ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2016, Vol. 42, No. 8, pp. 516–538. © Pleiades Publishing, Ltd., 2016.
Original Russian Text © E. Coropceanu, O. Bologa, I. Arsene, A. Vitiu, I. Bulhac, N. Gorinchioy, P. Bourosh, 2016, published in Koordinatsionnaya Khimiya, 2016, Vol. 42, No. 8, pp. 480–502.

Dedicated to the 110th anniversary of the discovery of the reaction of transition metals with α-dioximes
by Academician L.A. Chugaev and to the 110th birthday of Academician A.V. Ablov,
the founder of the school of coordination chemistry in Chisinau

Synthesis and Characterization of Inner-Sphere Substitution Products in Azide-Containing Cobalt(III) Dioximates

E. Coropceanu[a], O. Bologa[a], I. Arsene[a], A. Vitiu[b], I. Bulhac[a], N. Gorinchioy[a], and P. Bourosh[b], *

[a]*Institute of Chemistry, Academy of Sciences of Moldova, Chisinau, Republic of Moldova*
[b]*Institute of Applied Physics, Academy of Sciences of Moldova, Chisinau, Republic of Moldova*
**e-mail: bourosh.xray@phys.asm.md*

Received November 17, 2015

Abstract—New compounds of Co(III) dimethylglyoximate with the sulfanilamide derivative $[Co(N_3)(DmgH)_2(SAM)]$ ($DmgH^-$ is the dimethylglyoxime monoanion, and SAM is $-NH_2-C_6H_4-SO_2-NH-R$) are synthesized using the structural block $[Co(N_3)(DmgH)_2(H_2O)]$ as the initial one. The reaction products of various $[Co(N_3)(DmgH)_2(SAM)]$ with ligand L (L is pyridine (Py), thiourea (Thio), triphenylphosphine (PPh_3), nicotinamide (Nia), *iso*-nicotinamide (INia), isonicotinic acid (HINA), 4-pyridinaldoxime (4-PaoH), 4,4'-bipyridine (Bipy), and NH_4NCS) are synthesized. The compounds are studied by IR and NMR spectroscopy and X-ray diffraction analysis (CIF files CCDC 1414767–1414775 (**I**, **V–XII**)). The following facts are established. First, only the coordinated water molecule in $[Co(N_3)(DmgH)_2(H_2O)]$ is replaced by SAM. Second, SAM from different similar compounds also undergoes substitution by the aforementioned organic ligands. The exception is the compound obtained by the reaction of $[Co(N_3)(DmgH)_2(SAM)]$ with NH_4NCS, due to which the NCS^- anion replaces both SAM and inorganic anion N_3^-. The X-ray diffraction analysis shows that the substitution reactions give both mononuclear compounds $[Co(N_3)(DmgH)_2(Py)]$, $[Co(N_3)(DmgH)_2(PPh_3)]$, $[Co(N_3)(DmgH)_2(Thio)]$, $[Co(N_3)(DmgH)_2(Nia)]$ $[Co(N_3)(DmgH)_2(INia)]$, $[Co(N_3)(DmgH)_2(HINA)] \cdot H_2O$, $[Co(N_3)(DmgH)_2(4\text{-}PaoH)] \cdot DMF$, and $[Co(N_3)(DmgH)_2(Bipy)]$ and binuclear molecular complexes $[(Co(N_3)(DmgH)_2)_2(Bipy)] \cdot 0.5H_2O$ and $[(Co(N_3)(DmgH)_2)_2(Bipy)] \cdot H_2O$, as well as ionic complex $(NH_4)[Co(SCN)_2(DmgH)_2] \cdot 3H_2O$. The obtained compounds supplement a series of complexes that make it possible to evaluate the *trans* effect of the N_3^- anion on the bond lengths along the axial coordinate and on the Co–N bonds in the equatorial plane of the octahedron.

DOI: 10.1134/S1070328416070046

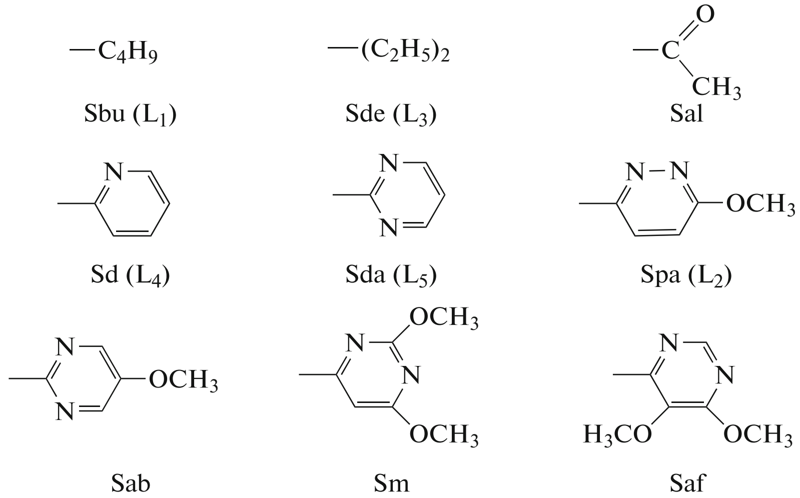
INTRODUCTION

Among a diversity of transition metal complexes, compounds containing polyfunctional ligands capable of coordinating via the polydentate mode to one of several metal atoms are very significant. The chelate dioximate complexes discovered by L.A. Chugaev in 1905 are of the first type [1]. L.A. Chugaev developed a general method for the preparation of complex cations of the type $[Co(DmgH)_2(A)_2]^+$, anions $[Co(DmgH)_2(X)_2]^-$, and molecular complexes $[Co(DmgH)_2(X)(A)]$, where DmgH is the monodeprotonated residue of dimethylglyoxime, X is the acid residue, and A is the neutral organic ligand [2]. Dioximates of some transition metals found practical use as catalysts of chemical processes [3], in biology (as antihistaminic drugs) [4], in biochemistry and medicine [5], in hydrogen production [6], and as biostimulators of physiological processes [7]. Cobalt α-dioximates in the crystalline state can serve as a basis for the production of semiconducting materials [8]. The cobalt dioximates were also proved to be good models of vitamin B_{12} [9]. Similar iron compounds are models of such important objects as hemoglobin, and results of studying them serve for the explanation of mechanisms of many reactions occurring in the human blood [10].

As it is found for the dioxime-based complexes containing atoms of one or several transition metals [11–13], strong intramolecular hydrogen bonds stabilize the *trans* configuration of dioximates and make these compounds convenient for studying inner-sphere substitution reactions. Dioximates in which two dioxime residues fall onto one cobalt atom but having special properties make it possible to suggest the *cis* configuration of the latter. It is established that *cis*-dioximates are stable only in neutral and alkaline media, whereas in an acidic medium they are quantitatively transformed into the *trans*-isomers [14]. However, classical cobalt(II) dioximines of the *cis*-configuration were obtained in a highly acidic medium, and α-dioximes act in them as neutral ligands [15]. A.V. Ablov and followers studied the mechanism and kinetics of substitution reactions of a whole series of ligands in the trivalent cobalt *trans*-dioximates [16, 17]. As a result, the qualitative order of ligand activity was established: Thios > Scarb, Thio, Seu, $NCSe^-$, $NCS^- > I^-$, NO_2^-, $HCO^- > Br^- > Cl^- >...H_2O$ [18], where Thios are various thiosemicarbazoles, Scarb are thiocarbamides, Thio is thiourea, and Seu is selenourea. In the series of dioximates containing thiocarbamide, thiourethane, or sulfanilamide, their reactivity and the influence of different substituents on the ability to complex formation were studied and conditions for the formation of heteroligand dioximates were determined [19]. The *cis–trans* effect was studied in the series of compounds with the same or different residues of dioximes [20], including the compounds containing the azide ion on the coordinate 1,6 and such molecules as H_2O, lutidine, pyridine, ammonia, triphenylphosphine, or different sulfanilamides were synthesized [21, 22]. The results of studying the influence of the replacement of equatorial ligands by axial ones are presented [23].

