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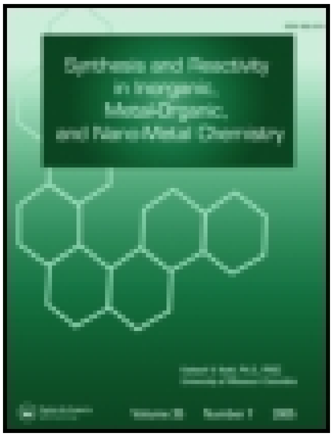

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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Synthesis and Crystal Structure of a Dioxovanadium(V) Complex with Schiff Base Derived from 2-[1-(2-Aminocyclohexylimino)ethyl]phenol

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Synthesis and Crystal Structure of a Dioxovanadium(V) Complex with Schiff Base Derived from 2-[1-(2-Aminocyclohexylimino)ethyl]phenol

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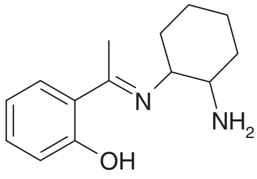
A new dioxovanadium(V) complex, $[VO_2L]_2 \cdot 2CH_3OH$, where L is the deprotonated form of 2-[1-(2-aminocyclohexylimino) ethyl]phenol, has been synthesized and characterized by I.R. spectra and single crystal X-ray diffraction. The compound consists of a centrosymmetric dinuclear dioxovanadium complex molecule and two methanol molecules of crystallization. Each V atom in the complex is six-coordinated through three bonds to oxo groups and through bonds to the tridentate Schiff base ligand, forming an octahedral geometry. The V···V distance is 3.188(2) Å. In the crystal structure, the dioxovanadium complex molecules are linked with the methanol molecules through intermolecular N−H···O and O−H···O hydrogen bonds, forming chains running along the *b* axis.

Keywords crystal structure, Schiff base, synthesis, vanadium complex

INTRODUCTION

Schiff bases and their metal complexes have received much attention in coordination chemistry and biological chemistry.[1–3] In recent years, the vanadium complexes have been reported to have interesting biological activities such as normalizing the high blood glucose levels and acting as models of haloperoxidases.[4–6] In order to investigate the synthesis and self-assembly of the vanadium complexes with Schiff bases, in this work, a new dioxovanadium(V) complex, $[VO_2L]_2 \cdot 2CH_3OH$, where L is the deprotonated form of 2-[1-(2-aminocyclohexylimino)ethyl]phenol (HL), has been synthesized and structurally characterized. It is notable that no complexes with HL have been reported previously.



HL

EXPERIMENTAL

Materials and Measurements

All chemicals used were commercially available with AR grade. The I.R. spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets in the 4000–400 cm^{-1} region.

Synthesis of the Schiff Base HL

A methanol solution (50 mL) of 1-(2-hydroxyphenyl) ethanone (1.0 mmol, 136.2 mg) was added dropwise to a stirred methanol solution (50 mL) of cyclohexane-1,2-diamine (1.0 mmol, 114.2 mg). The mixture was stirred for 30 minutes to give an amount of yellow precipitate. The precipitate was filtered out, washed three times with cold methanol, and dried in a vacuum over anhydrous $CaCl_2$. Yield: 93%. Selected I.R. data (KBr, cm^{-1}): 3207 (ν_{N-H}), 1639 ($\nu_{C=N}$).

Synthesis of $[VO_2L]_2 \cdot 2CH_3OH$

A methanol solution (5 mL) of $VO(acac)_2$(0.1 mmol, 26.5 mg) was added to a methanol solution (10 mL) of HL (0.1 mmol, 23.2 mg) with stirring. The mixture was stirred at room temperature for 30 min to give a yellow solution. The resulting solution was allowed to stand in air for a few days. Yellow block-shaped crystals suitable for X-ray single crystal diffraction were formed at the bottom of the vessel. The isolated product was washed three times with cold methanol, and dried in air. Yield: 67%. Selected I.R. data (KBr, cm^{-1}): 3413 (ν_{O-H}), 3205 (ν_{N-H}), 1627 ($\nu_{C=N}$), 930, 845 ($\nu_{V=O}$).

