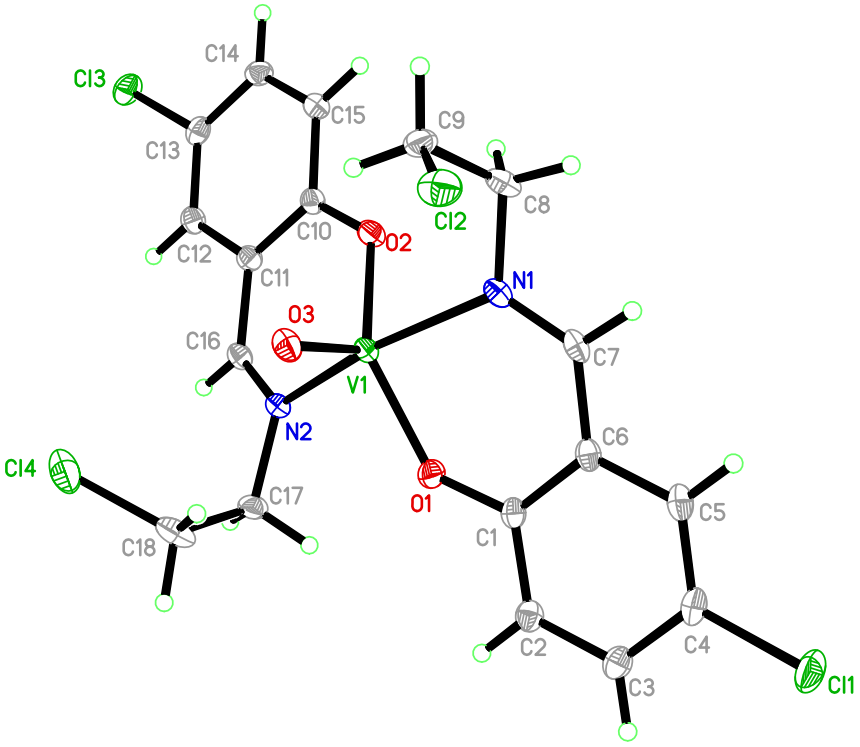
Wei Wei, Ya-Zhai Zhang, Heng-Qiang Zhang, Qi-Ying Zhang*, Zhao-Kun Xuan and Hong-Li Chen

The crystal structure of bis(4-chloro-2-(((2-chloroethyl)imino)methyl)phenolato-κ²*N*,*O*)-oxidovanadium(IV), $C_{18}H_{16}Cl_4N_2O_3V$



https://doi.org/10.1515/ncrs-2022-0179
Received April 7, 2022; accepted May 5, 2022;
published online May 20, 2022

Abstract

$C_{18}H_{16}Cl_4N_2O_3V$, orthorhombic, *Pbca* (no. 61), $a = 7.8555(3)$ Å, $b = 21.6645(7)$ Å, $c = 23.7584(8)$ Å, $V = 4043.3(2)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0296$, $wR_{ref}(F^2) = 0.0799$, $T = 296(2)$ K.

CCDC no.: 2170726

The asymmetric unit of the molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

In a 250 mL flask containing 50 mL of absolute methanol were added 5 mmol of 2-chloroethanamine hydrochloride

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.24 × 0.22 × 0.20 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	1.04 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, *φ* and *ω*
θ_{max}, completeness:	28.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	52,657, 5077, 0.037
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4204
$N(param)_{refined}$:	253
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

***Corresponding author: Qi-Ying Zhang**, Department of Chemistry, East China Normal University, Shanghai 200062, P. R. China, E-mail: qyzhang@163.com
Wei Wei, Department of Architechture Engineering, Chengde Petroleum College, Chengde 067000, P. R. China
Ya-Zhai Zhang, Heng-Qiang Zhang, Zhao-Kun Xuan and Hong-Li Chen, Department of Chemistry, Hebei Normal University for Nationalities, Chengde 067000, P. R. China. https://orcid.org/0000-0001-7138-2905 (H.-Q. Zhang)

