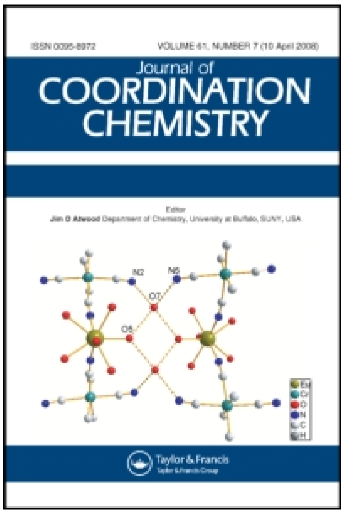

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Microwave-assisted aqueous phase synthesis and single crystal study of oxovanadium(IV) (2-hydroxybenzylideneamino) acetate

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Microwave-assisted aqueous phase synthesis and single crystal study of oxovanadium(IV) (2-hydroxybenzylideneamino) acetate

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Single crystal of oxovanadium(IV) (2-hydroxybenzylideneamino) acetate was synthesized by template method in aqueous phase using microwaves as the source of energy. A fine crystalline complex was obtained in high yield within a few minutes. All bond distances and angles were observed to study the effect of bonding of vanadium and distortion from normal. Other spectroscopic data are also reported.

Keywords: Microwave-assisted synthesis; Amino acid Schiff base; Vanadium(IV) complex; Single crystal

1. Introduction

Schiff-base compounds containing an imino group (–C=N–) are potential anticancer drugs, and their anticancer activity tends to increase when they form complexes with metal ions [1–8]. Many symmetric and asymmetric Schiff bases are derived from salicylaldehyde and other suitable amines to mimic biological systems. Unsymmetical ligands always attract the attention of researchers to resolve critical unsolved questions in physiology and biochemistry. Ligands derived from amino acids and salicylaldehyde are a good example taken from the earlier studies to understand the role of unsymmetrical ligands.

Metal complexes of Schiff bases were derived from amino acids; the paper which formed the foundation of our study was that of Theriot *et al.* [9] in 1969. Prior to that very little work was done in this area [10–12]. Many unsymmetrical Schiff bases and their metal complexes have been studied. Mn(II), Co(II), Fe(III), and VO(IV) complexes of unsymmetrical Schiff bases derived from amino acids were studied earlier [13–15]. The crystal structure of *N*-salicylideneglycinatoaquocopper(II) was studied for the first time by Professor Masao Kakudo and co-workers by X-ray crystal analysis.

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Recently, a detailed study of some electronegative oxovanadium(IV) Schiff-base complexes was reported by Bezaatpour *et al.* [16]. Insulin-enhancing activity of unsymmetrical Schiff-base oxovanadium(IV) complexes were reported by Nejo *et al.* [17]. Isomeric unsymmetric metal complexes were reported by Kolawole and Osowole [18].

Conventional synthesis of coordination compounds using reflux consumes energy, time, and solvents. Development of new energy efficient, green, clean, and economical methods for such synthesis is needed. In our literature survey, only one article was dedicated to the synthesis of coordination complexes using microwave irradiation method [19].

This article was aimed to synthesize and study the single crystal structure of oxovanadium(IV) (2-hydroxybenzylideneamino) acetate (**1**). Direct synthesis of single crystals was done in aqueous phase in a simple manner to obtain good crystalline compound in high yield by one pot microwave irradiation.

2. Experimental

2.1. *Materials*

All reagents were of analytical grade purchased from S.D. Fine Chemicals Ltd., Mumbai, and used as received. Vanadyl sulfate was $VOSO_4 \cdot 5H_2O$ by gravimetric analysis.