Sulfanilamide $NH_2–C_6H_4–SO_2–NH_2$ (Sam) and its derivatives in transition metal complexes can coordinate to the central atom as mono- and bidentate ligands. However, in the Co(III) [24–26] and Cu(II) dioximate complexes [27] with $NH_2–C_6H_4–SO_2–NH–R$, where R is the aminothiazole substituent (Sat), ligands of this class are monodentately coordinated through one nitrogen atom of the sulfanyl fragment. In the Cu(II) and Zn(II) complexes [28, 29], the coordination mode is also monodentate but occurs through the nitrogen atom of the thiazole fragment. The coordination mode in the Co(II) complex [30] is bidentate through two nitrogen atoms. It is also found that in the Co(II) and Cu(II) complexes [30, 31] Sal is bidentately coordinated to the metal atom through the terminal N and O atoms. In the Cu(II) complex [32], the derivative of this ligand Sm is tridentately coordinated to two metal atoms through a set of donor atoms N,N,N.

The series of SAM with different substituents R is presented in Scheme 1.



Scheme 1.

We have previously synthesized a series of Co(III) pyrimidinesulfamide dimethyl glyoximates, $[Co(N_3)(DmgH)_2(SAM)]$ (SAM = Sm, Saf, Sab, Sd, and Sal; Scheme 1), studied by IR and NMR spectroscopy and X-ray diffraction analysis [33]. All indicated SAM are coordinated to the metal atom only through the amino group ($Co \leftarrow NH_2C_6H_4SO_2NHR$). That is why, their position in the series of *trans* effect in the cobalt(III) dioximates is almost the same.

The purpose of this work is the development of procedures for the synthesis of mono- and binuclear Co(III) dioximates by the substitution of axial ligands from the already existing complexes using the latter as "building blocks" due to the stability of the equatorial fragment $Co(DmgH)_2$. For this purpose, we synthesized a new complex $[Co(N_3)(DmgH)_2(Sda)]$ (**I**) from $[Co(N_3)(DmgH)_2(H_2O)]$ by the substitution of water by sulfanilamide Sda. Then we carried out the reactions of various $[Co(N_3)(DmgH)_2(SAM)]$ with pyridine (Py), triphenylphosphine (PPh_3), thiourea (Thio), nicotinamide (Nia), isonicotinamide (INia), isonicotinic acid (HINA), 4-pyridinaldoxime (4-PaoH), 4,4'-bipyridine (Bipy), and NH_4NCS. The strength of sulfanilamide ligand retention in similar complexes and competitiveness of various ligands in coordination to the metal atom were used to study the substitution reactions and to perform quantum-chemical calculations in a series of molecules (predominantly pyridine-containing molecules). The latter contain several functional groups (amide/carboxyl and oxime), which made it possible to study and compare experimental and theoretical regularities of complex formation. As a result, the following complexes were obtained: $[Co(N_3)(DmgH)_2(Py)]$ (**II**), $[Co(N_3)(DmgH)_2(PPh_3)]$ (**III**), $[Co(N_3)(DmgH)_2(Thio)]$ (**IV**), $NH_4[Co(SCN)_2(DmgH)_2] \cdot 3H_2O$ (**V**), $[Co(N_3)(DmgH)_2(Nia)]$ (**VI**), $[Co(N_3)(DmgH)_2(INia)]$ (**VII**), $[Co(N_3)(DmgH)_2(HINA)] \cdot H_2O$ (**VIII**), $[Co(N_3)(DmgH)_2(4\text{-}PaoH)] \cdot DMF$ (**IX**), $[Co(N_3)(DmgH)_2(Bipy)]$ (**X**), $[(Co(N_3)(DmgH)_2)_2(Bipy)] \cdot 0.5H_2O$ (**XI**), and $[(Co(N_3)(DmgH)_2)_2(Bipy)] \cdot H_2O$ (**XII**). Their compositions and structures were studied by IR, UV, and NMR spectroscopy and X-ray diffraction analysis (except for compounds **II–IV**).

EXPERIMENTAL

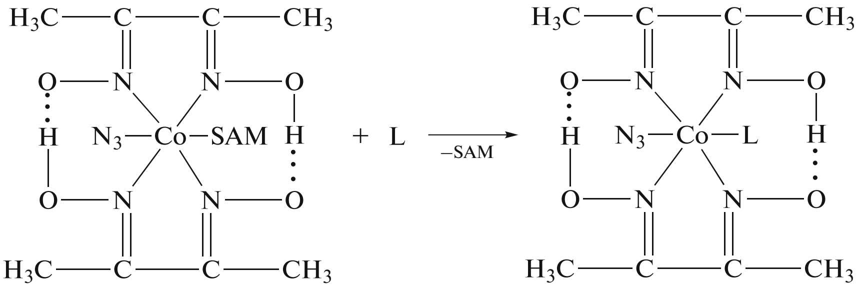
Synthesis. "Building block" **I** was obtained using different methods.

(1) The method using the oxidation with air oxygen of a mixture of the initial components (cobalt salt, dimethylglyoxime, sodium azide, and sulfanilamide taken in a molar ratio of 1 : 2 : 1 : 1 in a methanol–dimethylformamide (5 : 1) solvent) was applied. The mixture was oxidized on heating and permanent magnetic stirring. Rectangular brown prisms precipitated from the brown solution.

(2) Sodium azide NaN_3 was added to a hot solution of complex $[Co(Cl)(DmgH)_2(H_2O)]$ in a molar ratio of 1 : 1, and then the same amount of sulfanilamide was added.

Synthesis of compound I. Compound $[CoCl(DmgH)_2(H_2O)]$ (0.34 g, 1 mmol) was dissolved on heating in methanol (30 mL). Sodium azide (0.07 g, 1 mmol) was added to the obtained solution, and heating was continued. In 15 min, Sda (0.25 g, 1 mmol) was added, and heating was continued for 10 min. The hot brown solution was filtered and left for slow evaporation at room temperature. Brown crystals were precipitated from the solution.

To carry out inner-sphere substitution sreactions, some sulfamide complexes $[Co(N_3)(DmgH)_2(SAM)]$ were treated with several organic ligands L (Py, PPh_3, Thio, Nia, INia, HINA, 4-PaoH, or Bipy) according to the following scheme:



Scheme 2.

According to Scheme 2, compounds **II**, **III**, and **V–IX** were synthesized from the complex containing Sd; compounds **VI**, **VII**, and **X** were prepared from the complexes with ligand Sda; compounds **III** and **IV** were obtained from the complexes containing Sde and Spa, respectively; and compounds **XI** and **XII** were synthesized using the complexes containing ligand Sbu.

The elemental analysis results for compounds **I–XII** are presented in Table 1.

