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Crystal Structure and Vibrational Spectra of $[C(NH_2)_3]_2[Cr_3(\mu_3\text{-}O)(OOCC_2H_5)_6F_3]$

Christopher E. Anson, Nittayaporn Chai-Sa'ard, John P. Bourke, Roderick D. Cannon,*
Upali A. Jayasooriya, and Anne K. Powell

School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K.

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The title complex crystallises in the tetragonal system, $I4_1/a$, with $a = 14.741(2)$ Å, $c = 34.774(4)$ Å, and $Z = 8$. The trinuclear complex lies on a crystallographic 2-fold axis. The three Cr atoms form an almost equilateral triangle, with one F bonded to each: Cr–(μ_3-O) = 1.908(4), 1.909(2) Å; Cr–Cr = 3.308(1), 3.302(2) Å. The Cr–F distances (1.909(4), 1.914(3) Å) are the longest yet observed for any chromium(III) complex, and the Cr–F stretching frequencies (492 and 460 cm^{-1}) are the lowest.

Introduction

Trinuclear complexes of the general type $[M_3O(OOCR)_6L_3]^{n+}$ have a wide variety of interesting chemical and physical properties which in various ways are due to the presence of the oxide-centered triangular metal ion cluster.[1] Antiferromagnetic coupling between the metal ions and electron delocalization in cases when the metal ions form a mixed-valency cluster[2–4] are being actively studied. It is also becoming apparent that the bonding of the peripheral ligands L is of interest. A review of the early literature has suggested that in general these ligands are more labile than are the same ligands attached to the same metals in mononuclear complexes.[1] Two recent kinetic studies seem to confirm this: Sykes and co-workers studied anation reactions of the mixed-valence triiridium(IV,IV,III) complex $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$. They concluded that rate constants are relatively high for substitution at either Ir^{III} or Ir^{IV} and that the central nitrido ligand exerts a significant trans-labilizing effect.[5] Sasaki and co-workers have studied water replacement by methanol in the ruthenium(III) and rhodium(III) complexes $[M_3O(OOCCH_3)_6(H_2O)_3]^+$ (M_3 = Ru_3, Rh_3, Ru_2Rh).[6a] They have found labilization effects and have proposed predominantly dissociative mechanisms for these and other related substitutions.[6b,c] However there is still very little information on the stability or lability of similar complexes of metals of the first transition series.

Among the complexes of the type $[Cr^{III}_3O(OOCR)_6L_3]^{n+}$ with three identical ligands L, a number of anionic fluoride complexes were reported by Weinland and Lindner.[7] The best-characterized is the guanidinium salt of the hexakis(μ-propionato) complex. This was originally formulated as a dihydroxy species, $[C(NH_2)_3]_2[Cr_3(OH)_2(OOCC_2H_5)_6F_3]$, on the basis of an incorrect theory of the trinuclear structure.[7] Revising the formula of the complex to the oxo-centered form, it was conjectured[1] that the true formula might be anhydrous $[C(NH_2)_3]_2[Cr_3O(OOCC_2H_5)_6F_3]$, and this has proved to be the case. In preliminary kinetic studies, we have found that the compound does contain coordinated fluoride, which is only slowly released in aqueous solution at room temperature. We report here a crystal structure determination and a detailed study of the IR and Raman spectra of the complex. The results confirm that the chromium–fluoride bonds are indeed significantly weaker than those in mononuclear complexes, as shown both by greater bond lengths and by lower stretching frequencies.

Experimental Section

Preparations. The complex $[Cr_3O(OOCC_2H_5)_6(OH_2)_3]Cl{\cdot}3H_2O$ was prepared by a modification of the method previously used for the corresponding acetato complex.[8] A 33.3-g portion of hydrated chromic chloride, $CrCl_3{\cdot}6H_2O$ (0.125 mol), was dissolved in 300 mL of water, and 188 mL of 2 M sodium hydroxide (0.375 mol) was slowly added with stirring. The precipitated hydroxide was collected by filtration on double-thickness Whatman No. 1 filter paper, washed several times with water, then transferred to a deep Petri dish and mixed thoroughly with 18.5 g of anhydrous propionic acid (0.25 mol). After heating and stirring till all solid had dissolved, the mixture was allowed to evaporate to dryness on a steam bath. The sticky green solid was redissolved in 100 mL of 1.0 M hydrochloric acid and again evaporated to dryness. A granular green solid was obtained and this was recrystallized twice from 0.5 M HCl. Finally the dark green crystals were collected and dried between filter paper. Anal. Calcd: C, 28.66; H, 5.57; Cl, 4.71. Found: C, 28.68; H, 5.51; Cl, 4.62.

The complex $[C(NH_2)_3]_2[Cr_3(\mu_3\text{-}O)(OOCC_2H_5)_6F_3]$ was prepared by a modification of the method of Weinland and Lindner.[7] Finely ground guanidinium carbonate, $[C(NH_2)_3]_2(CO_3)$ (3.6 g, 0.2 mol), was added in small portions to a mixture of 2.0 g of anhydrous hydrofluoric acid and 10 g of water in a Teflon beaker. To this was added a solution of 7.4 g of the above propionato complex (0.1 mol) in 35 mL of water with stirring. After this mixture was allowed to stand over concentrated sulfuric acid in a closed Teflon jar for several days, dark green crystals were collected by filtration, usually in 70–80% yield. The crystals were of two forms: (A) long bundles of fused needles and (B) tetragonally elongated octahedra, the latter comprising only 2–3% of the total, but easily separated by hand. Both forms analyzed correctly for the title compound, and both gave essentially identical IR spectra, which differed only in the solid-state splittings of some bands. Anal. Calcd: C, 30.50; H, 5.33; N, 10.67; Cr, 19.8; F, 7.2. Found, form A: C, 30.11; H, 5.30; N, 10.70; Cr, 19.6; F, 6.5. Found, form B: C, 30.44; H, 5.31; N, 10.06. In addition to the dark green crystals, a paler green shiny crystalline material was also formed. When treated separately with water, the pale green material was found to be practically insoluble, while the dark green crystals dissolved less slowly—though only with decomposition. However when the reaction mixture was allowed to stand at room temperature for 1 week, the pale green material all dissolved and the yield of dark green material increased. The IR spectrum of the pale green material suggested the salt $[C(NH_2)_3]_3[CrF_6]{\cdot}H_2O$. Anal. Calcd: C, 9.81; H, 5.45; N, 34.33. Found: C, 10.0; H, 5.38; N, 33.2. To obtain the deuterioguanidinium complex, $[C(ND_2)_3]_2[Cr_3O(OOCC_2H_5)_6F_3]$, the salt $[C(ND_2)_3]F$ was prepared

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[1] Cannon, R. D.; White, R. P. *Prog. Inorg. Chem.* **1988**, *36*, 195.

