ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2015, Vol. 41, No. 7, pp. 456–461. © Pleiades Publishing, Ltd., 2015.

New μ-OAC Bridged Dinuclear Copper(II) Complex with Tridentate Schiff Base Ligand: Synthesis, Characterization, Crystal Structure, and CuO Nano-Particles Formation[1]

G. Grivani[a], *, V. Eigner[b], M. Dušek[b], B. Sadeghi[a], and A. D. Khalaji[c]
[a] *School of Chemistry, Damghan University, Damghan, 36715-364 Iran*
[b] *Institute of Physics ASCR, v. v. i., Na Slovance 2, 18221 Prague, Czech Republic*
[c] *Department of Chemistry, Faculty of Science, Golestan University, Gorgan, Iran*
**e-mail: grivani@du.ac.ir*

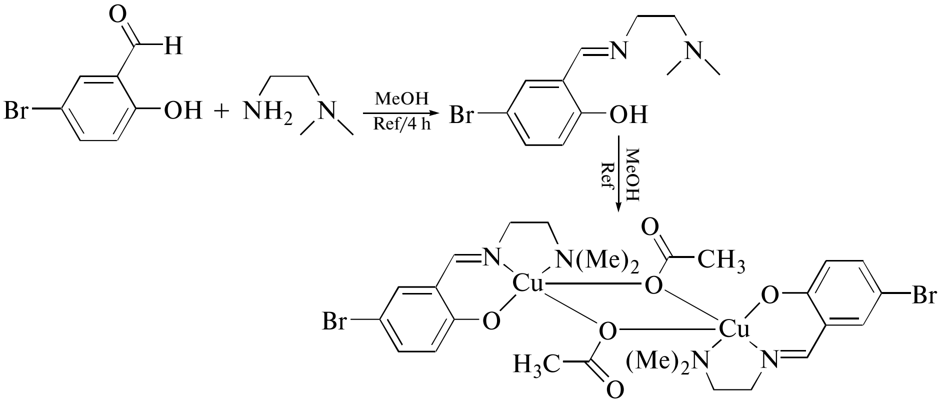
Received October 23, 2014

Abstract—A new (μ-acetato)-bridged dinuclear copper(II) complex $[Cu_2(L)_2(\mu\text{-}OAc)_2]$ (**I**) has been synthesized by the reaction of a tridentate N_2O Schiff base ligand (HL) with $Cu(OAC)_2$ in methanol at refluxed conditions and characterized by elemental analysis (CHN) and FT-IR spectroscopy. The crystal structure of **I** was investigated by single-crystal X-ray diffraction (CIF file CCDC no. 1013907). X-ray results showed that two OAC groups bridge the copper(II) ions in a Cu_2O_2 core of a binuclear complex. Each copper(II) ion adopts a distorted square-pyramidal geometry with one imine nitrogen, one amine nitrogen and one phenolato oxygen from the tridentate Schiff base ligand, completed by two acetate oxygen atoms. Finally, the complex was thermally decomposed in order to obtain CuO nano-particles. The particles were characterized by powder X-ray diffraction, which confirmed the formation of the CuO nano-particles with the average size of 24 nm.

DOI: 10.1134/S1070328415070027

INTRODUCTION

Schiff bases as chelating ligands play central role in the main group and transition metal coordination chemistry [1, 2] because of their simple preparation in one-pot condensation of aldehydes (or ketones) and Primary amines in an alcohol solvent. They are capable to bind with transition, non-transition,lanthanide and actinide metal ions to give complexes with suitableproperties for theoretical studies and/or practical applications [3–5]. The metal complexes with Schiff base ligands have been extensively investigated for more than one century and investigated in many different aspects, including biological studies [6–12], magneto chemistry [13], non-linear optics [14], photo physical studies [15], catalysis [16], materials chemistry [17], chemical analysis [18], absorption and transport of oxygen [19]. As an additional contribution to the synthesis, characterization, and crystal structure of transition metal Schiff base complexes and in the course of our ongoing studies of these kinds of materials [20–25], we describe here the synthesis, characterization and crystal structure of a new (μ-acetato)-bridged dinuclear copper(II) complex $[Cu_2(L)_2(\mu\text{-}OAc)_2]$ (**I**).



---

[1] The article is published in the original.

