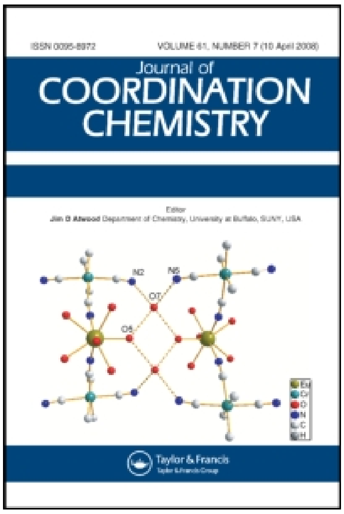

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# SYNTHESIS, CHARACTERIZATION AND THE CRYSTAL STRUCTURE OF A *CIS*-DIOXOVANADIUM(V) COMPLEX OF A TRIDENTATE SCHIFF BASE LIGAND

Hai-Xin Liu[a]; Wei Wang[a]; Xin Wang[a]; Min-Yu Tan[a]
[a] Instrumental Analysis and Research Centre, Lanzhou University, Lanzhou, P. R. China

**To cite this Article** Liu, Hai-Xin , Wang, Wei , Wang, Xin and Tan, Min-Yu(1994) 'SYNTHESIS, CHARACTERIZATION AND THE CRYSTAL STRUCTURE OF A *CIS*-DIOXOVANADIUM(V) COMPLEX OF A TRIDENTATE SCHIFF BASE LIGAND', Journal of Coordination Chemistry, 33: 4, 347 — 352

**To link to this Article: DOI:** 10.1080/00958979408024294

**URL:** http://dx.doi.org/10.1080/00958979408024294

*J. Coord. Chem.*, 1994, Vol 33, pp. 347–352
Reprints available directly from the publisher
Photocopying permitted by license only

# SYNTHESIS, CHARACTERIZATION AND THE CRYSTAL STRUCTURE OF A *CIS*-DIOXOVANADIUM(V) COMPLEX OF A TRIDENTATE SCHIFF BASE LIGAND

HAI-XIN LIU, WEI WANG, XIN WANG* and MIN-YU TAN

*Instrumental Analysis and Research Centre, Lanzhou University, Lanzhou 730000, P. R. China*

*(Received April 9, 1994; in final form July 14, 1994)*

The title complex, $[VO_2\{C_6H_5C(O)CHC(CH_3)NNC(O)CH_2(NC_5H_5)\}]\cdot C_2H_5OH$, was synthesized and characterized by elemental analysis and spectroscopy. Yellow crystals of the complex are monoclinic, space group $P2_1/a$ with $a = 10.690(2)$, $b = 16.008(3)$, $c = 13.164(4)$Å, $\beta = 107.03(2)$°, $V = 2153.9(18)$Å$^3$, $F(000) = 880$ and $Dc = 1.305$ g cm$^{-3}$ for $Z = 4$. X-ray structure analysis shows that the vanadium coordination number is five and the coordination polyhedron is a distorted trigonal bipyramid.

KEYWORDS: *cis*-dioxovanadium, Schiff base, terdentate, crystal structure

## INTRODUCTION

Recently, there has been considerable interest in the coordination chemistry of vanadium in view of its structure, catalytic activity and biological effects.[1–6] Although vanadium plays an increasingly recognized role as a biometal, little is still known of the structure and function of vanadium compounds in living organisms.[5] This understanding will depend, in part, on further knowledge of the coordination chemistry of vanadium in the +3, +4 and +5 states. Many vanadium-Schiff base complexes have been reported, and which include the *cis*- dioxovanadium (V) core. Pecoraro *et al.*[7] have recently reported the formation of a μ-dioxodivanadium(V) complex with a Schiff base ligand in the solid state, where the complex is converted to a mononuclear *cis*-dioxo form in DMSO solution. The present paper describes the preparation and characterization of a *cis*-dioxovanadium(V) complex with a terdentate Schiff base. As far as we know, there is no other such complex with other metal ions. X-ray analysis of the crystal structure has been undertaken. A comparison to related vanadium(V) complexes is made.

---

* Author for correspondence.

## EXPERIMENT

### *Materials and Measurements*

Girard's reagent P, $[NH_2NHCOCH_2(NC_5H_5)]Cl$, was obtained from the British Drug Houses Ltd. All other analytical grade reagents were purchased commercially and used without subsequent purification. $(C_2H_5)_4NVO_3$ was synthesized by a method similar to one reported in the literature[8]. The Schiff base ligand BAP was obtained by the reaction between benzoyl acetone and Girard's reagent P in the usual way.[9] Elemental analysis was performed with an Italy 1106 apparatus. IR spectra were recorded in KBr discs on a Nicolet 170SX spectrophotometer. Electronic spectra in DMSO solution were recorded on a Schimaden UV-260 spectrophotometer. Single crystal X-ray data were collected on automatic Enraf-Nonius CAD-4 diffractometer.

