ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2011, Vol. 37, No. 8, pp. 606–612. © Pleiades Publishing, Ltd., 2011.

Syntheses, Characterization, and Crystal Structures of Oxovanadium(V) Complexes with Similar Tridentate Hydrazones[1]

C. L. Yuan

Key Laboratory for Phytochemistry of Shaanxi Province, Department of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences, Baoji, Shaanxi 721013, PR. China

E-mail: chunlanyuan@163.com

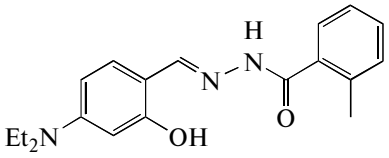
Received October 13, 2010

Abstract—Reactions of bis(acetylacetonato)oxovanadium(IV) with *N*'-[2-hydroxy-4-diethylaminobenzylidene)]-2-methylbenzohydrazide (H_2HMB) and *N*'-[5-bromo-2-hydroxy-3-methoxybenzylidene)]-2-methylbenzohydrazide (H_2BMB), respectively, produce two oxovanadium(V) species with the formulas $[VO(OMe)(HMB)]_2$ (**I**) and [VO(OMe)(HOMe)(BMB)] (**II**). The complexes have been characterized by elemental analysis, IR spectra, and single-crystal X-ray diffraction. The crystal of **I** is triclinic: space group $P\bar{1}$, a = 8.843(1), b = 9.937(1), c = 12.327(2) Å, α = 96.500(2)°, β = 110.070(2)°, γ = 104.220(2)°, V = 962.8(2) Å^3, Z = 1. The crystal of **II** is monoclinic: space group $P2_1/c$, a = 9.908(2), b = 19.968(3), c = 11.065(3), β = 109.362(3)°, V = 2065.3(8) Å^3, Z = 4. Compound **I** is the methoxide-bridged dimeric oxovanadium(V) complex, and **II** is the mononuclear oxovanadium(V) complex. Each V atom in the complexes is in an octahedral coordination.

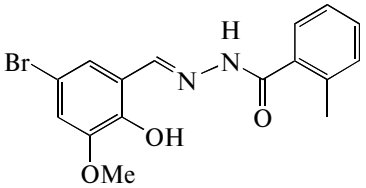
DOI: 10.1134/S1070328411070141

INTRODUCTION

Oxovanadium complexes, especially with bi- and tridentate chelating ligands bearing pharmacological activity, have been extensively investigated in recent years with respect to their remarkable efficiency as insulin-mimetic compounds [1–3]. In the last few years, the O-, N-, and S-containing hydrazone compounds have been proved to possess versatile biological activity [4–7]. Study on the structures of the oxovanadium complexes with hydrazones is very important in both coordination chemistry and medicinal chemistry. In this paper, the author reports the synthesis, characterization, and crystal structures of two new oxovanadium(V) complexes, $[VO(OMe)(HMB)]_2$ (**I**) and [VO(OMe)(HOMe)(BMB)] (**II**), where HMB and BMB are the deprotonated form of *N*'-[2-hydroxy-4-diethylaminobenzylidene)]-2-methylbenzohydrazide (**H_2HMB**) and *N*'-[5-bromo-2-hydroxy-3-methoxybenzylidene)]-2-methylbenzohydrazide (**H_2BMB**), respectively:



(H_2HMB)



(H_2BMB)

EXPERIMENTAL

Materials and methods. 4-(Diethylamino)salicylaldehyde, 5-bromo-3-methoxysalicylaldehyde, and 2-methylbenzohydrazide were purchased from Lancaster Chemical Co. The remaining reagents and solvents were purchased from local sources and used as received. C, H, and N elemental analyses were determined on a Carlo Erba MOD 1106 elemental analyzer. FT-IR spectra were recorded in the range 4000–400 cm^{-1} on a Nicolet Avatar-360 spectrometer using a KBr pellet.

Synthesis of H_2HMB and H_2BMB. The hydrazone compounds H_2HMB and H_2BMB were synthesized by the condensation of equimolar quantities of 2-methylbenzohydrazide with 4-(diethylamino)salicylaldehyde and 5-bromo-3-methoxysalicylaldehyde, respectively, in methanol, according to the literature method [8]. The yields were 93% for H_2HMB and 96% for H_2BMB. IR (KBr; ν, cm^{-1}): for H_2HMB – 3208 w, 1650 s, 1632 s, 1588 s, 1550 m, 1521 s, 1453 w, 1418 w, 1355 s, 1303 w, 1277 m, 1245 m, 1223 w, 1197 w, 1157 w, 1136 m, 1078 w, 1068 w, 1013 w, 972 w, 916 m, 873 w, 847 w, 788 m, 737 w,

[1] The article is published in the original.