EXPERIMENTAL

Materials and physical measurements. All reagents and solvents for synthesis and analysis were commercially available and purchased from Merck and used as received without further purifications. FT-IR spectrum was recorded in the range 400–4000 cm^{-1} on a PerkinElmer FT-IR spectrophotometer using KBr pellets. Elemental analyses were performed on a Heraeus CHN–O-Rapid analyzer and results agreed with calculated values. ^{1}H NMR spectrum was recorded on a BRUKER DRX-500 AVANCE spectrometer at 300 MHz for the Schiff base ligand. UV-Vis spectra were recorded by PerkinElmer Spectrometer Lambda 25.

Synthesis of HL. In a 100 mL round-bottmflask containing 70 mL methanol, 5-bromo-2-hydroxybenzaldehyde (10 mmol) and *N*,*N*-dimethyl ethylendiamin (10 mmol, 2.04 g) were added and the mixture was refluxed for 4 h with stirring. After evaporating the solvent, the yellow precipitate was collected and dried in air. The yield was 80%. M.p. = 51°C.

For $C_{11}H_{15}N_2OBr$

anal. calcd., %:	C, 48.73;	H, 5.50;	N, 10.29.
Found, %:	C, 48.72;	H, 5.53;	N, 10.33.

IR (KBr; ν, cm^{-1}): 1637 ν(C=N). ^{1}H NMR ($CDCl_3$; δ, ppm): 13.5 (s., 1H, O–H), 8.27 (s., 1H: H–C = N), 7.36 (m., 2H: phenyl-H), 3.71 (t., 2H: N–CH_2), 2.63 (t., 2H: CH_2–N) and 2.29 (s., 6H: $N(CH_3)_2$).

Synthesis of I. In a 100 mL round-bottom flask containing 60 mL methanol HL (1.8 mmol) and $Cu(OAc)_2 \cdot 2H_2O$ (0.9 mmol) were added and the content was refluxed for 2 h with stirring. After evaporating the solvent, the resulting green powder was dried in air and recrystallized in $CHCl_3$ by slow evaporation method. The greenish crystals that formed were filtered off, washed with *n*-hexane and dried in an oven. M.p. = 206°C.

For $C_{26}H_{34}N_4O_6Br_2Cu_2$

anal. calcd., %:	C, 39.79;	H, 4.32;	N, 7.11.
Found, %:	C, 39.75;	H, 4.33;	N, 7.13.

IR (KBr ν, cm^{-1}): 1629 ν(C=N).

X-ray structure determination. Suitable single crystal of I (0.11 × 0.07 × 0.02 mm) was chosen for X-ray diffraction study. Crystallographic measurements were done at room temperature with four circle CCD diffractometer Gemini of Oxford diffraction, Ltd., using MoK_α radiation ($\lambda = 1.5418$ Å), sealed X-ray tube collimated by mirrors and CCD detector Atlas. The crystal structure was solved by direct methods with program SIR2002 [26] and refined with program package Jana2006 [27] by full-matrix least-squares technique on F^2. The molecular structure plots were prepared by ORTEP III [28]. Hydrogen atoms were mostly discernible in difference Fourier maps and could be refined to reasonable geometry. According to common practice, they were nevertheless kept in ideal positions during the refinement. The isotropic atomic displacement parameters of hydrogen atoms were evaluated as $1.2U_{eq}$ of the parent atom. Crystallographic data, details of the data collection and structure solution and refinements are listed in Table 1, while the selected bond distances and angles are present in Table 2. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1013907) and it is available through an e-mail request at deposit@ccdc.cam.ac.uk or through a web form at http://www.ccdc.cam.ac.uk.

Table 1. Crystallographic data and structural refinement details of complex **I**

Parameter	Value
Formula weight	785.47
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	7.9195(3)
b, Å	8.8831(3)
c, Å	10.9520(4)
α, deg	96.854(3)
β, deg	99.641(3)
γ, deg	104.633(3)
V, Å^3	724.32(5)
Z	1
μ, mm^{-1}	5.45
$T_{\min}/T_{\max}$	0.683/0.885
Measured reflections/independent	10845/2540
$R_{\rm int}$	0.038
Reflections with $I > 3\sigma,(I)$	2540
$F(000)$	867.0
S	1.34
$R\ (F^2 > 2\sigma,(F_2)$	0.025
$wR\ (F^2)$	0.060
$\Delta\rho_{\max}/\Delta\rho_{\min}$, e Å^{-3}	0.56/–0.64

RESULTS AND DISCUSSION

The tridentate N_2O Schiff base ligand (HL) was prepared by the condensation of 5-bromo-2-hydroxybenzaldehyde and *N*,*N*-dimethyl ethlylenediamine in