It was established for compounds **II–IV** and **VI–X** that ligands SAM were substituted by ligands L to form

Table 1. Elemental analysis results for compounds **I–XII**

Complex	Empirical formula	Found/calculated, %			
		Co	C	H	N
$[Co(N_3)(Dmg)(DmgH_2)(Sda)]$ (**I**)	$C_{18}H_{24}N_{11}O_6SCo$	9.82/10.13	36.79/37.17	4.02/4.16	26.37/26.51
$[Co(N_3)(DmgH)_2(Py)]$ (**II**)	$C_{13}H_{19}N_8O_4Co$	14.28/14.36	37.92/38.05	4.47/4.67	27.19/27.35
$[Co(N_3)(DmgH)_2(PPh_3)]$ (**III**)	$C_{26}H_{29}N_7O_4PCo$	9.82/9.93	52.47/52.61	4.82/4.93	16.41/16.53
$[Co(N_3)(DmgH)_2(Thio)]$ (**IV**)	$C_9H_{18}N_9O_4SCo$	14.28/14.47	26.29/26.54	4.28/4.45	31.07/30.95
$NH_4[Co(SCN)_2(DmgH)_2] \cdot 3H_2O$ (**V**)	$C_{10}H_{24}N_7O_7S_2Co$	12.04/12.35	24.82/25.17	4.93/5.07	20.12/20.54
$[Co(N_3)(DmgH)_2(Nia)]$ (**VI**)	$C_{14}H_{20}N_9O_5Co$	12.56/13.00	36.82/37.07	4.26/4.54	27.56/27.83
$[Co(N_3)(DmgH)_2(INia)]$ (**VII**)	$C_{14}H_{20}N_9O_5Co$	12.68/13.00	36.74/37.07	4.40/4.54	27.46/27.83
$[Co(N_3)(DmgH)_2(HINA)] \cdot H_2O$ (**VIII**)	$C_{14}H_{21}N_8O_7Co$	12.03/12.48	35.41/35.59	4.23/4.48	23.56/23.74
$[Co(N_3)(DmgH)_2(4\text{-}PaoH)] \cdot DMF$ (**IX**)	$C_{17}H_{27}N_{10}O_6Co$	10.82/11.19	38.56/38.78	4.81/5.17	26.34/26.62
$[Co(N_3)(DmgH)_2(Bipy)]$ (**X**)	$C_{18}H_{22}N_9O_4Co$	11.78/12.09	44.07/44.35	4.32/4.55	25.71/25.88
$[(Co(N_3)(DmgH)_2)_2(Bipy)] \cdot 0.5H_2O$ (**XI**)	$C_{26}H_{37}N_{16}O_{8.5}Co_2$	13.86/14.24	37.46/37.73	4.43/4.51	26.83/27.10
$[(Co(N_3)(DmgH)_2)_2(Bipy)] \cdot H_2O$ (**XII**)	$C_{26}H_{38}N_{16}O_9Co_2$	13.83/14.09	37.21/37.32	4.34/4.58	26.67/26.80

mononuclear compounds. However, the reaction of $[Co(N_3)(DmgH)_2(Sbu)]$ with Bipy in a ratio of 2 : 1 gave binuclear complexes **XI** and **XII**. The reaction of $[Co(N_3)(DmgH)_2(Sd)]$ with salt NH_4NCS resulted in the substitution of both neutral organic ligand Sd and azide ion to form compound **V**.

The IR spectra of the ligands and metal complexes were recorded on a FT-IR PerkinElmer Spectrum 100 spectrophotometer in Nujol in a range of 4000–400 cm^{-1} and ATP in a range of 4000–650 cm^{-1}. The UV absorption spectra were obtained on a Perkin-Elmer Lambda 25 spectrophotometer in aqueous solutions at a concentration of 10^{-4} mol/L. ^1H and ^{13}C NMR spectra were recorded on a 400 Bruker spectrometer with a working frequency of 400.13 MHz (^1H) and 100.61 MHz for ^{13}C in DMSO-d_6 solutions using tetramethylsilane as an internal standard. The signals were expressed in ppm.

X-ray diffraction analysis. The determination of unit cell parameters for compounds **II** and **III** was confirmed by the formation of the known compounds $[Co(N_3)(DmgH)_2(Py)]$ and $[Co(N_3)(DmgH)_2(PPh_3)]$ [34, 35]. The full experimental data were obtained for compounds **I** and **V–XII** at room temperature (293 K) on an Xcalibur E diffractometer (MoK_α radiation, graphite monochromator). The full experiment was repeated for compound **V**, because the R factor of the earlier obtained structure $NH_4[Co(SCN)_2(DmgH)_2] \cdot 3H_2O$ [36] presented in the Cambridge Crystallographic Data Centre [37] is 0.116 for 479 independent nonzero reflections. The structures of compounds **I** and **V–XII** were solved by direct methods and refined by least squares in the anisotropic full-matrix variant for non-hydrogen atoms for F^2 (SHELX-97) [38]. The positions of the hydrogen atoms of the solvate water molecules in the complexes were determined from the difference Fourier synthesis, and the positions of other hydrogen atoms were calculated geometrically. All hydrogen atoms were isotropically refined in the rigid body model with $U_{\rm eff} = 1.2U_{\rm equiv}$ or $1.5U_{\rm equiv}$ of the corresponding O, N, and C atoms.

The crystallographic data and X-ray diffraction characteristics for compounds **I** and **V–XII** are given in Table 2. Selected interatomic distances and bond angles are listed in Table 3. The geometric parameters of hydrogen bonds are presented in Table 4. The positional and thermal parameters for the studied structures were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC 1414767–1414775 (**I** and **V–XII**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Quantum-chemical calculations. The electronic structures and molecular geometries of the ligands and complexes were calculated using the GAMESS quantum-chemical program package [39]. Geometry optimization was performed in the framework of the Hartree–Fock–Roothaan nonempirical method using the 6-31G basis set [40, 41] without any symmetry restraints. In order to refine spin states of the systems, the energies of electronic terms of different multiplicities were calculated taking into account the configurational interaction for the already optimized geometry. The configurational interaction matrices included all configurations formed by one- and two-electron excitations from five highest occupied molecular orbitals (HOMO) to six lowest unoccupied molecular

Table 2. Crystallographic data, experimental characteristics, and refinement prameters for structures **I** and **V–XII**

