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SYNTHESIS AND THE MOLECULAR AND CRYSTAL STRUCTURE OF AQUADIFLUOROOXO(1,10-PHENANTHROLINO)VANADIUM(IV), [$VOF_2(H_2O)$(1,10-PHENANTHROLINE)]

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SUMMARY

The complex, [$VOF_2(H_2O)$phen], has been isolated from an aqueous HF solution of VOF_2 and 1,10-phenanthroline. The molecular and crystal structure has been determined from three-dimensional X-ray data. The geometry around vanadium is distorted octahedral with two fluorine, two oxygen and two nitrogen atoms. Bond distances are as follows: V - O 1.623(4), V - OH_2 2.012(4), V - F 1.896(3) and 1.921(3), V - N 2.134(4) and 2.306(4) Å. The longer V - N distance is in trans position to terminal oxygen atom. Two hydrogen bonds O-H...F are 2.592(5) and 2.537(5) Å respectively.

INTRODUCTION

The chemistry of oxovanadium(IV) difluoride has received much attention in recent years [1-3]. Several fluorooxovanadates(IV) have an octahedral coordination about vanadium.

Neutral complexes of VOF_2 are little known although there is a report on the synthesis of [VOF_2L_2], [$VOF_2(H_2O)L$] and [VOF_2L] [4]. In the case of [$VOF_2(H_2O)L$] compounds, which have the same stoichiometry as that in the present work,

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the ligand L was acetonitrile, dioxal and dimethylformamide respectively. In this paper we describe the synthesis and molecular and crystal structure of the $[VOF_2(H_2O)L]$ complex with L = 1,10-phenanthroline.

EXPERIMENTAL

Preparation

1.00 g 1,10-phenanthroline hydrate was dissolved in 40% hydrofluoric acid (10 ml). A solution of 0.53 g VOF_2 in 20% HF (6 ml) was added. The compound precipitated out in a few seconds. Found: 17.10 % V. $[VOF_2(H_2O)phen]$ requires: 16.75 % V.

Crystals suitable for X-ray structure analysis were obtained by slow diffusion between the two solutions.

Crystal Data

$[VOF_2(H_2O)phen]$, M = 303.17, Monoclinic, a = 8.456(1), b = 7.252(2), C = 19.250(2) Å, β = 100.28(2)°, V = 1161.5 Å^3, D_m(by flotation) 1.68 gcm^{-3}, Z = 4, D_c = 1.734 gcm^{-3}, space group $P2_1/n$.

Preliminary cell dimensions and space group symmetry were determined from oscillation and Weissenberg photographs taken with Cu-Kα radiation. Accurate cell parameters were obtained by least-squares treatment of high-angle reflections, collected on an Enraf-Nonius CAD-4 automatic diffractometer, using graphite-monochromated Mo-Kα radiation. Intensity data were recorded with the ω-2θ scan technique in the interval $1.5 < \theta < 30.0^\circ$. Half a sphere of reflections (6963 in all) was measured. The symmetry-related reflections were averaged (mean discrepancy on I = 1.6%) to yield 3352 independent reflections of which 2007 with $I_o > 2\sigma(I_o)$ (obtained from counting statistics) were considered observed and used for the structure analysis. Lorentz-polarization corrections were applied, but no absorption corrections.