Table 2. Selected bond distances (Å) and angles (deg) of **I***

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–O(1)	1. 9401(19)	C(11)–N(12)	1.485(3)
Cu(1)–N(9)	1.9693(19)	N(12)–C(13)	1.479(3)
Cu(1)–N(12)	2.099(2)	N(12)–C(14)	1.477(4)
Cu(1)–O(1a)	1.9591(15)	O(1a)–C(2a)	1.291(3)
Br(1)–C(5)	1.904(2)	C(2a)–O(3a)	1.233(3)
C(8)–N(9)	1.284(3)	C(2a)–C(4a)	1.502(3)
N(9)–C(10)	1.470(4)	O(1)–C(2)	1.301(3)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(1)Cu(1)N(9)	90.91(8)	C(8)N(9)C(10)	118.4(2)
O(1)Cu(1)N(12)	171.40(8)	N(9)C(10)C(11)	108.0(2)
O(1)Cu(1)O(1a)	91.00(7)	C(10)C(11)N(12)	110.4(2)
N(9)Cu(1)N(12)	82.89(8)	Cu(1)N(12)C(11)	103.98(15)
N(9)Cu(1)O(1a)	175.02(8)	Cu(1)N(12)C(13)	114.99(17)
N(12)Cu(1)O(1a)	94.70(7)	Cu(1)N(12)C(14)	109.75(15)
Cu(1)O(1)C(2)	125.48(18)	C(11)N(12)C(13)	108.60(19)
O(1)C(2)C(3)	119.9(2)	C(11)N(12)C(14)	110.7(2)
O(1)C(2)C(7)	123.7(2)	C(13)N(12)C(14)	108.73(19)
Cu(1)N(9)C(8)	126.21(19)	Cu(1)O(1a)C(2a)	113.92(16)
Cu(1)N(9)C(10)	115.41(13)	O(1a)C(2a)O(3a)	122.7(2)
O(3a)C(2a)C(4a)	121.8(2)	O(1a)C(2a)C(4a)	115.6(2)

methanol in refluxed conditions and isolated by evaporation of the solvent. The corresponding dinuclear copper(II) complex **I** was synthesized by the reaction of $Cu(OAc)_2 \cdot H_2O$ with HL in methanol in refluxed conditions in two separated reactions. The ligand and complex are quite air stable as a solid as well as in a solution.

The HL ligand and its dinuclear copper(II) complex **I** were characterized by the FT-IR and UV-Vis spectroscopy and elemental (CHN) analysis. In addition, HL was characterized by ^1H NMR spectroscopy. The CHN analysis of HL and complex **I** clearly confirmed the predicted chemical composition of both compounds.

The ^1H NMR spectrum of HL is given in Fig. 1. The eight signals with the integrations ratio of 6 : 2 : 2 : 1 : 1 : 2 : 1 were seen in this spectrum due to the aliphatic and aromatic protons. A singlet resonance appeared at 2.29 was attributed to the protons of two CH_3 groups and two distinct triplet peaks at 2.62 and 3.71 ppm were corresponded to the aliphatic protons ($-CH_2-CH_2-$). The signals of aromatic protons were seen at 6.7–7.5 ppm. The resonance of iminic proton (–CH=N–) was seen at 8.27 ppm. The chemical shift of phenolic proton (OH) was strongly shifted to down field and exhibited at 13.50 ppm. This high chemical shift can be related to the intramolecular hydrogen bonding between nitrogen of imine and hydrogen of phenol.

In the FT-IR spectrum of HL, a sharp band was appeared at 1637 cm^{-1}, due to ν(C=N) of azomethine group. This band was shifted to the lower wave number and appeared at 1629 cm^{-1} in FT-IR spectrum of **I**, indicating the binding of azomethine nitrogen to copper ion.

The UV-Vis spectra of the HL and I are given in Fig. 2. There are two bands in the region of 230–500 nm at 256 and 334 nm for the HL ligand due to the intra-ligand ($\pi \to \pi^*$ and $n \to \pi^*$) transitions. These bands in the UV-Vis spectrum of **I** broadened and shifted to the higher wave lengths (red shift) and appeared at 257 and 398 nm, respectively, because of

