ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 7, pp. 496–503. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © O.V. Koval'chukova, S.B. Strashnova, A.I. Stash, V.K. Bel'skii, B.E. Zaitsev, 2009, published in Koordinatsionnaya Khimiya, 2009, Vol. 35, No. 7, pp. 505–512.

Geometric and Spectral Characteristic of the Tetrahalocuprate(II) Complexes $(HL)_2CuX_4$ (X = Cl, Br). Crystal and Molecular Structures of Bis(2-Methylimidazolium) Tetrabromocuprate(II)

O. V. Koval'chukova[a], S. B. Strashnova[a]*, A. I. Stash[b], V. K. Bel'skii[b], and B. E. Zaitsev[a]

[a] *Peoples Friendship University, ul. Miklukho-Maklaya 6, Moscow, Russia*

[b] *Karpov Research Institute of Physical Chemistry, ul. Vorontsovo pole 10, Moscow, 103064 Russia*

**E-mail: sstrashnova@mail.ru*

Received November 28, 2008

Abstract—The crystal and molecular structures of bis(2-methylimidazolium) tetrabromocuprate(II) are determined. The linear dependences of the degree of distortion of the $CuBr_4^{2-}$ coordination polyhedron on the protonation constant of the organic cation are revealed for the structures with $\theta < 140°$. The dependence of the hydrogen bond parameters (distances H···Br and N···Br, angle NHBr) on the degree of distortion of $CuBr_4^{2-}$ is shown. The degree of distortion of CuX_4^{2-} (X = Cl, Br) is determined by the type of the organic cation and is almost the same for the $CuBr_4^{2-}$ and $CuCl_4^{2-}$ polyhedra. The empirical equations relating the degree of distortion of CuX_4^{2-} (X = Cl, Br) and the position of the Cu ← X ligand-to-metal charge-transfer band (νLMCT) are obtained.

DOI: 10.1134/S1070328409070069

INTRODUCTION

It is known that the complex copper halides are used actively as catalysts for organic reactions. Their catalytic activity is determined by the structure of the coordination polyhedron, which changes (for tetracoordinate copper) from a square to a tetrahedron. The structure of the complexes and specific features of their properties can be determined by the dependence of the degree of distortion of the CuX_4^{2-} polyhedron on the nature of the organic cations and spectral characteristics of the complexes.

The present article continues the series of works devoted to the synthesis, structures, and spectral characteristics of the anionic chloro- and bromocuprate(II) complexes containing organic nitrogen-containing bases as counterions [1–5]. The generalization of the obtained experimental and literature data on the crystallographic and spectral properties of the tetrahalo(chloro, bromo)cuprate(II) anions made it possible to construct correlations that could be used for the estimation of the degree of distortion of the coordination copper(II) polyhedron by the spectral characteristics of the isolated polycrystalline complexes.

EXPERIMENTAL

Synthesis of $(HL)_2[CuBr_4]$ (I) (HL cation of 2-methylimidazolium $H_4N_2C_3(CH_3)$). A weighed sample corresponding to 5×10^{-4} mole of 2-methylimidazolium was dissolved in a minimum volume of ethanol. An ethanolic solution of copper(II) bromide containing 2.5×10^{-3} mole of Cu^{2+} ions was added along with a concentrated solution of HBr, which was added dropwise to pH 1–1.5. The reaction mixture was stored in a water bath for 30 min at 50°C. The single crystals formed after cooling were filtered off and dried over P_2O_5 to a constant weight. The yield was 45%. The violet crystals of complex **I** were unstable in polar solvents. The composition of complex **I** was determined by X-ray diffraction analysis.