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.96261 (19)	0.84000 (7)	0.91069 (7)	0.0223 (3)
C2	1.0490 (2)	0.88008 (7)	0.94715 (7)	0.0264 (3)
H2	1.120267	0.863977	0.974748	0.032*
C3	1.0295 (2)	0.94320 (8)	0.94254 (8)	0.0284 (3)
H3	1.088632	0.969354	0.966640	0.034*
C4	0.9214 (2)	0.96775 (8)	0.90186 (8)	0.0293 (4)
C5	0.8342 (2)	0.93004 (8)	0.86593 (8)	0.0290 (4)
H5	0.762365	0.946995	0.838921	0.035*
C6	0.85286 (19)	0.86547 (7)	0.86972 (7)	0.0238 (3)
C7	0.7533 (2)	0.82770 (7)	0.83193 (7)	0.0247 (3)
H7	0.687520	0.848394	0.805420	0.030*
C8	0.6319 (2)	0.74077 (8)	0.78918 (7)	0.0295 (4)
H8A	0.697539	0.713929	0.764757	0.035*
H8B	0.583882	0.773356	0.766106	0.035*
C9	0.4898 (2)	0.70435 (8)	0.81493 (8)	0.0332 (4)
H9A	0.536597	0.674730	0.841353	0.040*
H9B	0.430871	0.681592	0.785667	0.040*
C10	0.9680 (2)	0.60007 (7)	0.81768 (7)	0.0228 (3)
C11	1.0800 (2)	0.57444 (7)	0.85770 (7)	0.0230 (3)
C12	1.1414 (2)	0.51399 (7)	0.85043 (7)	0.0249 (3)
H12	1.214211	0.496880	0.877066	0.030*
C13	1.0942 (2)	0.48022 (7)	0.80427 (7)	0.0255 (3)
C14	0.9875 (2)	0.50524 (7)	0.76341 (7)	0.0268 (3)
H14	0.958389	0.482248	0.731792	0.032*
C15	0.9253 (2)	0.56427 (7)	0.77009 (7)	0.0258 (3)
H15	0.853922	0.580819	0.742744	0.031*
C16	1.1342 (2)	0.60697 (7)	0.90758 (7)	0.0240 (3)
H16	1.219538	0.588614	0.928934	0.029*
C17	1.1468 (2)	0.68071 (8)	0.97908 (7)	0.0285 (4)
H17A	1.167050	0.724806	0.976862	0.034*
H17B	1.254909	0.660500	0.986046	0.034*
C18	1.0268 (3)	0.66737 (10)	1.02690 (8)	0.0385 (4)
H18A	0.916831	0.685790	1.018956	0.046*
H18B	1.070585	0.685875	1.061143	0.046*
Cl1	0.89366 (7)	1.04766 (2)	0.89870 (2)	0.04335 (13)
Cl2	0.34173 (6)	0.75320 (2)	0.85067 (2)	0.04028 (12)
Cl3	1.16452 (6)	0.40416 (2)	0.79803 (2)	0.03444 (11)
Cl4	1.00140 (7)	0.58634 (3)	1.03715 (2)	0.05089 (15)
N1	0.74635 (17)	0.76841 (6)	0.83117 (5)	0.0228 (3)
N2	1.07598 (17)	0.65876 (6)	0.92533 (5)	0.0222 (3)
O1	0.98674 (15)	0.78001 (5)	0.91608 (5)	0.0269 (2)
O2	0.90385 (15)	0.65630 (5)	0.82275 (5)	0.0258 (2)
O3	0.72159 (15)	0.68821 (6)	0.92694 (5)	0.0292 (3)
V1	0.87579 (3)	0.70857 (2)	0.88741 (2)	0.01983 (8)

and 5 mmol of 3-chloro-2-hydroxybenzaldehyde. Then 5 mmol of NaOH was dissolved in 2 mL H_2O, added to the above solution and the contents were refluxed for 3 h at 343 K. After cooling to room temperature, we added 10 mL methanol containing 2.5 mmoL of vanadyl acetylacetonate. To this solution was added 30 mL trichloromethane and filtered off. The filtrate was refluxed with stirring for 3 h at 343 K. The yellow crystals that formed were filtered off and after 10 days at room temperature.

Experimental details

A suitable crystal was selected and mounted on a 'Bruker APEX–II CCD' diffractometer. Using Olex2 [2], the structure was solved with the XT [3] structure solution program and refined with the ShelXL [4] refinement package. All of hydrogen atoms were added using a riding model. Their U_{iso} values were set to $1.2U_{eq}$ of the parent atoms.