The positions of the vanadium and of six light atoms were determined from a three-dimensional Patterson map. The subsequent electron-density maps gave coordinates for all the non-hydrogen atoms. The oxygen atom of the vanadyl group could be established unequivocally from the short V-O bond distance. There were three possibilities of locating the oxygen atom of the water molecule. The best agreement was obtained (R = 0.093) by taking the longest distance from vanadium. This position also has two short contact distances to fluorine atoms which additionally account for the location of the second oxygen atom. After refinement with anisotropic temperature factors for all the atoms, R was 0.076. The difference electron-density map gave the hydrogen atoms of water molecule. Hydrogen atoms of the phenanthroline molecule were calculated. Hydrogen atoms were included in the refinement as invariants with isotropic thermal parameters, $U = 0.06\ Å^2$. This final refinement converged at R 0.068 $(=\Sigma|\Delta F|/|F_o|)$, and R_w 0.065 $\{=[\Sigma w(\Delta F)^2/\Sigma wF_o{}^2]^{1/2}\}$. The function minimized was $\Sigma w(F_o-F_c)^2$, where the weighting function $w = W_F W_S$ was determined empirically from $W_F(|F_o|<13.5)=(|F_o|/13.5)^{5.0}$, $W_F(F_o>33.0) = (33.0/|F_o|)^{1.5}$, and $W_F(13.5\leqslant F_o\leqslant 33.0) = 1.0$, and $W_S(\sin\Theta<0.28) = (\sin\Theta/0.28)^{1.5}$, $W_S(\sin\Theta>0.43) = (0.43/\sin\Theta)^{6.0}$, and $W_S(0.28\leqslant\sin\Theta\leqslant o.43) = 1.0$.

Atomic scattering factors for H atoms were taken from ref.[5] and for other atoms from ref. [6], those for V,O,F,N and C being corrected for the effects of anomalous scattering ($\Delta f'$,$\Delta f''$)[7]. All the calculations were made on an CDC CYBER 72 computer at RRC Ljubljana using the 'X-RAY 72' system of crystallographic programs [8].

RESULTS AND DISCUSSION

Table 1 shows positional parameters and Table 2 interatomic distances and angles. Vanadium is octahedrally coordinated by two fluorine atoms, two nitrogen atoms of the phenanthroline molecule, the oxygen atom of the vanadyl group and an oxygen atom of a water molecule (Figure 1).

TABLE 1

Atomic coordinates with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
V	0.2441(1)	0.2019(1)	0.1571(1)
F(1)	0.3760(4)	-0.0125(4)	0.1811(2)
F(2)	0.1806(3)	0.4529(4)	0.1497(2)
O(1)	0.0744(4)	0.1004(6)	0.1273(2)
O(2)	0.2485(5)	0.2222(5)	0.2617(2)
N(1)	0.4963(5)	0.3331(5)	0.1725(2)
N(10)	0.4126(4)	0.2042(6)	0.0557(2)
C(2)	0.5834(6)	0.4014(8)	0.2317(3)
C(3)	0.7442(7)	0.4572(8)	0.2349(3)
C(4)	0.8139(6)	0.4439(8)	0.1767(3)
C(5)	0.7826(6)	0.3675(8)	0.0474(3)
C(6)	0.6868(7)	0.3106(8)	-0.0128(3)
C(7)	0.4200(7)	0.1901(8)	-0.0739(3)
C(8)	0.2660(7)	0.1389(8)	-0.0688(3)
C(9)	0.2154(6)	0.1474(7)	-0.0035(3)
C(11)	0.4638(5)	0.2582(6)	-0.0505(2)
C(12)	0.5642(5)	0.3237(6)	0.1139(2)
C(13)	0.7237(5)	0.3781(7)	0.1126(3)
C(14)	0.5240(6)	0.2531(6)	-0.0131(3)
H(2)	0.5294	0.4131	0.2788
H(3)	0.8127	0.5128	0.2837
H(4)	0.9391	0.4839	0.1789
H(5)	0.9081	0.4014	0.0465
H(6)	0.7338	0.3125	-0.0620
H(7)	0.4622	0.1817	-0.1241
H(8)	0.1840	0.0914	-0.1159
H(9)	0.0917	0.1070	-0.0008
H(10)	0.2006	0.3239	0.2835
H(11)	0.2747	0.2114	0.2949

