

Syntheses and Crystal Structures of Oxovanadium(V) Complexes Derived from N'-[1-(2-Hydroxynaphthyl)Ethylidene]-4-Nitrobenzohydrazide and 2-Hydroxy-N'-[1-(2-Hydroxynaphthyl)Ethylidene]Benzohydrazide¹

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 P.R. China
e-mail: chunlanyuan@163.com

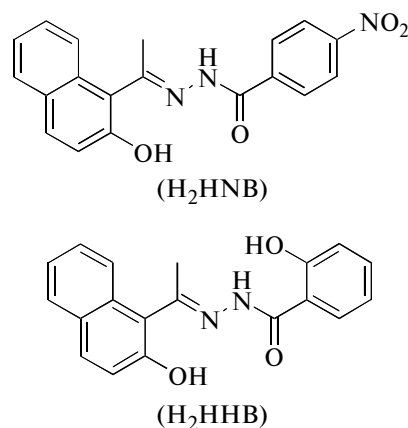
Received May 10, 2011

Abstract—Reactions of bis(acetylacetonato)oxovanadium(IV) with N'-[1-(2-hydroxynaphthyl)ethylidene]-4-nitrobenzohydrazide (H₂HNB) and 2-hydroxy-N'-[1-(2-hydroxynaphthyl)ethylidene]benzohydrazide (H₂HHB), respectively, product two oxovanadium(V) species with the formulas [VO(OMe)(HNB)]₂ (**I**) and [VO(OMe)(HHB)] (**II**). The complexes **I** and **II** have been characterized by elemental analysis, IR spectra, and single crystal X-ray diffraction. The crystal of **I** is monoclinic: space group *P*2₁/*n*, *a* = 8.208(2), *b* = 14.528(3), *c* = 16.418(3) Å, β = 97.887(3)°, *V* = 1939.3(7) Å³, *Z* = 2. The crystal of **II** is triclinic: space group *P*1̄, *a* = 8.334(2), *b* = 10.236(2), *c* = 11.337(2) Å, α = 80.91(3)°, β = 75.41(3)°, γ = 75.63(3)°, *V* = 902.0(3) Å³, *Z* = 2. Complex **I** is a methoxide-bridged dimeric oxovanadium(V) complex, and complex **II** is a mononuclear oxovanadium(V) complex. The V atom in **I** is in an octahedral coordination, and that in **II** is in a square pyramidal coordination.

DOI: 10.1134/S1070328412070111

INTRODUCTION

Oxovanadium complexes, especially with bi- and tridentate chelating ligands bearing pharmacological activity, have being 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)(HNB)]₂ (**I**) and [VO(OMe)(HHB)] (**II**), where HNB and HHB are the deprotonated form of N'-[1-(2-hydroxynaphthyl)ethylidene]-4-nitrobenzohydrazide (H₂HNB) and 2-hydroxy-N'-[1-(2-hydroxynaphthyl)ethylidene]benzohydrazide (H₂HHB), respectively:



EXPERIMENTAL

Materials and methods. 2-Acetyl-1-naphthol, 4-nitrobenzohydrazide, and 2-hydroxybenzohydrazide were purchased from Lancaster Chemical Co. The remaining reagents and solvents were purchased from local sources and were used as received. C, H,

¹ The article is published in the original.

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_2HNB and H_2HHB . The hydrazone compounds H_2HNB and H_2HHB were synthesized by the condensation of equimolar quantities of 2-acetyl-1-naphthol with 4-nitrobenzohydrazide and 2-hydroxybenzohydrazide, respectively, in methanol, according to the literature method [8]. The yields were 95% for H_2HNB and 93% for H_2HHB . IR (KBr; ν , cm^{-1}): for H_2HNB —3422 w, 3200 m, 1684 s, 1610 m, 1593 s, 1511 s, 1437 w, 1343 s, 1266 s, 1178 w, 1114 m, 1059 w, 864 w, 847 m, 822 w, 751 m, 689 w; for H_2HHB —3423 w, 3234 w, 1644 s, 1623 s, 1605 s, 1533 m, 1512 m, 1492 w, 1457 w, 1434 w, 1369 w, 1349 w, 1310 m, 1278 w, 1241 m, 1210 m, 1157 w, 953 w, 893 w, 818 m, 750 m.