[2] Blondin, G.; Girerd, J.-J. *Chem. Rev.* **1990**, *90*, 1359.

[3] Cannon, R. D.; Jayasooriya, U. A.; White, R. P. In *Mixed Valency Systems: Applications in Chemistry, Physics and Biology*; Prassides, K., Ed.; NATO ASI Series C: Mathematical and Physical Sciences 343; Kluwer: Dordrecht, The Netherlands, 1991; pp 283–298.

[4] Hendrickson, D. N. In *Mixed Valency Systems: Applications in Chemistry, Physics and Biology*; Prassides, K., Ed.; NATO ASI Series C: Mathematical and Physical Sciences 343; Kluwer: Dordrecht, The Netherlands, 1991; pp 67–90.

[5] Hills, E. F.; Richens, D. T.; Sykes, A. G. *Inorg. Chem.* **1986**, *25*, 3144.

[6] (a) Sasaki, Y.; Tokiwa, A.; Ito, T. *J. Am. Chem. Soc.* **1987**, *109*, 6341. (b) Nakata, K.; Nagasawa, A.; Soyama, N.; Sasaki, Y.; Ito, T. *Inorg. Chem.* **1991**, *30*, 1575. (c) Sasaki, Y. *Inorganic Mechanisms Discussion Group, 1991 Meeting*, Royal Society of Chemistry: London, 1991; Abstract L3.

[7] Weinland, R.; Lindner, J. *Z. Anorg. Allg. Chem.* **1930**, *190*, 285.

[8] White, R. P.; Chai Sa-ard, N.; Bollen, S. K.; Cannon, R. D.; Jayasooriya, U. A.; Robertson, S. T.; Steigenberger, U.; Tomkinson, J. *Spectrochim. Acta* **1990**, *46A*, 903.

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Table I. Crystallographic Data for $[C(NH_2)_3]_2[Cr_3O(OOCC_2H_5)_6F_3]$

chemical formula: $C_{20}H_{42}Cr_3F_3N_6O_{13}$	$Z = 8$
fw = 787.61	$T = 25$ °C
space group: $I4_1/a$	λ(Mo Kα) = 0.710 73 Å
$a = 14.741(2)$ Å	$\rho_{obsd} = 1.41$ g cm^{-3}
$c = 34.774(4)$ Å	$\rho_{calcd} = 1.40$ g cm^{-3}
$V = 7555.2$ Å^3	μ(Mo Kα) = 8.60 cm^{-1}
	R(unit weights) = 0.0494

separately by reacting guanidinium carbonate with aqueous HF, then deuterated by repeatedly dissolving in D_2O and evaporating to dryness, and the preparation was continued as above using D_2O in place of H_2O and working in a glovebox flushed with dry nitrogen.

In aqueous solution the visible absorption spectrum showed the expected two bands at 450 and 610 nm, and when the solution was allowed to stand, these progressively shifted to shorter wavelengths, with an isosbestic point at 508 nm, over a period of 8 h. Spectrophotometric measurements using the color developed by the zirconyl–alizarin reaction[9] confirmed the gradual release of fluoride ion, and the retention of the prominent shoulder at ca 660 nm, assigned to the enhanced quartet–doublet transitions of chromium(III),[10] confirmed that the oxo-centered trinuclear complex was largely retained during the period of reaction. Mixtures of the triaquo complex with fluoride, e.g. 1.0 M ammonium fluoride, showed the reverse spectral changes, consistent with a progressive anation reaction.

Analyses. Chromium was determined by oxidation to dichromate.[11] Weighed samples were boiled with excess aqueous potassium perdisulfate, $K_2S_2O_8$, in the presence of a small amount of silver nitrate. After continued boiling to destroy excess persulfate, the chromium(VI) was determined by adding a measured excess of ammonium iron(II) sulfate, and back-titrating with cerium(IV), using a platinum electrode. Fluoride was determined potentiometrically. An accurately weighed sample of the fluorocomplex (ca. 0.1 g) was dissolved in 5 mL 0.5 M NaOH. Aqueous "100 vol" hydrogen peroxide was added dropwise with heating and stirring until the color had changed from green to yellow (about 2 mL was required). After cooling, the solution was acidified to pH 6–7 with nitric acid and then titrated with 0.2 M thorium nitrate solution (pH 2.7), using a Corning SSISE fluoride-sensitive electrode. The thorium solution was standardized by titrating a commercially supplied standard KF solution. Satisfactory end points were achieved using unbuffered media as described. With buffers such as acetate (pH ≈ 5) the endpoints were less well-defined.

Vibrational Spectra. FT-IR spectra of KBr disks were recorded on a Digilab FTS-40/80 spectrophotometer at 90 K using a Beckman RIIC conventional low-temperature cell. Far-IR spectra of Nujol mulls were recorded at room temperature on a Nicolet 20F FTIR spectrophotometer. FT-Raman spectra were recorded on a Bruker FRA106/IFS66 spectrophotometer equipped with a Nd-YAG laser, lasing at 1064 nm.

X-ray Data Collection and Processing. (See Table I.) Systematic absences (hkl, $h + k + l = 2n + 1$; $hk0$, $h(k) = 2n+1$; $00l$, $l = 4n + 2$) are consistent with space group $I4_1/a$. Conditions: Nicolet-Siemens P3/V diffractometer, ω–2θ scan mode, scan width = 1.2°, variable scan speeds 1.5–14.65 deg min^{-1}, graphite monochromator Mo Kα radiation, 4343 unique reflections, $2.0° < 2\theta < 50°$ ($+h,+k,+l$), 2827 with $F_o > 6\sigma(F_o)$ were considered observed. Three standard reflections every 50 reflections showed no crystal decay. Lorentz and polarization corrections were applied to the data as well as an empirical absorption correction.[11]

