Russian Journal of Coordination Chemistry, Vol. 30, No. 4, 2004, pp. 269–274. Translated from Koordinatsionnaya Khimiya, Vol. 30, No. 4, 2004, pp. 288–294.
Original Russian Text Copyright © 2004 by Tsapkov, Chumakov, Antosyak, Bocelli, Samus', Gulya.

Synthesis, Structure and Properties of Some 3*d*-Element Complexes with 2-[2-(Hydroxybenzylidene)-amino]-2-hydoxymethylpropane-1,3-diol

V. I. Tsapkov*, Yu. M. Chumakov, B. Ya. Antosyak**, G. Bocelli***, N. M. Samus'*, and A. P. Gulya***

** Moldova State University, ul. Matteevicha 60, Chisinau, 277009 Moldova*

*** Institute of Applied Physics, Academy of Sciences of Moldova, Academiei 5, Chisinau, Moldova*

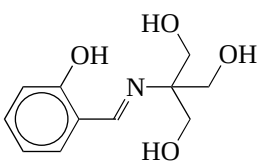
**** Center of Structural Diffractometry, Parma, Italy*

Received September 30, 2003

Abstract—2-[2-(Hydroxybenzylidene)-amino]-2-hydoxymethylpropane-1,3-diol (HL) reacts with cobalt, nickel, copper and zinc chlorides, bromides and acetates in water–ethanol solutions and gives $MLX \cdot nH_2O$ and $ML_2 \cdot nH_2O$ complexes (M = Co, Ni, Cu, Zn; X = Cl, Br; n = 0–5). Single crystals of CuLBr were grown, and its crystal structure was determined by X-ray diffraction analysis. The crystals are tetragonal, a = 17.024(2), c = 8.720(2) Å, space group $P\bar{4}2_1c$, Z = 8, R_1 = 0.0349. In the structure of this complex, the copper atom coordinates the deprotonated HL molecule. The coordination polyhedron of the central atom is an elongated tetragonal pyramid. Its base is built of the imine nitrogen atom, phenolic and alcoholic oxygen atoms, and bromine atom. The apex of the pyramid is occupied by the bromine atom of the adjacent complex connected with the initial complex by the plane of sliding reflection. Thus, the crystal contains infinite chains of complexes running along the c axis, the complexes being united by both bridging bromine atoms and O–H···O hydrogen bonds. The conclusions on the compositions and structures of the remaining compounds were made on the basis of elemental and combined thermal analyses, IR spectroscopy, and magnetic chemistry data. The copper halide complexes were found to have dimeric, and the other metal complexes monomeric, structures. In the synthesized complexes, the azomethine HL can function as a bidentate or tridentate ligand. The thermolysis of the coordination compounds proceeds through the stages of elimination of crystal water molecules (75–90°C) or inner-sphere water molecules (145–155°C) and complete thermal destruction (485–550°C).

2-Amino-2-hydroxymethylpropane-1,3-diol $[H_2NC(CH_2OH)_3]$ containing a number of donor atoms is known to form coordination compounds with transition-metal ions, where it can act as a mono-, bi-, and tridentate or bridging ligand [1–3]. The amino group of the ligand favors its condensation with aldehydes and ketones thus increasing the number of functional groups and dentate number. Complexation of transition metals with such ligands in solution was studied earlier in [4–7].

The purpose of this work was to find optimal conditions of isolation of cobalt, nickel, copper, and zinc complexes with the product of condensation of 2-amino-2-hydroxymethylpropane-1,3-diol with salicylic aldehyde, 2-[2-(hydroxybenzylidene)-amino]-2-hydoxymethylpropane-1,3-diol (HL)



(HL)

from a solution, determine the composition and structure, and to study their physicochemical properties.

