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Inorganica Chimica Acta 224 (1994) 199–201

Inorganica Chimica Acta

Note

Crystal structure of a binuclear vanadium(III) complex with a new tripodal ligand, $[V_2Cl_4(tped)(EtOH)_2]\cdot 2EtOH$

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Received by Editor 17 February 1994; received by Publisher 24 May 1994

Abstract

The reaction of $VCl_3(thf)_3$ (thf = tetrahydrofuran) with bis(2-pyridyl) ketone (pyke) gives a binuclear vanadium(III) complex, $[V_2Cl_4(tped)(EtOH)_2]\cdot 2EtOH$ (tped = tetrapyridyl-1,2-ethanediol), having a new type of tripodal ligand, which comes from the reductive coupling of the pyke. This is the first dinuclear vanadium(III) complex that contains both ionic and neutral alcohol oxygen. The complex crystallizes in monoclinic space group $P2_1/c$, with $a = 11.420(4)$, $b = 10.978(2)$, $c = 14.826(3)$ Å, $\beta = 103.53(2)°$, $V = 1807.1(8)$ Å^3, $Z = 2$, $D_{calc} = 1.463$ g cm^{-3}, μ(Cu Kα) = 77.16 cm^{-1}, $F(000) = 820.00$, $R = 0.040$, $R_w = 0.060$, $T = 296(1)$ K for 1998 observed reflections.

Keywords: Crystal structures; Vanadium complexes; Tripodal ligand complexes; Dinuclear complexes

1. Introduction

Bis(2-pyridyl) ketone (pyke) can afford two types of chelate structures, depending on the donor atoms: a five-membered chelate by (N,O) coordination and a six-membered chelate by (N,N) coordination [1]. Among the many transition-metal complexes synthesized so far [2–7], the six-membered structure is found quite frequently. The copper(II) complexes take a five-membered form, which can also convert to a six-membered ring [4] because of the affinity of copper(II) for both nitrogen and oxygen donors. Similarly, vanadium complexes would favor a five-membered (N,O) ring because of vanadium's oxophilicity. The interest in the present compound is based not only on the type of coordination but also on the recent discovery of the reductive coupling of carbonyl compounds in the presence of a vanadium compound [8]. This work is concerned with a unique reaction product of pyke with vanadium(III), and its X-ray crystallographic structure.

2. Experimental

All operations were performed under anaerobic conditions by using standard Schlenk techniques. Solvents were purified by standard methods before use. $VCl_3(thf)_3$ was prepared according to the literature methods [9]. Di-2-pyridyl ketone was purchased from Aldrich.

2.1. Synthesis

$VCl_3(thf)_3$ (0.2 g, 0.5 mmol) was dissolved in 2 ml of ethanol. To this solution, an ethanolic solution of di-2-pyridyl ketone (0.27 g, 1.5 mmol) was added. The solution mixture was stirred and subsequently filtered. Hexane was layered slowly on the resulting green solution. Blue prismatic crystals were obtained within two months (40% yield).

2.2. X-ray crystallography

A blue crystal having approximate dimensions of 0.4 × 0.25 × 0.10 mm was mounted in a glass capillary. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Cu Kα radiation. The cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 16 carefully centered reflections in the range $40.29 < 2\theta < 42.51°$, corresponded to a primitive monoclinic cell. The data were collected at room temperature. Over the course of data collection,

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0020-1693/94/$07.00
SSDI 0020-1693(94)04122-C

the standards decreased by 13.8%. A polynomial correction factor was applied to the data to account for this phenomenon. An empirical absorption correction using the program DIFABS [10] was applied which resulted in transmission factors ranging from 0.74 to 1.456. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. The nonhydrogen atoms were refined anisotropically. The final positions of the hydrogen atoms were calculated after the last cycle of refinement. The final cycle of full-matrix least-squares refinement was based on 1998 observed reflections ($I > 3\sigma(I)$) and 209 variable parameters, and converged with the unweighted and weighted agreement factors $R = 0.040$ and $R_w = 0.060$, respectively.

3. Results and discussion

The molecular structure of [V_2Cl_4(tped)(EtOH)$_2$] (**1**), together with the atomic numbering scheme, is given in Fig. 1. Selected bond distances and angles are listed in the caption of Fig. 1. Complex **1** has a crystallographic inversion center at the midpoint of the C(6)–C(6′) bond. The two equivalent vanadium(III) ions are bridged by the tped ligand. Each vanadium ion is coordinated in a distorted octahedral geometry by the $N_2O_2Cl_2$ donor set. Owing to the difference in bond distances for nitrogen and chloride atoms, the two respective N and Cl atoms afford a trapezoid-basal plane, while the two oxygen atoms sit over both sides of the plane; the difference in the two V–O distances is large (0.116 Å), and the V–O–V unit reveals a bent form (an angle of 170.7(1)°). One of the oxygen atoms comes from neutral ethanol, and thus both vanadium centers are formally trivalent. The tped ligand is composed of two N_2O^- donor sets and is considered to be a coupled-tripodal ligand, which apparently forms from two pyke molecules by a reductive coupling reaction.