Structure Analysis and Refinement. The chromium atoms were located from a Patterson synthesis. The remaining non-hydrogen atoms were located from successive least-squares refinements and Fourier difference maps. The methyl carbon of one of the ethyl groups was found to be disordered; it was modeled as two half-carbons in subsequent refinements. The high magnitude and anisotropy of the methyl carbon atoms in the final structure suggests that further unresolved disorder of these atoms is also present. Further cycles of refinement and Fourier difference maps located all six of the guanidinium hydrogen atoms. These were refined without geometrical constraint. Hydrogens were placed in calculated positions for the two ordered ethyl groups with half-hydrogens in calculated positions on the disordered methyl. No attempt was made to model th hydrogens on the disordered methylene carbons. All hydrogen atoms were assigned isotropic thermal parameters $U = 1.2U_{iso}$, where values of U_{iso} relate to the atoms to which the hydrogens are bonded. All non-hydrogen atoms were then assigned anisotropic temperature factors and the structure was refined to convergence, using unit weights. Attempts to introduce a weighting scheme gave no improvement in the analysis of variance. The final residual was $R = 0.0494$. The maximum |shift/esd| in the final cycle was 0.205. The largest peak in the final difference Fourier map was 0.364 e Å^{-3}, 1.29 Å from Cr(1). Atomic coordinates are listed in Table II.

Table II. Atomic Coordinates and Thermal Parameters U_{eq}[a] (with Esd) for $[C(NH_2)_3]_2[Cr_3(\mu_3\text{-}O)(OOCC_2H_5)_6F_3]$

atom	x/a	y/b	z/c	U(eq)
Cr(1)	1.00000[b]	0.00000[b]	0.84765(3)	0.0422(5)
Cr(2)	0.89460(5)	0.03788(5)	0.76522(2)	0.0462(4)
O(1)	1.0000[b]	0.0000[b]	0.7928(1)	0.042(2)
F(1)	1.0000[b]	0.0000[b]	0.9025(1)	0.062(2)
F(2)	0.7854(2)	0.0748(2)	0.7399(1)	0.064(2)
O(11)	0.8751(2)	−0.0450(2)	0.8534(1)	0.059(2)
C(11)	0.8157(3)	−0.0706(3)	0.8295(1)	0.051(3)
C(12)	0.7462(4)	−0.1375(4)	0.8429(2)	0.071(4)
C(13)	0.7783(7)	−0.2292(5)	0.8386(4)	0.182(10)
O(12)	0.8132(2)	−0.0444(2)	0.7949(1)	0.056(2)
O(21)	0.9633(2)	0.1289(2)	0.8507(1)	0.061(2)
O(21)	0.9159(3)	0.1743(3)	0.8280(2)	0.059(3)
O(22)	0.9045(6)	0.2757(4)	0.8347(2)	0.099(5)
O(23A)	0.9499(16)	0.3254(10)	0.8050(7)	0.175(20)
C(23B)	0.9530(14)	0.3158(10)	0.8637(6)	0.147(16)
O(22)	0.8747(2)	0.1435(2)	0.7991(1)	0.067(2)
O(31)	0.8987(2)	−0.0615(3)	0.7276(1)	0.073(2)
C(31)	0.9582(4)	−0.1173(4)	0.7183(2)	0.070(4)
C(32)	0.9296(6)	−0.1886(7)	0.6890(3)	0.141(7)
C(33)	0.9948(10)	−0.2571(14)	0.6810(5)	0.522(32)
O(32)	0.9615(2)	0.1190(3)	0.7304(1)	0.075(3)
C(01)	0.8955(4)	−0.1460(4)	0.9586(2)	0.065(3)
N(01)	0.8561(4)	−0.0736(4)	0.9448(2)	0.087(4)
H(911)	0.8948(40)	−0.0312(39)	0.9287(17)	0.092[c]
H(912)	0.8191(42)	−0.0487(42)	0.9607(18)	0.092[c]
N(92)	0.8557(4)	−0.1915(4)	0.9871(2)	0.080(4)[c]
H(921)	0.8032(40)	−0.1623(39)	0.9975(17)	0.088[c]
H(922)	0.8871(40)	−0.2297(41)	0.9992(17)	0.088[c]
N(93)	0.9716(4)	−0.1752(4)	0.9431(2)	0.084(4)
H(931)	1.0034(40)	−0.1300(40)	0.9274(17)	0.092[c]
H(932)	1.0075(40)	−0.2164(40)	0.9566(17)	0.092[c]

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$. [b] Parameter value required by crystal symmetry. [c] Parameter value fixed in refinement.

Table III. Selected Bond Lengths and Hydrogen-Bonding Distances (Å) in $[C(NH_2)_3]_2[Cr_3O(OOCC_2H_5)_6F_3]$

Cr(1)–Cr(2)	3.308(2)	Cr(2)–Cr(2′)	3.302(1)
Cr(1)–O(1)	1.908(4)	Cr(2)–O(1)	1.909(2)
Cr(1)–F(1)	1.907(4)	Cr(2)–F(2)	1.914(3)
Cr(1)–O(11)	1.966(3)	Cr(1)–O(21)	1.978(3)
Cr(2)–O(12)	1.995(3)	Cr(2)–O(22)	1.975(4)
Cr(2)–O(31)	1.966(4)	Cr(2)–O(32)	1.966(4)
C(11)–O(11)	1.254(5)	C(11)–O(12)	1.264(5)
C(21)–O(21)	1.249(6)	C(21)–O(22)	1.257(6)
C(31)–O(31)	1.245(7)	C(31)–O(32′)	1.257(7)
C(91)–N(91)	1.306(6)	C(91)–N(92)	1.331(7)
C(91)–N(93)	1.319(7)	N(91)–N(911)	1.01(6)
N(91)–H(912)	0.86(6)	N(92)–H(921)	0.96(6)
N(92)–H(922)	0.84(6)	N(93)–H(931)	0.98(6)
N(93)–H(932)	0.93(6)		
N(91)···F(1)	2.800	H(911)–F(1)	1.86
N(93)···F(1)	2.973	H(931)–F(1)	2.08
N(92)···F(2′)	2.818	H(921)–F(2′)	1.90
N(91)···F(2′)	3.084	H(912)–F(2′)	2.37
N(93)···F(2″)	2.754	H(932)–F(2″)	1.84
N(92)···F(2″)	3.513	H(922)–F(2″)	2.88

Results

Structure. Selected bond distances and angles are listed in Tables III and IV. Diagrams of molecular structures are shown in Figures 1 and 2. The unit cell contains eight symmetry-related formula units.

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(9) Vogel, A. I. *A Textbook of Qualitative Chemical Analysis*, 3rd ed.; Longmans: London, reprinted 1951; p 272.