Parameter	Value								
	I	**V**	**VI**	**VII**	**VIII**	**IX**	**X**	**XI**	**XII**
FW	581.47	477.41	453.32	453.32	472.32	522.89	487.38	827.58	836.58
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$Pnma$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a, Å	12.8214(10)	8.5067(3)	7.9499(4)	8.5933(3)	10.2498(9)	14.2860(6)	8.0905(6)	7.8421(5)	7.8380(5)
b, Å	12.8403(9)	12.2129(4)	25.0052(11)	17.3639(6)	11.3240(8)	12.5375(6)	13.4459(9)	14.5713(6)	10.9547(8)
c, Å	14.6945(11)	10.0448(3)	18.9942(7)	13.1980(5)	20.0536(9)	13.5313(5)	19.161(2)	15.5422(6)	11.2757(10)
α, deg	90	90	90	90	76.005(5)	90	90	91.330(3)	88.431(6)
β, deg	91.410(6)	95.327(3)	94.262(4)	94.396(3)	77.722(5)	90	97.712(8)	90.975(4)	72.474(7)
γ, deg	90	90	90	90	64.090(7)	90	90	95.208(4)	73.531(6)
V, Å^3	2418.4(3)	1039.07(6)	3765.4(3)	1963.53(13)	2016.2(2)	2423.6(2)	2065.6(3)	1767.87(15)	883.56(12)
Z	4	2	8	4	4	4	4	2	1
ρ_{calcd}, g/cm^3	1.597	1.526	1.599	1.533	1.556	1.433	1.567	1.555	1.572
μ, mm^{-1}	0.856	1.072	0.961	0.921	0.906	0.761	0.879	1.010	1.013
F(000)	1200	496	1872	936	976	1082	1008	854	432
Crystal size, mm	0.22 × 0.12 × 0.03	0.24 × 0.12 × 0.08	0.25 × 0.1 × 0.06	0.22 × 0.20 × 0.03	0.12 × 0.06 × 0.05	0.45 × 0.12 × 0.09	0.35 × 0.25 × 0.20	0.35 × 0.15 × 0.03	0.15 × 0.10 × 0.08
θ range, deg	3.16–25.05	2.93–25.50	2.97–25.50	2.98–25.50	2.87–25.50	3.01–25.05	2.89–25.05	2.94–25.00	3.07–25.49
Index ranges	$-9 \leqslant h \leqslant 15$ $-15 \leqslant k \leqslant 15$ $-15 \leqslant l \leqslant 17$	$-9 \leqslant h \leqslant 10$ $-8 \leqslant k \leqslant 14$ $-7 \leqslant l \leqslant 12$	$-9 \leqslant h \leqslant 9$ $-30 \leqslant k \leqslant 28$ $-15 \leqslant l \leqslant 23$	$-10 \leqslant h \leqslant 10$ $-20 \leqslant k \leqslant 20$ $-7 \leqslant l \leqslant 15$	$-12 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 13$ $-24 \leqslant l \leqslant 2$	$-16 \leqslant h \leqslant 17$ $-14 \leqslant k \leqslant 13$ $-16 \leqslant l \leqslant 16$	$-9 \leqslant h \leqslant 6$ $-10 \leqslant k \leqslant 15$ $-22 \leqslant l \leqslant 22$	$-9 \leqslant h \leqslant 9$ $-17 \leqslant k \leqslant 14$ $-18 \leqslant l \leqslant 17$	$-9 \leqslant h \leqslant 9$ $-13 \leqslant k \leqslant 12$ $-13 \leqslant l \leqslant 11$
Reflections collected/unique (R_{int})	7790/4243 (0.0573)	3629/1924 (0.0282)	13325/6935 (0.0568)	6747/3630 (0.0418)	11962/7453 (0.0391)	1082/2246 (0.0272)	2.89/6563 (0.0479)	9025/6111 (0.0219)	4994/3272 (0.0293)
Completeness, %	99.0 (θ = 25.05°)	99.4 (θ = 25.50°)	99.0 (θ = 25.50°)	99.3 (θ = 25.50°)	99.1 (θ = 25.50°)	99.8 (θ = 25.05°)	99.0 (θ = 25.05°)	98.1 (θ = 25.00°)	99.3 (θ = 25.49°)
Reflections with $I > 2\sigma(I)$	2355	1498	4159	2376	4548	1834	1857	4297	2132
Parameters	334	129	532	266	549	183	287	486	308
GOOF	1.006	1.001	1.003	1.005	1.007	1.006	1.005	1.003	1.003
R factor ($I > 2\sigma(I)$)	$R_1 = 0.0625$ $wR_2 = 0.0870$	$R_1 = 0.0425$ $wR_2 = 0.0865$	$R_1 = 0.0631$ $wR_2 = 0.0731$	$R_1 = 0.0573$ $wR_2 = 0.1118$	$R_1 = 0.0656$ $wR_2 = 0.1189$	$R_1 = 0.0714$ $wR_2 = 0.2471$	$R_1 = 0.0822$ $wR_2 = 0.1814$	$R_1 = 0.0570$, $wR_2 = 0.1589$	$R_1 = 0.0614$ $wR_2 = 0.1341$
R factor (for all data)	$R_1 = 0.1300$ $wR_2 = 0.1003$	$R_1 = 0.0611$ $wR_2 = 0.0950$	$R_1 = 0.1225$ $wR_2 = 0.0843$	$R_1 = 0.0999$ $wR_2 = 0.1280$	$R_1 = 0.1185$ $wR_2 = 0.1387$	$R_1 = 0.0813$ $wR_2 = 0.2591$	$R_1 = 0.1664$ $wR_2 = 0.2141$	$R_1 = 0.0858$ $wR_2 = 0.1772$	$R_1 = 0.1034$ $wR_2 = 0.1538$
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	0.367, –0.446	0.305, –0.243	0.408, –0.455	0.516, –0.313	0.793, –0.586	1.506, –0.415	1.549, –1.303	0.659, –0.447	0.409, –0.296

Table 3. Selected interatomic distances and bond angles in structures **I** and **V–XII***

Bond	*d*, Å								
	I	**V**	**VI** (*A*/*B*)	**VII**	**VIII** (*A*/*B*)	**IX**	**X**	**XI**	**XII**
Co(1)–N(1)	1.897(4)	1.908(2)	1.891(3)/1.888(3)	1.891(3)	1.888(4)/1.901(4)	1.898(3)	1.889(6)	1.898(4)/1.896(4)	1.884(3)/1.893(3)
Co(1)–N(2)	1.883(4)	1.885(3)	1.888(3)/1.885(3)	1.890(4)	1.881(4)/1.898(4)		1.892(5)	1.892(4)/1.890(4)	1.883(3)/1.898(3)
Co(1)–N(3)/N(2)	1.902(4)		1.904(3)/1.907(3)	1.900(3)	1.879(4)/1.889(4)	1.891(3)	1.898(6)	1.885(4)/1.907(4)	
Co(1)–N(4)	1.895(4)		1.901(3)/1.903(3)	1.895(4)	1.897(4)/1.887(4)		1.903(5)	1.901(4)/1.898(4)	
Co(1)–N(5)/S(1)/N(4)	1.963(4)	2.2920(8)	1.977(4)/1.960(4)	2.017(3)	2.024(5)/1.975(4)	2.031(4)	2.024(6)	1.966(5)/1.963(4)	1.916(6)/2.017(6)
Co(1)–N(8)/N(3)	2.014(3)		1.975(3)/1.975(4)	1.970(3)	1.973(3)/1.971(4)	1.961(4)	1.969(6)	1.975(3)/1.984(3)	2.081(4)/1.935(3)
N(1)–O(1)	1.334(4)	1.343(3)	1.334(4)/1.327(4)	1.329(4)	1.342(5)/1.356(4)	1.336(6)	1.326(7)	1.342(5)/1.323(5)	1.338(4)/1.357(4)
N(2)–O(2)	1.331(4)	1.353(3)	1.329(4)/1.333(4)	1.331(4)	1.323(5)/1.343(5)		1.345(7)	1.341(5)/1.350(5)	1.356(4)/1.346(3)
N(3)–O(3)	1.350(4)		1.342(4)/1.346(4)	1.344(4)	1.348(5)/1.336(4)	1.330(5)	1.336(7)	1.346(4)/1.334(5)	
N(4)–O(4)	1.353(4)		1.353(4)/1.347(4)	1.352(4)	1.337(6)/1.330(5)		1.338(7)	1.338(5)/1.358(5)	
N(1)–C(1)	1.293(5)	1.296(4)	1.299(5)/1.301(4)	1.297(5)	1.295(6)/1.292(6)	1.289(5)	1.297(8)	1.290(6)/1.300(6)	1.302(5)/1.296(5)
N(2)–C(2)	1.306(5)	1.295(4)	1.307(5)/1.306(4)	1.289(5)	1.304(6)/1.298(7)	1.293(5)	1.289(8)	1.291(6)/1.281(6)	1.279(5)/1.287(4)
N(3)–C(3)	1.283(5)		1.293(5)/1.285(5)	1.289(5)	1.303(6)/1.288(6)		1.290(9)	1.301(6)/1.295(6)	
N(4)–C(4)	1.292(5)		1.276(5)/1.295(4)	1.298(5)	1.281(7)/1.289(6)		1.279(8)	1.295(6)/1.289(6)	
C(1)–C(2)/C(1)$^{\#1}$	1.466(6)	1.468(4)	1.471(6)/1.459(5)	1.465(6)	1.447(8)/1.465(7)	1.425(12)	1.465(10)	1.491(7)/1.468(7)	1.488(6)/1.461(5)
C(3)–C(4)	1.461(7)		1.474(5)/ 1.463(6)	1.453(6)	1.467(9)/1.456(7)		1.459(11)	1.473(7)/1.465(7)	