### *Synthesis of* $[VO_2\{C_6H_5C(O)CHC(CH_3)NNC(O)CH_2(NC_5H_5)\}]\cdot C_2H_5OH$

$(C_2H_5)_4NVO_3$ (1.0 mmol) was added to the ethanol solution of BAP (1.0 mmol) at room temperature. The reaction mixture was heated to reflux and stirred for 2h. Filtration afforded a yellow solid, which was washed with cold ethanol and dried *in vacuo* at room temperature over $P_2O_5$. The product was dissolved in DMSO solution, which was evaporated slowly at room temperature. The resulting yellow crystals were suitable for X-ray analysis. Yield, 75%. Found: C, 53.67; N, 10.10; H, 5.12%; Calc. for $C_{19}H_{22}N_3O_5V$: C, 53.91; N, 9.93; H, 5.24%.

### *Crystal structure determination*

A selected single crystal with approximate dimensions 0.15 × 0.20 × 0.25 mm was mounted on a glass fibre. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Cu$-K_\alpha$ radiation ($\lambda = 1.54184$ Å) using the $\omega$-$2\theta$ scan mode [scan width: $0.6 + 0.140 \tan\theta$]. A total of 3483 reflections in the range $2° \leq 2\theta \leq 120°$ were measured ($-12 \leq h \leq 12$, $0 \leq k \leq 17$, $0 \leq l \leq 14$). Some 2352 reflections with $I > 3.0\sigma(I)$ were used for structure solution and refinement. An empirical $\psi$-scan absorption correction were applied (min./max. transmission factors 0.398/0.999).

### *Crystal data*

$VC_{19}H_{22}N_3O_5$, $M = 423.34$, monoclinic, space group $P2_1/a$, $a = 10.690$ (2), $b = 16.008$ (3), $c = 13.164$ (4) Å, $\beta = 107.03$ (2)°, $V = 2153.9$ (18) Å$^3$, $Dc = 1.305$ g cm$^{-3}$, $Z = 4$, $\mu(Cu-K_\alpha) = 43.664$ cm$^{-1}$, $F(000) = 880$.

The structure was solved by direct and difference Fourier methods. Full-matrix least-squares was used to refine the structure on a PDP 11/44 computer with the SDP program. Positions of H atoms localized in a difference Fourier map were included in the calculations but not refined. The structure was refined to final $R = 0.085$, $R_w = 0.089$ and $(\Delta/\sigma)_{max} = 0.15$. Minimum and maximum peaks in the final difference Fourier map were $-0.903$ and $1.315$ eÅ$^{-3}$, respectively.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography (1974).*

## RESULTS AND DISCUSSION

### *Crystal structure studies*

Atomic coordinates of non-hydrogen atoms and thermal parameters are given in Table 1. Selected bond lengths and angles are listed in Table 2. The molecular structure of the compound is shown in Figure 1. X-ray analysis reveals that the molecule possess a *cis*-$VO_2$ moiety. The ligand acts as terdentate anionic ligand and bonds to the *cis*-$VO_2$ unit through ONO to form a distorted trigonal bipyramid configuration. Thus, the coordination number of vanadium(V) is five. Chelation gives rise to one five-membered and one six-membered ring, which make the molecules stable. In the structure, the $VO_2$ moiety is in the *cis* configuration with an OVO angle of 107.9(2)°,[10–13] and the two V–O distances [1.616(3) and 1.601(3) Å] are typical of V=O interactions[7]. Bond distances of the other two oxygen atoms bonding to the vanadium atom, V–O3 [1.929(4) Å] and V–O4 [1.980(4) Å], are in the range of other vanadium-Schiff base complexes.[14] The V–N1 distance is 2.133 (4) Å, which is similar as compared to analogues.[15] The sum of three angles O1–V–O2, O2–V–N1 and O1–V–N1 is 359.3(6)°, and the angle O3–V–O4 is 149.2(2)°. In view of these features it may be considerated that the vanadium atom is in the O1–O2–N1 plane. Atoms O3 and O4 are on the conic nodes of the distorted