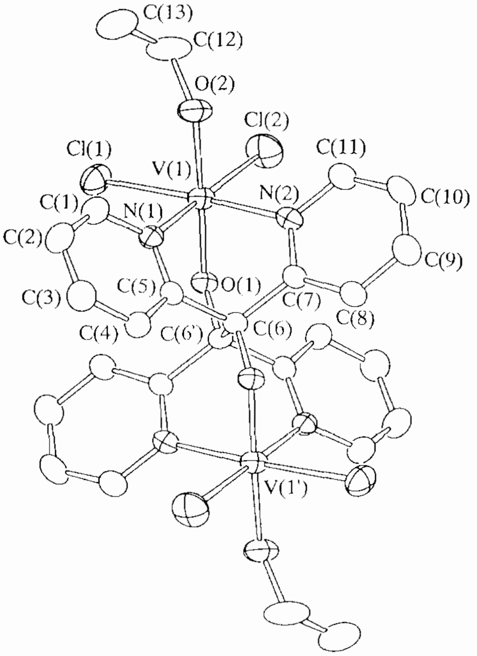

Fig. 1. ORTEP drawing of [V_2Cl_4(tped)(EtOH)$_2$] molecule showing the atom-labeling scheme. Two molecules of uncoordinated ethanol are present but omitted in this figure. Atoms are represented by their 50% probability ellipsoids. Selected bond distances (Å) and angles (°): V(1)···V(1′) 5.844(2), V(1)–Cl(1) 2.409(1), V(1)–Cl(2) 2.351(2), V(1)–O(1) 1.846(3), V(1)–O(2) 2.060(3), V(1)–N(1) 2.142(3), V(1)–N(2) 2.114(3), Cl(1)–V(1)–Cl(2) 93.38(5), Cl(2)–V(1)–N(2) 91.71(9), N(1)–V(1)–N(2) 83.9(1), N(1)–V(1)–Cl(1) 91.03(9), Cl(1)–V(1)–O(2) 90.72(9), O(2)–V(1)–N(2) 89.5(1), O(1)–V(1)–O(2) 170.7(1), N(2)–V(1)–O(1) 87.1(1), O(1)–V(1)–Cl(1) 91.93(9), Cl(2)–V(1)–O(1) 97.00(9), O(1)–V(1)–N(1) 85.9(1), N(1)–V(1)–O(2) 85.1(1), O(2)–V(1)–Cl(2) 91.73(9).

The long V–V separation (5.844(2) Å) is indicative of no V–V interaction. The V–Cl (2.410(1) and 2.351(2) Å) and V–N (2.141(3) and 2.112(3) Å) bond distances are close to those found in complexes of pyridine derivatives [11,12]. 2,2′-Bipyridine (bpy), as a congener of pyke, also forms a five-membered ring, which is found in [$V_2(bpy)_4Cl_2(\mu\text{-}O)]^{2+}$ [12]. The N–V–N chelate angles of bpy are 74.8(2) and 76.8(2)°. On the other hand, complex **1** has a six-membered chelate ring formed by py–C(6)–py–V(1), with a chelate angle N(1)–V(1)–N(2) of 83.9(1)°. This six-membered chelate moiety, V(1)N(1)C(5)C(6)C(7)N(2), is in a boat conformation, and the mean plane passing through N(1)C(5)C(7)N(2) leaves the V(1) and C(6) atoms out of the plane by 1.0 and 0.7 Å, respectively. The other two chelate rings, V(1)N(1)C(5)C(6)C(6′)O(1) and V(1)N(2)C(7)C(6)C(6′)O(1), are also in the boat conformation. These chelate angles of N–V–O are 86.0(1) and 87.1(1)°, respectively. The V–O(1) bond distance is 1.844(3) Å, the shortest among those found for the vanadium(III) complexes having alcoholate oxygen. On the other hand, the V–O(2) bond distance of 2.060(3) Å is the longest among those for vanadium(III) containing neutral alcohol. The elongation of the V–O(2) bond is ascribed to the *trans* influence of anionic O(1). Complex **1** is the first dinuclear vanadium(III) complex that contains both ionic and neutral alcohol oxygen.

It is well known that the N,N-coordinated pyke reacts with various nucleophiles and provides a tridentate chelation [13]; the keto carbon of pyke readily undergoes an addition reaction in the presence of Pd(II), Pt(II) and Au(III) to afford the geminal diol ligand [6], whose metal complexes are all mononuclear. In our case, two molecules of pyke react with each other so that a 1,2-diol forms instead of a geminal diol, resulting in a new type of coupled-tripodal tped. Recently, the stereoselective coupling of aldehydes employing the vanadium(II) complex [$V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ has been found [8]. The ligand was produced by the reductive coupling of two carbonyls. The formation of tped from pyke indicates that a similar type of coupling reaction of ketones also occurs even in the vanadium(III) system.

Acknowledgements

This work was supported in part by a Grant-in-Aid for Scientific Research (No. 05225226) from the Ministry of Education, Science and Culture.

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