719 w, 701 w, 666 w; for H_2BMB – 3447 br. w, 3219 w, 1655 s, 1604 m, 1569 m, 1541 m, 1469 s, 1441 m, 1386 w, 1355 m, 1318 w, 1249 s, 1155 m, 1113 w, 1097 w, 1075 w, 975 m, 896 m, 863 w, 837 w, 741 m, 694 w, 661 w.

For H_2HMB ($C_{16}H_{16}N_2O_2$)			
anal. calcd., %:	C, 71.62;	H, 6.01;	N, 10.44.
Found, %:	C, 71.45,	H, 6.13;	N, 10.63.
For H_2BMB ($C_{16}H_{15}BrN_2O_3$)			
anal. calcd., %:	C, 52.91;	H, 4.16;	N, 7.71.
Found, %:	C, 52.72,	H, 4.27;	N, 7.78.

Synthesis of complex I. A methanol solution (20 ml) of H_2HMB (0.134 g, 0.5 mmol) was added to a stirred methanol solution (20 ml) of $VO(Acac)_2$ (0.132 g, 0.5 mmol). The mixture was stirred for 30 min at room temperature. The deep red solution was left to slow evaporation for a few days, yielding dark red block-shaped single crystals. The crystals were isolated by filtration. The yield was 83%. IR (KBr; ν, cm^{-1}): 1607 s, 1579 s, 1521 m, 1505 s, 1482 m, 1446 w, 1405 m, 1378 w, 1354 s, 1320 s, 1244 s, 1190 w, 1141 s, 1079 w, 1024 m, 971 m, 825 w, 791 w, 771 w, 728 w, 714 m, 629 w, 597 w, 565 w, 478 w.

For $C_{40}H_{48}N_6O_8V_2$			
anal. calcd., %:	C, 57.01;	H, 5.74;	N, 9.97.
Found, %:	C, 56.78;	H, 5.81;	N, 9.90.

Synthesis of complex II. A methanol solution (20 ml) of H_2BMB (0.182 g, 0.5 mmol) was added to a stirred methanol solution (20 ml) of $VO(Acac)_2$ (0.132 g, 0.5 mmol). The mixture was stirred for 30 min at room temperature. The deep red solution was left to slow evaporation for a few days, yielding dark red block-shaped single crystals. The crystals were isolated by filtration. The yield was 77%. IR (KBr; ν, cm^{-1}): 3475 w, 1617 s, 1552 s, 1518 m, 1485 w, 1459 s, 1438 s, 1423 m, 1357 s, 1289 s, 1251 s, 1213 w, 1147 w, 1121 m, 1099 w, 1040 s, 976 s, 920 w, 882 w, 838 w, 807 m, 782 m, 738 m, 702 w, 629 s, 600 s, 512 w, 466 w, 450 w.

For $C_{18}H_{20}BrN_2O_6V$			
anal. calcd., %:	C, 44.01;	H, 4.10;	N, 5.70.
Found, %:	C, 43.80,	H, 4.05;	N, 5.82.

X-Ray structure determination. Diffraction intensities for the complexes were collected at 298(2) K on a Bruker SMART APEX-II CCD diffractometer equipped with a graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). Absorption corrections were applied using SADABS [9]. The structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs [10]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The methanol hydrogen atom in **II** found in an electron-density difference Fourier map was refined isotropically with O–H distance restrained to 0.85(1) Å and with U_{iso} restrained to 0.08 $Å^2$. Other hydrogen atoms were added in ideal positions and were not refined. Crystallographic data are listed in Table 1, and selected bond distances and angles are given in Table 2.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 792715 (**I**) and 792716 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The reaction of $VO(Acac)_2$ with the hydrazone compounds readily affords the oxovanadium(V) complexes. The vanadium in $VO(Acac)_2$ is in the V(IV) oxidation state; however, it appears to be V(V) in the complexes, indicating that it was oxidized by oxygen during the reaction and crystallization procedures.