The reaction of aqueous solutions of chlorides, bromides, and acetates of the indicated metals with HL (taken at the 1 : 1 and 1 : 2 molar ratios) results in finelycrystalline compounds $MLX \cdot nH_2O$ (**I**, **II**, **IV**, **VI**, **VII**, **IX**) and $ML_2 \cdot nH_2O$ (**III**, **V**, **VIII**, **X**), where M = Co (**I**–**III**), Ni (**IV**, **V**), Cu (**VI**–**VIII**), Zn (**IX**, **X**); X = Cl (**I**, **IV**, **VI**, **IX**), Br (**II**, **VII**); n = 0 (**VI**, **VII**, **IX**), 2 (**X**), 3 (**V**, **VIII**), 4 (**II**), 5 (**I**, **III**, **IV**).

EXPERIMENTAL

The initial HL was prepared as described elsewhere [8].

Synthesis of I. To 30 ml of hot aqueous solution (50–55°C) containing 10 mmol of cobalt(II) chloride hexahydrate, 20 ml of C_2H_5OH containing 10 mmol of HL was added. The resulting reaction mixture was heated to 50–55°C with continuous stirring for 25–30 min. After cooling the solution, dark brown fine crystals precipitated; they were filtered on a glass filter, washed with small quantities of alcohol and ether, and dried in air.

1070-3284/04/3004-0269 © 2004 MAIK "Nauka / Interperiodica"

Table 1. Results of elemental analysis and magnetochemical study of complexes **I**–**X**

Compound	Empirical formula	Yield, %	Content (found/calculated), %			μ_{eff}, μ_B (294 K)
			Hal	M	N	
I	$C_{11}H_{24}ClCoNO_9$	69	8.42/8.69	14.19/14.44	3.30/3.43	4.96
II	$C_{11}H_{22}BrCoNO_8$	73	18.15/18.39	13.31/13.56	2.94/3.22	5.06
III	$C_{22}H_{38}CoN_2O_{13}$	75		9.59/9.88	4.35/4.69	4.90
IV	$C_{11}H_{24}ClNNiO_9$	71	8.51/8.69	14.15/14.44	3.18/3.43	2.98
V	$C_{22}H_{34}N_2NiO_{11}$	74		10.35/10.52	5.16/4.99	3.18
VI	$C_{11}H_{14}ClCuNO_4$	65	10.79/10.97	19.54/19.78	4.18/4.33	1.65
VII	$C_{11}H_{14}BrCuNO_4$	68	21.45/21.74	17.28/17.39	3.64/3.80	1.60
VIII	$C_{22}H_{34}CuN_2O_{11}$	72		11.07/11.31	4.68/4.95	2.06
IX	$C_{11}H_{14}ClNO_4Zn$	70	10.69/10.94	19.75/20.03	4.03/4.31	
X	$C_{22}H_{32}N_2O_{10}Zn$	75		11.60/11.84	4.86/5.10	

Similarly, compounds **II**, **IV**, **VI**, **VII**, and **IX** were prepared using corresponding cobalt, nickel, copper, and zinc chlorides or bromides and HL (1 : 1 molar ratio) as initial reagents.

Complexes **III**, **V**, **VIII**, and **X** were synthesized by the reaction of the indicated metal acetate hydrates with HL (1 : 2 molar ratio) using a similar procedure.

Complexes **I**–**X** are readily soluble in water, alcohols, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) and insoluble in ether. The results of the elemental analysis and selected physicochemical parameters of complexes **I**–**X** are given in Table 1.

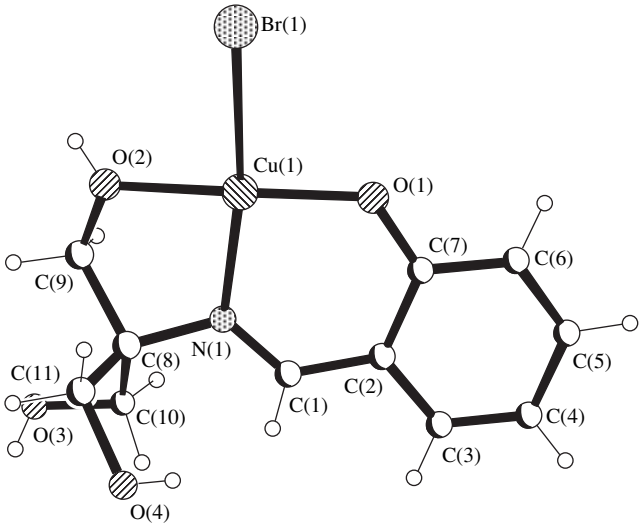


Fig. 1. Structure of complex **VII**.