Comment

Vanadium compounds as insulin mimics have been studied for more than 20 years [5, 6]. A great number of organic vanadium compounds were synthesized, including oxovanadium, peroxovanadium and vanadium hydroxylamido compounds [7, 8]. These complexes contain a five or seven-coordinated vanadium. However, due to the complexity of vanadium coordination mode, the possible correlation between the biological activity and the coordination structure of the vanadium compounds is still very elusive [9]. These results prompted us to choose structurally similar ligands that could engage in multiple, simultaneous coordination modes and to use such molecular in the assembly of novel complexes.

The crystallographic data revealed that the vanadium(IV) ion was surrounded by two oxygen and two nitrogen atoms from two Schiff base ligands and one oxygen atom from an oxo ligand in the five-coordinated geometry (see the Figure). The geometry around the vanadium(IV) ion is a tetragonal pyramidal, as indicated by the unequal metal-ligand bond distances and angles: i.e. V1\O1 = 1.9023(12) Å, V1\O2 = 1.9212(11) Å, V1\N1 = 2.1213(13) Å, V1\N2 = 2.1093(13) Å and V1\O3 = 1.5949(12) Å. All distances and angles in the title complex agree well with the same distances in other vanadium(IV) complexes [10–12]. There are also exist weak non-classical C–H···O and C–H···Cl hydrogen bonds stabilizing the structure.

Acknowledgements: We thank the Center of Testing and Analysis, East China Normal University, for support.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: The authors thank the projects of the program for Hebei Provincial Department of Human Resources and Social Security (No. A202001082).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. BRUKER. *SAINT, APEX2 and SADABS*. Bruker AXS Inc., Madison, WI, 2009.
2. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, *42*, 339–341.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Sheldrick G. M. A short history of *SHELX*. *Acta Crystallogr.* 2008, *A64*, 112–122.
5. You Z. L., Cui Y. M., Ma Y. P., Wang C., Zhou X. S., Li K. Synthesis, characterization and urease inhibitory activity of oxovanadium(V) complexes with similar Schiff bases. *Inorg. Chem. Commun.* 2011, *14*, 636–640.
6. Ren D. X., Xing N., Shan H., Chen C., Cao Y. Z., Xing Y. H. Novel vanadium(III) complexes with rigid phenylpolycarboxylate ligands: synthesis, structures and application in C–H bond activation. *Dalton Trans*. 2013, *14*, 5355–5365.
7. Lemons B. G., Richens D. T., Anderson A., Sedgwick M., Crans D. C., Johnson M. D. Stabilization of a vanadium(V)-catechol complex by compartmentalization and reduced solvation inside reverse micelles. *New J. Chem.* 2013, *24*, 75–81.
8. Leon I. E., Di Virgilio A. L., Barrio D. A., Arrambide G., Gambino D., Etcheverry S. B. Hydroxylamido-amino acid complexes of oxovanadium(V). toxicological study in cell culture and in a zebrafish model. *Metallomics* 2012, *4*, 1287–1296.
9. Crans D. C., Smee J. J., Gaidamauskas E., Yang L. Q. The chemistry and biochemistry of vanadium and the biological activities exerted by vanadium compounds. *Chem. Rev.* 2004, *104*, 849–902.
10. Wei W., Xia J., Zhang W.-Y., Zhang H.-Q., Fang F.-J., Xin Y., Zheng X.-J. Crystal structure of bis(4-bromo-2-(((3-bromopropyl) imino)methyl) phenolato-κ^2*N,O*)-oxido-vanadium(IV), $C_{20}H_{20}Br_4N_2O_3V$. *Z. Kristallogr. N. Cryst. Struct.* 2021, *236*, 1355–1357.
11. Wei W., Wu Q., Zhang H.-Q., Liu R., Chen H.-L. Crystal structure of bis(4-bromo-2-(((3-chloropropyl)imino)methyl)phenolato - κ^2*N,O*)-oxidovanadium(IV), $C_{20}H_{20}Br_2Cl_2N_2O_3V$. *Z. Kristallogr. N. Cryst. Struct.* 2019, *234*, 443–444.
12. Grivani G., Ghavami A., Kučeráková M., Dušek M., Khalaji A. D. Synthesis, characterization, crystal structure determination, thermal study and catalytic activity of a new oxidovanadium Schiff base complex. *J. Mol. Struct.* 2014, *1076*, 326–332.