The IR spectra of the hydrazone compounds exhibit two absorption bands in the regions 3208–3219 and 1650–1655 cm^{-1} due to the ν(N–H) and ν(C=O) stretches. The absence of these bands in the spectra of the complexes is consistent with the enoliation of the amide functionality and subsequent proton replacement by the vanadium atom. The weak band observed at 3475 cm^{-1} in the spectrum of **II** due to the O–H stretch of the coordinated methanol molecule is absent in the spectrum of **I**. The new bands appearing in the 1244–1289 cm^{-1} range are assigned to the stretching vibration of the enolic groups. The strong bands at 1607 and 1617 cm^{-1} in complexes **I** and **II**, respectively, are assigned to the conjugate C=N–N=C moieties [11]. The bands observed at 971 and 976 cm^{-1} in **I** and **II**, respectively, are assigned to the V=O stretches [12, 13].

The molecular structure of **I** is shown in Fig. 1. The complex is a methoxide-bridged centrosymmetric dinuclear oxovanadium(V) complex. The V···V distance is 3.391(2) Å. The dianionic tridentate ligand HMB binds the V atom through the phenolate O, imine N, and deprotonated amide O atoms, forming six- and five-membered chelate rings. Each V atom is in a distorted NO_5 octahedral coordination with the three donor atoms of the hydrazone ligand and one methoxide O atom, defining the basal plane, and with one oxo O and one symmetry-related methoxide O atom, occupying the axial positions. The mean deviation of the four basal donor atoms from the least-squares plane is 0.029(3) Å. The displacement of the V atom towards the oxo group from the plane is 0.323(2) Å. The distances of V=O and other coordination bonds in the complex are comparable to those observed in other similar oxovanadium(V) complexes [14, 15]. The molecules are stacked along the *x* axis with no obvious short contacts (Fig. 2).

Table 1. Crystallographic data and details of the experiment and refinement of structures **I** and **II**

Parameter	Value	
	I	**II**
Fw	842.72	491.21
Crystal shape/colour	Block/red	Block/red
Crystal size, mm	0.32 × 0.30 × 0.30	0.28 × 0.27 × 0.26
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a, Å	8.8430(10)	9.908(2)
b, Å	9.9370(10)	19.968(3)
c, Å	12.327(2)	11.065(3)
α, deg	96.500(2)	90
β, deg	110.070(2)	109.362(3)
γ, deg	104.220(2)	90
V, Å^3	962.8(2)	2065.3(8)
Z	1	4
μ (MoK_α), mm^{-1}	0.547	2.451
T_{min}	0.8444	0.5470
T_{max}	0.8531	0.5683
Reflections/parameters	4015/257	4362/259
Independent reflections	3047	2876
F(000)	440	992
Goodness of fit on F^2	1.024	1.037
R_1, wR_2 ($I \geq 2\sigma(I)$)*	0.0538, 0.1129	0.0481, 0.1026
R_1, wR_2 (all data)*	0.0751, 0.1234	0.0851, 0.1173

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w[(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond lengths (Å) and bond angles (deg) for **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
		I	
V(1)–O(1)	1.838(2)	V(1)–O(2)	1.9212(19)
V(1)–O(3)	1.578(2)	V(1)–O(4)	1.8230(19)
V(1)–N(1)	2.099(2)	V(1)–O(4*A*)	2.353(2)
		II	
V(1)–O(1)	1.852(2)	V(1)–O(2)	1.942(3)
V(1)–O(4)	1.575(3)	V(1)–O(5)	1.776(2)
V(1)–O(6)	2.334(3)	V(1)–N(1)	2.136(3)
Angle	ω, deg	Angle	ω, deg
		I	
O(3)V(1)O(4)	100.48(10)	O(3)V(1)O(1)	101.86(11)
O(4)V(1)O(1)	102.08(9)	O(3)V(1)O(2)	99.27(10)
O(4)V(1)O(2)	93.75(8)	O(1)V(1)O(2)	150.68(9)
O(3)V(1)N(1)	96.69(11)	O(4)V(1)N(1)	160.56(9)
O(1)V(1)N(1)	83.09(9)	O(2)V(1)N(1)	74.42(9)
O(3)V(1)O(4*A*)	172.48(9)	O(4)V(1)O(4*A*)	72.08(9)
O(1)V(1)O(4*A*)	81.14(9)	O(2)V(1)O(4*A*)	80.50(8)
N(1)V(1)O(4*A*)	90.50(8)		
		II	
O(4)V(1)O(5)	101.23(13)	O(4)V(1)O(1)	100.44(14)
O(5)V(1)O(1)	100.58(11)	O(4)V(1)O(2)	99.37(14)
O(5)V(1)O(2)	96.89(11)	O(1)V(1)O(2)	150.38(11)
O(4)V(1)N(1)	92.37(13)	O(5)V(1)N(1)	164.84(12)
O(1)V(1)N(1)	83.29(11)	O(2)V(1)N(1)	74.09(11)
O(4)V(1)O(6)	174.79(12)	O(5)V(1)O(6)	83.97(11)
O(1)V(1)O(6)	78.05(11)	O(2)V(1)O(6)	80.24(11)
N(1)V(1)O(6)	82.52(11)		