Single crystals of complex **VII** suitable for the X-ray diffraction analysis were obtained by recrystallization of the compound from the water–ethanol (1 : 1) solution.

Molar conductivity of the solutions of complexes **I**–**X** in DMF (20°C, c_M = 0.01 mol/l) was measured with a R-38 slide-wire bridge.

IR spectra of the complexes were recorded on an Specord M80 spectrophotometer with mineral and fluorinated oil mulls.

Magnetic susceptibility was measured at room temperature by the Gouy method with $Co[Hg(NCS)_4]$ as a standard.

Thermal curves for **I**–**X** were recorded on an OD-102 derivatograph at the rate of 5 K/min in the 20–1000°C temperature range in air.

X-ray diffraction study of complex **VII** was carried out on a Bruker AXS Smart diffractometer with a CCD detector (MoK_α radiation, room temperature). Absorption was corrected with the SHELXTL-NT V5.1 programs [9]. Structure **VII** was solved by the direct method and refined by the least-squares method in anisotropic approximation for non-hydrogen atoms and isotropic approximation for hydrogen atoms with the use of the SHELX97 programs [10]. Hydrogen atoms were located from Fourier difference syntheses.

The details of the experiment are given in Table 2. Coordinates and thermal parameters of basis atoms are

Table 2. Crystallographic data and details of experiment and refinement of structure **VII**

M	364.66
Wave length, Å	0.71073
Crystal system	Tetragonal
Space group	$P\bar{4}2_1/c$
Unit cell parameters	
a, Å	17.024(2)
c, Å	8.720(2)
V, Å^3	2527.2(7)
Z	8
ρ (calcd), g/m^3	1.917
μ, mm^{-1}	4.895
F(000)	1440.0
Crystal size, mm	0.2 × 0.3 × 0.4
θ, deg	1.69–25.01
Index range	$-20 \le h \le 20$, $-20 \le k \le 20$, $-10 \le l \le 10$
Number of measured reflections	24415
Number of unique reflections	2232 (R_{int} = 0.084)
Number of reflections with $I > 2\sigma(I)$	1769
Number of refined parameters	178
GOOF	0.967
Final R factor ($I > 2\sigma(I)$)	R_1 = 0.0349, wR_2 = 0.0624
R factor for total array	R_1 = 0.0586, wR_2 = 0.0667
Δρ(max) and Δρ(min), e Å^{-3}	0.334 and –0.261

Table 3. Atomic coordinates (×10^4) and equivalent isotropic thermal parameters U_{eq} (×10^3) in structure **VII**

Atom	x	y	z	U_{eq}, Å^2
Cu(1)	8161(1)	7455(1)	9030(1)	30(1)
Br(1)	7086(1)	7715(1)	10723(1)	37(1)
O(1)	7839(2)	6413(2)	8630(5)	33(1)
O(2)	8658(3)	8455(3)	9687(5)	35(1)
O(3)	10855(3)	8700(3)	7653(5)	34(1)
O(4)	9242(3)	8452(3)	4940(5)	33(1)
N(1)	9073(3)	7425(3)	7672(5)	24(1)
C(1)	9234(3)	6836(4)	6786(7)	27(2)
C(2)	8820(3)	6103(3)	6720(8)	27(1)
C(3)	9103(3)	5536(3)	5684(9)	37(2)
C(4)	8774(4)	4797(4)	5557(8)	41(2)
C(5)	8150(4)	4617(4)	6522(7)	42(2)
C(6)	7848(4)	5158(4)	7533(8)	38(2)
C(7)	8159(4)	5920(3)	7656(6)	28(2)
C(8)	9549(3)	8156(3)	7633(6)	21(1)
C(9)	9472(3)	8515(3)	9240(7)	32(1)
C(10)	10421(3)	8000(4)	7302(7)	30(2)
C(11)	9192(4)	8729(3)	6465(6)	28(2)

listed in Table 3; interatomic distances and bond angles are presented in Table 4.