(10) Dubicki, L.; Day, P. *Inorg. Chem.* **1972**, *11*, 1868.

(11) (a) Vogel, A. I. *A Textbook of Quantitative Inorganic Analysis*, 3rd ed., Longmans: London, 1961; p 311. (b) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

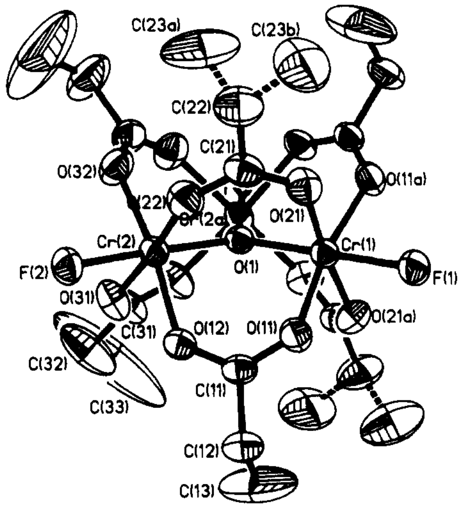

Figure 1. Structure of the complex anion in $[C(NH_2)_3]_2[Cr_3O(OOCC_2H_5)_6F_3]$.

Table IV. Selected Bond Angles (deg) in $[C(NH_2)_3]_2[Cr_3O(OOCC_2H_5)_6F_3]$

Cr(1)–O(1)–Cr(2)	120.2(1)	Cr(2)–O(1)–Cr(2)	119.6(2)
O(1)–Cr(1)–F(1)	180	O(1)–Cr(2)–F(2)	177.1(1)
O(11)–C3(1)–F(1)	84.3(1)	O(22)–Cr(2)–F(2)	86.0(2)
O(21)–Cr(1)–F(1)	87.0(1)	O(32′)–Or(2)–F(2)	86.0(2)
O(12)–Cr(2)–F(2)	84.5(1)		
O(11)–Cr(1)–O(1)	95.7(1)	O(22)–Cr(2)–O(1)	92.9(1)
O(21)–Cr(1)–C(1)	93.0(1)	O(31)–Cr(2)–O(1)	95.2(1)
O(12)–Cr(2)–O(1)	93.0(1)	O(32)–Cr(2)–O(1)	95.2(1)
O(11)–C(11)–O(12)	124.5(4)	O(31)–C(31)–O(32)	126.1(6)
O(21)–C(21)–O(22)	125.4(5)		
C(11)–C(12)–C(13)	110.0(6)	C(23)–C(22)–C(23)	93.9(10)
C(21)–C(22)–C(23)	108.5(10)	C(31)–C(32)–C(33)	114.2(7)
C(21)–C(22)–C(23)	118.1(9)		
N(91)–C(91)–N(92)	119.3(6)	H(911)–N(91)–H(912)	110.(7)
N(91)–C(91)–N(93)	120.0(6)	H(921)–N(92)–H(912)	110.(7)
N(92)–C(91)–N(93)	120.6(6)	H(921)–N(93)–H(932)	110.(7)

The trichromium complex anions are located on sites of C_2 symmetry. The Cr_3O triangle is thus planar by imposed symmetry. The thermal ellipsoid of the central oxygen shows no significant elongation in the direction perpendicular to the plane, thus indicating that the planarity is real and not merely the result of disorder (Figure 1). The metal ion triangle is slightly but just significantly nonequilateral, with Cr–Cr distances of 3.308(1), 3.308(1), and 3.302(2) Å. The central oxygen is within less than one esd of the center of gravity of the three chromiums. Of the six symmetry-distinct Cr–(carboxylate O) distances, five lie in the range 1.978–1.966 Å and show no significant differences. The sixth one, Cr(2)–O(12), at 1.995(3) Å is slightly longer. As shown in Figure 2, the atom O(12) is hydrogen-bonded to two guanidinium NH_2 groups. The Cr–F distances are effectively equivalent, 1.907, 1.914, and 1.914 Å, with average esd = 0.004 Å. In summary, there appear to be only minimal differences between the coordination environments of the three chromium atoms.

The guanidinium ions are on general sites, but the CN_3 units do not deviate significantly from planarity or trigonal symmetry. As mentioned above, the H atoms of the NH_2 groups were located and refined. They do not lie in the CN_3 plane. They are significantly hydrogen bonded to the fluorines, as shown in Figure 2, and the fluorines lie 0.71, 0.41, and 0.94 Å to one side of the plane.

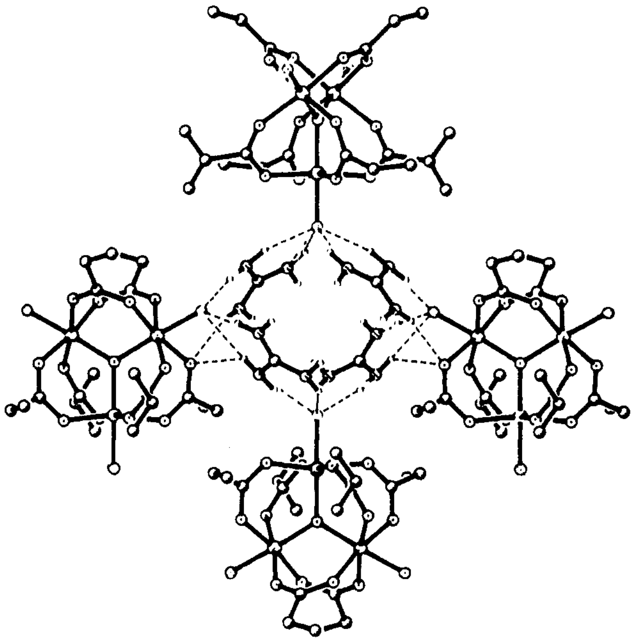

Figure 2. Hydrogen bonding of the guanidinium cations in $[C(NH_2)_3]_2[Cr_3O(OOCC_2H_5)_6F_3]$.

