Manganese(III) Complexes with Tetradentate (N₂O₂) Schiff Bases and Dicyanamide

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Abstract—New Mn(III) complexes with Schiff bases and dicyanamide are synthesized: $[Mn(Salpn)N(CN)_2]_n$ (two polymorphous modifications, **Ia** and **Ib**), $\{[Mn(5-BrSalen)N(CN)_2] \cdot CH_3OH\}_n$ (**II**), and $[Mn(3-MeOSalen)N(CN)_2(H_2O)]$ (**III**), where $SalpnH_2 = N,N'$ -bis(salicylidene)-1,3-diamino-propane, 5-BrSalenH_2 = N,N'-bis(5-bromosalicylidene)-1,2-diaminoethane, and 3-MeOSalenH_2 = N,N'-bis(3-methoxysalicylidene)-1,2-diaminoethane. Complexes **Ia**, **Ib**, and **II** have the polymer structure in which the dicyanamide anion binds the paramagnetic Mn(III) complexes with the Schiff bases into one-dimensional chains. Unlike them, in complex **III** the monomer units containing water and the dicyanamide anion as terminal ligands form dimers due to hydrogen bonds. The study of the magnetic properties of complexes **Ia** and **II** shows a weak antiferromagnetic interaction between the Mn³⁺ ions through the dicyanamide bridges in these complexes.

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Manganese with the charge +3 forms high-spin (S=2) complexes with tetradentate (N_2O_2) Schiff bases of the N,N'-bis(salicylidene)-1,2-diaminoethane (SalenH₂, Scheme 1) type. Depending on steric

features of the Schiff base, the nature of the terminal ligands, and the solvent, the complexes can exist in the monomer paramagnetic or dimeric antiferromagnetic and ferromagnetic forms (Scheme 2) [1-7].



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Scheme 2.

These complexes are building blocks for the preparation of mono- and heterometallic magnetic materials of different dimensionalities by the replacement in them of neutral terminal ligands by diamagnetic or

paramagnetic bridging groups [8-20]. For these purposes, pseudohalide anions N₃, CN, NCS, and NCO are widely used as bridging ligands [8-14]. At the same time, the polydentate dicyanamide anion $[N(CN)_2]^{-1}$ (Dca) forming polymer structures of different dimensionalities [21-26] was poorly used as an apical ligand in the Mn(III) complexes with Schiff bases. Only two published works are known that describe three coordination polymer Mn complexes with Schiff bases containing $[N(CN)_2]^-$ as bridging ligands [27, 28]. In this work we synthesized new Mn(III) complexes with Schiff bases (Salpn, 5-BrSalen, and 3-MeOSalen; Scheme 1) and dicyanamide: $[Mn(Salpn)N(CN)_2]_n$ (two polymorphous modification Ia and Ib), {[Mn(5-BrSalen)N(CN)₂] · CH₃OH}_n (II), and [[Mn(3- $MeOSalen)N(CN)_2(H_2O)$] (III). The syntheses and crystal structures of these complexes and the magnetic properties of complexes **Ia** and **II** are described.

EXPERIMENTAL

The following reagents were used for the syntheses of the complexes: Mn(II) acetate tetrahydrate ($\geq 99\%$, Fluka), Mn(III) acetate dihydrate (97%, Aldrich), N,N'bis(salicylidene)-1,3-diaminopropane (SalpnH₂, 99%), 2-hydroxy-5-bromobenzaldehyde (98%), 2-hydroxy-3methoxybenzaldehyde (98%), ethylenediamide (99%, Sigma-Aldrich), and methanol (reagent grade). Complex $[Mn(Salpn)(H_2O)](ClO_4)$ and simple and complex Mn(II) and Ni(II) dicyanamides were synthesized according to described procedures [1, 29, 30]. IR spectra were recorded on a Varian 3100 FT-IR instrument in the range from 600 to 4000 cm⁻¹ using polycrystalline samples. Absorption bands in the IR spectra were assigned on the basis of literature data [31]. Elemental analyses for C, H, and N were carried out on a Vario MICRO Cube analyzer. Magnetic measurements were carried out on an MPMS-5-XL SQUID magnetometer (Quantum Design) in a field of 100 Oe. The diamagnetic contributions from the sample holder and internal diamagnetism of the complexes calculated using Pascal's tables were taken into account in the calculation of the paramagnetic component of magnetic susceptibility γ .