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TABLE 1
Crystal data for the complex

Formula	$C_{30}H_{46}N_4O_8V_2$
FW	692.6
Crystal shape/color	block/yellow
Crystal size/mm	0.23 × 0.21 × 0.21
Crystal system	Triclinic
Space group	P-1
a /Å	8.816(2)
b /Å	8.920(2)
c /Å	11.114(3)
α /°	94.494(2)
β /°	96.906(2)
γ /°	109.058(2)
V/Å^3	813.6(3)
Z	1
T /K	298(2)
D_c/g cm^{-3}	1.414
$F(000)$	364
μ/mm^{-1} (Mo-Kα)	0.628
$T_{\min}$	0.869
$T_{\max}$	0.879
Reflections/parameters	3119/201
Independent reflections	2241
Restraints	0
Goodness of fit on F^2	1.021
R_1, wR_2 $[I \geq 2\sigma(I)]^a$	0.0529 0.1093
R_1, wR_2 (all data)^a	0.0814 0.1226

$^aR_1 = \sum||Fo| - |Fc||/\sum|Fo|$, $wR_2 = [\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2]^{1/2}$, $w = [\sigma^2 Fo^2 + (0.0467(Fo^2 + 2Fc^2)/3)^2 + 0.5212(Fo^2 + 2Fc^2)/3]^{-1}$.

TABLE 2
Selected bond lengths (Å) and bond angles (°) for the complex

V1-O1	1.899(3)	V1-O2	1.617(3)
V1-O3	2.395(3)	V1-O3^i	1.661(3)
V1-N1	2.212(3)	V1-N2	2.111(3)
O2-V1-O3^i	106.56(13)	O2-V1-O1	104.35(13)
O3^i-V1-O1	97.68(11)	O2-V1-N2	96.31(12)
O3^i-V1-N2	92.90(11)	O1-V1-N2	152.93(11)
O2-V1-N1	94.34(12)	O3^i-V1-N1	157.92(11)
O1-V1-N1	83.59(11)	N2-V1-N1	77.50(11)
O2-V1-O3	172.15(11)	O3-V1-O3^i	77.87(11)
O1-V1-O3	81.14(10)	N2-V1-O3	76.82(10)
N1-V1-O3	80.58(9)		

Symmetry code: (i) $1 - x$, $1 - y$, $1 - z$.

TABLE 3
Hydrogen-bond geometry (Å, °) for the complex

D–H···A	D–H	H···A	D···A	D–H···A
N2–H2A···O4^i	0.90	2.23	3.045(5)	150
N2–H2B···O1^i	0.90	2.13	2.929(4)	147
O4–H4···O2^{ii}	0.82	2.00	2.775(4)	158

Symmetry codes: (i) $1 - x$, $1 - y$, $1 - z$; (ii) x, $1 + y$, z.

Crystal Structure Determination

Diffraction intensities for the complex were collected at 298(2) K using a Bruker SMART 1000 CCD area-detector with Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). The collected data were reduced using the SAINT program,[7] and empirical absorption corrections were performed using the SADABS program.[8] The structure was solved by direct methods and refined against F^2 by full-matrix least-squares methods using the SHELXTL package.[9] All of the non-hydrogen atoms were refined anisotropically. H atoms in the complex were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data for the complex are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. Hydrogen bonds are listed in Table 3.

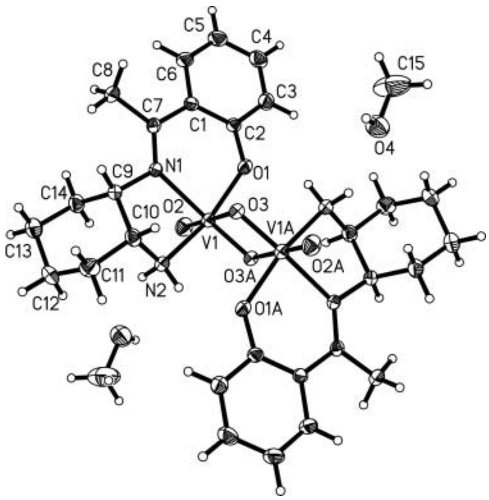
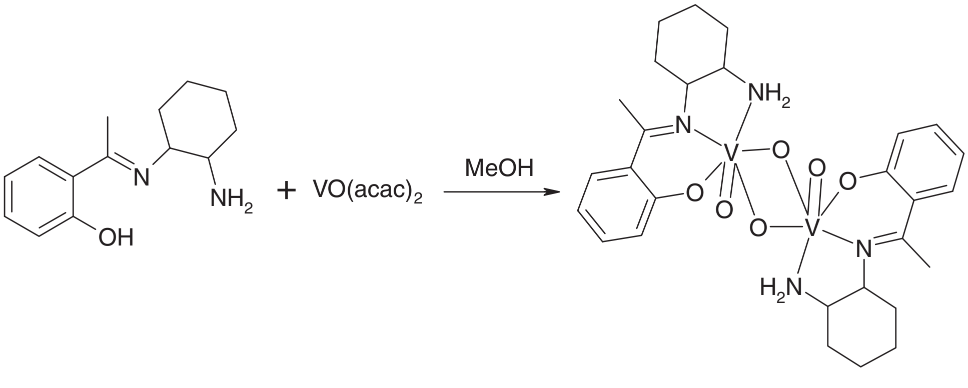


FIG. 1. Molecular structure of the complex at 30% probability displacement.

