Potassium Hexanitratocobaltate(III)

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Potassium hexanitratocobaltate(III) has been prepared by treating potassium hexafluorocobaltate(III) with dinitrogen pentaoxide at 273 K. Solution properties of the product in water and anhydrous organic solvents are reported. The product has been characterized by its magnetic susceptibility, and by i.r. and electronic spectra. These properties are clearly consistent with an octahedrally co-ordinated $t_{2g}{}^6$ low-spin complex ion. Decomposition of the product in acetonitrile has been monitored by electronic spectroscopy.

HEXANITRATO-COMPLEXES of metals have been a subject of interest for many investigators. Some of those reported for heavier metals in oxidation states IV and V are: $Mg[Th(NO_3)_6]\cdot 8H_2O$,[1] $[NEt_4]_2[Th(NO_3)_6]$,[2] $[NO_2]_2[Th(NO_3)_6]$,[3] $[NH_4]_2[Ce(NO_3)_6]$,[4] $M[Pa(NO_3)_6]$ [5] (M = Cs, NEt$_4$, or NMe$_4$), $Cs_2[Sn(NO_3)_6]$,[6] $[NMe_4]_2[Zr(NO_3)_6]$,[7] $[NEt_4]_2[Zr(NO_3)_6]$,[6] $K_2[Ir(NO_3)_6]$,[8] and $K_2[Pt(NO_3)_6]$.[8] So far as tripositive metals are concerned, Rosolovskii and his co-workers [9] recently reported the isolation of the complex $K_3[Al(NO_3)_6]$ and the possibility of synthesising first-row transition(3*d*)-metal counterparts of this species has been under investigation in our laboratories for some years. Preparation of the chromium analogue, $K_3[Cr(NO_3)_6]$, by treating $K_3[Cr(C_2O_4)_3]$ with N_2O_5, has been claimed,[10] but recent work [11] leads to the conclusion that a mixture of the compounds $K_2[Cr(NO_3)_5]$ and $K[NO_3]$ is obtained by this procedure.

Previous attempts to prepare $[Co(NO_3)_6]^{3-}$ in the Nottingham laboratories yielded only $M_2[Co(NO_3)_4]$ where M = Na or K,[12,13] however, isolation of this elusive species has now been achieved. The preparation and some properties of this first authenticated example of a 3*d* hexanitratometallate(III) complex are reported below.

EXPERIMENTAL

Potassium hexafluorocobaltate(III), $K_3[CoF_6]$, was prepared by passage of a mixture (1 : 1 by volume) of gaseous fluorine and nitrogen over a heated (553 K) mixture (3 : 1 molar proportion) of potassium chloride and anhydrous cobalt(II) chloride. Dinitrogen pentaoxide was prepared by dropwise addition of fuming nitric acid to phosphoric oxide. The dinitrogen pentaoxide vapour was carried through a column filled with alternating 3-cm bands of loosely packed phosphoric oxide and glass wool and into a receiving vessel, maintained at 195 K, in a slow stream of ozonised oxygen which converted any dinitrogen tetraoxide impurity into the pentaoxide.

Analytical Methods.—Cobalt was determined by titration with ethylenediaminetetra-acetate after reduction to Co^{II}. Nitrogen was determined by treatment with Devarda's alloy in sodium hydroxide solution and distillation of the ammonia into excess of 2% boric acid solution, which was then titrated against standard hydrochloric acid using Bromocresol Green–Methyl Red as indicator. The sample was first hydrolysed by breaking a closed ampoule, containing a known weight, in a known volume of 2 mol dm^{-3} sodium hydroxide solution in a closed vessel and aliquots were taken for analysis. Potassium was determined by flame photometry.

Physical Techniques.—Magnetic susceptibility was measured by means of a Gouy balance at ambient temperature. Infrared spectra were recorded for Nujol, Halocarbon, and Fluorolube mulls between silver chloride plates using a Perkin-Elmer 457 spectrometer. Electronic spectra were obtained using a Unicam SP 800 spectrophotometer equipped with a diffuse-reflectance attachment. Magnesium carbonate was used as reference material in the diffuse-reflectance studies. *X*-Ray powder data were obtained using a Philips diffractometer with an 11-cm camera and Cu-K_α radiation.