Synthesis of complex Ia. Method (A). A solution of Schiff base SalpnH₂ (0.352 g, 1.25 mmol) in methanol (10 mL) was added to a solution of Mn(III) acetate dihydrate (0.335 g, 1.25 mmol) in methanol (10 mL). The mixture was heated to 50° C and stirred for 30-40 min, then (Bu₄N)Mn[N(CN)₂]₃ (0.309 g, 0.625 mmol) in methanol (10 mL) was added, and the mixture was stirred for 30-40 min more. Then water (20 mL) was poured to the hot solution, and the solution was filtered. The mother liquor was left to evaporate slowly at ambient temperature for a week. Dark brown crystals that precipitated were washed with a minimum amount of water and dried in vacuo. The yield was 72%.

For C₁₉H₁₆N₅O₂Mn

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anal. calcd. (%):	C, 56.86;	Н, 3.99;	N, 17.45.
Found (%):	C, 56.58;	Н, 3.89;	N, 17.31.

IR, v, cm⁻¹: 2228, 2158 v(C=N); 1609 v(C=N).

Method (B). A solution of tetraphenylphosphonium dicyanamide $(Ph_4P)[N(CN_2)]$ (0.091 g, 0.213 mmol) in methanol (10 mL) was added to a solution of complex $[Mn(Salpn)(H_2O)](ClO_4)$ (0.1 g, 0.213 mmol) in methanol (20 mL). The mixture was heated to 50°C and stirred for 30–40 min, then hot water (20 mL) was added, and the solution was filtered. The mother liquor was left to evaporate at ambient temperature for a week. Dark brown crystals that precipitated were washed with a minimum amount of water and dried in vacuo. The yield was 63%.

For $C_{19}H_{16}N_5O_2Mn$					
anal. calcd. (%):	C, 56.86;	Н, 3.99;	N, 17.45.		
Found (%):	C. 57.04:	H. 3.88:	N. 17.40.		

IR, v, cm⁻¹: 2228, 2159 v(C=N); 1608 v(C=N).

Synthesis of complex Ib was carried out according to method (A) using $Mn[N(CN)_2]_2$ in a methanolic solution as a precursor of the dicyanamide anion. The yield was 65%.

IR, v, cm⁻¹: 2226, 2159 v(C=N); 1610 v(C=N).

Synthesis of complex II. Method (B). A dry mixture of manganese(II) acetate tetrahydrate (0.123 g, 0.5 mmol) and 2-hydroxy-5-bromobenzaldehyde (0.201 g, 1 mmol) was dissolved in methanol (20 mL) with stirring for 10-15 min, and then ethylenediamine (0.03 g, 0.5 mmol) was poured dropwise. The reaction mixture was heated to 50°C and stirred for 30-40 min, then $(Bu_4N)Ni[N(CN)_2]_3$ (0.244 g, 0.5 mmol) in methanol (10 mL) was added, and the mixture was stirred for 30-40 min more. Then water (20 mL) was poured to the hot solution, and the resulting solution was filtered. The mother liquor was left to evaporate slowly at ambient temperature for a week. Dark brown crystals that precipitated were washed with a minimum amount of water and dried in vacuo. The yield was 48%.

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IR, v, cm⁻¹: 2226, 2159 v(C=N); 1610 v(C=N).

Synthesis of complex III was similar to that of complex **II** (method C) using 2-hydroxy-3-methoxybenzaldehyde instead of 2-hydroxy-5-bromobenzaldehyde. The yield was 68%.

For $C_{20}H_{20}N_5O_5Mn$				
anal. calcd. (%):	C, 51.61;	H, 4.30;	N, 15.05.	
Found (%):	C, 51.72;	H, 4.51;	N, 14.97.	

IR, v, cm⁻¹: 2251, 2144 v(C=N); 1622 v(C=N).

Complex III was synthesized by the same method using $Ni(Dca)_2$ in a methanolic solution as a precursor of the dicyanamide anion. The yield was 65%.

For $C_{20}H_{20}N_5O_5Mn$				
anal. calcd. (%):	C, 51.61;	H, 4.30;	N, 15.05.	
Found (%):	C, 51.76;	Н, 4.52;	N, 14.99.	