* Symmetry formation used to generate equivelant atoms: $(A) - x, 1 - y, - z$.

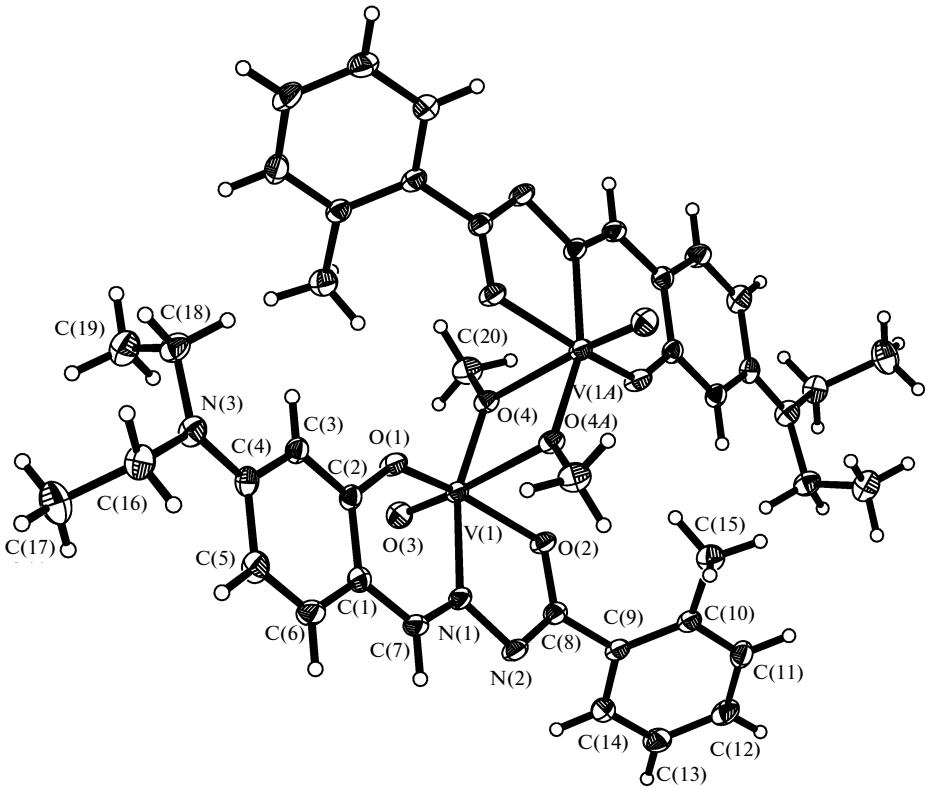


Fig. 1. Molecular structure of **I** with 30% thermal ellipsoids. Unlabelled atoms are related to the symmetry operation $-x, 1-y, -z$.

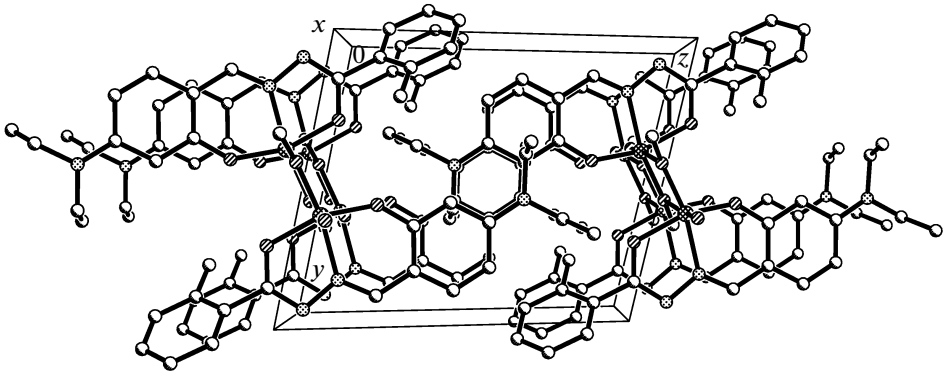


Fig. 2. Molecular packing structure of **I** viewed along the *x* axis.