X-Ray diffraction analysis. The crystals of complex **I** are monoclinic, space group $P\bar{1}$, $a = 7.903(2)$, $b = 8.350(2)$, $c = 12.997(3)$ Å, $\alpha = 90.74(3)°$, $\beta = 103.97(3)°$, $\gamma = 100.14(3)°$, $V = 817.9(3)$ Å^3, ρcalcd = 2.231 g/cm^3, $Z = 2$. The experimental data were obtained on an Enraf-Nonius CAD-4 automated four-circle diffractometer (MoK_α radiation, graphite monochromator, $\theta/2\theta$ scan mode, $\theta_{max} = 25.47°$). The total number of measured independent reflections was 3240 in the index range: $-9 \le h \le 9$, $0 \le k \le 10$, $-15 \le l \le 15$. In calculations, 3031 independent reflections with $I > 2\sigma(I)$ were used. The structure was solved by a direct method and

refined by least squares in the full-matrix anisotropic approximation for non-hydrogen atoms. The coordinates of hydrogen atoms were revealed from the difference Fourier synthesis and included into the refinement with the fixed coordinates and isotropic thermal parameters. The final R factor values were $R = 0.0391$, $wR_2 = 0.0910$ (for reflections with $I > 2\sigma(I)$), the goodness-of-fit being 0.888. All calculations were performed by the SHELX-97 program package [6]. The coordinates of atoms and other parameters of structure **I** were deposited with the Cambridge Crystallographic Data Centre (no. 711 564; deposit@ccdc.cam.ac.uk).

Electronic absorption spectra were recorded in the interval from 50000 to 15000 cm^{-1} on a Specord UV-VIS spectrometer as a suspension in Nujol.

Table 1. Hydrogen bond geometry in the structure of compound $(HL)_2CuBr_4$

N–H···Br*	Distance, Å			Angle NHBr, deg
	H–N	H···Br	N···Br	
N(2)–H(2)···Br(2)#1	0.92	2.49	3.370(6)	162
N(5)–H(5)···Br(4)#2	0.93	2.57	3.376(6)	145
N(8)–H(8)···Br(3)#1	0.91	2.44	3.302(6)	159
N(11)–H(11)···Br(3)#3	0.91	2.55	3.320(6)	143

* Coordinates of the Br atoms: #1 0.81531(9), 0.59763(9), 0.69756(6); #2 0.47301(9), 0.42186(10), 0.82640(6); #3 0.26778(9), 0.65861(8), 0.61318(7).

RESULTS AND DISCUSSION

According to the X-ray diffraction data (Fig. 1a), the structural units of complex **I** are the $CuBr_4^{2-}$ anion in the partial position in the 2-fold axis and two independent 2-methylimidazolium cations ($\mathbf{HL}^+$). The coordination polyhedron of the Cu^{2+} ion is a distorted tetrahedron. The Cu–Br distances are nearly aligned, being 2.3590–2.3963 Å. The BrCuBr angles vary from 100.02(5)° to 131.64(5)°. The imidazole cycle protonated at the nitrogen atom is almost planar, and its geometric parameters are close to the corresponding parameters of the 2-methylimidazolium cation [5].

The cations and anions in the crystal are joined by the NH···Br hydrogen bonds into infinite ribbons (Fig. 1b). Each $CuBr_4^{2-}$ anion is linked with four organic cations, and each cation is bound to two anions (Table 1).

The electronic absorption spectrum of polycrystalline sample **I** has a broad absorption band with a maximum at 16800 cm^{-1} corresponding to the Br⟶Cu ligand-to-metal charge-transfer band (LMCT), which is absent from the spectrum of imidazole.

The analysis of the published data on the structures and spectra of the copper(II) halide complexes made it possible to examine the change in the average value of the *trans*-XCuX angle (θ) for the CuX_4^{2-} structure (X = Cl, Br) (Table 2). The plot of the degree of distortion of the CuX_4^{2-} coordination polyhedron vs. the halide ion (Fig. 2) is linear, and the θ values for $CuCl_4^{2-}$ and $CuBr_4^{2-}$ are similar for the structure with the same counterions. Therefore, it can be concluded that the degree of distortion of the coordination polyhedron depends slightly on the halogen (Cl, Br) nature and is mainly determined by the nature of the organic cation.

As known, the *trans*-angle value close to 109° corresponds to the tetrahedral configuration (T_d) of the $CuBr_4^{2-}$ ion, whereas the flattening of the structure to the D_{4h} configuration increases θ to 180°. The analysis of the dependence of the degree of distortion of the $CuBr_4^{2-}$ polyhedron on the protonation constant of the organic cation (Fig. 3) suggests that for the structure close to tetrahedral (θ = 100°–140°) the degree of distortion of the $CuBr_4^{2-}$ coordination polyhedron increases with an increase in the basicity of the organic base. We failed to reveal the character of the dependence at larger *trans* angles.