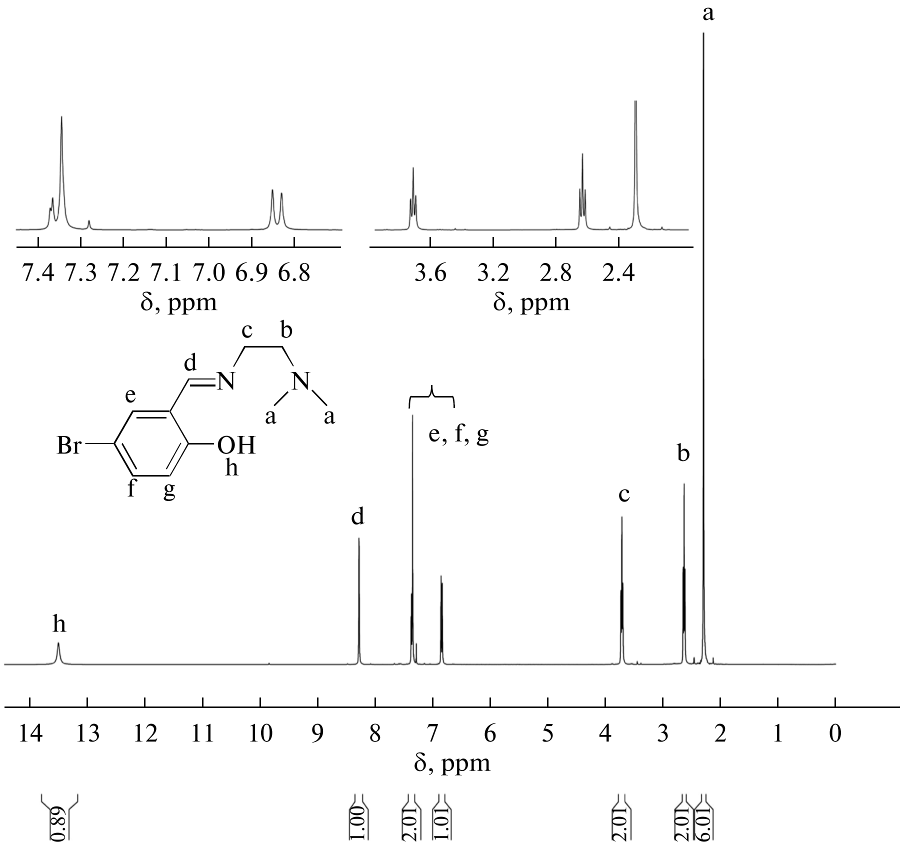


Fig. 1. The ^{1}H NMR spectrum of HL.

the anionic form of HL coordination (as phenolate) and resonance of charge in the longer route. In addition, a new band at 626 nm with very low intensity was appeared which was attributed to the *d–d* transitions of Cu^{2+} ion.

The molecular structure including the atom-numbering scheme of dinuclear copper(II) complex of **I** is shown in Fig. 3. The selected bond lengths and angles are listed in Table 2. Single crystal X-ray diffraction analysis reveals that the complex of **I** consists of two deprotonated Schiff base ligands with NNO^- donor set, two acetate ions acting as bridging ligands and two copper(II) cations. The copper(II) ions as well as the two halves of the complex are related by the inversion center located between the copper(II) ions. The copper(II) ion has a distorted square pyramidal geometry with $\tau = 0.06$ ($\tau = (\beta - \alpha)/60$) [29], where β and α are the two largest LCuL angles O(1)Cu(1)N(12) 171.40(8)° and N(9)Cu(1)O(1a) 175.02(8)°. The basal plane is formed by two N atoms and one O atom of the HL ligand and one O atoms of the bridging acetate ion. The fifth coordination position of the square pyramid is occupied by the oxygen atom of the bridging acetate ion forming the CuOCu bridge (Cu···Cu distance 3.470 Å). Bond angles around the copper(II) ions are in the range 82.89(8)°–171.40(8)°. The bond distances Cu(1)–O(1) (1.9401(19) Å), Cu(1)–O(1a) (1.9591(15) Å), Cu(1)–N(9) (1.9693(19) Å) and Cu(1)–N(12) (2.099(2) Å) are in the range observed for similar compounds [30]. The Cu(1)O(1a)Cu(1a) angle is found to be ~105.24(2)° in this complex.

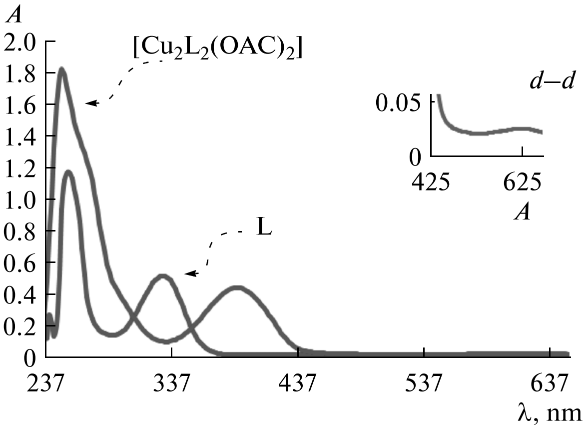


Fig. 2. The UV-Vis spectra of HL and complex **I**.