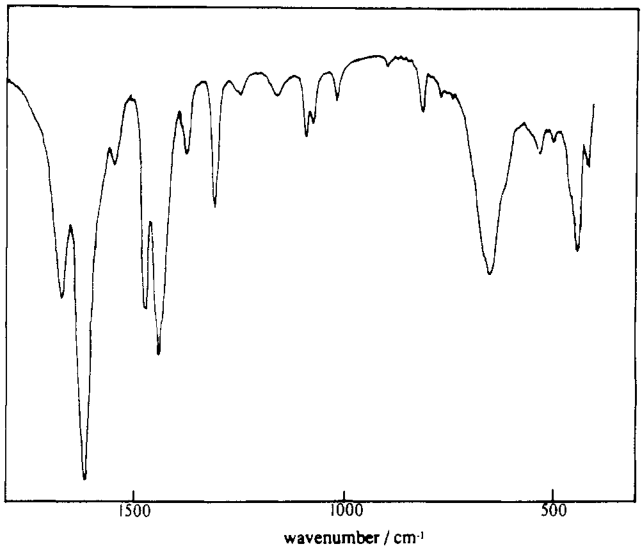

Figure 3. IR spectrum of $[C(NH_2)_3]_2[Cr_3O(OOCC_2H_5)_6F_3]$ from 1600 to 400 cm^{-1}. Conditions: $T = 100$ K. Vertical scale, transmittance/arbitrary units.

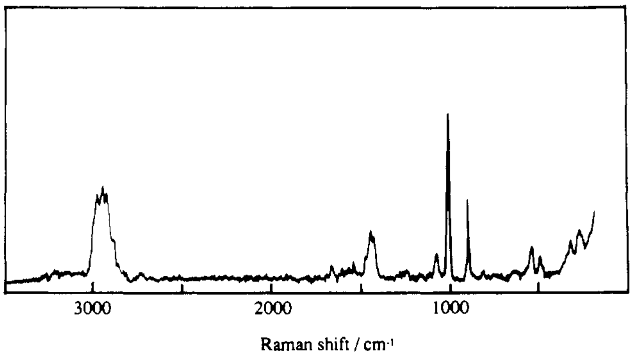

Figure 4. Raman spectrum of $[C(NH_2)_3]_2[Cr_3O(OOCC_2H_5)_6F_3]$. Conditions: $T = 100$ K. Vertical scale, scattering intensity/arbitrary units.

Vibrational Spectra. IR and Raman spectra of the title compound are shown in Figures 3–6, and selected frequencies and assignments are listed in Table V. In the range above 800

Table V. Selected Vibrational Frequencies (cm^{-1}) in IR and Raman Spectra of Complexes $[Cr_3O(OOCC_2H_5)_6X_3]^{n\pm}$

	[F-adduct][a]		[H$_2$O-adduct][b]	[C(NH$_2$)$_3$]Cl[c]		EtCOONa[d]
assignment	IR	R	IR	IR	R	IR
$\nu(H_2O)$			3380 vs, br			
$\nu(NH_2)$ + overtones	3416 vs			3396 vs	3410	
	3347 sh			3300 sh		
					3328	
					3275	
	3253 mw			3230 vw		
		3300–3200 vbr				
	3148 ms			3152 m	3192 vw	
	3095 m					
$\nu(CH)$ + overtones	2986 w		2993 mw			2974
	2973 w	2976 m	2962 mw			2955
	2947 w	2948 s	2940 w			2943
	2917 w	2924 m				2936
	2876 w		2879 vw			2906
	2848 w		2852 w			2874
$\nu_a(CN_3)$	1671 ms	≈1700 w		1660s 1843 s	1660 sh 1630 w	
$\nu_a(CO_2)$	1616 vs		1595 vs			1565
$\delta(NH_2)$	1542 mw	1544 w		1553 vw	1553 s	
$\delta_a(CH_3)$	1472 ms		1467			1464 1443
$\nu_s(CO_2)$	1441 s	1450 m 1434 m	1438 s			1430
$\delta(CH_2)$	obsc		obsc			1417
$\delta_s(CH_3)$	1372 mw 1367 sh		1378 m			1376 1369
$\omega(CH_2)$	1306 m		1310 m			1298
$\tau(CH_2)$	1244 w	≈1260 w	1243 w			1250
$\rho(NH_2)$	1158 w			1120 mw		
$\nu_a(CCC)$	1088 1071	1077 mw	1099 1074		1076	
$\rho(CH_3)$	1016 mw		1021 mw			1004
$\nu_s(CN_3)$		1013 vs			1007 vs	
$\nu_s(CCC)$	895 vw	903 s	896 vw			881
$\rho(CH_2)$	809 m		813 m			815
overtone?	766 w		754 w			
$\pi(CN_3)$	738 w		724 w			
$\nu_a(Cr_3O)$	663 m,sh		688 m			
$\delta(CO_2)$	651 s		663 s			647
$\rho(CO_2)$	≈640 m, sh		632 m			581
$\pi(CO_2)$	618 w, sh		612 w, sh			508
$\delta_a(CN_3)$	541 wsh	541 m		529 w	526 m	
$\omega_s(NH_2)$	531 mw			518 m		
$\omega_a(NH_2)$	499 w			490 m		
$\nu_s(CrF)$		492 mw				
$\nu_a(CrF)$	460 m, sh					
$\nu_d(CrO_4)$	444s 415 m		438 s 434 mw			
$\nu_s(CrO_4)$	c 335 vw	325 m				
$\pi(Cr_3O)$	≈270 w?					
EtCO$_2$[e]		270 m				286
$\pi(CrO_4)$	240 m	219				
$\nu_s(Cr_3O)$		165 s				

[a] $[C(NH_2)_3]_2[Cr_3O(OOCC_2H_5)_6F_3]$. [b] $[Cr_3O(OOCC_2H_5)(OH_2)_3]Cl\cdot 3H_2O$. [c] Reference 13. [d] Reference 17. [e] Skeletal mode.

cm^{-1} the assignments were straightforwardly based on previous studies of oxo-centered trinuclear carboxylate complexes,[12] together with comparisons with spectra of $[Cr_3O(OOCC_2H_5)_6(OH_2)_3]Cl\cdot 3H_2O$ and of C_2H_5COONa[17] and $[C(NH_2)_3]Cl$[13] as previously reported in the literature. (Of the various guanidinium salts which have been studied, the chloride is the most appropriate, as the X-ray crystal structure[14] indicates a pattern of hydrogen bonding of the NH_2 groups very similar to what we have found here.) Our main interest in the spectra was in the vibrations of the metal–oxygen framework and in locating the chromium–fluorine stretches.

