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LETTER

The X-ray structure of the divanadyl complex, $[(VO)_2Cl_2(C_8H_6N_2)_2(OC_2H_5)_2]$

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Among a vast body of vanadyl complexes [1], only a limited number of divanadyl complexes have been synthesized and characterized by X-ray diffraction methods [2–6], although divanadyl complexes are intriguing concerning their physiological and physicochemical properties. In this paper we describe the X-ray crystallographic characterization of the first bis(μ-ethoxo)-bridged complex of vanadium(IV). In addition, this work also presents a rare coordination form of 1,8-naphthyridine (napy), where one nitrogen atom is coordinated to the vanadium ion while another one has a very close contact with the vanadium ion.

Experimental

Synthesis of the title compound (1)

A total of 78.1 mg (6.0×10^{-4} mol) of napy was added to a green ethanol solution (10 cm^3) of VCl_3 (32 mg, 2×10^{-4} mol) and the mixture was stirred for 1 h, giving a clear brown solution. This solution was allowed to stand overnight, and brick-shaped crystals were obtained (20.0 mg, 36%). IR (Nujol) 989 cm^{-1} (ν(V=O)). UV–Vis (ethanol) 439 nm ($\epsilon = 235$ M^{-1} cm^{-1}).

X-ray crystallography of 1

A brown crystal of **1** was attached to the end of a glass fiber and mounted on a Rigaku AFC-6 automated diffractometer. Preliminary examinations showed that the crystal belonged to the monoclinic system, space group *C2/c*. The unit cell dimensions were obtained by a least-squares fit of 25 strong reflections. Intensity data were measured by ω–2θ scans at 22 °C and were corrected for Lorentz and polarization effects. Empirical absorption corrections were carried out.

Crystal data for $V_2Cl_2O_4N_4C_{20}H_{22}$: $M = 555.2$, monoclinic, space group *C2/c*, $a = 19.878(8)$, $b = 8.780(2)$, $c = 18.942(8)$ Å, $\beta = 131.96(3)°$, $U = 2458.3$ Å^3, $Z = 4$, $D_c = 1.50$ g cm^{-3}, $F(000) = 1128$ electrons, μ(Mo Kα) $= 9.86$ cm^{-1}, $T = 295$ K.

The structure was solved via MULTAN, which yielded the position of most of the non-hydrogen atoms. Subsequent Fourier syntheses revealed the location of all remaining non-hydrogen atoms. Idealized positions of the H atoms bound to carbon atoms of the napy and ethanolate were calculated in the final refinement cycles with fixed isotropic thermal parameters. A final difference Fourier synthesis was essentially featureless, and the structure was judged to be complete: $R = 0.0562$ ($R_w = 0.0571$).

Results and discussion

The crystal structure of **1** contains discrete dinuclear molecules. This molecule is depicted in Fig. 1, where the atom labelling scheme is defined. The complex cation has a crystallographically imposed centrosymmetry. Important interatomic distances and angles are listed in the caption of Fig. 1. Each vanadium(IV) center has a distorted square-pyra-