For H_2HNB ($\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_3$)

anal. calcd., %	C, 65.32;	H, 4.33;	N, 12.03.
Found, %	C, 65.09;	H, 4.37;	N, 12.15.

For H_2HHB ($\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_3$)

anal. calcd., %	C, 71.24;	H, 5.03;	N, 8.74.
Found, %	C, 71.10;	H, 5.11;	N, 8.87.

Synthesis of complex I. A methanol solution (20 mL) of H_2HNB (0.175 g, 0.5 mmol) was added to a stirred methanol solution (20 mL) of $\text{VO}(\text{Acac})_2$ (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 72%. IR (KBr; ν , cm^{-1}): 1615 m, 1592 m, 1569 m, 1547 s, 1515 m, 1444 w, 1425 w, 1376 m, 1340 s, 1243 m, 1050 w, 1022 m, 982 m, 866 w, 824 w, 757 w, 710 m, 618 m, 593 m, 419 w.

For $\text{C}_{40}\text{H}_{32}\text{N}_6\text{O}_{12}\text{V}_2$ (I)

anal. calcd., %	C, 53.94;	H, 3.62;	N, 9.44.
Found, %	C, 53.63;	H, 3.71;	N, 9.32.

Synthesis of complex II. A methanol solution (20 mL) of H_2HHB (0.160 g, 0.5 mmol) was added to a stirred methanol solution (20 mL) of $\text{VO}(\text{Acac})_2$ (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 80%. IR (KBr; ν , cm^{-1}): 3455 w, 1619 m, 1595 s, 1535 s, 1508 m, 1490 m, 1450 w, 1430 w, 1373 m, 1310 w, 1246 s,

1159 m, 1074 w, 1022 s, 987 s, 827 w, 750 s, 695 w, 671 w, 615 s, 603 s, 487 w, 430 w.

For $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_5\text{V}$ (II)

anal. calcd., %	C, 57.70;	H, 4.12;	N, 6.73.
Found, %	C, 57.86;	H, 4.15;	N, 6.60.

X-ray structure determination. Diffraction intensities for the complexes were collected at 298(2) K on a Bruker APEX-II CCD diffractometer equipped with a graphite-monochromatized MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). Absorption corrections were applied using SADABS [9]. The structures were solved by direct methods and refined with the full-matrix least-squares technique using SHELXS-97 and SHELXL-97 programs [10]. All non-hydrogen atoms were refined with anisotropic thermal parameters. All 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 (nos. 792717 (I) and 792718 (II); deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

RESULTS AND DISCUSSION

The reaction of $\text{VO}(\text{Acac})_2$ with hydrazone compounds readily affords the oxovanadium(V) complexes. The vanadium in the $\text{VO}(\text{Acac})_2$ is in 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 3200–3234 and 1644–1684 cm^{-1} due to the $\nu(\text{N}-\text{H})$ and $\nu(\text{C}=\text{O})$ stretches. The absence of these bands in the spectra of the complexes is consistent with the enolisation of the amide functionality and subsequent proton replacement by the vanadium atom. The weak band observed at 3455 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 1243–1246 cm^{-1} range are assigned to the stretching vibration of the enolic groups. The bands at 1615 and 1619 cm^{-1} in complexes I and II, respectively, are assigned to the conjugate $\text{C}=\text{N}-\text{N}=\text{C}$ moieties [11]. The bands observed at 982 and 987 cm^{-1} in I and II, respectively, are assigned to the $\text{V}=\text{O}$ 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 3.360(2) \AA . The dianionic tridentate ligand HNB binds the V atom through the phenolate-O, imine-N, and deprotonated amide-O atoms, forming a six- and a five-membered chelate rings. Each V atom is in a distorted NO_5 octahedral coordination, with the