RESULTS AND DISCUSSION

Preparation of HL and the Complex

The Schiff base HL was prepared by the reaction of equimolar quantities of 1-(2-hydroxyphenyl)ethanone and cyclohexane-



SCH. 1.

1,2-diamine in methanol. To obtain HL with high purity, 1-(2-hydroxyphenyl)ethanone was slowly added to the methanol solution of cyclohexane-1,2-diamine. If the sequence was reversed, an amount of the bis-Schiff base 2,2′-[(1,2-cyclohexanediyl)bis(nitriloethylidyne)]bisphenol was obtained.

The complex was readily synthesized according to the standard procedure (Scheme 1), crystallized as yellow crystals, which is stable in air at room temperature. The crystal of the complex is soluble in DMSO, DMF, MeCN, MeOH and EtOH, and insoluble in water.

Structure Description of the Complex

The molecular structure of the complex is shown in Figure 1. The compound consists of a centrosymmetric dinuclear dioxovanadium complex molecule and two methanol molecules of crystallization. The V···V distance is 3.188(2) Å. Each V atom in the complex is six-coordinated through three bonds to oxo groups and through bonds to the tridentate Schiff base ligand, forming an octahedral geometry. The distance between atoms V1 and O2 is 1.617(2) Å, indicating a typical V=O bond. The O3 atom is involved in the bridge between V1 and V1A, strongly coordinated to V1A [1.661(2) Å] and weakly coordinated to V1 [2.395(2) Å]. The coordinate bond lengths are comparable to those observed in other similar vanadium complexes.[10–12] The distortion of the octahedral coordination can be observed by the coordinate bond angles, ranging from 76.8(2) to 106.6(2)° for the perpendicular angles, and from 152.9(2) to 172.2(2)° for the diagonal angles.

In the crystal structure, the dioxovanadium complex molecules are linked with the methanol molecules through intermolecular N—H···O and O—H···O hydrogen bonds, forming chains running along the *b* axis (Figure 2).

SUPPLEMENTARY MATERIALS

Supplementary crystallographic data are available from the CCDC, Union Road, Cambridge CB2 1EZ, UK on request quoting the deposition number CCDC 761789 (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

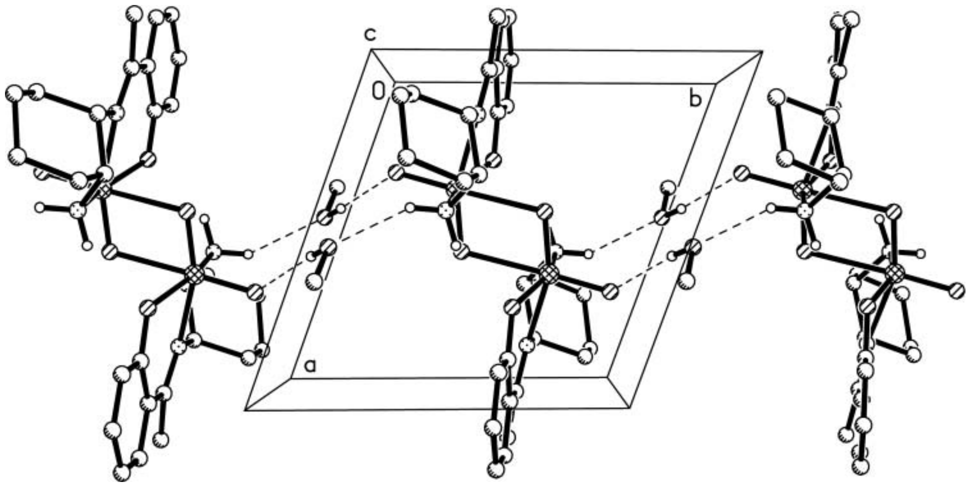


FIG. 2. Molecular packing arrangement of the complex. Viewed along the *c* axis. Intermolecular hydrogen bonds are shown as dashed lines.

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