RESULTS AND DISCUSSION

The copper atom in structure **VII** coordinates the deprotonated HL molecule (Fig. 1). The coordination polyhedron of the central atom is an elongated tetragonal pyramid. Its base is built of the imine N(1) atom, phenolic and alcoholic O(1) and O(2) atoms, and Br(1) atom. Deviations of these atoms from the mean plane they determine fall within the 0.091–0.119 Å range; the copper atom extends from this plane by 0.064 Å. The bond lengths are as follows: Cu(1)–O(1) 1.888(4), Cu(1)–O(2) 1.981(4), Cu(1)–N(1) 1.953(5), Cu(1)–Br(1) 2.392(1) Å. The Br(1) atom occupies the apex of the Cu(1)' coordination polyhedron of the adjacent complex[1] (Cu(1)'–Br(1) 3.340 Å). The angles between this bond and the coordination bonds of the atoms in the base of pyramid vary in the range of 80.4°–103.3°. Thus, the crystal contains infinite chains of complexes running along the *c* axis, the complexes being united by both bridging bromine atoms and hydrogen bonds (O(1)···O(4)' 2.72(8), O(1)···H(11)' 1.8(6) Å, angle

[1] Coordinates of the atoms labeled with primes are ' y + 1.5, x + 1.5, z – 0.5; " y, x + 2, $-z$ + 2; '" $-y$ + 2, x, $-z$ + 1.

Table 4. Interatomic distances and bond angles in structure **VII**

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–O(1)	1.888(4)	C(1)–C(2)	1.435(8)
Cu(1)–N(1)	1.953(5)	C(2)–C(3)	1.408(8)
Cu(1)–O(2)	1.981(4)	C(2)–C(7)	1.424(8)
Cu(1)–Br(1)	2.3923(9)	C(3)–C(4)	1.382(8)
O(1)–C(7)	1.314(6)	C(4)–C(5)	1.389(9)
O(2)–C(9)	1.438(7)	C(5)–C(6)	1.389(9)
O(3)–C(10)	1.434(7)	C(6)–C(7)	1.405(8)
O(4)–C(11)	1.413(7)	C(8)–C(9)	1.534(8)
N(1)–C(1)	1.296(7)	C(8)–C(10)	1.536(8)
N(1)–C(8)	1.485(7)	C(8)–C(11)	1.405(8)
Angle	ω, deg	Angle	ω, deg
O(1)Cu(1)N(1)	95.5(2)	C(3)C(4)C(5)	117.5(6)
O(1)Cu(1)O(2)	169.4(2)	C(6)C(5)C(4)	121.8(6)
N(1)Cu(1)O(2)	81.5(2)	C(5)C(6)C(7)	121.8(6)
O(1)Cu(1)Br(1)	93.7(1)	O(1)C(7)C(6)	118.8(6)
N(1)Cu(1)Br(1)	170.7(1)	O(1)C(7)C(2)	124.0(5)
O(2)Cu(1)Br(1)	89.7(1)	C(6)C(7)C(2)	117.1(6)
C(7)O(1)Cu(1)	126.7(4)	N(1)C(8)C(9)	105.4(4)
C(9)O(2)Cu(1)	113.6(3)	N(1)C(8)C(10)	112.7(4)
C(1)N(1)C(8)	121.3(5)	N(1)C(8)C(11)	109.4(4)
C(1)N(1)Cu(1)	123.3(4)	C(9)C(8)C(10)	108.9(4)
C(8)N(1)Cu(1)	115.2(4)	C(11)C(8)C(10)	111.6(5)
N(1)C(1)C(2)	126.4(6)	C(9)C(8)C(11)	108.7(5)
C(3)C(2)C(7)	119.2(6)	O(2)C(9)C(8)	106.8(5)
C(3)C(2)C(1)	117.0(6)	O(3)C(10)C(8)	106.8(5)
C(7)C(2)C(1)	123.8(6)	O(4)C(11)C(8)	112.9(5)
C(4)C(3)C(2)	122.5(7)		