2.2. *Physical measurements*

Microwave oven of ONIDA make, 2450 MHz frequency, 700 W output with digital timer, and clock was used for synthesis. Elemental analysis was carried out on a Perkin Elmer elemental analyzer model PE2400. Infrared (IR) spectra were recorded on a Perkin Elmer spectrophotometer GX FT-IR using KBr pellets (1% w/w). ^{1}H-NMR spectra were recorded on a Bruker Avance II model at 400 MHz using dimethyl sulfoxide (DMSO). Chemical shifts for proton resonances are reported in ppm (δ) relative to tetramethylsilane (TMS). Electronic spectra were recorded on a Cintra 10e UV-Vis spectrophotometer. The mass spectra were recorded by electronspray ionization method on a Waters Q-Tof micro mass spectrometer. Electron spin resonance (ESR) spectra were recorded at room temperature in solid state as well as using DMSO on a Varian E-112 ESR spectrophotometer. Magnetic susceptibilities of the solid complexes were measured employing a Gouy balance at room temperature (31°C) using mercury(II) tetrathiocynato cobaltate, $Hg[Co(CNS)_4]$, as a calibrant for standardizing the Gouy balance. Melting points of ligands were recorded by open capillary method and were uncorrected. The single crystal X-ray was obtained using an Enraf-Nonius single crystal X-ray diffractometer.

2.3. *Synthesis of oxovanadium(*IV*) (2-hydroxybenzylideneamino) acetate (1)*

Glycine (3 mmol, 225 mg) was dissolved in 15 mL water in a 150 mL conical flask. A buffer solution prepared by adding two drops of acetic acid and 80 mg of sodium acetate in 8 mL water was added dropwise to the solution of glycine to adjust the pH from 5.8 to 6.0. $VOSO_4$ (3 mmol, 785 mg) was added to the above-mentioned solution and warmed to 70°C. Salicylaldehyde (3 mmol, 3.6 mL) was added to this warm solution and mixed thoroughly. The reaction mixture was irradiated in a microwave oven for 2.5 min at 210 W. The irradiation was done for 10 s at a time so as to avoid the reaction becoming violent. The reaction mixture turned to a clear dark blue solution, cooled gradually to 40°C and then kept at room temperature. Fine blue crystals appeared at the bottom. Yield: 640 mg, 87%. The complex was soluble in dimethylformamide (DMF) and DMSO but insoluble in ethanol, methanol, and other common solvents.

IR data (KBr, cm^{-1}): 3026 (broad), 1635 (st, intense), 1370 (st, intense), 1006 (st, intense), 961, 578, and 459; ^{1}H-NMR data: (δ-ppm, DMSO-d_6): 8.45 (1H, s, –CH=N–), 7.5–6.8 (4H, m, ArH), and 4.3 (2H, s, –CH_2–); UV-Vis [DMSO, λ_{max} (nm)]: 216.8, 285.2, 366.8, 386.0, and 399.2. Electron spectra (ES) [multispectral imaging (MSI)]: Calcd (*m*/*z*): 262.11, 244.1, Found: 262, 244.8; Anal. Calcd for $C_9H_7NO_4V \cdot H_2O$ (%): C, 41.40; H, 3.09; N, 5.36; and V, 19.51. Found (%): C, 41.52; H, 3.14; N, 5.64; and V, 19.02. Magnetic moment μ $BM_{eff} = 1.69$.

2.4. *Single crystal analysis of 1*

Crystal with dimensions of $0.25 \times 0.20 \times 0.19\,mm^3$ was selected to obtain the data. The intensity data were collected on an Enraf-Nonius single crystal X-ray diffractometer with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation at 296(2) K. The structure was solved by direct methods using SHELXL-97. The vanadium was first located and carbon, nitrogen, and oxygen were found in difference Fourier maps. Hydrogens residing on carbon and oxygen were placed geometrically and refined riding on their parent atoms. All non-hydrogen atoms were refined anisotropically. Details of the final refinement and intermolecular interactions in **1** are given in tables 1 and 2, respectively.

3. Results and discussion

Crystal structure of the complex clearly shows that the oxovanadium(V=O) is out of the plane of the ligand formed from glycine and salicylaldehyde (figures 1 and 2). Both V–O–C bonds push vanadium out of the plane of the ligand resulting in distorted square pyramidal geometry. The two V–O–C bond angles are 126.7 and 120.4 Å (table 3). The VO unit is lifted 0.685 Å above the plane of the phenyl ring and 0.593 Å above the plane of the ligand. A water is attached to vanadium at 2.005 Å suggesting coordinated water. Bond valence calculations for V(IV) amount to 3.57. Thus, vanadium is V(IV) and the deficient electron density is compensated by the formation of a coordinate bond with imine (–CH=N) nitrogen and oxygen from coordinated water.