The molecular structure of **II** is shown in Fig. 3. The methoxide group lies in the *trans* position to the imine N atom. The methanol ligand is *trans*-coordinated to the oxo group. The dianionic tridentate ligand BMB binds the V atom through the phenolate O, imine N, and deprotonated amide O atoms, forming a six- and a five-membered chelate rings. The V atom is in a distorted NO_5 octahedral coordination with the three donor atoms of the hydrazone ligand and one methoxide O atom, defining the basal plane, and with one oxo O and one methanol O atom, occupying the axial positions. The mean deviation of the four basal donor atoms from the least-squares plane is 0.059(3) Å. The displacement of the V atom towards the oxo group from the plane is 0.289(2) Å. The distances of V=O and other coordination bonds in the complex are comparable with those observed in **I** and other similar oxovanadium(V) complexes [14, 16, 17]. In the crystal structure of the complex, the molecules are linked through intermolecular O–H···N hydrogen bonds, forming 1D chains running along the *z* axis (Fig. 4).

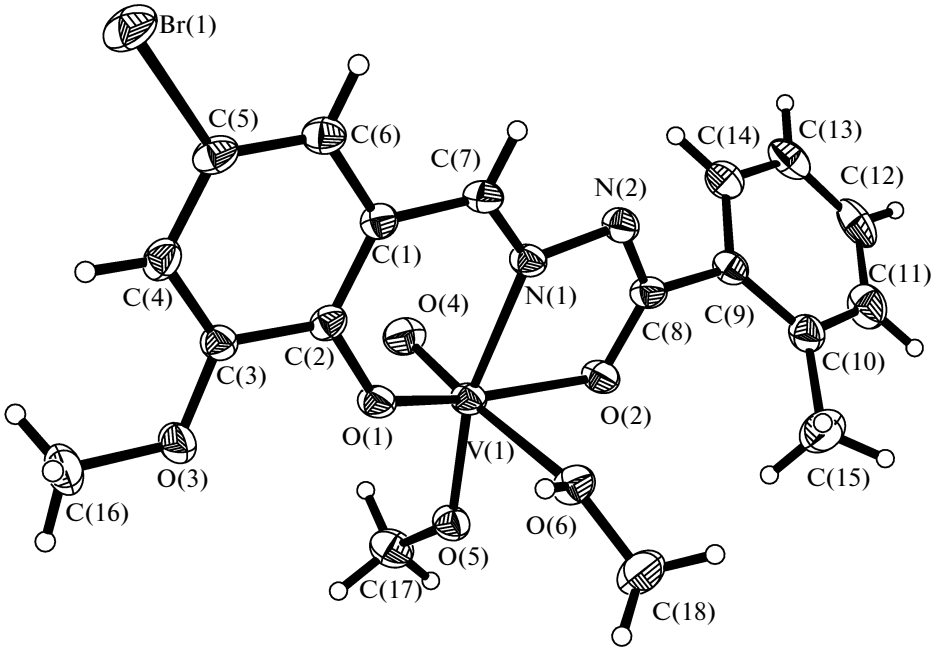


Fig. 3. Molecular structure of **II** with 30% thermal ellipsoids.