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

Parameter	Value	
	I	II
<i>F</i> _w	890.60	416.30
Crystal shape/colour	Block/red	Block/red
Crystal size, mm	0.30 × 0.27 × 0.27	0.23 × 0.20 × 0.20
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	8.208(2)	8.3340(17)
<i>b</i> , Å	14.528(3)	10.236(2)
<i>c</i> , Å	16.418(3)	11.337(2)
α , deg	90	80.91(3)
β , deg	97.887(3)	75.41(3)
γ , deg	90	75.63(3)
<i>V</i> , Å ³	1939.3(7)	902.0(3)
ρ_{calcd} , g/cm ³	1.525	1.533
<i>Z</i>	2	2
$\mu(\text{MoK}\alpha)$, mm ^{−1}	0.556	0.586
<i>F</i> (000)	912	428
θ Range, deg	1.88–27.00	1.87–27.00
Index ranges <i>h</i> , <i>k</i> , <i>l</i>	−10 ≤ <i>h</i> ≤ 10, −18 ≤ <i>k</i> ≤ 18, −20 ≤ <i>l</i> ≤ 20	−10 ≤ <i>h</i> ≤ 10, −13 ≤ <i>k</i> ≤ 13, −14 ≤ <i>l</i> ≤ 14
<i>T</i> _{max} / <i>T</i> _{min}	0.8645/0.8510	0.8918/0.8770
Reflections	4155	3746
Independent reflections (<i>R</i> _{int})	3057(0.0397)	3268 (0.0205)
Parameters	273	255
Goodness of fit on <i>F</i> ²	1.017	1.029
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> ≥ 2σ(<i>I</i>))*	0.0507, 0.1159	0.0393, 0.1027
<i>R</i> ₁ , <i>wR</i> ₂ (all data)*	0.0743, 0.1258	0.0452, 0.1074
Largest diff. peak and hole, e/Å ³	0.388 and −0.199	0.343 and −0.274

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

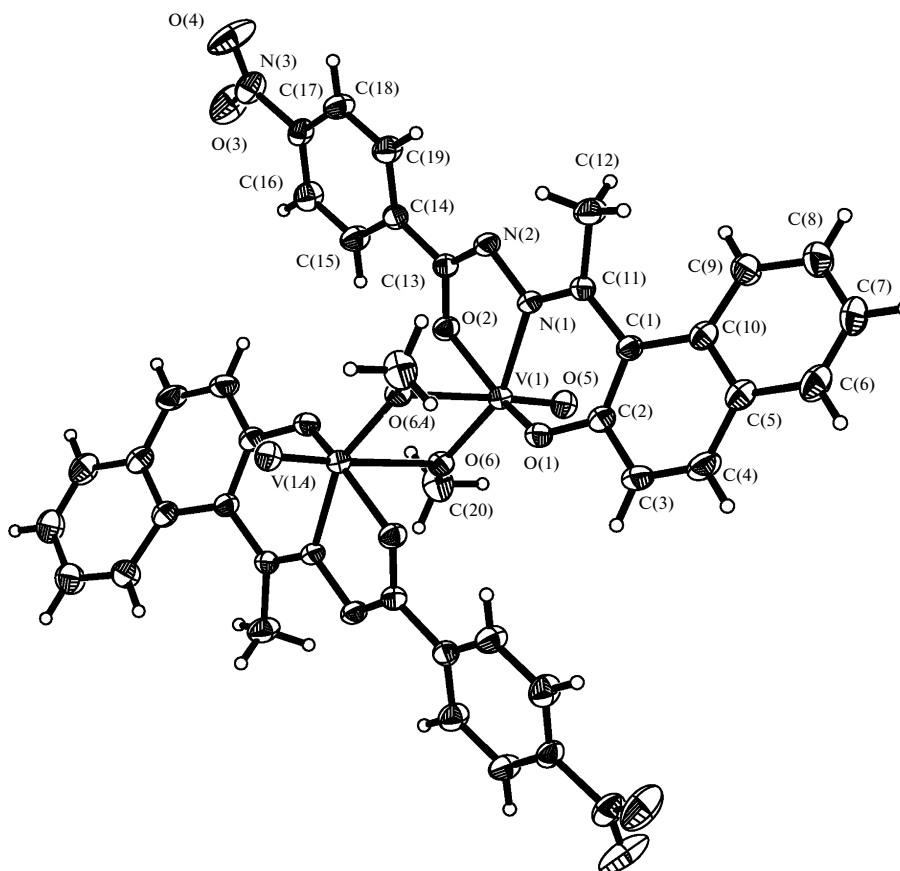
three donor atoms of the hydrazone ligand, and one methoxide O atom defining the basal plane, and with one oxo O and one symmetry-related methoxide O atom occupying the axial positions. The mean deviation of the four equatorial donor atoms from the least-squares plane is 0.014(3) Å. The displacement of the V atom towards the oxo group from the plane is 0.356(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).