IR, v, cm⁻¹: 2251, 2145 v(C=N); 1622 v(C=N).

X-ray diffraction analysis. Unit cell parameters were determined for single crystals of all four complexes, and three-dimensional arrays of reflection intensities were collected on a four-circle diffracto-

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Parameter	Value				
Turumeter	Ia	Ib	П	III	
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	
FW	401.31	401.31	577.13	465.35	
Space group; Z	$P2_1/n; 4$	<i>P</i> 2 ₁ / <i>c</i> ; 4	<i>P</i> 2 ₁ / <i>c</i> ; 4	$P2_{1}/c; 4$	
a, Å	9.308(1)	7.2102(8)	9.907(1)	11.383(1)	
b, Å	14.858(2)	15.177(1)	16.480(2)	22.017(2)	
<i>c</i> , Å	13.117(1)	16.511(2)	13.477(1)	8.6293(8)	
β, deg	99.32(1)	95.70(1)	102.448(9)	108.80(1)	
<i>V</i> , Å ³	1790.1(3)	1797.9(3)	2148.6(4)	2047.3(3)	
$\rho_{calcd}, g/cm^3$	1.489	1.483	1.784	1.51	
μ , cm ⁻¹	7.62	7.59	43.64	6.88	
θ scan range, deg	2.09-28.28	1.83-31.1	1.98-32.85	1.89-29.55	
Range of indices h, k, l	-12 < h < 12, -19 < k < 19, -17 < l < 17	-5 < h < 10, -20 < k < 20, -24 < l < 19	-13 < h < 14, -24 < k < 24, -18 < l < 20	-14 < h < 15, -27 < k < 30, -11 < l < 11	
N measured	18340	11971	28791	19423	
N independent	4446	4952	7366	5054	
$R_{\rm int}, R_{\sigma}$	0.044, 0.04	0.041, 0.029	0.037, 0.034	0.039, 0.038	
Number of parameters	245	244	273	288	
S	1.072	1.053	1.05	1.068	
R factor ($I > 2\sigma(I)$)	0.042	0.04	0.043	0.043	
$\Delta \rho_{\text{max}} / \Delta \rho_{\text{min}}, e \text{ Å}^{-3}$	0.729/-0.374	1.016/-0.946	0.276/-0.349	0.631/-0.346	

Table 1. Main crystallographic data and refinement parameters for structures Ia, Ib, II, and III

meter with a CCD detector (Oxford Diffraction GeminiR, MoK_{α} radiation, ω scan mode, graphite monochromator) at ambient temperature. An absorption correction was applied on intensities of diffraction reflections using the SCALE3 ABSPACK algorithm of the CrysAlisPro program [32]. The crystal structures of complexes Ia and III were determined by a direct method using the SIR2004 program [33], and those of crystals Ib and II were determined by the abinitio method using the Superflip program [34] and refined by the least-squares method using the SHELXL program [35]. All non-hydrogen atoms

were refined in the anisotropic approximation, and hydrogen atoms were specified geometrically with the thermal parameters $U_{iso}(H) = 1.2U_{eq}(C)$ and $U_{iso}(H) = 1.5U_{eq}(O)$. The main crystallographic data and refinement parameters for the structures are listed in Table 1. Selected bond lengths and bond angles are given in Table 2. All crystallographic data **Ia**, **Ib**, **II**, **III** were deposited with the Cambridge Crystallographic Data Centre (nos. 875317, 875318, 875319, and 875320; deposit@ccdc.cam.ac.uk or http://www.ccdc. cam.ac.uk/data_request/cif).

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Type of bond	Ia	Ib	п	III
Mn–O _{eq} , Å	1.887(1) 1.888(1)	1.876(1) 1.895(1)	1.873(2) 1.889(2)	1.883(1) 1.874(1)
$Mn-N_{eq}, Å$	2.036(2) 2.048(2)	2.027(2) 2.052(1)	1.984(2) 1.995(2)	1.981(2) 1.980(2)
Mn–N _{ax} , Å	2.266(2) 2.319(2)	2.260(2) 2.329(2)	2.295(2) 2.333(2)	
(Mn-O _{ax})				2.262(2) 2.321(2)
(NMnN) _{ax} , deg	175.90(7)	174.60(6)	171.91(8)	
(NMnO)				173.99(7)
(Mn-Mn) _{chain} , Å	8.637	7.871	8.407	
(Mn-Mn) _{interchain} , Å	7.405	7.210	7.003	4.890 (in dimer)
(CNC) _{Dca} , deg	122.3(2)	119.8(2)	121.4(3)	121.9(3)