The relationship between the geometry of the anion and hydrogen bond geometry is discussed using the tetrachlorocuprate complexes as an example [26]. The authors [26] believe that almost no hydrogen bonding is observed between the $CuCl_4^{2-}$ ions and organic counterions in the structure close to tetrahedral with the angles θ < 132°. The enhancement of the hydrogen bonds elongates the corresponding coordination Cu–Cl bond and increases the degree of distortion of the tetrahedron, i.e., results in the flattening of the inorganic anion structure.

The hydrogen bond characteristics and the Cu–Br bond lengths for some compounds are given in Table 2. The constructed graphical correlations of the hydrogen bond parameters (r(H–Br)/r(N–Br) (Fig. 4a) and angle NH···Br/θ (Fig. 4b)) are linear and similar to those for the tetrachlorocuprate(II) complexes [5]. Thus, the determining factor for hydrogen bond formation is the type of the outer-sphere organic cation in the $(HL)_2CuX_4$ compounds rather than the nature of the inorganic ligand (Cl, Br).

Although a restricted number of compounds with the known crystal structures was accessible for analysis of the position of the Cu⟵X LMCT band (Table 2), the correspondence of the frequencies of the LMCT bands and the degree of distortion of the CuX_4^{2-} coordination polyhedron is distinctly seen in Fig. 5. As mentioned above, the coordination polyhedron of