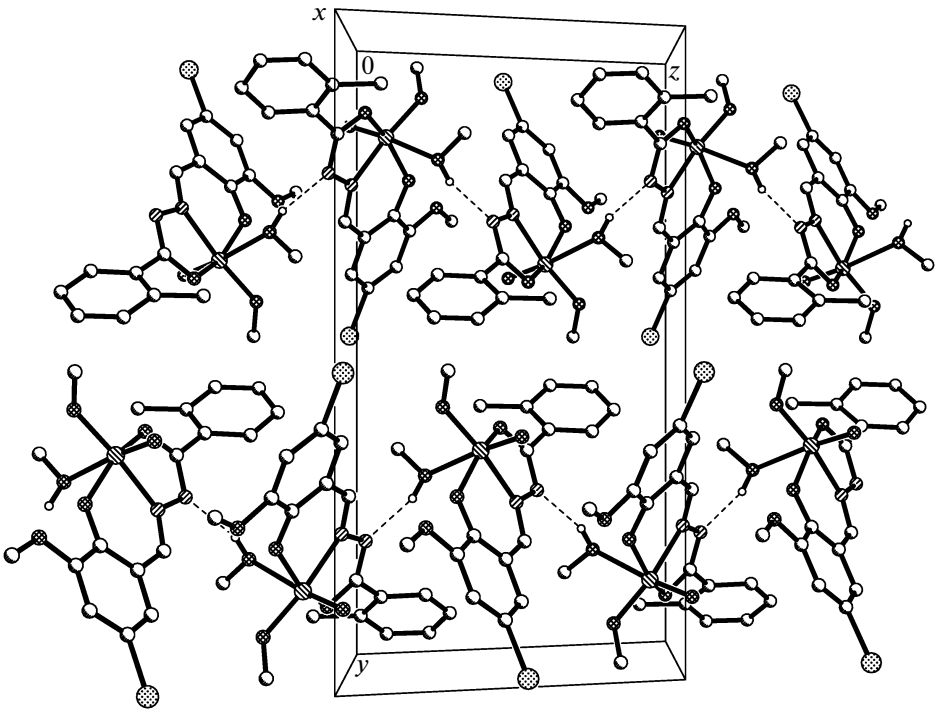


Fig. 4. Molecular packing structure of **II**, viewed along the *x* axis. Intermolecular hydrogen bonds are drawn as dashed lines.

ACKNOWLEDGMENTS

I am grateful for the financial support from the industrialization foster (no. 06JC25) of Shaanxi Province and the main project (no. 04JS37) of the Key Laboratory of Shaanxi Province, P.R. China.

REFERENCES

1. Zhang, Y., Yang, X.D., Wang, K., and Crans, D.C., *J. Inorg. Biochem.*, 2006, vol. 100, no. 1, p. 80.
2. Sheela, A., Roopan, S.M., and Vijayaraghavan, R., *Eur. J. Med. Chem.*, 2008, vol. 43, no. 10, p. 2206.

3. Garribba, E., Micera, G., Lodyga-Chruscinska, et al., *Eur. J. Inorg. Chem*., 2005, vol. 24, no. 21, p. 4953.
4. Horiuchi, T., Nagata, M., Kitagawab, M., et al., *Bioorg. Med. Chem*., 2009, vol. 17, no. 23, p. 7850.
5. Avaji, P.G., Kumar, C.H.V., Patil, S.A., et al., *Eur. J. Med. Chem*., 2009, vol. 44, no. 9, p. 3552.
6. Ajani, O.O., Obafemi, C.A., Nwinyi, O.C., and Akinpelu, D.A., *Bioorg. Med. Chem*., 2010, vol. 18, no. 1, p. 214.
7. Deep, A., Jain, S., Sharma, P.C., et al., *Acta Pol. Pharm*., 2010, vol. 67, no. 3, p. 255.
8. Deflon, V.M., de Oliveira, D.M., de Sousa, G.F., et al., *Z. Anorg. Allg. Chem*., 2002, vol. 628, no. 5, p. 1140.
9. Sheldrick, G.M., SADABS, In: *Program for Empirical Absorption Correction of Area Detector*, Göttingen (Germany): Univ. of Göttingen, 1996.
10. Sheldrick, G.M., SHELXS, SHELXL-97: *Program for the Refinement of Crystal Structure*, Göttingen (Germany): Univ. of Göttingen, 1997.
11. El-Sayed, L. and Iskander, M.F., *J. Inorg. Nucl. Chem*., 1971, vol. 33, no. 2, p. 435.
12. Rath, S.P., Rajak, K.K., Mondal, S., and Chakravorty, A., *Dalton Trans*., 1998, no. 12, p. 2097.
13. Kwiatkowski, E., Romanowski, G., Nowicki, W., et al., *Polyhedron*, 2003, vol. 22, no. 7, p. 1009.
14. Mondal, B., Drew, M.G.B., Banerjee, R., and Ghosh, T., *Polyhedron*, 2008, vol. 27, no. 15, p. 3197.
15. Seena, E.B., Mathew, N., Kuriakose, M., and Kurup, M.R.P., *Polyhedron*, 2008, vol. 27, no. 5, p. 1455.
16. Liu, J.-H., Wu, X.-Y., Zhang, Q.-Z., et al., *Chin. J. Inorg. Chem*., 2006, vol. 22, no. 6, p. 1028.
17. Dinda, R., Sengupta, P., Sutradhar, M., et al., *Inorg. Chem*., 2008, vol. 47, no. 13, p. 5634. l