The molecular structure of **II** is shown in Fig. 3. There is an intramolecular O—H...N hydrogen bond stabilizing the molecular conformation. The methox-

ide group lies *trans* to the imine-N atom. The dianionic tridentate ligand HHB 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 NO₄ square pyramidal coordination, with the three donor atoms of the hydrazone ligand, and one methoxide O atom defining the basal plane, and with one oxo O atom occupying the apical position. The mean deviation of the four basal donor atoms from the least-squares plane is 0.084(3) Å. The displacement of the V atom towards the oxo group from the plane is 0.387(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].

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

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
I			
V(1)–O(1)	1.8368(19)	V(1)–O(2)	1.9351(18)
V(1)–O(5)	1.580(2)	V(1)–O(6)	1.8283(18)
V(1)–N(1)	2.088(2)	V(1)–O(6A)	2.3588(18)
II			
V(1)–O(2)	1.9327(15)	V(1)–O(3)	1.8856(14)
V(1)–O(4)	1.5759(17)	V(1)–O(5)	1.7669(15)
V(1)–N(2)	2.1081(19)		
Angle	ω, deg	Angle	ω, deg
I			
O(5)V(1)O(6)	102.81(9)	O(5)V(1)O(1)	100.77(10)
O(6)V(1)O(1)	105.51(8)	O(5)V(1)O(2)	101.21(9)
O(6)V(1)O(2)	89.39(7)	O(1)V(1)O(2)	149.85(8)
O(5)V(1)N(1)	97.53(10)	O(6)V(1)N(1)	156.54(8)
O(1)V(1)N(1)	81.71(8)	O(2)V(1)N(1)	75.18(7)
O(5)V(1)O(6A)	176.69(9)	O(6)V(1)O(6A)	73.96(8)
O(1)V(1)O(6A)	79.60(7)	O(2)V(1)O(6A)	79.64(7)
N(1)V(1)O(6A)	85.78(7)		
II			
O(4)V(1)O(5)	102.53(8)	O(4)V(1)O(3)	101.57(8)
O(5)V(1)O(3)	101.09(6)	O(4)V(1)O(2)	106.14(8)
O(5)V(1)O(2)	94.01(7)	O(3)V(1)O(2)	144.60(7)
O(4)V(1)N(2)	95.92(8)	O(5)V(1)N(2)	160.55(7)
O(3)V(1)N(2)	80.94(6)	O(2)V(1)N(2)	74.75(7)

* Symmetry formation used to generate equivalent atoms: (Å) $2 - x, 1 - y, 2 - z$.**Fig. 1.** Molecular structure of **I** with 30% thermal ellipsoids. Unlabelled atoms are related to the symmetry operation $2 - x, 1 - y, 2 - z$.