Table 2. Selected bond lengths and bond angles in complexes Ia, Ib, II, and III*

* (NMnN)_{ax} is the angle between the axial bonds at Mn; (Mn-Mn)_{chain} is the closest distance between Mn in the chain; (Mn-Mn)_{interchain} is the closest Mn-Mn distance between the chains; and (CNC)_{Dca} is the angle at the central N atom in the dicyanamide bridge.

RESULTS AND DISCUSSION

The Mn^{3+} complexes with Schiff bases Salpn²⁻, 5-BrSalen²⁻, 3-MeOSalen²⁻) and dicyanamide were synthesized using the following three approaches: (A) the reaction between Mn^{3+} acetate, the corresponding Schiff base, and a precursor of the dicyanamide ligand, (B) the substitution of the terminal ligand (H₂O) in the starting Mn^{3+} complexes with Schiff bases { $[Mn(BS)H_2O]ClO_4$ } for the dicyanamide ligand; and (C) the reaction between Mn^{2+} diacetate, the corresponding salicylaldehyde and diamine, and a precursor of the dicyanamide ligand. Precursors of the dicyanamide ligands were $NaN(CN)_2$, $PPh_4N(CN)_2$, $M[N(CN)_2]_2$ (M = Mn, Ni) and *n*-Bu₄N{M[N(CN)_2]_3} $(M = Mn^{2+}, Ni^{2+})$. It was assumed that the Mn(III) complexes with Schiff bases containing paramagnetic anions $\{M[N(CN)_2]_3\}^-$ as bridging ligands could possibly be synthesized in the case of complex Mn²⁺ and Ni²⁺ dicyanamides. However, regardless of the nature of the precursor of the dicyanamide ligand and the synthesis method, we obtained complexes containing only the dicyanamide anion either as the bridging ligand (two polymorphous modifications **Ia** and **Ib** and complex **II**), or as the terminal ligand (complex **III**). The latter is the first Mn(III) complex with the Schiff base containing the Dca⁻ anion as the terminal ligand. Probably, this is related to steric features of the Schiff base (3-MeOSalen²⁻) bearing the methoxy group in position 3.

The molecular structures of complexes **I**–**III** are shown in Fig. 1. The central Mn atom in all structures has the octahedral coordination with the equatorial plane formed by the O and N atoms of the Schiff base. In complexes **Ia**, **Ib**, and **II** the axial positions are occupied by the N atoms of the Dca ligand, whereas in structure **III** the O atom of the water molecule occupies one of the axial positions. The shape of the octahedron is extended along the axial axis, which is characteristic of the Jahn–Teller ion of Mn(III) (Table 2). The Mn–O_{eq}, Mn–N_{eq}, and Mn–N_{ax} bond lengths in the synthesized complexes are close to similar distances in complex [Mn(Salen)N(CN)₂]_n [27, 28].

Structures Ia, Ib, and II are characterized by the chain structure through the bridging Dca groups in the



Fig. 1. Molecular structures of complexes Ia, Ib, II, and III with 30% thermal ellipsoids.

axial positions, whereas structure **III** is built of discrete dimers $[Mn(3-MeOSalen)N(CN)_2(H_2O)]\cdots[Mn(3-MeOSalen)N(CN)_2(H_2O)].$

The projections of the crystal structures of polymorphous phases **Ia** and **Ib** along the *x* direction are shown in Fig. 2. The structures of these phases differ by the internal structure of the polymer chain. First, the angle between the Jahn–Teller axes in the chain is 44.5° for complex **Ia** and 69.9° for complex **Ib**. In addition, the Mn(Salpn) fragments have different conformations: the dihedral angles between the planes of salicylideneimines (C_7NO) are 52.5° in complex **Ia** and 73.6° in complex **Ib**. The chains in structures **Ia** and **Ib** pass along the directions [-1 0 1] and [0 1 0], respectively. Both structures are characterized by shortened contacts between the C–H…O, C–H…C, and C…C chains (π – π interactions).