O(1)H(11)'O(4)' 157(5)°) (Fig. 2). The chains are also linked by hydrogen bonds: O(2)···O(3)" 2.62(1), O(3)"···H(2) 1.8(1) Å, angle O(2)H(2)O(3)" 178(4)°; O(3)'"···O(4) 2.71(8), O(4)···H(10)'" 1.8(9) Å, angle O(3)'"H(10)'"O(4) 169(5)°.

In compound **VII**, the six-membered metal cycle Cu(1)O(1)N(1)C(1)C(2)C(7) is slightly bent along the O(1)···N(1) line. The angle between the Cu(1)O(1)N(1) and O(1)N(1)C(1)C(2)C(7) planes is 4.1°. In di(μ–$O_{phenoxy}$)-bis{nitrato-2-[2-hydroxyethylimino)-methyl]-phenolo-imidazolecopper [11], nitrato-2-oxy-ethylimino-2-oxy-1-benzaldehyde-3-picolinecopper [12], and 3-hydroxypropylsalicylaldiminatocopper [13], it is equal to 20.6°, 14.9°, and 22.7°, respectively. At the same time, nitrato-2-[2-(hydroxyethylimino)-methyl]-phenolocopper [14], nitrato-2-[2-(hydroxyethylimino)-

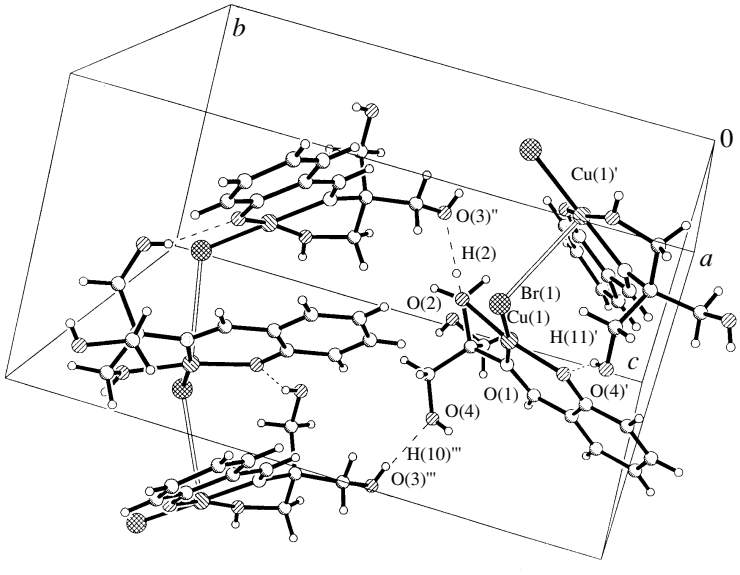


Fig. 2. Fragment of packing of complexes in crystals of **VII**.

methyl]-phenolo-4-picolinecopper [15], and 2-[2-(hydroxoethylimino)-methyl]-phenolocopper [16] do not exhibit such a bend. The benzene ring (*A*) lies nearly in the plane of the O(1)N(1)C(1)C(2)C(7) fragment (*B*) of the six-membered metal cycle; the angle between the *A* and *B* planes is 2.9°. The five-membered metal cycle Cu(1)O(2)N(1)C(8)C(9) has a *gauche* conformation; deviations of the C(8) and C(9) atoms from the Cu(1)O(2)N(1) plane are –0.209(8) and 0.312(9) Å, respectively.