The V=O bond distance is 1.580(3), shorter than usually found for a six-coordinate vanadium [20]. The bond distances of V–O_{phenyl}, V–$O_{caboxyl}$, and V–N_{imine} are 1.916, 1.980, and 2.044 Å, respectively.

Table 1. Crystallographic details of **1**.

CCDC number	741713
Empirical formula	$C_9H_7NO_4V$
Formula weight	244.10
Color	Blue
Crystal morphology	Block
Temperature (K)	293(1)
Radiation	Mo-Kα
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P\ 2(1)/n$
Unit cell dimensions (Å, °)	
a	11.1322(14)
b	7.3477(10)
c	12.5660(16)
α	90.00
β	102.942(6)
γ	90.00
Volume (Å^3), Z	1001.7(2), 4
Calculated density (g mL^{-1})	1.62
Absorption coefficient, μ (mm^{-1})	0.981
$F(0\,0\,0)$	491.9
θ range for data collection (°)	2.2–25.0
Reflections collected	1760
Parameters	181
Goodness-of-fit on F^2	1.071
R_obs, wR_2_obs	0.042, 0.114
$\Delta\rho_{\min}$, $\Delta\rho_{\max}$ (eÅ^{-3})	−0.360, 0.804

Table 2. Intermolecular interactions in **1**.

D–H···A	r(D–H) (Å)	r(D–A) (Å)	r(H···A) (Å)	∠D–H···A (°)	Symmetry
C3–H1···O4	0.74(3)	3.366(5)	2.802(8)	134(3)	$-x+1/2, +y-1/2, -z+1/2+1$
C4–C4···O4	0.96(4)	3.595(5)	2.703(7)	154(3)	$x-1/2, -y+1/2, +z+1/2$
C5–H3···O2	0.93(4)	3.696(5)	2.933(5)	139(2)	$x-1/2, -y+1/2, +z+1/2$
C8–H6···O1	0.94(4)	3.716(4)	2.928(9)	141(3)	$x, +y-1, +z$
O5–H12···O3	0.95(5)	2.720(4)	1.761(2)	178(5)	$-x+1/2+1, +y+1/2, -z+1/2+1$
O5–H11···O3	0.59(4)	2.754(4)	2.160(7)	175(5)	$x, +y+1, +z$
C8–H7···Cg1[a]	1.05(1)	3.646(4)	2.660(1)	157(1)	$1/2-x, -1/2+y, 3/2-z$

[a] Cg1 is a center of gravity of the ring formed by the atoms C1, C2, C3, C4, C5, and C6.

The complex shows a sharp intense peak for azomethine (–CH=N–) at 1635 cm^{-1} [21] and a peak for V=O at 961 cm^{-1}. Also observed are sharp peaks at 535 and 459 cm^{-1} corresponding to V–O and V–N, respectively. A broad peak at 3026 cm^{-1} corresponds to lattice water [22].

^{1}H-NMR spectra of the complex show a singlet at 8.45 ppm for azomethine hydrogen and peaks beyond 10 ppm suggesting that carboxylic and phenolic proton are replaced to form V–O bonds. Spectra show a multiplet in aromatic region from salicylaldehyde and a singlet for methylene of glycine.

Mass spectra recorded by electron spray ionization show a peak corresponding to the molecular weight of the complex at 262. A base peak at 244.8 indicates loss of water.

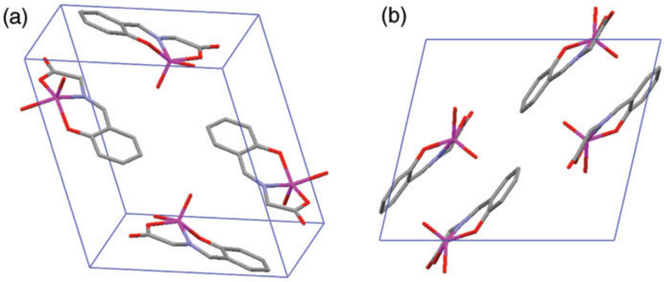

Figure 1. Packing diagram (two views a and b) for **1**.