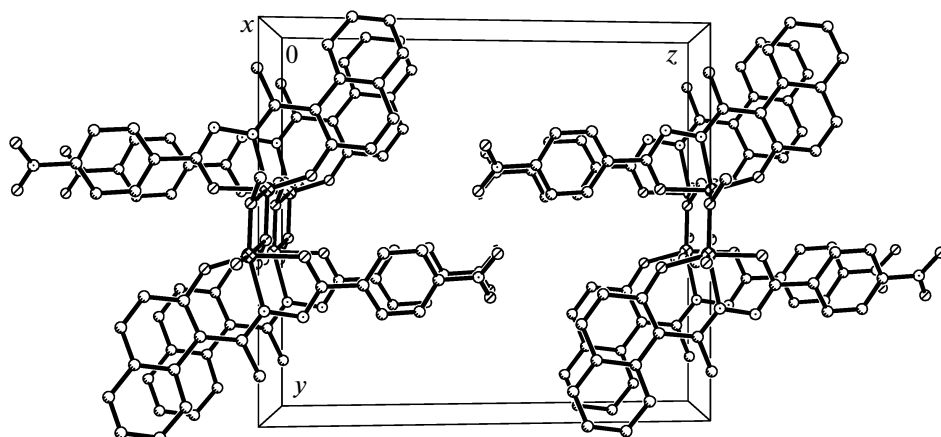


Fig. 2. Molecular packing structure of **I** viewed along the *x* axis.

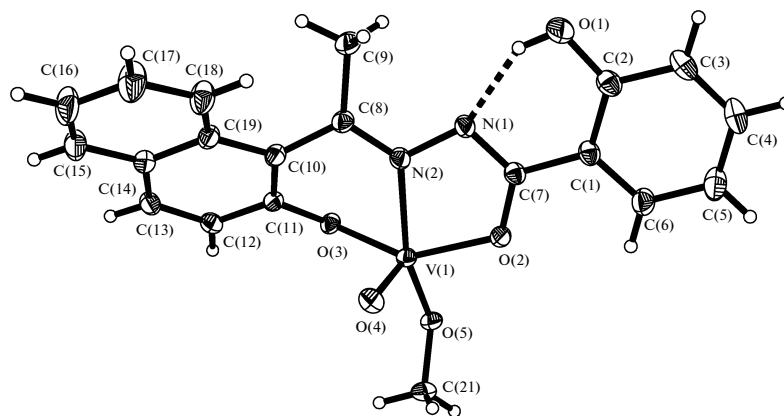


Fig. 3. Molecular structure of **II** with 30% thermal ellipsoids. Intramolecular O—H...N hydrogen bond is shown as a dashed line.

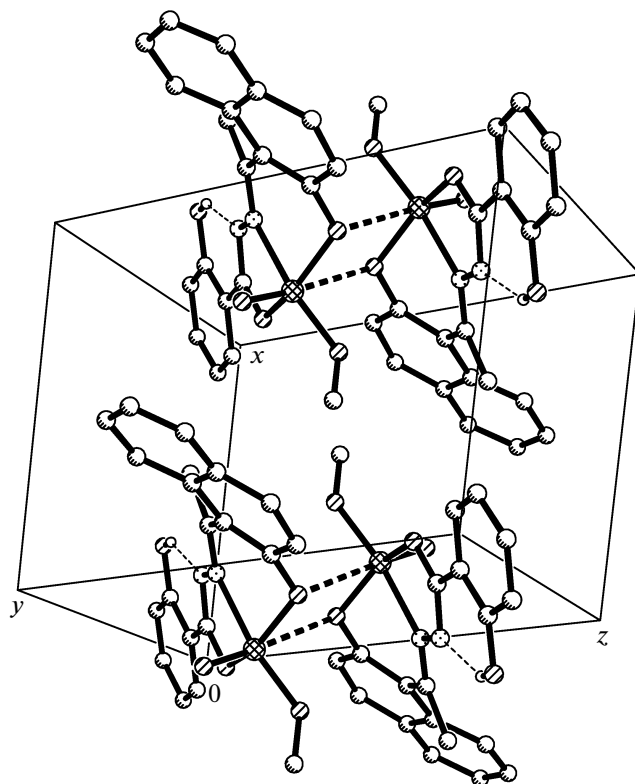


Fig. 4. The weak V...O linked dimeric structure of **II**.

It is notable that there exists weak V...O_{phenolate} interactions (V...O 2.359(2) Å) between the adjacent two molecules (Fig. 4).

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, E., 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., 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, 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.