Table 5. Thermal analysis of complexes **I**–**X**

Compound	Number of effect in thermal curve	*T*, °C	Mass loss		Kinetic parameters of process		Temperature of complete decomposition, °C
			found/calculated, %	corresponds to the elimination of	E_{ac}, kJ/mol*	log*Z***	
I	1	75	13.0/13.2	$3H_2O$	40.1	3.7	515
	2	175	8.5/8.8	$2H_2O$	89.9	8.7	
II	1	80	8.0/8.3	$2H_2O$	49.9	5.0	500
	2	165	8.2/8.3	$2H_2O$	68.9	6.8	
III	1	90	15.0/15.1	$5H_2O$	37.6	3.4	540
IV	1	80	13.5/13.2	$3H_2O$	36.9	3.5	500
	2	165	9.0/8.8	$2H_2O$	75.1	7.0	
V	1	90	9.5/9.6	$3H_2O$	45.4	4.2	525
VI	1	75	5.5/5.3	H_2O	35.1	3.4	485
VII							470
VIII	1	85	9.5/9.5	$3H_2O$	42.6	4.0	500
IX							520
X	1	90	6.5/6.6	$2H_2O$	37.3	3.6	550

* E_{ac} is the activation energy of the solid-phase reaction.
** *Z* is the preexponential factor.

The visual microscopic study of powdered complexes **I**–**VI** and **VIII**–**X** revealed their homogeneity. Because single crystals of the complexes were not available, we used IR spectroscopy, magnetic chemistry, and combined thermal analysis (TA) methods in order to identify them and study their structures.

The absorption bands in the IR spectrum of compound **VII** were assigned with account of its structural data. The tridentate chelating function of monodeprotonated ligand L^- was confirmed by (a) disappearance of the absorption band $\delta(OH)_{phenol}$ that was observed for a free azomethine in the 1237–1230 cm^{-1} range; (b) shift of the band $\nu(C{=}N)$ by 20–18 cm^{-1} toward lower frequencies as compared to the band in the initial HL (1635 cm^{-1}); (c) split and low-frequency shift (by 15–10 cm^{-1}) of the absorption bands due to the alcoholic OH groups at 3290–3270 ($\nu(OH)_{alcohol}$) and 1055–1050 cm^{-1} ($\nu(C–O)_{alcohol}$) and broadening of the band $\nu(C–O)_{phenol}$ at 1540 cm^{-1}; (d) appearance of new bands corresponding to $\nu(Cu–N)$ (510 and 405 cm^{-1}) and $\nu(Cu–O)$ (470 cm^{-1}).

Comparison of the IR spectra of complex **VII** and of the remaining nine compounds revealed identical positions of the main characteristic absorption bands. This indicates the same mode of coordination of L^- to the central ions. Negligible difference is found only for compound **VIII** in the region of the absorption bands of the alcoholic OH groups; they have almost the same position as the bands in the initial HL. Probably, in complex **VIII**, L^- functions as a bidentate ligand that is coordinated to the central atom through the deprotonated phenol O atom and azomethine N atom, while in the remaining complexes, it acts as a tridentate ligand (as in complex **VII**).

The determination of the molar conductivity of the dimethylformamide solutions of the complexes obtained suggests that all of them, like compound **VII**, are nonelectrolytes (μ^{20}_{1000} = 3–7 Ω^{-1} cm^2 mol^{-1}).

The data of the magnetochemical study show (Table 1) that the cobalt compounds **I**–**III** have effective magnetic moments (μ_{eff}) corresponding to three unpaired electrons and an oxidation number of the central ion equal to +2. Complexes **IV** and **V** are paramagnetic; judging from their μ_{eff}, the Ni^{2+} ion has a pseudooctahedral ligand surrounding. Compound **VIII** is monomeric, since its magnetochemical data at room temperature correspond to the spin value for one unpaired electron. Complex **VI** with the lowered value of μ_{ef} is a polynuclear compound like complex **VII**.