Preparation of Potassium Hexanitratocobaltate(III).—An excess of dinitrogen pentaoxide was collected at 195 K in a reaction vessel vented to the air through a phosphoric oxide guard tube. Potassium hexfluorocobaltate(III) was added against a counter current of pure dry nitrogen at 195 K. The vessel was removed from the cooling bath and allowed to warm to 273 K whilst still protected with the guard tube. After the light blue crystals of potassium hexafluorocobaltate(III) had completely changed to a green solid, nitryl fluoride and excess of dinitrogen pentaoxide were swept out of the vessel with pure dry nitrogen and any residual traces were removed by brief evacuation. The light green powdery product, being both oxygen and moisture sensitive, was collected and stored under pure dry nitrogen. The products of two independent preparations were subjected to analysis {Found: (1) Co, 10.5; K, 21.1; N, 15.5; (2) Co, 10.7; K, 20.7; N, 15.7. $K_3[Co(NO_3)_6]$ requires Co, 10.8; K, 21.4; N, 15.3%}.

The value $[NO_3{}^-] = 3.8 \times 10^{-2}$ mol dm^{-3} was calculated from the absorbance (0.53) of the band characteristic of nitrate ion at 33 200 cm^{-1} ($\varepsilon_{max.} = 7.01$ dm^3 mol^{-1} cm^{-1}) exhibited by a hydrolysate of the product (0.033 7 g) in 2 mol dm^{-3} sodium hydroxide solution (10 cm^3) contained in a 2 cm cell. The nitrate concentration expected for this hydrolysate, on the basis of the formula $K_3[Co(NO_3)_6]$, was 3.7×10^{-2} mol dm^{-3}. The reaction achieved can therefore be represented as in the equation.

$$K_3[CoF_6] + 6N_2O_5 \longrightarrow K_3[Co(NO_3)_6] + 6NO_2F$$

RESULTS AND DISCUSSION

Solution Properties.—The salt $K_3[Co(NO_3)_6]$ dissolves in water to give a green solution which gradually becomes violet, with effervescence, presumably as cobalt(II) species are formed, with evolution of oxygen. So far as organic solvents are concerned, the complex is soluble only in donors which can compete effectively with nitrate ligands for co-ordination positions. However, reactivity of the complex towards such solvents results in reduction to cobalt(II) species, with precipitation of $K[NO_3]$. Cobalt(III) nitrate undergoes a similar reduction in organic donor solvents.[14] In solvents such as CCl_4, $CHCl_3$, CH_2Cl_2, C_6H_6, and C_6H_{12} in which $Co(NO_3)_3$ forms reasonably stable green solutions [14] the insolubility and non-reactivity of $K_3[Co(NO_3)_6]$ discount any possibility that this reaction product is simply a mixture of cobalt(III) nitrate and potassium nitrate.

I.r. Spectrum.—The i.r. spectrum observed for freshly prepared mulls of $K_3[Co(NO_3)_6]$ is presented in Table 1 along with those for two other nitrate species for the purpose of comparison. The compound was unstable in all three mulling agents, decomposing to a pink cobalt(II) species.

TABLE 1

Infrared spectra (cm^{-1}) of $K_3[Co(NO_3)_6]$ and related compounds

$[NMe_4]_2[Zr(NO_3)_6]$[7] N,H,*	$Co(NO_3)_3$[14] S	$K_3[Co(NO_3)_6]$ N,H
1 600	1 658 (sh)	1 620 (sh)
1 572 } vs	1 624s	1 593s
1 544	1 528w	1 520br
		1 470s
1 292		1 290
} vs		} s
1 280	1 161 (sh)	1 270
	1 146s	1 100w
		1 047
		} w
1 021		1 035
} vs		
1 010	968s, sp	995
		990 } s, sp
		978
762s	770 (sh)	805w
	764s, sp	780 (sh)
731m		738vs
	681w, sp	690w
	505 (sh)	
	502s	490s, sp

N = Nujol mull, H = Halocarbon mull, S = solid film (100 K).

* Bands arising from NMe_4^+ not included.