As has been discussed before,[12a] the expected vibrations of the central Cr_3O cluster are the in-plane asymmetric stretch, ν_{as}, usually at ca. 650–670 cm^{-1}, the out-of-plane deformation π-(Cr_3O), ca. 300 cm^{-1}, and the in-plane symmetric stretch, ν_s, ca. 150 cm^{-1}. The fourth predicted mode, δ_{as}, has never been observed and is presumed to be below 100 cm^{-1}. In the present case we find ν_s prominent in the Raman at 165 cm^{-1}. In the region 300–250 cm^{-1} of the IR there are numerous weak features, but as yet we cannot unambiguously assign $\pi(Cr_3O)$ (the IR band at ca. 270 cm^{-1} is probably the best candidate). The very broad and strong IR band in the region 700–600 cm^{-1} has at least three main overlapping features. In a rather better-resolved spectrum

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(12) (a) Johnson, M. K.; Powell, D. B.; Cannon, R. D. *Spectrochim. Acta* **1981**, *37A*, 995. (b) Montri, L.; Cannon, R. D. *Spectrochim. Acta* **1985**, *41A*, 643. (c) Meesuk, L.; Jayasooriya, U. A.; Cannon, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 2009. (d) Meesuk, L.; Jayasooriya, U. A.; Cannon, R. D. *Spectrochim. Acta* **1987**, *43A*, 687. (e) Meesuk, L.; White, R. P.; Templeton, B. G.; Jayasooriya, U. A.; Cannon, R. D. *Inorg. Chem.* **1990**, *29*, 2389.

(13) (a) Angell, C. L.; Sheppard, N.; Yamaguchi, A.; Shimanouchi, T.; Miyazawa, T.; Mizushima, S. *Trans. Faraday Soc.* **1957**, *53*, 589. (b) Bonner, O. D. *J. Phys. Chem.* **1977**, *81*, 2247.

(14) Haas, D. J.; Harris, D. R.; Mills, H. H. *Acta Crystallogr.* **1965**, *19*, 676.

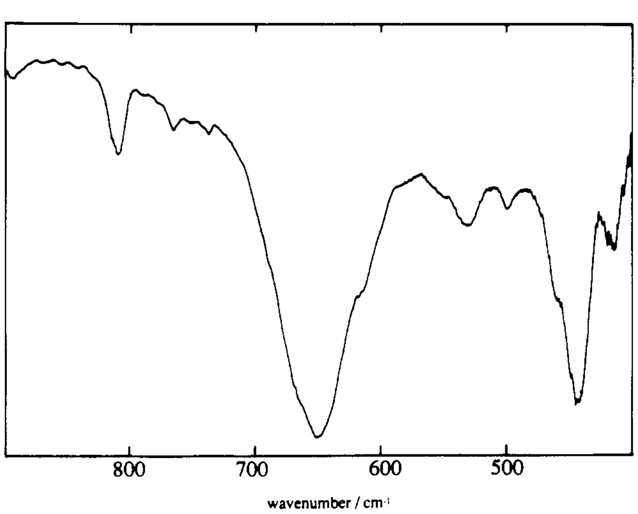

Figure 5. IR spectrum of $[C(NH_2)_3]_2[Cr_3O(OOCC_2H_5)_6F_3]$. Conditions: T = 100 K. Vertical scale, transmittance/arbitrary units.

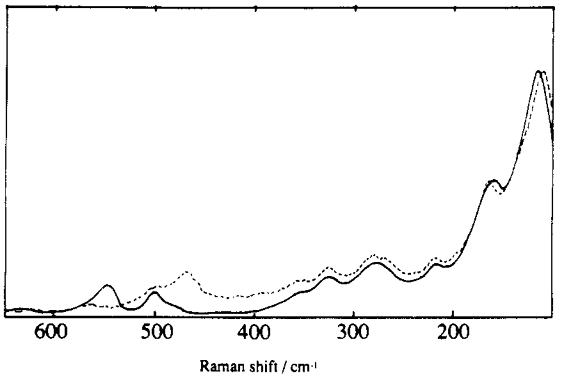

Figure 6. Raman spectra of $[C(NH_2)_3]_2[Cr_3O(OOCC_2H_5)_6F_3]$ (full line) and $[C(ND_2)_3]_2[Cr_3O(OOCC_2H_5)_6F_3]$ (broken line). Conditions: T = 100 K. Vertical scale, scattering intensity/arbitrary units.

of the triaquo complex (not shown) we assign three features at 663, 632, and 612 cm^{-1} to the $\delta(CO_2)$, $\rho(CO_2)$, and $\pi(CO_2)$ modes of the propionate ligands, respectively, on the basis of comparisons with the free anion in the sodium salt and frequency shifts on coordination of the same modes of the acetate ion. In the spectrum of the fluoro complex, the modes are assigned similarly, although $\rho(CO_2)$ is not clearly seen and presumably forms a shoulder on the low-frequency side of the very sharp $\delta(CO_2)$ band. We assign the shoulder at 663 cm^{-1} in the fluoro complex (688 cm^{-1} in the aquo complex) to $\nu_{as}(Cr_3O)$.

The chromium–carboxylate oxygen (CrO_4) modes can be assigned by reference to the published assignments of the acetato complexes.[12] We find that modes of the three CrO_4 units couple significantly under the idealized D_{3h} symmetry. The IR bands (with no Raman counterparts) at 444 and 415 cm^{-1} are assigned to the a_2'' and e' components of $\nu_d(CrO_4)$, where $\nu_d(CrO_4)$ is the mode which would correlate with the e_u component of $\nu(CrO_4)$ in a CrO_4 unit of D_{4h} symmetry. The Raman band at 325 cm^{-1} is assigned to the a_1' $\nu_s(CrO_4)$ mode, while the very weak IR shoulder at ca. 335 cm^{-1} may result from the e' component of this mode. The Raman band at 219 cm^{-1} and the IR band at 240 cm^{-1} are assigned to the a_1' and e' components of the out-of-plane CrO_4 deformation $\pi(CrO_4)$, and the 270 cm^{-1} Raman band is assigned to a propionato skeletal mode.