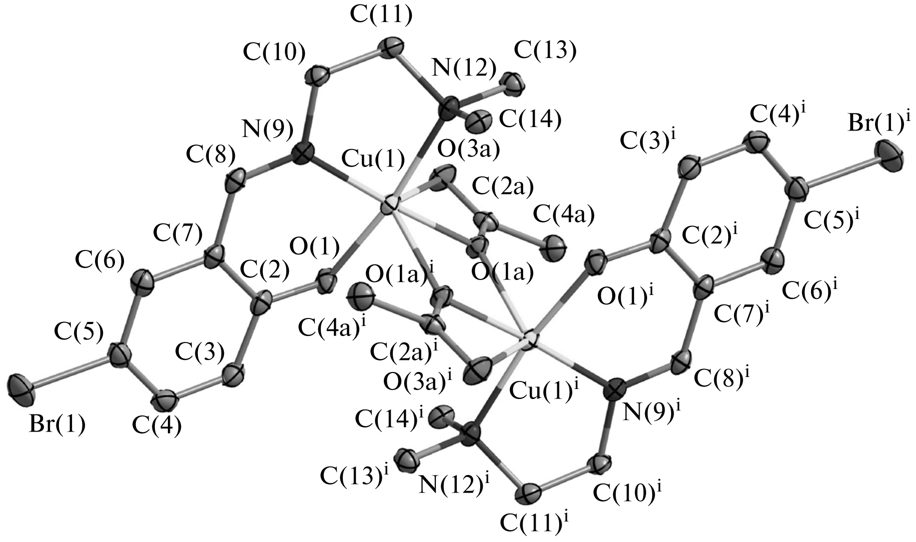


Fig. 3. Molecular structure of **I**. Ellipsoids are drawn from 50% probability label.

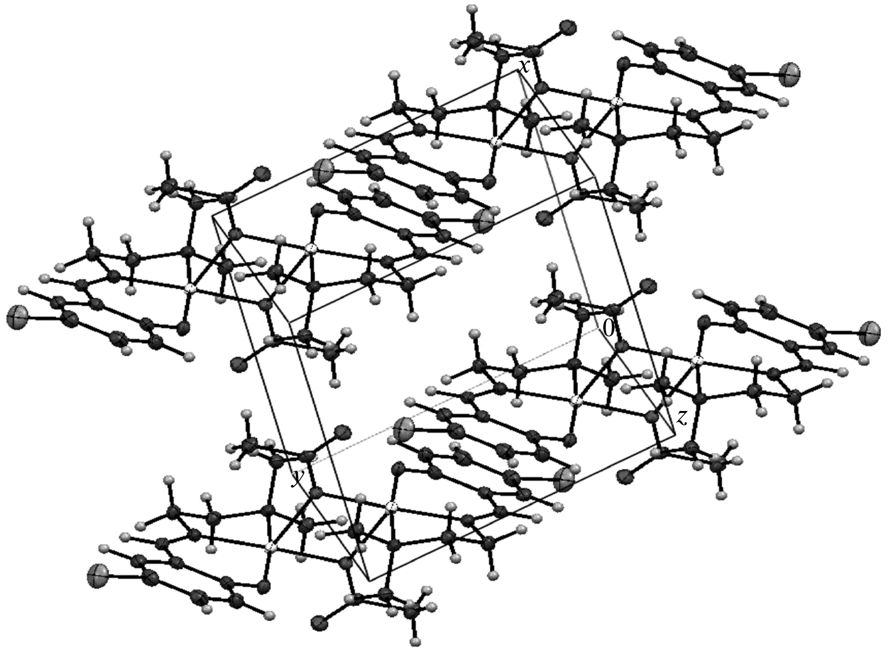


Fig. 4. The packing of the binuclear complex **I** in the unit cell.

Packing of four molecules of the binuclear complex in the unit cell is shown in Fig. 4.

Finally, we prepared the CuO nano-particles by thermal decomposition of the complex of **I**. The complex was thermally decomposed in an oven at 700°C. Based on the XRD pattern of the resulting powder, the average crystallite size calculated by using Scherrer's formula was found to be around 24 nm.