The i.r. spectrum obtained 30 min after preparation of a Nujol mull exhibited a strong band at 1 600 cm^{-1} and weak bands at 1 730 and 3 300 cm^{-1}. These bands were not observed in the spectrum obtained from a freshly prepared mull and are attributed to the formation of an alkyl nitrate (1 600 cm^{-1}) and a carboxylic acid (1 730 and 3 300 cm^{-1}) by reactions of the complex with Nujol.[15]

For a freshly prepared mull, no bands were found in the 1 350—1 400 cm^{-1} region where the doubly degenerate stretching vibration of ionic nitrate occurs, and the through-the-plane rocking mode of NO_3^- at 830 cm^{-1} was also absent. This clearly indicates that all the nitrate groups are covalently bound to the central metal ion but in the absence of Raman data, which could not be obtained due to sample absorption and decomposition under laser excitation, it is not possible to distinguish between uni- and bi-dentate bonding. However, six bidentate ligands bound to the metal would generate a co-ordination number of 12, and this seems unlikely for Co^{III} which could achieve its preferred octahedral co-ordination if bonded to six unidentate nitrate groups.

Magnetic Properties.—The molar magnetic susceptibility of the product, χ_m, measured at 295.5 K and corrected for ligand diamagnetism, was 2.798×10^{-5} cm^3 mol^{-1} yielding $\mu_{eff.} = 0.819\mu_B$, consistent with the presence of a low-spin (t_{2g}^6) octahedral cobalt(III) complex. For comparison purposes, solid $Co(NO_3)_3$ exhibits $\mu_{eff.} = 0.94\mu_B$ at the same temperature.[14] Both of these values appear somewhat high, even allowing for a rather large contribution to the moment from temperature-independent paramagnetism (t.i.p.). This effect, predicted for octahedral low-spin d^6 complexes, usually produces moments in the range of 0.0—0.5μ_B. Some decomposition of $K_3[Co(NO_3)_6]$ to a paramagnetic cobalt(II) species during loading of the tube was suspected to be responsible for the high values obtained.

X-Ray Powder Diffraction Parameters.—The *d* spacings and relative intensities of the *X*-ray powder lines are presented in Table 2.

Electronic Spectra.—The diffuse-reflectance spectra of solid $K_3[Co(NO_3)_6]$ and $Co(NO_3)_3$ [14] (the latter recorded in the present work for purposes of comparison) showed marked similarities {$\nu_{max.}$: $K_3[Co(NO_3)_6]$, 15 800, 22 000 (sh), 25 000; $Co(NO_3)_3$, 16 300, 25 000 cm^{-1}}. A single-crystal *X*-ray crystallographic study [16] of the latter compound shows it to be composed of discrete, molecular $Co(NO_3)_3$ species involving the symmetrical bonding of three bidentate nitrate groups to give an irregular octahedral oxygen environment possessing D_3 symmetry about the cobalt atom. Furthermore, i.r. and electronic spectroscopic results show that this structure is retained when the compound is dissolved in essentially non-interacting solvents such as CCl_4.

TABLE 2

X-Ray powder diffraction data for $K_3[Co(NO_3)_6]$

d spacing (Å)	Intensity	*d* spacing (Å)	Intensity
12.653 9	5	2.572 4	5
9.184 1	10	2.447 2	5
6.645 9	10	2.351 8	100
5.533 4	10	2.272 1	10
5.165 9	5	2.210 8	30
4.680 4	90	2.117 0	30
4.372 9	30	2.035 6	80
4.113 1	10	1.875 2	5
3.611 7	5	1.743 3	5
3.460 1	30	1.661 6	20
3.154 4	40	1.572 1	20
3.019 0	10	1.444 4	30
2.881 5	80	1.376 7	5
2.764 6	10	1.293 0	20
2.696 0	5		

The positions of the absorption maxima recorded for a freshly prepared green solution of $K_3[Co(NO_3)_6]$ in acetonitrile are presented in Table 3. The reasonably close correspondence of the bands at 15 200 ($\varepsilon_{max.}$ 84), 22 500 ($\varepsilon_{max.}$ 100 dm^3 mol^{-1} cm^{-1}), and 25 500 cm^{-1} to those observed in the diffuse-reflectance spectrum of the complex indicates that the $[Co(NO_3)_6]^{3-}$ anion is present, initially, in the acetonitrile solution. Moreover, the data in Table 3 for some other cobalt(III) complexes support the low-spin octahedral character of $[Co(NO_3)_6]^{3-}$. The band at 25 500 cm^{-1} in the solution spectrum of the latter can be assigned to the highest energy ${}^1E_{1g} \leftarrow {}^1A_{1g}$