TABLE 2*

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

a) Intramolecular distances and angles in vanadium polyhedra

V-F(1)	1.921(3)	F(2)-V-N(10)	92.48(15)
V-F(2)	1.896(3)	F(2)-V-N(1)	81.76(13)
V-N(10)	2.134(4)	F(2)-V-O(1)	100.83(17)
V-N(1)	2.306(4)	F(2)-V-O(2)	87.65(15)
V-O(1)	1.623(4)	N(10)-V-N(1)	73.66(14)
V-O(2)	2.012(4)	N(10)-V-O(1)	92.72(18)
F(1)-V-F(2)	159.76(13)	N(10)-V-O(2)	162.86(15)
F(1)-V-N(10)	89.21(14)	N(1)-V-O(1)	166.28(19)
F(1)-V-N(1)	79.58(13)	N(1)-V-O(2)	89.42(15)
F(1)-V-O(1)	99.02(17)	O(1)-V-O(2)	104.10(19)
F(1)-V-O(2)	84.96(14)		

c) Atomic contacts

O(2)-H(10)...F(1^{I})	2.537(5)	O(2)-H(11)...F(2^{II})	2.592(5)

Symmetry code: I; 1/2-x, 1/2+y, 1/2-z; II; 1/2-x, -1/2+y, 1/2-z

*The atomic thermal parameters and observed and calculated structure amplitudes are available from the authors.

There are no other crystal structures known for neutral complexes of vanadyl fluoride, however, in all structurally characterized fluorooxovanadates(IV) the octahedral coordination of vanadium was found. The observed V - O distance in the vanadyl group is in the range characteristic for the V - O double bond, e.g. 1.607 Å in $[NMe_4]_2[V_2O_2F_6(OH_2)_2]$ [9], 1.612 Å in $(NH_4)_2[VOF_4]$ [10], or 1.602 Å in $Cs_2[VOF_4(OH_2)]$ [11]. The $VO_2F_2N_2$ octahedra in the present complex are very distorted, not only due to the short V - O distance in vanadyl group, but also because of the the presence of the chelate ring resulting in a N - V - N bond angle of 73.66 (14)°. The difference in

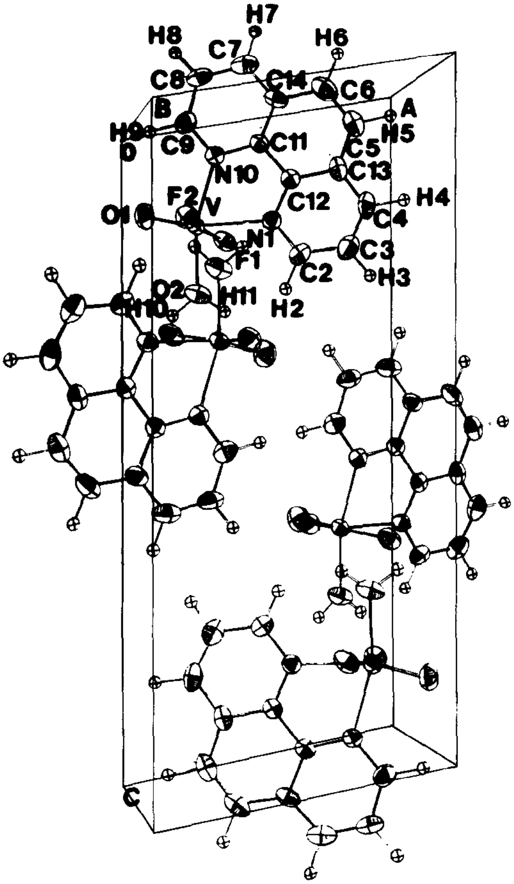

Fig. 1. View of the unit cell and numbering scheme used for $[VOF_2(H_2O)phen]$

V - N bond lengths can be ascribed to the trans influence already found in other oxovanadium complexes. The oxygen atom of the water molecule is at 2.012 Å which is short as compared to other fluorooxovanadates(IV), e.g. 2.074 Å in $[NMe_4]_2[V_2O_2F_6(OH)_2]$ [9] or 2.268 Å in $Cs_2[VOF_4(OH_2)]$ [11]. Bond distances and angles in 1,10-phenanthroline are close to the literature data [12]. There are two short hydrogen bonds O-H...F 2.537 and 2.592 Å which bound together two molecules related by the screw axis.

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