ACKNOWLEDGMENTS

We acknowledge the Damghan University (DU) and Golestan University (GU) for support of this work. Crystallography was supported by the project 14-03276S of the Czech Science Foundation.

REFERENCES

1. Shebl, M., *Spectrochim. Acta, Part A*, 2008, vol. 70, p. 850.
2. Hobady, M. and Smith, T.D., *Coord. Chem. Rev.*, 1973, vol. 9, p. 311.
3. Motekaitis, B.J., Martell, A.E., and Nelson, D.A., *Inorg. Chem.*, 1984, vol. 23, p. 275.
4. Nishinaga, A., Tomita, H., Nishizawa, K., et al., *Dalton Trans.*, 1981, p. 1504.
5. Coleman, W.M., *Inorg. Chim. Acta*, 1981, vol. 49, p. 205.
6. Rajasekar, M., Sreedaran, S., Prabu, R., et al., *J. Coord. Chem.*, 2010, vol. 63, p. 136.
7. Abdallah, S.M., Mohamed, G.G., Zayed, M.A., et al., *Spectrochim. Acta, A,* 2009, vol. 73, p. 833.
8. Dhanaraj, C.J. and Nair, M.S., *J. Coord. Chem.*, 2009, vol. 62, p. 4018.
9. Karthikeyan, M.S., Parsad, D.J., Poojary, B., et al., *Bioorg. Med. Chem.*, 2006, vol. 14, p. 7482.
10. Panneerselvam, P., Nair, R.R., Vijayalakshmi, G., et al., *Eur. J. Med. Chem.*, 2005, vol. 40, p. 225.
11. Wang, C., Wu, X., Tu, S., et al., *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.,* 2009, vol. 39, p. 78.
12. Liu, Q.R., Xue, L.W., and Zhao, G.Q., *Russ. J. Coord. Chem.*, 2014, vol. 40, p. 757.
13. Murray, K.S., *Inorg. Chem.,* 1995, vol. 43, p. 261.
14. Houlton, A., Jasim, N., Roberts, R.M.G., et al., *Dalton Trans.*, 1992, p. 2235.
15. Lu, J.W., Huang, Y.H., Lo, S.I., et al., *Inorg. Chem. Commun.*, 2007, vol. 10, p. 1210.
16. Di Bella, S. and Fragala, I., *New J. Chem.*, 2002, vol. 26, p. 285.
17. Cozzi, P.G., Dolci, L.S., Garelli, A., et al., *New J. Chem.*, 2003, vol. 27, p. 692.
18. Gianneschi, N.C., Nguyen, S.T., and Mirkin, C.A., *J. Am. Chem. Soc.*, 2005, vol. 127, p. 1644.
19. Morris, G.A., Zhou, H., Stern, C.L., et al., *Inorg. Chem.*, 2001, vol. 40, p. 3222.
20. Komatsu, H., Ochiai, B., Hino, T., et al., *J. Mol. Catal., A*, 2007, vol. 273, p. 289.
21. Wang, Y., Ouyang, X.M., Li, Y.Z., and Sun, W.Y., *Bull. Chem. Soc. Jpn.*, 2003, vol. 76, p. 1403.
22. Khalaji, A.D., Grivani, G., Rezaei, M., et al., *Polyhedron*, 2011, vol. 30, p. 2790.
23. Khalaji, A.D., Grivani, G., Seyyedi, M., et al., *Polyhedron*, 2013, vol. 49, p. 19.
24. Grivani, G., Bruno, G., Rudbari, H.A., et al., *Inorg. Chem. Commun.*, 2010, vol. 18, p. 15.
25. Khalaji, A.D., Gholinejadi, M., and Triki, S., *Russ. J. Coord. Chem.*, 2013, vol. 39, p. 209.
26. Palatinus, L. and Chapuis, G., *J. Appl. Crystallogr.*, 2007, vol. 40, p. 786.
27. Petricek, V., Dusek, M., and Palatinus, L., *Z. Kristallogr.*, 2014, vol. 229, p. 345.
28. Farrugia, L.J., *J. Appl. Crystallogr.,* 1997, vol. 30, p. 656.
29. Thakurta, S., Roy, P., Gomez-Garcia, C.J., et al., *Polyhedron*, 2009, vol. 28, p. 695.
30. Biswas, M., Pilet, G., Tercero, J., et al., *Inorg. Chim. Acta*, 2009, vol. 362, p. 2915.