The projection of crystal structure II along the *x* direction is shown in Fig. 3. The Mn(BrSalen) fragment in structure II is nearly planar: the angle between the planes of bromosalicylideneimines is 7.8° . The Jahn–Teller axes of the adjacent Mn(III) atoms in the chain are arranged at an angle of 56.6°. The crystals include the MeOH solvent molecule that is localized between the chains and forms hydrogen

bonds $C-H\cdots Br$ and $O-H\cdots O$ with the salicylideneimine fragments of the complex.

The crystal structure of complex **III** is built of centrosymmetric dimers linked by hydrogen bonds $O-H\cdots O$ (Fig. 4a). The interplanar distance in the dimer is 3.26 Å, and the type of overlapping is shown in Fig. 4b. In crystal the dimers are formed into layers perpendicular to the *y* direction (Fig. 4c). Inside the layer, the Jahn–Teller axes at Mn(III) are parallel and the angle between these axes from the adjacent layers is 85.4°. The central fragment Mn(MeOSalen) is nearly planar, and the angle between the planes of methoxysalicylideneimines is 10.3°.

The magnetic properties of polycrystalline samples of complexes **Ia** and **II** were studied in a range of 2.0–300 K. The temperature dependences of $\chi_M T$ and χ_M^{-1} are presented in Figs. 5 and 6. For both complexes, the product $\chi_M T$ is almost temperature-independent down to ~50 K and decreases sharply with the further temperature decrease down to 2 K. The values of $\chi_M T$ at 300 K (2.88 cm³ K/mol and 2.90 cm³ K/mol for complexes **Ia** and **II**, respectively) almost coincide with a theoretical value of 3.00 cm³ K/mol for the magnetically noninteracting Mn³⁺ ions with S = 2 and g = 2. The temperature dependences of the inverse susceptibility are well described by the Curie–Weiss



Fig. 2. Projections of crystalline structures Ia and Ib along the x chain (hydrogen atoms are omitted for clarity).



Fig. 3. Projection of crystal structure II along the *x* direction.



Fig. 4. (a) General view of the dimer, (b) overlapping of molecules in the dimer, and (c) the projection of crystal structure **III** along the *x* direction (hydrogen atoms are omitted for clarity).







Fig. 6. Temperature dependences of (a) $\chi_M T$ and (b) χ_M^{-1} for complex II.

equation ($\chi = C/T - \theta$) in the whole temperature range with parameters $C = 2.89 \text{ cm}^3 \text{ K/mol}$, $\theta = -2 \text{ K}$ and $C = 2.9 \text{ cm}^3 \text{ K/mol}$, $\theta = -0.7 \text{ K}$ for complexes Ia and II, respectively (Figs. 5b and 6b). The low negative values of Weiss constants indicate the existence of weak antiferromagnetic exchange interactions between the high-spin Mn³⁺ ions in the chains of complexes Ia and II through the bridging dicyanamide ligands [N=C-N-C=N]⁻. In complex Ia the Mn-N distances in the chains are shorter than those in complex II (Table 2), which probably results in a higher Weiss constant.

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REFERENCES

- 1. Ashmawy, F.M., McAuliffe, C.A., (Dick) Parish, R.V., and Tames, J., *Dalton Trans.*, 1985, no. 7, p. 1391.
- Hulme, Ch.E., Watkinson, M., Haynes, M., et al., *Dal*ton Trans., 1997, no. 11, p. 1805.
- Sakamoto, F., Sumiya, T., Fujita, M., et al., *Chem. Lett.*, 1998, vol. 27, no. 11, p. 1127.
- Garcia-Deibe, A., Sousa, A., Bermejo, M.R., et al., *Chem. Commun.*, 1991, no. 8, p. 728.
- 5. Miyasaka, H., Clerac, R., Ishii, T., et al., *Dalton Trans.*, 2002, no. 7, p. 1528.
- Lecren, L., Wernsdorfer, W., Lindigni, Y.-G., et al., J. Am. Chem. Soc., 2007, vol. 129, no. 16, p. 5045.
- Shyu, H.-L., Wei, H.-H., and Wang, Yu., *Inorg. Chim.* Acta, 1999, vol. 290, no. 1, p. 8.
- Reddy, K.R., Rajasekharan, M.V., and Tuchagues, J.-P., *Inorg. Chem.*, 1998, vol. 37, no. 23, p. 5978.
- Li, H., Zhong, Zh.J., Duan, Ch.-Y., et al., *Inorg. Chim. Acta*, 1998, vol. 271, nos. 1–2, p. 99.
- 10. Khalaji, A.D. and Ng, S.W., *Russ. Chem. Coord. Chem.*, 2011, vol. 37, no. 1, p. 26.
- 11. Matsumoto, N., Sunatsuki, Y., Miyasaka, H., et al., *Angew. Chem., Int. Ed. Engl.*, 1999, vol. 38, no. 12, p. 171.
- 12. Natase, S., Tuna, F., Maxim, C., et al., *Cryst. Growth Des.*, 2007, vol. 7, no. 9, p. 1825.