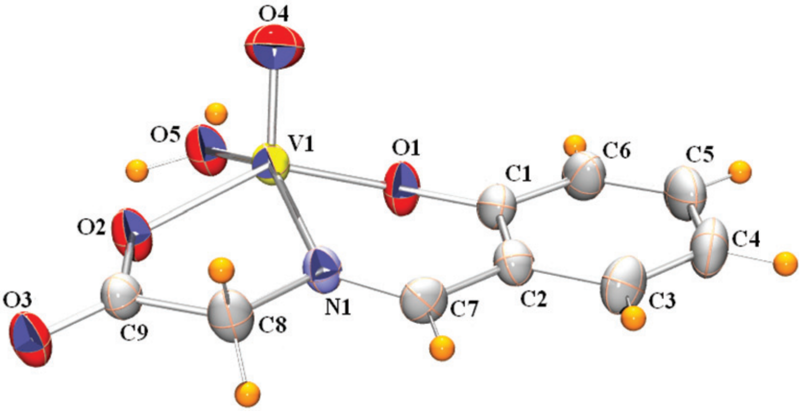

Figure 2. ORTEP diagram (50% probability) showing the molecule with a slightly distorted square pyramidal geometry and V=O lifted above the plane of the ligand.
V, yellow; C, gray; N, blue; O, red; H, orange; hydrogens were refined isotropically and are shown as spheres.

Electron paramagnetic resonance (EPR) spectra of the complex in DMSO clearly show an eight-line hyperfine splitting which indicates interaction of a single unpaired electron with ^{51}V ($I = 7/2$).

Bond valence calculations were done using the software *Valence*. The vanadium was first considered as 5+ and the bond valence sum was found to be 4.319. The calculations were also done by considering V as 4+ and the bond valence sum was found to be 4.199. Both the results are given in "Supplementary material." The oxidation state of V in the given complex seems to be 4+.

4. Conclusion

Synthesis of inorganic complexes using microwave irradiation is less studied. Single crystals of metal complexes are normally grown either by slow evaporation or diffusion

Table 3. Bond distances (Å) and angles (°) of all bonds except bond angles including hydrogen.

Atoms	Bond distance (Å)	Atoms	Bond angle (°)
V1–O4	1.580(3)	O7–V1–O1	107.96(13)
V1–O1	1.916(2)	O7–V1–O2	108.97(13)
V1–O2	1.980(2)	O1–V1–O2	142.80(11)
V1–O5	2.005(3)	O7–V1–O5	107.55(15)
V1–N1	2.044(3)	O1–V1–O5	88.22(11)
N1–C7	1.280(4)	O2–V1–O5	84.90(12)
N1–C8	1.468(4)	O7–V1–N1	105.19(13)
O3–C9	1.228(4)	O1–V1–N1	87.80(10)
O1–C1	1.332(4)	O2–V1–N1	78.53(10)
O2–C9	1.280(4)	O5–V1–N1	146.62(13)
O5–H12	0.96(5)	C7–N1–C8	119.5(3)
O5–H11	0.59(4)	C7–N1–V1	126.6(2)
C8–C9	1.519(5)	C8–N1–V1	114.0(2)
C8–H6	0.95(4)	C1–O1–V1	126.7(2)
C8–H7	1.06(4)	C9–O2–V1	120.4(2)
C7–C2	1.438(5)	N1–C8–C9	108.0(3)
C7–H5	0.86(3)	N1–C7–C2	124.3(3)
C2–C3	1.406(5)	O3–C9–O2	123.2(3)
C2–C1	1.409(5)	O3–C9–C8	121.1(3)
C6–C5	1.368(5)	O2–C9–C8	115.6(3)
C6–C1	1.398(5)	C3–C2–C1	119.0(3)
C6–H4	0.83(4)	C3–C2–C7	118.2(3)
C5–C4	1.386(6)	C1–C2–C7	122.8(3)
C5–H3	0.94(4)	C5–C6–C1	121.0(4)
C3–C4	1.366(6)	C6–C5–C4	121.4(4)
C3–H1	0.74(3)	O1–C1–C6	119.2(3)
C4–H2	0.96(4)	O1–C1–C2	122.7(3)
		C6–C1–C2	118.1(3)
		C4–C3–C2	121.9(4)
		C3–C4–C5	118.4(4)