To identify the Cr–F stretches we turn to direct comparisons of the spectra of the trifluoro and triaquo complexes $[C(NH_2)_3]_2[Cr_3O(OOCC_2H_5)_6F_3]$ and $[Cr_3O(OOCC_2H_5)_6(OH_2)_3]Cl\cdot 3H_2O$. In the range 600–400 cm^{-1} of the IR, three features are present in the former and not in the latter, i.e. medium to weak bands at 531 and 499 cm^{-1} and a shoulder of medium intensity at 460 cm^{-1}. The first two of these are similar in frequency to the bands assigned to $\delta(CN_3)$ and $\omega(NH_2)$ in previous studies of guanidinium salts[13] and were found to shift on deuteration of the guanidinium cation. In the Raman spectrum of $[C(NH_2)_3]_2[Cr_3O(OOCC_2H_5)_6F_3]$, two bands are found in this region at 541 and 492 cm^{-1}. The former is assigned to $\delta(CN_3)$, since it shifts to 470 cm^{-1} on deuteration, and the latter to $\nu(CrF)$ since it shows no deuteration shift (Figure 6). Evidently the frequencies 492 and 460 cm^{-1} represent the a_1' and e' components of the coupled $(CrF)_3$ system. This frequency separation is perhaps larger than might be expected. The two (CrF) modes are likely to couple strongly with the $\nu(Cr_3O)$ modes of the same symmetry. These are respectively above and below the frequency of ν(Cr–F); hence, coupling with $\nu_{as}(Cr_3O)$ will lead to a lowering of the frequency of the e' component of $\nu[(CrF)_3]$, and coupling with $\nu_s(Cr_3O)$ will raise the frequency of the a_1' component.

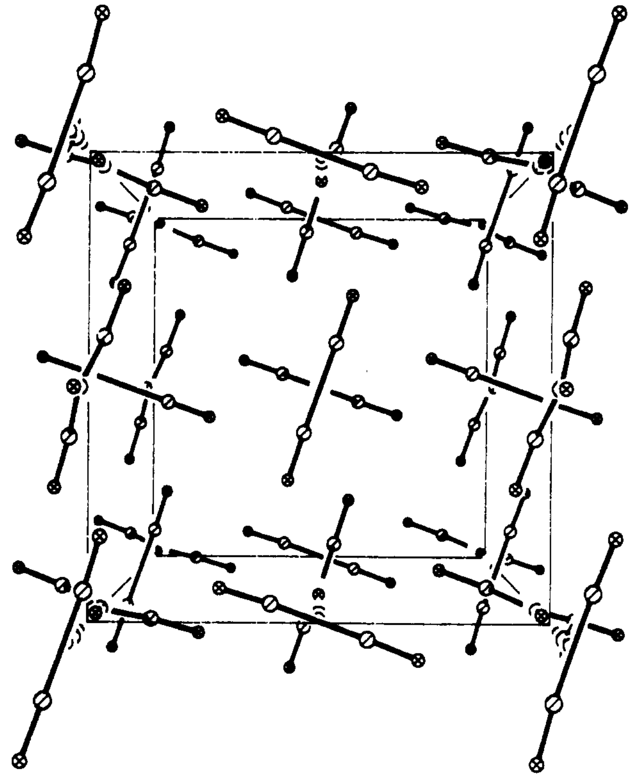

Figure 7. Packing diagram of the salt $[C(NH_2)_3]_2[Cr_3O(OOCC_2H_5)_6F_3]$, viewed along the c axis.

Discussion

Although a good many trinuclear complexes of this type are known, very few of them have the site symmetry consistent with the full idealized 3-fold geometry of the complex.[1] The present complex also does not have crystallographic 3-fold symmetry. The site symmetry is C_2, but if the ethyl groups are disregarded, it is only very slightly distorted from D_{3h}. More significantly, the C_2 axis and absence of disordered solvent of crystallisation make it one of the simplest of known oxo-centered trinuclear complexes, and a good model system for future physical studies. As shown in Figure 7, the complex anions occur in sets, the planes of the trinuclear metal clusters being parallel within a set, with the sets perpendicular to each other. It is therefore possible to apply an electromagnetic field parallel to the planes of all the triangles, or alternatively parallel to half the planes and perpendicular to the other half. This compound is therefore a promising material for future magnetic and photophysical experiments.

The Cr–F bond distances are the longest so far found. A survey of previous data on chromium(III) complexes containing linear units A–Cr–F reveals a correlation between the Cr–F bond length and the nature of the trans ligand A, increasing in the order OH^-

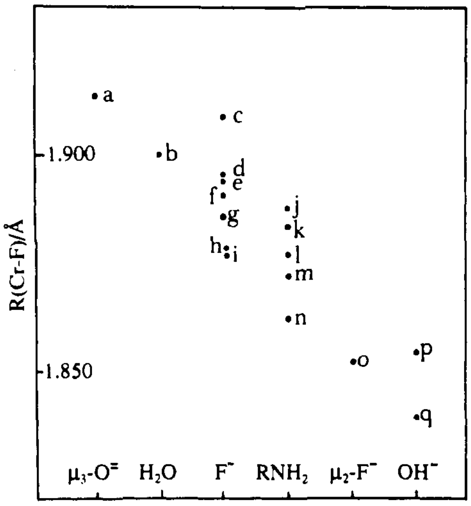

Figure 8. Chromium(III)-fluoride distances in six-coordinated complexes $[CrL_4AF]^{n+}$, grouped according to the nature of the ligand A trans to the fluoride. Key: (a) $[C(NH_2)_3]_2[Cr_3O(OOCC_2H_5)_6F_3]$, this work; (b) *trans*-$[CrF(OH_2)(pn)_2]^{2+}$;[21] (c) $NaK_2[CrF_6]$;[31] (d) *trans*-$[CrF_2(en)_2]Cl$;[29] (e) *trans*-$[CrF_2(NH_3)_4]I\cdot H_2O$;[18] (f) *trans*-$Li[CrF_2(pdda)_2]\cdot 2H_2O$;[28] (g) *trans*-$[CrF_2(OH_2)(en)]Cl$;[27] (h) *trans*-$[CrF_2(pn)_2]Na(ClO_4)_2$;[24] (i) *trans*-$[CrF_2(en)_2](ClO_4)_2$;[21] (j) *cis*-$[CrF_2(NH_3)_4](ClO_4)$;[18] (k) *cis*-$[CrF_2(en)_2](ClO_4)$;[26] (l) *cis*-$[CrF_2(en)_2]Na(ClO_4)_2$;[25] (m) *trans*-$[CrF(NH_3)(pn)_2](ClO_4)$;[30] (n) *trans*-$[CrF(NH_3)(en)_2](ClO_4)_2$;[23] (o) $Cs_3[Cr_3F_{12}]$;[22] (p) *trans*-$[CrF(OH)(en)_2]^+$;[21] (q) *trans*-$[CrF(OH)(pn)_2]^+$.[21] en = 1,2-diaminoethane, pn = 1,3-diaminopropane, pdda = 1,3-diaminopropane-*N*,*N*′-diacetate.