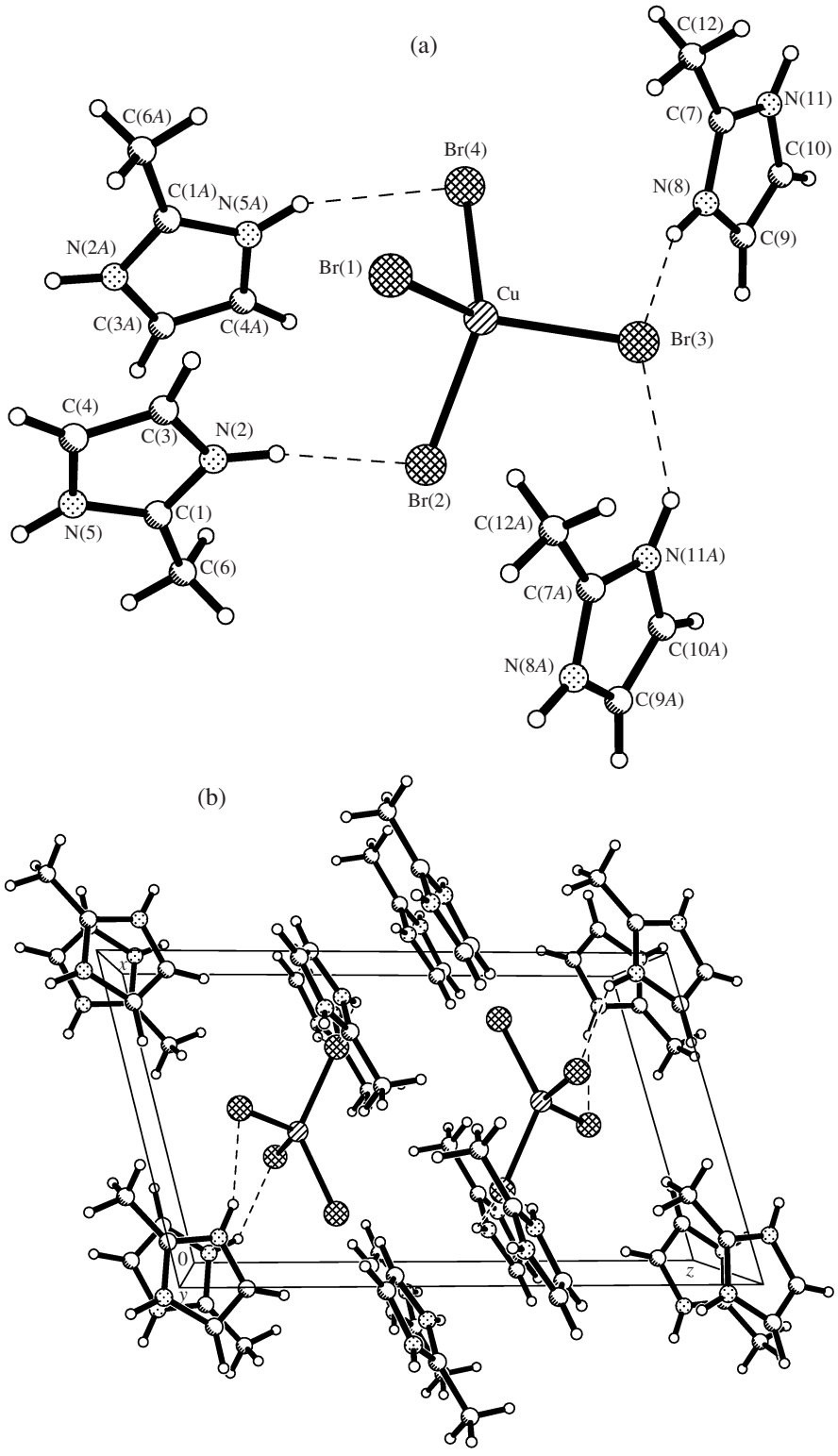


Fig. 1. (a) Molecular and (b) crystal structures of $(HL)_2CuBr_4$ (L is 2-methylimidazole); hydrogen bonds are shown by dotted lines.

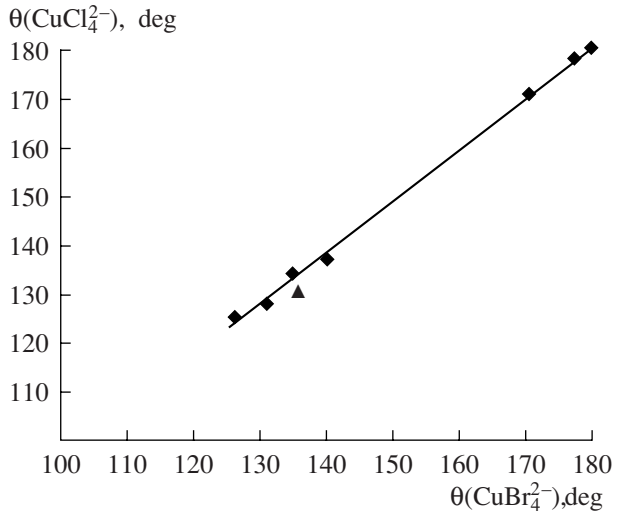


Fig. 2. Plots of the degree of distortion of the CuX_4^{2-} coordination polyhedron vs. inorganic anion nature: ■ are literature data, and ▲ are the data of the present work.

CuX_4^{2-} should be the same for the chloride and bromide complexes containing identical cations (organic bases).

The analysis of the data in Fig. 5 made it possible to obtain the empirical dependences of the degree of distortion of the CuX_4^{2-} polyhedron in the $(HL)_2CuX_4$ structure on the position of the Cu←X ν_{LMCT}: for the $(HL)_2CuCl_4$ $\theta = 0.0272\nu_{LMCT} - 544.56$ at the approximation reliability $R^2 = 0.9718$, whereas for $(HL)_2CuBr_4$ $\theta = 0.001\nu_{LMCT} + 113.97$ ($R^2 = 0.9963$).