**Table 1** Atomic coordinates and thermal parameters for non-hydrogen atoms of the complex.

| Atom | *x/a* | *y/b* | *z/c* | *Beq* |
|---|---|---|---|---|
| V | 0.2057(1) | 0.07695(8) | 0.7397(1) | 3.49(3) |
| O1 | 0.1153(4) | 0.1492(3) | 0.7674(4) | 4.2(1) |
| O2 | 0.1200(5) | 0.0282(4) | 0.6367(5) | 5.8(2) |
| O3 | 0.2032(5) | 0.0039(4) | 0.8557(5) | 5.2(1) |
| O4 | 0.3005(5) | 0.1589(4) | 0.6769(5) | 4.8(1) |
| N1 | 0.4036(5) | 0.0351(4) | 0.7789(5) | 3.8(1) |
| N2 | 0.4827(5) | 0.0770(4) | 0.7267(5) | 3.9(1) |
| N3 | 0.5900(5) | 0.1543(4) | 0.5903(5) | 3.7(1) |
| C1 | 0.2018(7) | - 0.1160(6) | 0.9572(7) | 4.5(2) |
| C2 | 0.2412(8) | - 0.1978(6) | 0.9838(8) | 5.2(2) |
| C3 | 0.1737(9) | - 0.2445(6) | 1.0416(7) | 5.5(2) |
| C4 | 0.0774(9) | - 0.2123(7) | 1.0726(7) | 5.7(2) |
| C5 | 0.040(1) | - 0.1333(8) | 1.0466(9) | 8.0(3) |
| C6 | 0.101(1) | - 0.0865(7) | 0.9912(9) | 7.7(3) |
| C7 | 0.2698(7) | - 0.0612(6) | 0.8970(7) | 4.4(2) |
| C8 | 0.3925(8) | - 0.0773(6) | 0.8930(7) | 5.2(2) |
| C9 | 0.4612(7) | - 0.0284(6) | 0.8367(7) | 4.6(2) |
| C10 | 0.5988(8) | - 0.0531(7) | 0.8433(9) | 6.5(3) |
| C11 | 0.4151(7) | 0.1391(5) | 0.6754(6) | 4.0(2) |
| C12 | 0.4792(7) | 0.1957(5) | 0.6134(7) | 4.2(2) |
| C13 | 0.5743(8) | 0.1122(6) | 0.5005(7) | 4.8(2) |
| C14 | 0.6755(9) | 0.0722(6) | 0.4802(8) | 5.6(2) |
| C15 | 0.7980(8) | 0.0747(6) | 0.5536(8) | 5.7(2) |
| C16 | 0.8119(8) | 0.1172(6) | 0.6453(8) | 5.1(2) |
| C17 | 0.7078(7) | 0.1584(5) | 0.6637(6) | 4.3(2) |
| O5 | 0.287(1) | 0.165(1) | 0.374(1) | 8.1(4) |
| C18 | 0.052(2) | 0.149(1) | 0.403(2) | 12.1(6) |
| C19 | 0.1588(6) | 0.2064(5) | 0.3665(9) | 5.3(2) |
| C20 | 0.1559(7) | 0.1394(6) | 0.3222(7) | 4.8(2) |

* $Beq = 4/3[a^2B_{11}+b^2B_{22}+c^2B_{33}+ab(\cos\gamma)B_{12}+ac(\cos\beta)B_{13}+bc(\cos\alpha)B_{23}]$.

**Table 2** Selected bond distances (Å) and angles (°) for the complex.

| Distances (Å) | | | | | |
|---|---|---|---|---|---|
| V | O1 | 1.616(3) | N1 | N2 | 1.405(5) |
| V | O2 | 1.601(3) | N1 | C9 | 1.309(6) |
| V | O3 | 1.929(4) | N2 | C11 | 1.297(6) |
| V | O4 | 1.980(4) | C1 | C2 | 1.388(8) |
| V | N1 | 2.133(4) | C7 | C8 | 1.353(7) |
| O3 | C7 | 1.290(6) | C8 | C9 | 1.422(8) |
| O4 | C11 | 1.271(6) | C9 | C10 | 1.501(7) |

| Angles (°) | | | | | | | |
|---|---|---|---|---|---|---|---|
| O1 | V | O2 | 107.9(2) | N1 | N2 | C11 | 107.3(4) |
| O1 | V | O3 | 96.2(2) | O3 | C7 | C1 | 113.7(4) |
| O1 | V | O4 | 91.9(2) | O3 | C7 | C8 | 123.9(5) |
| O1 | V | N1 | 141.9(2) | C1 | C7 | C8 | 122.3(5) |
| O2 | V | O3 | 103.7(3) | C7 | C8 | C9 | 124.8(5) |
| O2 | V | O4 | 101.9(2) | N1 | C9 | C8 | 120.3(4) |
| O2 | V | N1 | 109.5(2) | N1 | C9 | C10 | 121.6(6) |
| O3 | V | O4 | 149.2(2) | C8 | C9 | C10 | 118.2(5) |
| O3 | V | N1 | 82.(1) | O4 | C11 | N2 | 125.1(5) |
| O4 | V | N1 | 73.5(1) | O4 | C11 | C12 | 116.7(5) |
| N2 | N1 | C9 | 113.9(4) | N2 | C11 | C12 | 118.0(4) |