$< \mu_2\text{-}F^- < RNH_2 < F^- < H_2O < \mu_3\text{-}O^{2-}$ (Figure 6). There are not enough vibrational data to establish such a correlation for vibrational frequencies, and in any case the situation is complicated by coupling between Cr–F vibrators and also between Cr–F and other Cr–ligand modes. The most detailed analysis available is for *trans*-$[Cr(en)_2F_2]I$. Flint and Matthews assigned $\nu_{as}(CrF_2)$ and $\nu_s(CrF_2)$ to strong bands at 520 and 512 cm^{-1} in the IR and Raman respectively (at $T = 5$ K), confirmed by observations of fine structure in the visible luminescence spectrum.[15] Other bands assigned to $\nu(CrF)$ in various complexes fall in the range 490–535 cm^{-1} (Table VI). Compared with these, the frequencies of $\nu(CrF)$ in the present complex are very low, 492 and 460 cm^{-1}, with a weighted average of 471 cm^{-1}.

Table VI. Infrared Vibrational Frequencies, Cr–F stretch (cm^{-1})

cis-$[CrF_2(NH_3)_4](ClO_4)$	515	490	*a*
trans-$[CrF_2(en)_2[(ClO_4)$	513		*b*
trans-$[CrF_2(NH_3)_4]I\cdot H_2O$	505		*a*
trans-$[CrF_2(en)_2]I$	520^{e}	512^{e,f}	*b*
trans-$[CrF(en)_2(ONO)](ClO_4)$	515		*c*
trans-$[CrF(en)_2(H_2O)](ClO_4)_2$	526		*c*
trans-$[CrF(en)_2Cl](ClO_4)$	517		*c*
cis-$[CrF_2(en)_2]I$	525	517	*c*
cis-$[CrF(en)_2Cl]Cl$	520		*c*
trans-$[CrF(en)_2(H_2O)]Br_2\cdot DMF\cdot H_2O$	530		*c*
$Na[CrF_2(en)_2](ClO_4)\cdot H_2O$	525	500	*c*
$K_3[CrF_6]$	535	522	*d*
$[C(NH_2)_3]_2[Cr_3(\mu_3\text{-}O)(OOCC_2H_5)_6F_3]$	492^{g}	460^{f,g}	this work

[a] Reference 18. [b] Reference 15. [c] Reference 19. [d] Reference 20. [e] $T = 5$ K. [f] Raman spectrum. [g] $T = 100$ K.

Previously, Antsyshkina et al. reported the structure of the corresponding triaquo adduct $[Cr_3O(OOCC_2H_5)_6(H_2O)_3](NO_3)\cdot 2H_2O$.[16] Although their structure was of low accuracy the Cr–Cr distances, 3.273(8) and 3.277(4) Å, are significantly shorter than in the present complex, and the Cr–(central O) distances must be shorter as well. Consistently with this, the frequency of the in-plane Cr–O stretch, $\nu_{as}(Cr_3O)$, is lower in the fluoro than in the aquo adduct, 663 and 688 cm^{-1}, respectively. Evidently the peripheral fluoride ions weaken the bonding to the central oxygen, just as the oxygen weakens the bonds to the fluorine.

In conclusion, it was predicted from the limited kinetic data reviewed above that the bridging oxide ion should have a kinetic trans-effect, labilizing the terminal ligand by several orders of magnitude in rate: the present data show clearly that there is a static trans-effect as well.

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Supplementary Material Available: Table S1, atomic coordinates for $[C(NH_2)_3]_2[Cr_3O(OOCC_2H_5)_6F_3]$, and Table S2, interatomic distances and bond angles (9 pages). Ordering information is given on any current masthead page.

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(15) Flint, C. D.; Matthews, A. P. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1307.

(16) Antsyshkina, A. S.; Porai-Koshits, M. A.; Arkhangel'skii, I. V.; Diallo, I. N. *Zh. Neorg. Khim.* **1987**, *32*, 2928; *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1987**, *32*, 1700.

(17) Spinner, E.; Yang, P.; Wong, P. T. T.; Mantsch, H. H. *Aust. J. Chem.* **1986**, *39*, 475.

(18) Brencic, J. V.; Ceh, B.; Leban, I. *Monatsh. Chem.* **1981**, *112*, 1359.

(19) Vaughn, J. W.; DeJovine, J. M.; Seiler, G. J. *Inorg. Chem.* **1970**, *9*, 684.

(20) Peacock, R. D.; Sharp, D. W. A. *J. Chem. Soc.* **1959**, 2762.

(21) Solans, X.; Font-Altaba, M.; Brianso, J. L.; Solans, A.; Casabo, J.; Ribas, J. *Cryst. Struct. Commun.* **1982**, *11*, 1199; *Chem. Abstr.* **1983**, *98*, 207878m.

(22) Babel, D.; Knoke, G. *Z. Anorg. Allg. Chem.* **1978**, *442*, 151.

(23) Beveridge, K. A.; Bushnell, G. W.; Kirk, A. D. *Acta Crystallogr.* **1985**, *C41*, 899.

(24) Vaughn, J. W.; Rogers, R. D. *J. Crystallogr. Spectrosc. Res.* **1985**, *15*, 281; *Chem. Abstr.* **1985**, *103*, 46201q.

(25) Brencic, J. V.; Leban, I.; Polanc, I. *Z. Anorg. Allg. Chem.* **1987**, *551*, 109.

(26) Brencic, J. V.; Leban, I.; Polanc, I. *Acta Crystallogr.* **1987**, *C43*, 885.

(27) Vaughn, J. W. *J. Crystallogr. Spectrosc. Res.* **1983**, *13*, 231; *Chem. Abstr.* **1983**, *99*, 31148c.

(28) Bianchini, R. J.; Geiser, U.; Place, H.; Kaizaki, S.; Morita, Y.; Legg, J. I. *Inorg. Chem.* **1986**, *25*, 2129.

(29) Brencic, J. V.; Leban, I. *Vestn. Slov. Kem. Drus.* **1985**, *32*, 209; *Chem. Abstr.* **1985**, *104*, 13305u.

(30) Vaughn, J. W. *Inorg. Chem.* **1981**, *20*, 2397.

(31) Massa, W.; Babel, D.; Epple, M.; Ruedorff, W. *Rev. Chim. Miner.* **1986**, *23*, 508; *Chem. Abstr.* **1987**, *106*, 186945x.