TA of the synthesized complexes shows that their thermolysis proceeds in several stages (Table 5). Thermal curves of complexes **I**–**V**, **VIII**, and **X** have endothermic effects at 75–90°C; the weight loss corresponds to elimination of crystal water molecules. Compounds **I**, **II**, and **IV** show the second endothermic effect at 165–175°C corresponding to elimination of two inner-sphere water molecules. On the last stage of thermolysis (470–550°C), thermal oxidative destruction of the coordinated azomethine occurs (accompanied by exothermic effect). As follows from Table 5, the temperature of complete decomposition (T) of the complexes depends on the nature of the central atom and its ligand surrounding; for the compounds with the same composition, it decreases in the series $T_{Zn} > T_{Co} > T_{Ni} > T_{Cu}$. The nature of the acido ligand and the number of azomethine molecules also affect the T value. Introduction of the second L^- ligand into the complex increases the temperature by 15–40°C; with the same central atom, $T_{Cl} > T_{Br}$.

REFERENCES

1. Evreev, V.N., *Doctoral (Chem.) Dissertation*, Rostov-on-Don: Rostov State Univ., 1980.
2. Kovalenko, A.L., *Cand. Sci. (Chem.) Dissertation*, Chisinau: Chisinau State Univ., 1987.
3. Evreev, V.N., Bogdanov, A.P., and Zelentsov, V.V., *Koord. Khim.*, 1978, vol. 4, no. 11, p. 1718.
4. Sreenivasulu, R., Raghavendra, R.V.S., and Sreenivasulu, J., *J. Electrochem. Soc. Ind.*, 1987, vol. 36, no. 2, p. 131.
5. Sreenivasulu, R., Raghavendra, R.V.S., and Reddy, H.K., *J. Electrochem. Soc. Ind*., 1985, vol. 34, no. 3, p. 209.
6. Tsapkov, V.I., Popov, M.S., Fam Ngok Fung, and Samus', N.M., *Zh. Obshch. Khim.*, 1994, vol. 64, no. 4, p. 634.
7. Samus', N.M., Tsapkov, V.I., and Rudenko, O.V., *Zh. Obshch. Khim.*, 1995, vol. 65, no. 8, p. 1258.
8. Chumakov, Yu.M., Antosyak, B.Ya., Mazus, M.D., *et al.*, *Kristallografiya*, 2000, vol. 45, no. 6, p. 1025.
9. Bruker Axs Inc., 6300 Enterprise Lane, Madison, WI 53719-1173, USA.
10. Sheldrick, G.M., *SHELX97. Program for the Refinement of Crystal Structure*, Göttingen (Germany): Univ. of Göttingen, 1997.
11. Chumakov, Yu.M., Biyushkin, V.N., Malinovskii, T.N., *et al.*, *Koord. Khim.*, 1989, vol. 15, no. 3, p. 354.
12. Chumakov, Yu.M., Antosyak, B.Ya., Mazus, M.D., *et al.*, *Crystallogr. Reports*, 1998, vol. 43, no. 5, p. 859.
13. Chumakov, Yu.M., Biyushkin, V.N., Malinovskii, T.N., *et al.*, *Koord. Khim.*, 1988, vol. 14, no. 9, p. 1273.
14. Chumakov, Yu.M., Biyushkin, V.N., Malinovskii, T.N., *et al.*, *Koord. Khim.*, 1989, vol. 15, no. 8, p. 1074.
15. Chumakov, Yu.M., Biyushkin, V.N., Malinovskii, T.N., *et al.*, *Koord. Khim.*, 1990, vol. 16, no. 7, p. 945.
16. Raptopoulou, C.P., Papadopoulos, A.N., Malamatari, D.A., *et al.*, *Inorg. Chim. Acta*, 1998, vol. 272, p. 283.