- 13. Lu, Z., Yuan, M., Pan, F., et al., *Inorg. Chem.*, 2006, vol. 45, no. 9, p. 3538.
- 14. Sailaja, S., Reddy, K.R., Rajasekharan, M.V., et al., *Inorg. Chem.*, 2003, vol. 42, no. 1, p. 180.
- 15. Choi, H.-L., Sokol, J.J., and Long, J.R., *Inorg. Chem.*, 2004, vol. 43, no. 5, p. 1606.
- 16. Zhou, H.-B., Wang, J., Wang, H.-Sh., et al., *Inorg. Chem.*, 2011, vol. 50, no. 15, p. 6868.
- 17. Ababei, R., Li, Y.-G., Roubeau, O., et al., *New J. Chem.*, 2009, vol. 33, no. 6, p. 1237.
- Ferbinteanu, M., Miyasaka, H., Wernsdorfer, W., et al., J. Am. Chem. Soc., 2005, vol. 127, no. 9, p. 3090.
- 19. Pan, F., Wang, Z.-M., and Gao, S., *Inorg. Chem.*, 2007, vol. 46, no. 24, p. 10221.
- 20. Sun, H.-L., Wang, Z.-M., and Gao, S., *Coord. Chem. Rev.*, 2010, vol. 254, nos. 1–2, p. 1081.
- 21. Manson, J.L., Kmety, C.R., Huang, Q.Z., et al., *Chem. Mater.*, 1998, vol. 10, no. 9, p. 2552.
- 22. Kurmoo, M. and Kepert, C., New J. Chem., 1998, vol. 22, no. 12, p. 1515.
- 23. Batten, S.R., Jensen, P., Kepert, C.J., et al., *Dalton Trans.*, 1999, no. 24, p. 2987.
- 24. Van der Werff, P., Batten, S.R., Jensen, P., et al., *Polyhedron*, 2001, vol. 20, nos. 11–14, p. 1129.
- 25. Van der Werff, P.M., Batten, S.R., Jensen, P., et al., *Cryst. Growth Des.*, 2004, vol. 4, no. 3, p. 503.
- 26. Schlueter, J.A., Manson, J.L., and Geiser, U., *Inorg. Chem.*, 2005, vol. 44, no. 9, p. 3194.
- 27. Shi, Q., Cao, R., Li, X., et al., New J. Chem., 2002, vol. 26, no. 10, p. 1397.
- Price, D.J., Batten, S.R., Moubaraki, B., and Murray, K.S., *Indian J. Chem., Sect. A: Inorg., Bioinorg., Phys., Theor. Anal. Chem.*, 2003, vol. 42, p. 2256.
- 29. Batten, S.R., Jensen, P., Moubaraki, B., et al., *Chem. Commun.*, 1998, no. 3, p. 439.
- 30. Kmety, C.R.Q., Huang, Q., Jeffrey, W., et al., *Phys. Rev.*, 2000, vol. 62, no. 9, p. 5576.
- 31. Nakamoto, K., *Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 1986.
- CrysAlisPro. Agilent Technologies. Version 1.171.35.19. 2011.
- 33. Burla, M.C., Caliandro, R., Camalli, M., et al., *J. Appl. Crystallogr.*, 2005, vol. 38, p. 381.
- 34. Palatinus, L. and Chapuis, G., *J. Appl. Crystallogr.*, 2007, vol. 40, p. 786.
- 35. Sheldrick, G.M., Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, vol. 64, p. 112.