trigonal bipyramid. The torsion angles C1–C7–C8–C9, N2–N1–C9–C8 and C9–N1–N2–C11 are 179.3(8), −179.3(7) and −178.3(7)°, respectively. A difference Fourier synthesis suggested that the solvent molecule $C_2H_5OH$ in the complex is disordered, and successive attempts showed that C19 and C20 are present statistically with occupancy factors each of 0.5. The higher *R* value is due to the disorder of the solvent molecule.

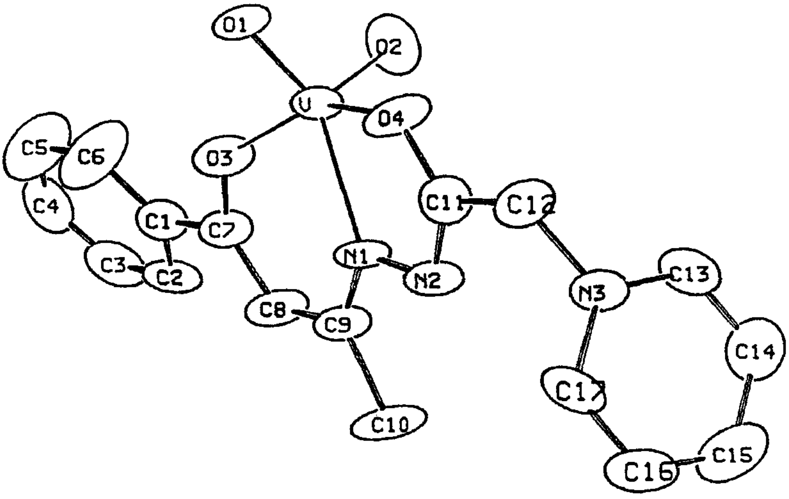

**Figure 1** A view of the [$VO_2$(BAP)] molecule with atom numbering. Hydrogen atoms have been omitted for clarity.

## *Comparison of structures of related vanadium(V) complexes*

In previous papers, we have reported two *cis*-dioxovanadium (V) monomers [$VO_2$(Sal−P)]·$CH_3OH$ (**I**) and [$VO_2$(Sal−T)] (**II**) that have very similar coordination environments with that herein reported for the title complex [$VO_2$(BAP)] (**III**). In these complexes, the Schiff base ligands are all present as terdentate donors coordinating through ONO, and which form a distorted square pyramid configuration in complex **I** and a trigonal bipyramid configuration in **II** and **III**, respectively. Pecoraro *et al.*[7] have recently reported a dimeric complex [$VO_2$(1,2-pnSal)]$_2$ (**IV**) which has a similar terdentate Schiff base ligand with ONN coordination to V(V) in the solid state. In the structure of complex **IV**, there are two distinct oxo groups [V−O, 1.619(6) and 1.665(4) Å], while the two V=O bond lengths are basically identical [1.616(3) and 1.601(3) Å)] in complex **III**. They believe that the reason why dimeric forms are converted to monomeric forms in DMSO solution is that the solvent breaks the weak bridging interactions observed in the solid state. In addition, the two ligand nitrogen atoms separated by an ethyl group in complex IV are *cis* to each other and are both coordinated to V(V). In the first three complexes, only one of the two ligand nitrogen atoms is coordinated to V(V), due to direct linking of the two nitrogen atoms.

## *IR spectra*

Selected infrared data for BAP and the complex are listed in Table 3. The characteristic ligand band $\nu$C=N at 1601.7 $cm^{-1}$ displays a shift to higher frequency (1610.1, 1636.2 $cm^{-1}$) in the complex, indicating coordination of the azomethine nitrogen atom to vanadium[16]. The expected $\nu$C=O ligand band is absent in the ligand, suggesting that it exists in the enol form. In spectra of the ligand, a medium intensity band at 3317.1 $cm^{-1}$ may be assigned to $\nu$OH. In the complex, the $\nu$OH shift to higher frequency (3375.6 $cm^{-1}$) indicates its deprotonation on coordination and this band may also be caused by ethanol OH. The enolic $\nu$C−O (1256.5 $cm^{-1}$) band of the ligand shifts to lower frequency (1225.7 $cm^{-1}$) in the complex. This indicates that both hydroxyl groups are involved in coordination. Two new strong bands in the complex at 928.6 and 902.9 $cm^{-1}$ may be assigned to sym. $\nu$O=V=O and asym. $\nu$O=V=O, respectively.[13,17] The two bands at 505.0 $cm^{-1}$ and 429.1 $cm^{-1}$ are absent in the spectra of the ligand and can be associated with V−O and V−N stretching vibrations. IR results are in good agreement with the X-ray analysis.