method. For complexes soluble only in highly polar solvents like DMSO and DMF, it is not easy to obtain the single crystals. This study is useful to obtain single crystals of coordination compounds. The only limitation found in this study was that one reactant organic species should be soluble in water which can take up the metal in the beginning. Gradual, stepwise, and controlled cooling of the reaction mixture results in fine crystalline complex. We are working to extend this technique to single crystals of coordination complexes without slow vaporization.

Supplementary material

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (deposition no. CCDC-741713). The data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

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References

[1] M.A. Sharpe, R. Ollosson, V.C. Stewart, J.B. Clark. *Biochem. J.*, **97**, 366 (2002).
[2] P. Yang, S. Chiu, L. Lin. *Toxicol. Sci.*, **85**, 551 (2005).
[3] M. Baudry, S. Etienne, A. Bruce, M. Palucki, E. Jacobsen, B. Malfroy. *Biochem. Biophys. Res. Commun.*, **192**, 964 (1993).
[4] P. Pietikainen. Mn-salen catalyzed asymmetric epoxidation: search for new oxidation systems. Academic dissertation, University of Helsinki, Finland (2001) (unpublished).
[5] O. Pouralimardan, A. Chamayou, C. Janiak, H. Hosseini-Monfared. *Inorg. Chim. Acta*, **360**, 1599 (2007).
[6] N. Raman, J.D. Raja, A. Sakthivel. *J. Chem. Sci.*, **119**, 303 (2007).
[7] W. Aoam, C.R. Saha-Moeller, P. Ganeshpure. *Ind. J. Chem.*, **43A**, 56 (2004).
[8] G. Liu, J. Liao, S. Huang, G. Shen, R. Yu. *Anal. Sci.*, **17**, 1031 (2001).
[9] L.J. Theriot, G.O. Carlisle, H.J. Hu. *J. Inorg. Nucl. Chem.*, **3**, 2841 (1969).
[10] G.L. Eichhorn, J.W. Dawes. *J. Am. Chem. Soc.*, **76**, 5663 (1954).
[11] G.L. Eichhorn, N.D. Marchand. *J. Am. Chem. Soc.*, **78**, 2668 (1956).
[12] A. Nakahara, H. Yamamoto, H. Matsumoto. *Sci. Rep. Coll. Gen. Educ., Osaka Univ.*, **12**, 11 (1963).
[13] Y. Kemin, Z. Wen, L. Gui. *Sci. China, Ser. B*, **42**, 2 (1999).
[14] G.B. Roy. *Inorg. Chim. Acta*, **362**, 1709 (2009).
[15] A.M.A. Hassaan. *J. Islamic Acad. Sci.*, **4**, 271 (1991).
[16] A. Bezaatpour, M. Behzad, D.M. Boghaei. *J. Coord. Chem.*, **62**, 1127 (2009).
[17] A.A. Nejo, G.A. Kolawole, A.R. Opoku, C. Muller, J. Wolowska. *J. Coord. Chem.*, **62**, 3411 (2009).
[18] G.A. Kolawole, A.A. Osowole. *J. Coord. Chem.*, **62**, 1437 (2009).
[19] R. Pagadala, P. Ali, J.S. Meshram. *J. Coord. Chem.*, **62**, 4009 (2009).
[20] C. Holloway, M. Melnik. *Rev. Inorg. Chem.*, **7**, 75 (1985).
[21] J. Costa Pessoa, I. Cavaco, I. Correia, M.T. Duarte, R.D. Gillard, R.T. Henriques, F.J. Higes, C. Madeira, I. Tomaz. *Inorg. Chim. Acta*, **1**, 293 (1999).
[22] J.C. Pessoa, I. Tomaz, R.T. Henriques. *Inorg. Chim. Acta*, **356**, 121 (2003).