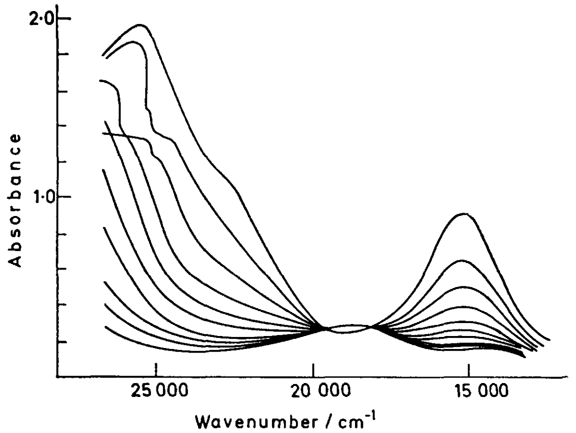
transition of a low-spin octahedral t_{2g}^6 system, this band usually being obscured by very intense charge-transfer bands.

Complete reduction to pink cobalt(II) species, with concurrent precipitation of $K[NO_3]$, occurred in the acetonitrile solution of $K_3[Co(NO_3)_6]$ over a period of 1—2 h. This process was monitored by successively recording visible spectra every 10 min (Figure). The progress of the conversion was apparent from the gradual decrease in intensity and eventual disappearance of the bands at 15 200, 22 500, and 25 500 cm^{-1} and the appearance of a band at 18 500 cm^{-1} assigned to the highest energy $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ spin-allowed transition of octahedrally co-ordinated high-spin cobalt(II) ($t_{2g}^5e_g^2$). The two isosbestic points at 18 100 and 19 500 cm^{-1} (Figure) indicate that a simple one-step reaction is occurring, most probably involving only two species.

TABLE 3

Energies (cm^{-1}) of electronic absorption maxima for some cobalt(III) complexes

	Complex						
	$[CoF_6]^{3-}$	$[Co(OH_2)_6]^{3+}$	$[Co(CO_3)_3]^{3-}$	$[Co(C_2O_4)_3]^{3-}$	$Co(NO_3)_3$ in CCl_4 (ref. 14)	$[Co(NO_3)_6]^{3-}$ in MeCN	Assignment
high spin	11 800 14 000						$^5E_g \leftarrow {}^5T_{2g}$
low spin		16 500	15 700	16 500	16 400	15 200	$^1T_{1g} \leftarrow {}^1A_{1g}$
		24 950	22 800	23 800	23 150	22 500	$^1T_{2g} \leftarrow {}^1A_{1g}$
						25 500	$^1E_g \leftarrow {}^1A_{1g}$



Electronic spectra of $K_3[Co(NO_3)_6]$ in acetonitrile recorded at 10-min intervals

Ligand-field Parameters for $[Co(NO_3)_6]^{3-}$.—The spectrum of $K_3[Co(NO_3)_6]$ in acetonitrile solution (freshly prepared) was analysed using the assignments given in Table 3 and the relevant Tanabe–Sugano diagram, yielding values of $\Delta_0 = 16\,200$ and $B = 466$ cm^{-1}. Comparison with the values obtained from the electronic spectrum of $Co(NO_3)_3$ in CCl_4 solution ($\Delta_0 = 17\,500$, $B = 508$ cm^{-1}) might be taken to suggest that Δ_0 and B values for nitrate ligands are somewhat sensitive to the manner in which the ligands are bound; as noted previously, nitrate co-ordination in $Co(NO_3)_3$ is known to be symmetrically bidentate and the ligands in $[Co(NO_3)_6]^{3-}$ are likely to be unidentate in view of the small ionic radius of Co^{3+} (0.63 Å). It is also interesting to recall that a theoretical Δ_0 value of 17 800 cm^{-1} was calculated for the $[Co(NO_3)_6]^{3-}$ complex by application of the average-environment rule to the spectra of $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_5(NO_3)]^{2+}$, assuming unidentate nitrate co-ordination.[12]

The fact that Co^{III} exists in the low-spin state in the complex $K_3[Co(NO_3)_6]$, where Δ_0 has been shown to have the rather low value of 16 200 cm^{-1}, implies that the average pairing energy P for this complex must be reduced at least 20% below the free-ion value of 22 000 cm^{-1}.

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