## *Electronic spectra*

Electronic absorption spectra were measured in DMSO. BAP exhibits three absorption bands at 259.2 nm ($\varepsilon = 1.40 \times 10^4\ M^{-1}\ cm^{-1}$), 276.0 nm ($\varepsilon$ = 1.26 ×

**Table 3** Infrared data for the ligand and complex ($cm^{-1}$).

| | $\nu$OH | enolic $\nu$C=O | C=N | $\nu$V=O | $\nu$V=O |
|---|---|---|---|---|---|
| ligand (BAP) | 3317.1 | 1256.5 | 1601.7 | | |
| Complex | 3375.6 | 1225.7 | 1610.1 | 928.6 | 505.0 |
| | | | 1636.2 | 902.9 | |

$10^4$ $M^{-1}$ $cm^{-1}$) and 316.2 nm ($\varepsilon$ = 1.91 × $10^4$ $M^{-1}$ $cm^{-1}$), which may be due to $\pi$–$\pi^*$ transitions in the ligand. In the spectra of the complex, there is only one strong band at 262.0 nm ($\varepsilon$ = 1.27 × $10^4$ $M^{-1}$ $cm^{-1}$) and a shoulder at 286.0 nm ($\varepsilon$ = 5.51 × $10^3$ $M^{-1}$ $cm^{-1}$).

## SUPPLEMENTARY MATERIAL

Atomic coordinates for the hydrogen atoms, thermal parameters, full lists of bondlengths, bond angles, torsion angles and observed and calculated structure factors for the complex are available from the authors on request.

## *References*

1. N.D. Chasteem, Ed., *Vanadium in Biological Systems,* (Kluwer Academic Publishers, Dordrecht, The Netherlands, 1990).
2. D. Rehder, *Angew. Chem. Int. Ed. Engl.,* **30,** 148 (1991).
3. J.J.R. Frausto da Silva, *Chem. Speciation and Bioavailability,* **1,** 139 (1989).
4. R. Wever and K. Kustin, *Adv. Inorg. Chem.,* **35,** 103 (1990).
5. N.D. Chasteen, J.K. Grady and C.E. Holloway, *Inorg. Chem.,* **25,** 2754 (1986).
6. V. Vergopoulos, W. Priebsch, M. Fritzsche and D. Rehder, *Inorg. Chem.,* **32,** 1844 (1993).
7. C.A. Root, J.D. Hoeschele, C.R. Cornman, J.W. Kampf and V.L. Pecoraro, *Inorg. Chem.,* **32,** 3855 (1993).
8. K.F. Jahr, J. Fuchs and O. Oberhauser, *Chem. Ber.,* **101,** 482 (1968).
9. C.J. Carrano, C.M. Nunn, R. Quan, J.A. Bonadies and V.L. Pecoraro, *Inorg. Chem.,* **29,** 944 (1990).
10. W.R. Scheidt, R. Countryman and J.L. Hoard, *J. Amer. Chem. Soc.,* **93,** 3878 (1971).
11. W.R. Scheidt, C. Tsai and J.L. Hoard, *J. Amer. Chem. Soc.,* **93,** 3867 (1971).
12. W.R. Scheidt, D.M. Collins and J.L. Hoard, *J. Amer. Chem., Soc.,* **93,** 3873 (1971).
13. X.-H. Li, M.S. Lah and V.L. Pecoraro, *Inorg. Chem.,* **27,** 4657 (1988).
14. A. Giacomelli, C. Floriani, A. Ofir De Souza Duarte, A. Chiesi-Villa and C. Guastini, *Inorg. Chem.,* **21,** 3310 (1982).
15. A. Hills, D.L. Hughes, G.J. Leigh and J.R. Sanders, *J. Chem. Soc., Dalton Trans.,* 61 (1991).
16. N.S. Biradar and V.H. Kulkarni, *Rev. Roum. Chim.,* **16,** 1203 (1971).
17. X. Wang, X.-M. Zhang and H.-X. Liu, *Inorg. Chim. Acta.,* in press.