Angle	ω, deg								
	I	**V**	**VI** (*A*/*B*)	**VII**	**VIII**	**IX**	**X**	**XI**	**XII**
N(1)Co(1)N(2)/N(1)$^{\#1}$	82.1(2)	80.91(11)	82.7(2)/82.6(2)	81.9(2)	82.2(2)/80.9(2)	80.5(2)	81.3(2)	80.9(2)/81.5(2)	81.5(1)/80.7(1)
N(1)Co(1)N(3)/N(1)$^{\#1}$/N(2)	179.3(2)	180.0	177.0(2)/178.2(2)	179.2(2)	177.5(2)/177.3(2)	178.9(1)	179.0(3)	178.1(2)/179.8(2)	180.0/180.0
N(1)Co(1)N(4)/N(2)$^{\#1}$	99.2(2)	99.09(11)	98.7(2)/97.8(2)	98.6(2)	97.1(2)/99.7(2)	98.7(2)	99.0(3)	98.6(2)/99.0(2)	98.5(1)/99.32(12)
N(1)Co(1)N(5)/S(1)	91.5(2)	91.16(7)	89.0(2)/90.6(2)	87.8(1)	87.4(2)/90.1(2)	89.92(11)	91.2(2)	87.7(2)/89.3(2)	92.4(2)/86.1(2)
N(1)Co(1)N(8)/S(1)$^{\#1}$/N(3)	87.3(2)	88.84(7)	92.9(1)/91.9(1)	89.7(1)	92.0(2)/90.4(2)	90.48(11)	89.1(2)	89.3(2)/88.7(2)	85.0(2)/86.9(1)
N(2)Co(1)N(3)	98.5(2)		98.3(2)/99.1(2)	98.9(2)	98.9(2)/97.9(2)		98.8(3)	98.7(2)/98.6(2)	
N(2)Co(1)N(4)/N(2)$^{\#1}$	178.7(2)	180.0	178.3(2)/178.1(2)	178.9(2)	177.2(2)/178.0(2)		179.2(3)	179.1(2)/178.2(1)	180.0

Table 3. (Contd.)

Angle	ω, deg								
	I	**V**	**VI** (*A*/*B*)	**VII**	**VIII**	**IX**	**X**	**XI**	**XII**
N(2)Co(1)N(5)/S(1)	87.1(2)	93.73(7)	87.2(2)/91.5(2)	88.5(1)	88.7(2)/90.7(2)		87.7(2)	92.7(2)/86.5(2)	89.1(2)/89.3(2)
N(2)Co(1)N(8)/S(1)$^{\#1}$/N(3)	90.6(2)	86.27(7)	91.8(1)/90.7(1)	89.9(1)	91.9(2)/90.3(2)		90.2(2)	87.8(2)/88.4(2)	88.1(1)/89.2(2)
N(3)/N(2)Co(1)N(4)/N(2)$^{\#1}$	80.2(2)		80.3(2)/80.5(2)	80.7(2)	81.7(2)/81.5(2)	82.0(2)	80.9(3)	81.7(2)/81.0(2)	–
N(3)/N(2)Co(1)N(5)	88.2(2)		88.2(2)/88.7(2)	91.9(1)	90.5(2)/87.5(2)		87.8(2)	90.5(2)/90.9(2)	87.6(2)/93.9(2)
N(3)/N(2)Co(1)N(8)/N(3)	93.0(2)		89.9(1)/88.8(2)	90.7(1)	90.2(2)/92.1(2)		91.9(2)	92.6(2)/91.2(2)	85.0(2)/93.1(1)
N(4)Co(1)N(5)	92.5(2)		91.8(2)/86.6(2)	90.6(1)	88.6(2)/87.3(2)		91.5(2)	86.5(2)/ 91.8(2)	90.9(29)/90.7(2)
N(4)Co(1)N(8)	89.9(1)		89.2(1)/91.1(2)	91.1(1)	90.9(2)/91.6(2)		90.6(2)	93.0(2)/ 93.3(2)	88.1(1)/90.83(15)
N(5)/N(4)Co(1)N(8)/N(3)	177.5(2)	180.0	177.7(1)/176.8(1)	177.1(1)	179.1(2)/178.9(2)	179.5(1)	177.9(2)	176.8(1)/174.7(2)	176.4(2)/173.0(2)
O(1)N(1)Co(1)	122.0(3)	122.0(2)	122.3(3)/122.4(2)	122.0(3)	124.0(3)/122.9(3)	122.7(3)	122.1(5)	122.6(3)/122.5(3)	123.6(2)/122.8(2)
C(1)N(1)Co(1)	115.5(3)	116.2(2)	115.4(3)/115.6(3)	115.7(3)	115.6(4)/117.4(3)	116.2(4)	116.1(5)	116.6(3)/116.0(3)	116.6(3)/117.2(2)
O(1)N(1)C(1)	122.5(4)	121.8(2)	122.2(4)/122.0(3)	122.4(4)	120.3(5)/119.3(4)	121.0(4)	121.7(6)	120.8(4)/121.5(4)	119.6(4)/119.8(3)
O(2)N(2)Co(1)	122.0(3)	123.5(2)	122.4(3)/122.1(2)	122.0(3)	122.6(3)/122.6(3)		123.1(4)	122.1(3)/122.5(3)	122.2(3)/121.6(2)
C(2)N(2)Co(1)	116.2(4)	117.7(2)	115.5(3)/115.3(3)	116.3(3)	115.5(4)/116.1(4)		116.9(5)	116.2(3)/116.5(3)	117.4(3)/116.7(2)
O(2)N(2)C(2)	121.7(4)	118.7(3)	122.0(4) 122.5(3)	121.7(4)	121.9(4)/121.3(4)		120.0(6)	121.5(4)/120.9(4)	120.4(3)/121.7(3)
O(3)N(3)Co(1)/O(2)N(2)Co(1)	123.4(3)		122.5(3)/124.4(2)	122.2(3)	123.2(3)/122.8(3)	121.4(3)	122.0(5)	122.7(3)/121.9(3)	
C(3)N(3)Co(1)/C(2)N(2)Co(1)	117.3(4)		117.5(3)/116.8(3)	116.7(3)	117.0(4)/116.2(4)	115.6(3)	116.4(5)	116.7(3)/116.1(3)	
O(3)N(3)C(3)/O(2)N(2)C(2)	119.3(4)		120.0(4)/118.9(3)	121.0(4)	119.8(5)/121.0(5)	122.9(4)	121.6(6)	120.6(4)/122.1(4)	
O(4)N(4)Co(1)	123.0(3)		123.7(3)/123.7(2)	123.3(3)	122.9(4)/121.4(3)		121.5(5)	122.0(3)/122.7(3)	
C(4)N(4)Co(1)	117.5(4)		117.4(3)/117.2(3)	116.9(3)	115.5(4)/116.3(3)		116.5(5)	115.9(3)/117.2(3)	
O(4)N(4)C(4)	119.5(4)		118.8(4)/119.1(3)	119.8(4)	121.6(5)/122.2(4)		122.0(6)	121.8(4)/120.0(3)	
N(1)C(1)C(2)/C(1)$^{\#1}$	113.7(4)	113.1(3)	113.5(4)/113.0(4)	113.2(4)	113.3(5)/111.7(5)	113.5(3)	113.2(6)	112.5(5)/112.5(4)	111.8(4)
N(2)C(2)C(1)	112.3(4)	112.0(3)	112.8(4)/113.5(4)	112.2(4)	113.4(5)/113.6(4)		112.2(6)	113.2(4)/113.3(4)	112.4(3)
N(3)C(3)C(4)/ N(2)C(2)C(2)$^{\#1}$	112.7(4)		111.6(4)/113.4(4)	113.1(4)	111.3(5)/113.1(5)	113.4(3)	112.9(6)	112.3(4)/113.4(4)	
N(4)C(4)C(3)	112.2(5)		113.1(4)/112.2(4)	112.6(4)	114.4(5)/112.9(4)		113.3(6)	113.2(4)/112.4(4)	

* Atoms multiplied by the symmetry procedure: for **V**, $^{\#1}$ $-x + 1, -y + 1, -z + 1$; for **IX**, $^{\#1}$ $x, -y + 1/2, z$; for **XII**, $^{\#1}$ $-x, -y + 2, -z + 1$; $^{\#2}$ $-x + 1, -y + 1, -z$.

