Co(NH_3)_6][VOF_5]$	Yellow	15.89(15.76)	30.60(31.61)	29.80(29.41)	9.891(1)	2.18	2.218	4
$[Rh(NH_3)_6][VOF_5]$	Light Blue	13.99(13.88)			9.980(5)	2.39	2.453	4

*Found(calc.).

TABLE III. Frequencies (cm^{-1}) and Assignments of Infrared Bands.

	$[Co(NH_3)_6][VOF_5]$	$[Cr(NH_3)_6][VOF_5]$	$[Rh(NH_3)_6][VOF_5]$
ν(N–H)	3300vs,b 3250vs,sh 3170vs,sh 3125v,sh	3320vs,b 3250vs,sh 3160vs,sh	3300vs,b 3120vs,sh
$2\delta_{sim}(NH_3)$	2715m 2620w	2565w	2690vw 2608w
$\rho(NH_3) + \delta_{sim}(NH_3)$	2200w	2105w	2260vw 2180w
	2090vw		
$2\rho(NH_3)$	1750w 1665m,sh		1750w 1685m,sh
$\delta_e(NH_3)$	1625m,sh 1595s	1640vs 1600vs,sh	1605s 1560m,sh
$\delta_{sim}(NH_3)$	1335vs	1320vs,sh 1300vs	1328vs
	1140vw	1150vw 1085vw	1150vw
ν(V–O)	905vs	907vs	913vs
$\rho(NH_3)$	885s 805m	805vs 725m	895vs 820m
ν(Me–N), ν(V–F)	495vs,sh 470vs	490vs 460vs	490vs 470vs
$\delta(MeN_6)$	340s,sh		320s
$\delta(VOF_5^{3-})$	310vs	325m	300s

ν(V–O) frequencies, at 947 and 937 cm^{-1}, were found for $(NH_4)_3VOF_5$ [9].

In the present study, extremely low V–O stretchings were found. Assuming the same situation as in $[Cr(NH_3)_6]MF_6$ [7], three hydrogen bonds are formed to each ligand, causing a decrease in their donating ability. The reduced donation of fluorides should increase the ν(V–O) frequency, whereas lowering of the V–O bond order should cause a decrease of the same frequency.

We may conclude therefore, that multiple hydrogen bonding considerably affects $p\pi$–$d\pi$ donation by the oxygen, with a decrease of ν(V–O) frequency of at least 25 cm^{-1}, as compared to $(NH_4)_3VOF_5$.

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