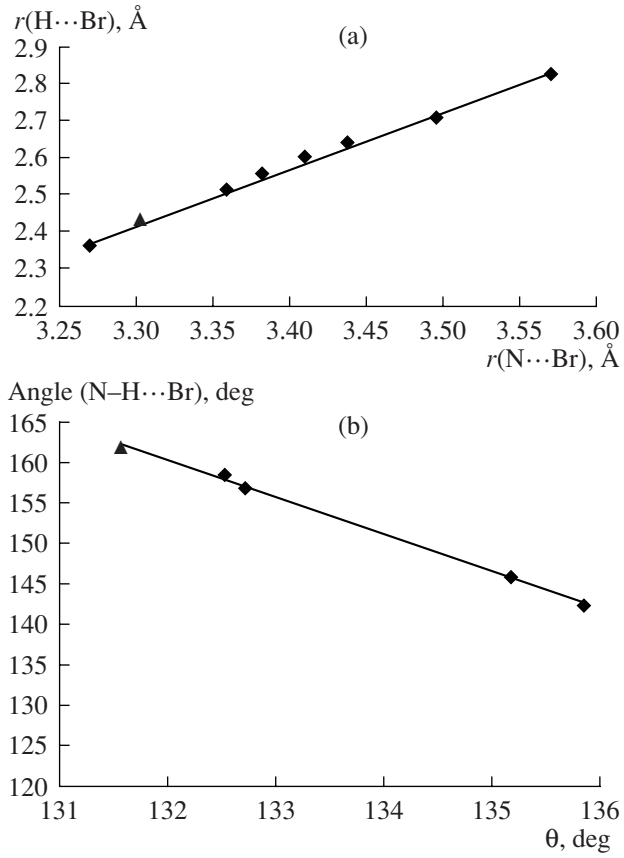


Fig. 4. Selected characteristics of hydrogen bonds in the $(HL)_2CuBr_4$ structures: (a) the dependence of the H···Br distance on N···Br and (b) the dependence of the degree of distortion of the coordination polyhedron (θ) on the N–H···Br angle in the hydrogen bonds of the $(HL)_2CuBr_4$ structure; ◆ are literature data, and ▲ are the data of the present work.

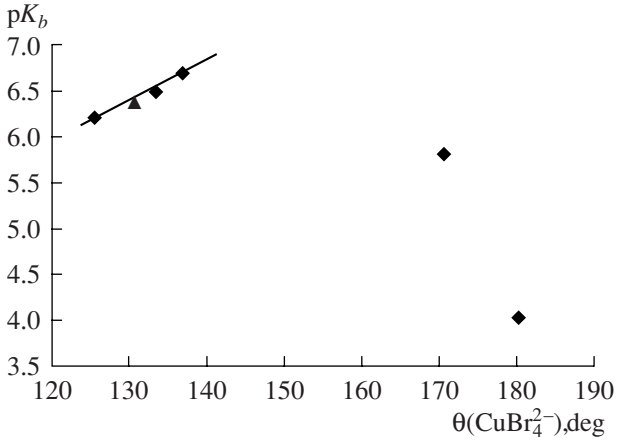


Fig. 3. Plots of the degree of distortion of the $CuBr_4^{2-}$ coordination polyhedron vs. protonation constant of the organic counterion pK_b: ■ are literature data, and ▲ – are the data of the present work.

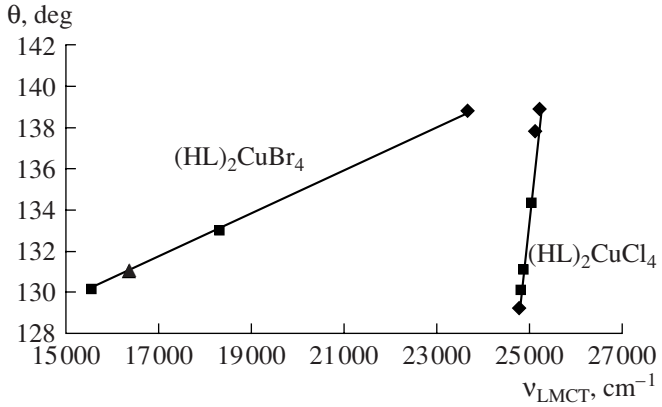


Fig. 5. Plots of the position of the Cu←Br and Cu←Cl charge-transfer bands (ν_{LMCT}) vs. degree of distortion of the coordination polyhedron in the $(HL)_2CuX_4$ complexes (X = Cl, Br): ■ are literature data, and ▲ are the data of the present work.