Table 4. Geometric parameters of intra- and intermolecular hydrogen bonds in structures **I** and **V–XII**

Contact D–H···A	Distance, Å			Angle DHA, deg	Coordinates of atoms A
	D–H	H···A	D···A		
I					
O(3)–H(1)···O(2)	0.82	1.70	2.493(4)	161	x, y, z
O(4)–H(1)···O(1)	0.82	1.72	2.516(4)	162	x, y, z
N(8)–H(1)···O(1)	0.90	2.08	2.908(5)	153	$-x + 1, -y + 1, -z + 1$
N(8)–H(2)···O(5)	0.90	2.07	2.920(5)	158	$x, -y + 3/2, z - 1/2$
N(9)–H(1)···O(2)	0.86	2.07	2.828(5)	147	$-x, y + 1/2, -z + 3/2$
V					
O(2)–H(1)···O(1)	0.82	1.77	2.526(3)	153	$-x + 1, -y + 1, -z + 1$
N(4)–H(1)···O(1)	0.73	2.32	3.04(3)	171	x, y, z
N(4)–H(2)···N(3)	0.76	2.24	2.99(4)	168	$-x + 1, -y + 1, -z$
N(4)–H(3)···O(1*w*)	0.72	2.05	2.74(4)	163	$-x, -y + 1, -z$
N(4)–H(4)···O(1*w*)	0.75	1.90	2.61(3)	159	x, y, z
O(1*w*)–H(1)···O(1)	0.87	1.97	2.832(3)	171	$-x + 1/2, y - 1/2, -z + 1/2$
O(1*w*)–H(2)···O(2*w*)	0.68	2.24	2.917(3)	175	x, y, z
O(1*w*)–H(3)···O(2*w*)	0.81	2.26	2.88(3)	134	$-x, -y + 1, -z$
O(2*w*)–H(1)···O(1)	0.73	2.08	2.81(2)	172	x, y, z
O(2*w*)–H(2)···N(3)	0.76	2.18	2.91(3)	164	$-x + 1, -y + 1, -z$
VI					
O(3*A*)–H(1)···O(2*A*)	0.82	1.69	2.481(4)	162	x, y, z
O(4*A*)–H(1)···O(1*A*)	0.82	1.74	2.523(4)	160	x, y, z
O(3*B*)–H(1)···O(2*B*)	0.82	1.77	2.553(4)	159	x, y, z
O(4*B*)–H(1)···O(1*B*)	0.82	1.69	2.483(3)	161	x, y, z
N(9*A*)–H(1)···N(7*A*)	0.86	2.42	3.163(6)	145	$x - 1/2, -y + 3/2, z + 1/2$
N(9*A*)–H(2)···O(2*B*)	0.86	2.30	3.132(5)	164	$-x + 1/2, y + 1/2, -z + 3/2$
N(9*B*)–H(1)···O(1*A*)	0.86	2.10	2.934(5)	164	$x + 1/2, -y + 3/2, z + 1/2$
N(9*B*)–H(2)···O(5*A*)	0.86	2.13	2.975(5)	169	x, y, z
VII					
O(3)–H(1)···O(2)	0.82	1.69	2.487(4)	163	x, y, z
O(4)–H(1)···O(1)	0.82	1.70	2.492(4)	161	x, y, z
N(9)–H(1)···O(5)	0.86	2.04	2.878(5)	163	$-x + 2, -y + 2, -z + 2$
N(9)–H(2)···N(7)	0.86	2.46	3.217(7)	148	$x + 1, -y + 3/2, z + 1/2$
VIII					
O(1*A*)–H(1)···O(4*A*)	0.82	1.68	2.465(6)	161	x, y, z
O(3*A*)–H(1)···O(2*A*)	0.82	1.71	2.501(5)	161	x, y, z
O(1*B*)–H(1)···O(4*B*)	0.82	1.74	2.521(5)	160	x, y, z
O(3*B*)–H(1)···O(2*B*)	0.82	1.67	2.467(5)	164	x, y, z
O(6*A*)–H(1)···O(2*w*)	0.82	1.89	2.641(4)	152	$x - 1, y, z$
O(6*B*)–H(1)···O(1*w*)	0.82	1.79	2.593(4)	168	$x - 1, y, z$
O(1*w*)–H(1)···O(4*B*)	0.82	1.91	2.718(4)	169	$x, y + 1, z$
O(1*w*)–H(2)···O(5*A*)	0.83	2.31	2.920(5)	130	x, y, z
O(2*w*)–H(1)···N(5*B*)	0.83	2.15	2.900(6)	151	$x, y + 1, z$
O(2*w*)–H(2)···O(5*B*)	0.83	2.09	2.903(5)	166	$x + 1, y, z$

Table 4. (Contd.)

Contact D–H···A	Distance, Å			Angle DHA, deg	Coordinates of atoms A
	D–H	H···A	D···A		
IX					
O(1)–H(1)···O(2)	0.82	1.69	2.480(6)	162	$x, -y + 1/2, z$
O(3)–H(1)···N(6)	0.82	2.01	2.822(8)	171	$x, -y + 1/2, z + 1$
O(3)–H(1)···N(7)	0.82	1.94	2.642(8)	143	$x, -y + 1/2, z + 1$
X					
O(2)–H(1)···O(3)	0.82	1.71	2.504(7)	161	x, y, z
O(4)–H(1)···O(1)	0.82	1.68	2.481(7)	164	x, y, z
XI					
O(1*A*)–H(1)···O(4*A*)	0.82	1.70	2.491(5)	161	x, y, z
O(2*A*)–H(1)···O(3*A*)	0.82	1.69	2.481(5)	162	x, y, z
O(2*B*)–H(1)···O(3*B*)	0.82	1.70	2.485(5)	160	x, y, z
O(4*B*)–H(1)···O(1*B*)	0.82	1.73	2.517(5)	161	x, y, z
O(1*w*)–H(1)···N(5*A*)	1.13	1.68	2.789(8)	166	x, y, z
O(1*w*)–H(1)···N(6*A*)	1.13	2.15	3.206(8)	156	x, y, z
O(1*w*)–H(2)···O(1*B*)	0.92	2.17	2.878(7)	133	x, y, z
XII					
O(1*A*)–H(1)···O(2*A*)	0.82	1.70	2.487(4)	160	$-x, -y + 2, -z + 1$
O(1*B*)–H(1)···O(2*B*)	0.82	1.72	2.509(4)	161	$-x + 1, -y + 1, -z$
O(1*w*)–H(1)···O(2*B*)	0.85	1.86	2.675(11)	160	$-x + 1, -y + 1, -z + 1$
O(1*w*)–H(2)···N(4*A*)	0.90	2.04	2.896(98)	158	x, y, z
O(2*w*)–H(1)···O(2*B*)	0.82	2.34	3.00(2)	137	$-x + 1, -y + 1, -z + 1$

orbitals (LUMO). The calculations showed that the spin singlet ($S = 0$) was the ground state of all considered compounds.

RESULTS AND DISCUSSION

The analysis of the UV spectra shows that the studied compounds **I–XII** contain a band at 235–255 nm by analogy with the earlier obtained spectra for cobalt(III) dioximates assigned to the stable group $Co(DmgH)_2$. This band can be ascribed to the π–π^* transition [42].

The IR spectrum of compound **I** exhibits the following absorption bands (cm^{-1}): ~1574 ν(C=N), ~1431 $\delta_{as}(CH_3)$, ~1377 $\delta_s(CH_3)$, ~1236 ν_{as}(N–O), ~1089 ν_s(N–O), ~977 γ(OH), ~514 $\nu_{as}(\text{Co–N})_{\text{DmgH}}$, and ~417 $\nu_s(\text{Co–N})_{\text{DmgH}}$, indicating the coordination of dimethylglyoxime to the complexing metal. The bands at ~1615 ν(CN), 1465 δ(CCH), 1322 $\nu_{as}(SO_2)$, and 1153 $\nu_s(SO_2)$ cm^{-1} are characteristic of the bond between the SAM ligand arranged on the apical coordinate and the metal. An intense band characteristic of the azide ion is observed at 2014 cm^{-1}. The IR spectra of other complexes (except for complex **V**) contain a strong band $\nu_{as}(N_3^-)$ in a range of 2024–2016 cm^{-1} and absorption bands of the $Co(DmgH)_2$ fragment.