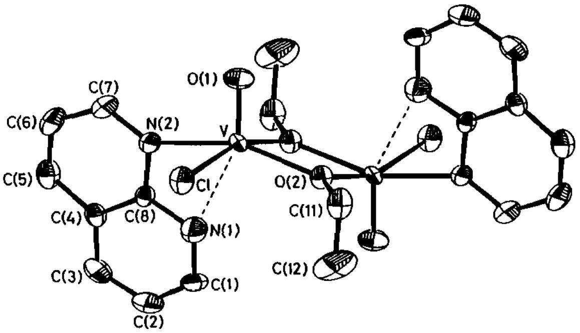

Fig. 1. Structure of $[(VO)_2(napy)_2Cl_2(OC_2H_5)_2]$ (**1**) showing the 30% probability thermal ellipsoids and atom labelling scheme. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°) are as follows: V–O(1), 1.582(4); V–Cl, 2.358(2); V–O(2), 1.958(4); V–N(1), 2.524(5); V–N(2), 2.126(5); V–O(2′), 1.995(4); N(1)–C(8), 1.362(6); N(2)–C(8), 1.349(4); V–V′, 3.101(1); N(1)–V–N(2), 56.9(1); O(2)–V–O(2′), 76.6(1); O(1)–V–O(2), 110.1(1); O(1)–V–O(2′), 101.5(1); O(1)–V–Cl, 99.2(1); O(1)–V–N(2), 97.0(1); O(1)–V–N(1), 154.0(1); O(2)–V–N(1), 95.3(1); O(2)–V–N(2), 151.6(1); O(2)–V–Cl, 93.4(1); Cl–V–O(2′), 158.97(8); Cl–V–N(2), 89.7(1); Cl–V–N(1), 83.54(11); N(1)–V–O(2′), 79.13(14); N(2)–V–O(2′), 151.66(10); V–O(2)–V′, 103.3(1); V–N(1)–C(8), 86.3(3); V–N(2)–C(8), 104.6(3); V–N(2)–C(7), 137.7(2); N(1)–C(8)–N(2), 111.8(4).

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midal environment with apical oxo anion; equatorial Cl^-, N atom of napy and two O^-(ethanolate) anions.

The V=O distance of 1.582(4) Å is in the range (1.63(2) to 1.55(1) Å) found in five-coordinate vanadyl complexes [1], as well as its stretching frequencies, $\nu(VO) = 989$ cm^{-1}, characteristic of a double bond. The V–Cl and V–N(2) distances fall within the range of vanadyl complexes. The distance of V–O(2) corresponds well to that of hydroxo(OH) and methoxo(CH_3O) bridged vanadyl complexes [2, 3], while the difference of 0.037(4) Å between the two bridging moieties, V–O(2) and V–O(2′), is larger than that of the hydroxo and methoxo complexes.

Interestingly, the unique feature of this structure is the coordination mode of napy. Usually napy provides three types of coordination mode; (A) monodentate ($[PtCl(napy)(PEt_3)_2]^+$ [7] and $[Mn(napy)(phen)(CO)_3]ClO_4^+$ [8]); (B) bidentate chelate ($[Fe(napy)_4]^{2+}$) [9]; (C) bidentate bridge ($[Ni_2(napy)_4Br_2]^+$ [10] and $[Cu_2(napy)_2]^{2+}$ [11]). The mode in **1** cannot be described by any of (A)–(C) but it is considered as quasi-bidentate coordination. The V–N(2) distance is 2.126(5) Å, the N(2) atom undoubtedly coordinated to V, while V–N(1) is 2.524(5) Å, longer than the normal V–N bond distance. The C–N–V angle illustrates well the structural aspect. In the case of the typical monodentate type (A), such as Pt and Mn complexes [7, 8], the C–N–M angles are 120(1) and 118.7(6)°. Hence, the distance between V and the uncoordinate N is over 3 Å, indicative of no interaction. The angle 120° exhibits good agreement between the direction of the nitrogen lone pair and the N–V bond axis. In the case of **1**, the angle, C(7)–N(2)–V, is 137.7(2)°, much greater than 120 °, and this tilt makes a close V–N(1) contact (2.524(5) Å) possible. There could be some additional interaction of N(1) and V because of no significant intermolecular interaction in the crystal. The V=O distance of **1** encounters no apparent *trans* influence of N(1), but the participation of N(1) cannot be excluded because the short V=O distances, close to 1.58 Å, have been found in octahedral vanadyl complexes [12]. A similar interaction of napy has been found in $[Hg_2(napy)_2](ClO_4)_2$ [13], where the distance of a long Hg–N bond and the angle of C–N–Hg are 2.78(1) Å and 138(2)°, respectively.

Supplementary material

Tables of fractional atomic coordinates, thermal parameters, interatomic bond distances and angles are available on request from author S.K..

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