Table 2. Basicity constants of the organic counterions, selected characteristics of the coordination polyhedron, hydrogen bond parameters, and positions of the ν_{LMCT} bands in the electronic absorption spectra of the complexes containing CuX_4^{2-} (X = Cl, Br)

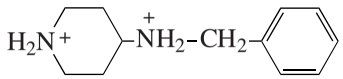
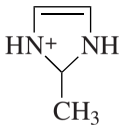
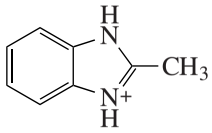
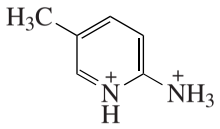
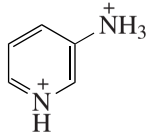
Outer-sphere cation	pK_b	X = Br							X = Cl		
		θ, deg	hydrogen bond parameters			r(Cu–Br), Å	ν_{LMCT}, cm^{-1}	literature	θ, deg	ν_{LMCT}, cm^{-1}	literature
			r(N–Br), Å	r(H–Br), Å	Angle NH···Br						
Cs^+		128.4						[7]	124	24730	[8]
	6.22 [9]	125.6						[10]	133		[11]
	6.25 [12]	131.64	3.302 3.376	2.44 2.57	143–162	2.369–2.396	16800	This work	134.4	25000	[5]
	6.29 [13]	134.2	3.34	2.64	147	2.430		[14]	134.69		[14]
	6.68 [15]	137						[16]	140		[16]
	5.8 [15]	170.6	3.44	2.62		2.439 2.435 2.430		[17]	170.56		[17]

Table 2. (Contd.)

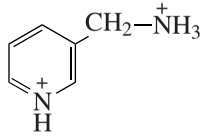
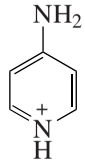
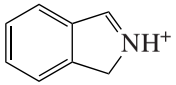
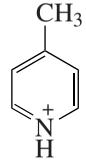
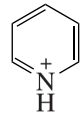
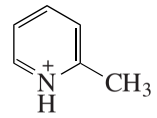
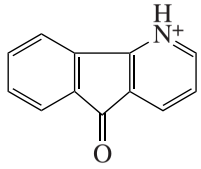
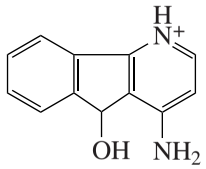
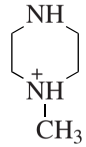
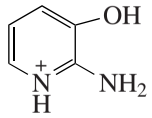
Outer-sphere cation	pK_b	X = Br							X = ël		
		θ, deg	hydrogen bond parameters			r(Cu–Br), Å	ν_{LMCT}, cm^{-1}	literature	θ, deg	ν_{LMCT}, cm^{-1}	literature
			r(N–Br), Å	r(H–Br), Å	Angle NH···Br						
		178						[18]	177.4		[18]
$H_3\overset{+}{N}-CH_2-CH_2-\overset{+}{N}H_3$	4.02 [19]	180						[20]	180		[21]
		132.57	3.48	2.61	159	2.390	18320	[22]			
		132.7	3.327	2.46	155	2.430		[23]			
		135.8	3.27 3.36	2.36 2.55	146	2.389 2.384		[24]			
		131.28	3.50	2.68	142	2.377		[24]			

Table 2. (Contd.)

Outer-sphere cation	pK_b	X = Br							X = Cl		
		θ, deg	hydrogen bond parameters			r(Cu–Br), Å	ν_{LMCT}, cm^{-1}	literature	θ, deg	ν_{LMCT}, cm^{-1}	literature
			r(N–Br), Å	r(H–Br), Å	Angle NH···Br						
		135.19	3.41	2.60	144	2.387		[24]			
							16400	[3]	130.98	24900	[5]
							15520	[3]		24820	[5]
							23810	[25]		25640	[25]
									137.8	25100	[5]

Taking into account the equal degree of distortion of the $(HL)_2CuX_4$ coordination polyhedron (X = Cl, Br), the relation between the ν_{LMCT} in the electronic absorption spectra of the complexes for the same counterion is expressed as follows:

$$\nu_{LMCT}(CuBr_4^{2-}) = 272\nu_{LMCT}(CuCl_4^{2-}) - 658530.$$

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 07-03-00020-a.