The signal at 2.52 (CH_3, 12H) ppm in the ^{1}H NMR spectrum of complex **I** corresponds to the CH_3 groups in the dimethylglyoxime residues. The ^{13}C NMR spectrum of free dimethylglyoxime exhibits signals at 9.2 ppm from the CH_3 groups and 153.10 ppm of the quaternary carbon atoms. Upon coordination, the signal of the methyl groups of dimethylglyoxime in compound **I** undergoes a downfield shift ($\delta(CH_3)$ = 12.63 ppm), whereas the signal of the quaternary carbon atoms undergoes an upfield shift (δ(C=N) = 152.53 ppm).

The X-ray diffraction analysis proved that the reaction of $[Co(N_3)(DmgH)_2(H_2O)]$ with sulfanilamide derivative Sda afforded a new molecular complex **I** (Fig. 1a), whose structure is similar to those described earlier [33] and can be attributed to the class of compounds with the general formula $[CoX(DioxH)_2A]$ [2]. A usual octahedral coordination of Co(III) is observed in complex **I**. Two $DmgH^-$ residues coordinated via the bidentate chelating mode through the nitrogen atoms lie in the equatorial plane, and the api-

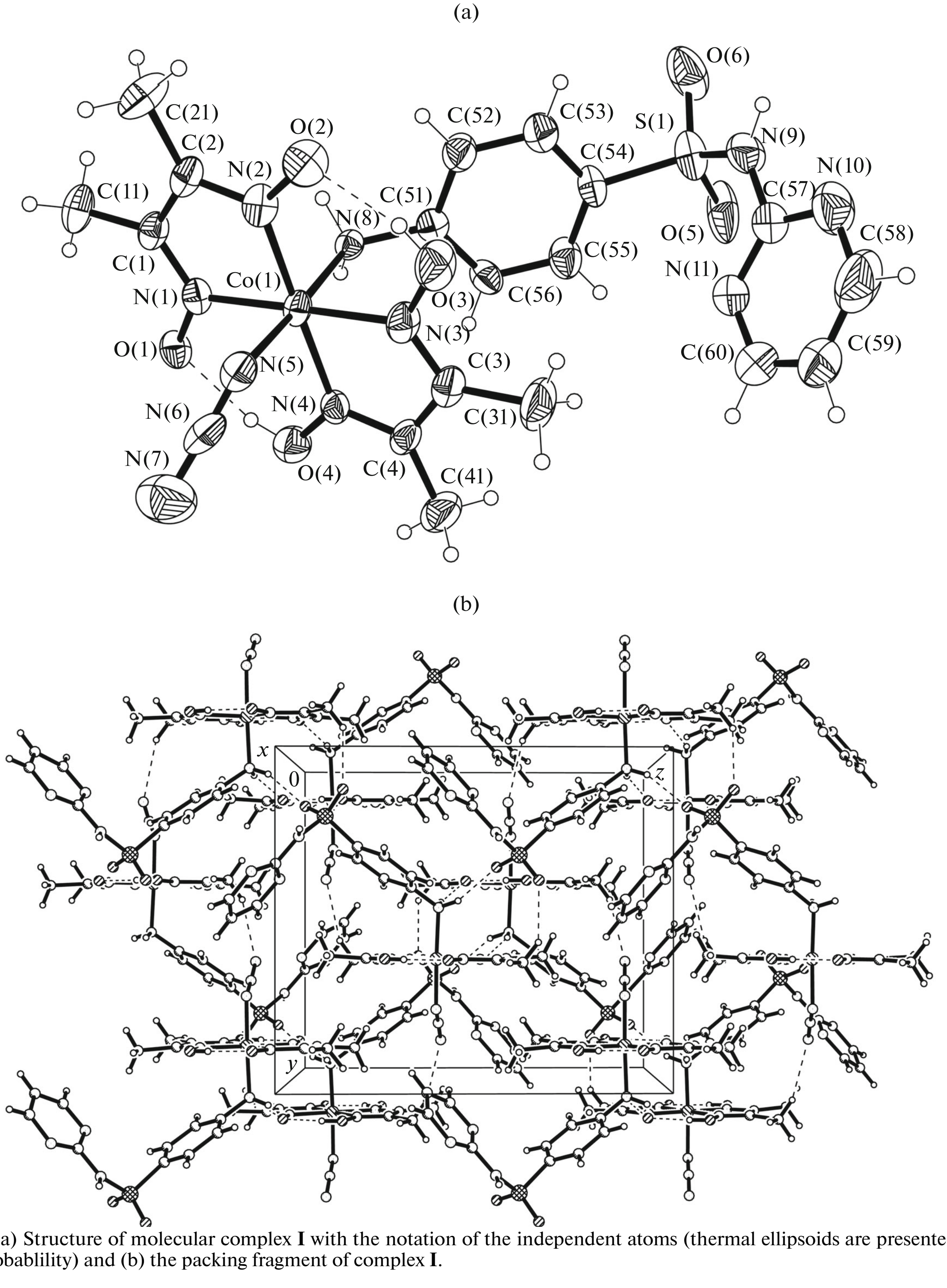


Fig. 1. (a) Structure of molecular complex **I** with the notation of the independent atoms (thermal ellipsoids are presented with 50% probablility) and (b) the packing fragment of complex **I**.

cal coordinates contain organic ligand Sda coordinated through the aminic nitrogen atom and inorganic anion N_3^-. Two $DmgH^-$ residues are joined by the O–H···O hydrogen bonds (Fig. 1a, Table 4) to form the stable fragment $Co(DmgH)_2$, which is characteristic of Co(III) dioximates. The interatomic distances Co–N(DmgH) range from 1.883(4) to 1.902(4) Å and the Co–N(Sad) distances are in a range of 2.014(3) Å (Table 3), which is consistent with similar values in the Co(III) complexes with dioximes [24–26, 33]. The interatomic distance metal–coordinated anion Co–N equal to 1.963(4) Å is shorter than that in similar compounds with the sulfanilamide derivatives [33] in

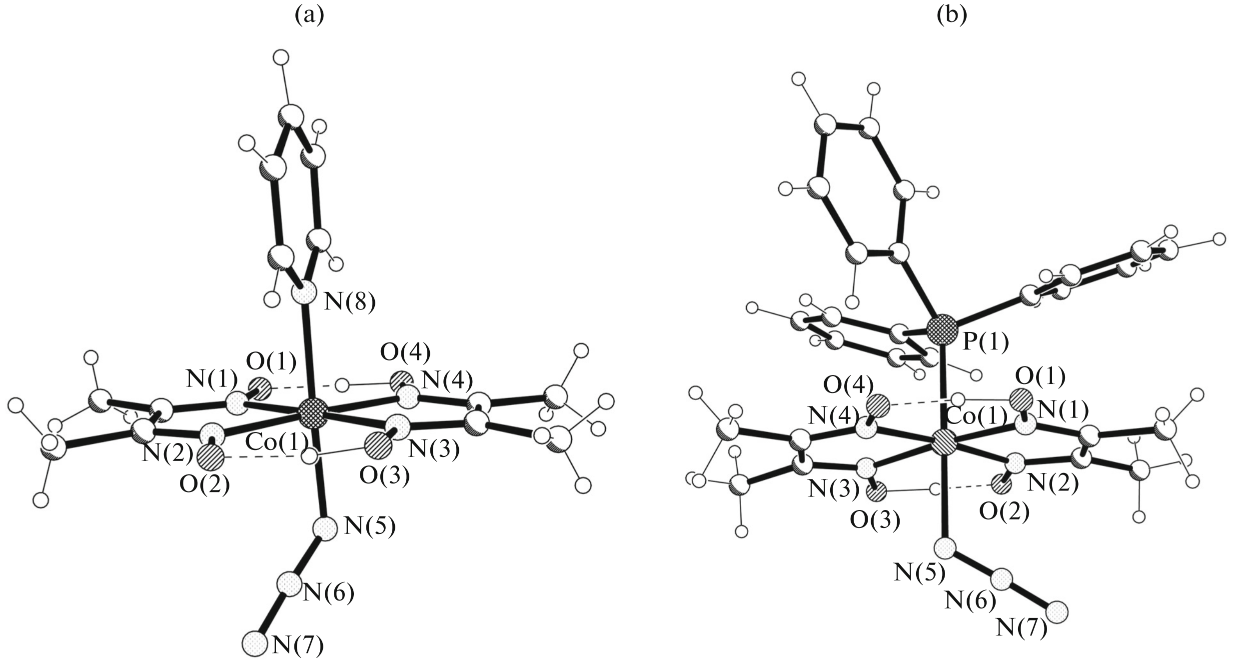


Fig. 2. Structures of complexes (a) $[Co(N_3)(Dmg)(DmgH_2)(Py)]$ (**II**) [34] and (b) $[Co(N_3)(DmgH)_2(PPh_3)]$ **(III)** [35].