REFERENCES

1. Kuz'mina, N.E., Palkina, K.K., Koval'chukova, O.V., et al., *Zh. Neorg. Khim.,* 2002, vol. 47, no. 11, p. 1843 [*Russ. J. Inorg. Chem.* (Engl. Transl.), vol. 47, no. 11, p. 1693].
2. Kuz'mina, N.E., Palkina, K.K., Koval'chukova, O.V., et al., *Zh. Neorg. Khim.*, 2003, vol. 48, no. 2, p. 257 [*Russ. J. Inorg. Chem.* (Engl. Transl.), vol. 48, no. 2, p. 205].
3. Koval'chukova, O.V., Palkina, K.K., Tran Tkhan Tun, et al., *Zh. Neorg. Khim.,* 2007, vol. 52, no. 5, p. 798 [*Russ. J. Inorg. Chem.* (Engl. Transl.), vol. 52, no. 5, p. 733].
4. Koval'chukova, O.V., Stash, A.I., Strashnova, S.B., et al., *Kristallografiya*, 2008, vol. 53, no. 3, p. 484 [*Crystallogr. Rep.* (Engl. Transl.), vol. 53, no. 3, p. 451].
5. Koval'chukova, O.V., Palkina, K.K., Strashnova, S.B., et al., *Koord. Khim.*, 2008, vol. 34, no. 11, p. 837 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 34, no. 11, p. 830].
6. Sheldrick, G.M., *SHELXL-97. Program for the Refinement of Crystal Structures*, Göttingen (Germany): Univ. of Göttingen, 1997.
7. Morosin, B. and Lingafelter, E.C., *Acta Crystallogr.*, 1960, vol. 13, no. 4, p. 807.
8. Doering, W.E. and Sachdev, K., *J. Am. Chem. Soc.*, 1974, vol. 96, no. 4, p. 1168.
9. Hall, H.K., *J. Am. Chem. Soc.*, 1957, vol. 79, no. 20, p. 5441.
10. Place, H. and Willett, R.D., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1988, vol. 44, no. 1, p. 34.
11. Antolini, L., Menabue, L., Pellacani, G.C., et al., *Dalton Trans.*, 1981, no. 8, p. 1753.
12. Bruice, T.C. and Schmir, G.L., *J. Am. Chem. Soc.,* 1958, vol. 80, no. 1, p. 148.
13. Lane, T.J. and Quinlan, K.P., *J. Am. Chem. Soc.*, 1960, vol. 82, no. 12, p. 2994.
14. Bhattacharya, R., Chanda, S., Bocelli, G., et al., *J. Chem. Crystallogr.*, 2004, vol. 34, no. 6, p. 393.
15. Angyal, S.J. and Angyal, C.L., *J. Chem. Soc.,* 1952, p. 1461.
16. Place, H. and Willett, R.D., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1987, vol. 43, no. 6, p. 1050.
17. Willett, R., Place, H., and Middleton, M., *J. Am. Chem. Soc.*, 1988, vol. 110, no. 26, p. 8639.
18. Long, G.S., Wei, M., and Willett, R.D., *Inorg. Chem.*, 1997, vol. 36, no. 14, p. 3102.
19. Braude, E.A. and Nachod, F.C., *Determination of Organic Structures by Physical Methods*, New York: Academic Press, 1955.
20. Rubenacker, G.V., Haines, D.N., and Drumheller, J.E., *J. Magn. Magn. Mater.*, 1984, vol. 43, no. 3, p. 238.
21. Tichý, K., Benes, J., Hälg, W., et al., *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1978, vol. 34, no. 10, p. 2970.
22. Roman, P., Sertucha, J., Luque, A., et al., *Polyhedron*, 1996, vol. 15, no. 8, p. 1253.
23. Tosik, A. and Bukowska-Strzyzewska, M., *J. Crystallogr. Spectr. Res.*, 1989, vol. 19, no. 4, p. 707.
24. Luque, A., Sertucha, J., Castillo, O., et al., *New J. Chem.*, 2001, vol. 25, p. 1208.
25. Marcotrigiano, G., Menabue, L., and Pellacani, G.C., *J. Coord. Chem.*, 1979, vol. 9, p. 141.
26. Murphy, B. and Hathaway, B., *Coord. Chem. Rev.*, 2003, vol. 243, nos. 1–2, p. 237.