which the Co–N interatomic distances range from 1.99(2) to 2.030(6) Å.

The analysis of the interatomic distances N–O in the dimethylglyoxime residues of complex **I** (Table 3) shows that the latter are coordinated via the bidentate mode; however, one of them is coordinated as a neutral ligand $DmgH_2$, whereas another is coordinated in the bideprotonated form Dmg^{2-}. As a result, the formula of compound **I** would be written more correctly as $[CoN_3(Dmg)(DmgH_2)(Sda)]$.

Intermolecular hydrogen bonds N–H···O (Table 4) joining the complexes into a 3D structure (Fig. 1b) are observed in crystal **I**. The amino (N(8)) and amido groups (N(9)) of ligand Sda always act as proton donors in the system of intermolecular hydrogen bonds. The crystal structure in compound **I** is additionally stabilized by weak intermolecular hydrogen bonds C–H···O and C–H···N (Table 4).

It was proved by X-ray diffraction analysis that the reactions of $[Co(N_3)(DmgH)_2(Sd)]$ with Py and PPh_3 afforded complexes **II** and **III**, respectively. The latter completely coincide with the compounds obtained earlier by the direct synthesis (Fig. 2) [34, 35], which confirms the substitution reaction.

The reaction of $[Co(N_3)(DmgH)_2(Sde)]$ with thiourea leads to the formation of compound **IV**, which was confirmed by the IR spectral method only, because single crystals suitable for X-ray diffraction analysis were not obtained. The formation of complex **V** described earlier [36] was confirmed by X-ray diffraction analysis. It was proved that both the sulfanilamide molecule and azide ion were substituted under the action of NH_4NCS (Fig. 3a) to form an anionic complex consisting of cation NH_4^+, centrosymmetrical octahedral anion $[Co(SCN)_2(DmgH)_2]^-$, and water molecules. The nitrogen atoms of the NH_4^+ cation and the oxygen atoms of the water molecules localized in the general position are randomly distributed over four positions each. The coordination polyhedron of the metal atom in the complex anion is formed by four nitrogen atoms of two monodeprotonated dimethylglyoxime residues coordinated via the chelating mode and by two sulfur atoms of two SCN^- anions coordinated to the metal through the sulfur atoms. Two $DmgH^-$ residues are joined by hydrogen bond O–H···O (O···O 2.526(3) Å (Table 4, Fig. 5)) to form the stable fragment $[Co(DmgH)_2]$, which is characteristic of Co(III) dioximates. The Co–N(DmgH) distances in compound **V** equal to 1.908(2) and 1.885(3) Å and the Co–S distance equal to 2.2920(8) Å are consistent with similar values in the Co(III) complexes with dioximes [26, 33–36].

In crystal **V**, the complex anions $[Co(SCN)_2(DmgH)_2]^-$ are bound into chains via intermolecular hydrogen bonds N(4)–H···O(1), N(4)–H···N(3) ($-x + 1$, $-y + 1$, $-z$), O(2*w*)–H···O(1), and O(2*w*)–H···N(3) ($-x + 1$, $-y + 1$, $-z$)

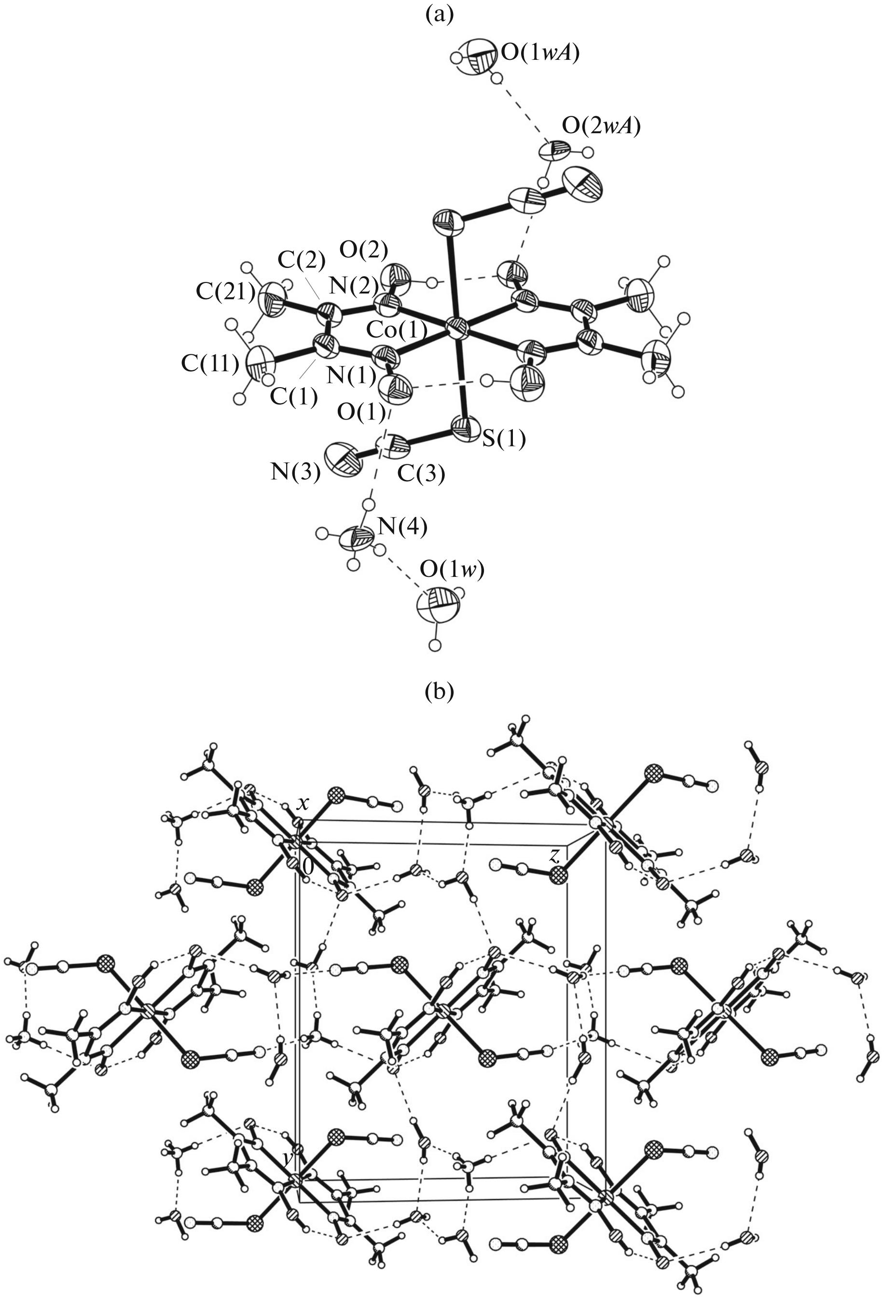
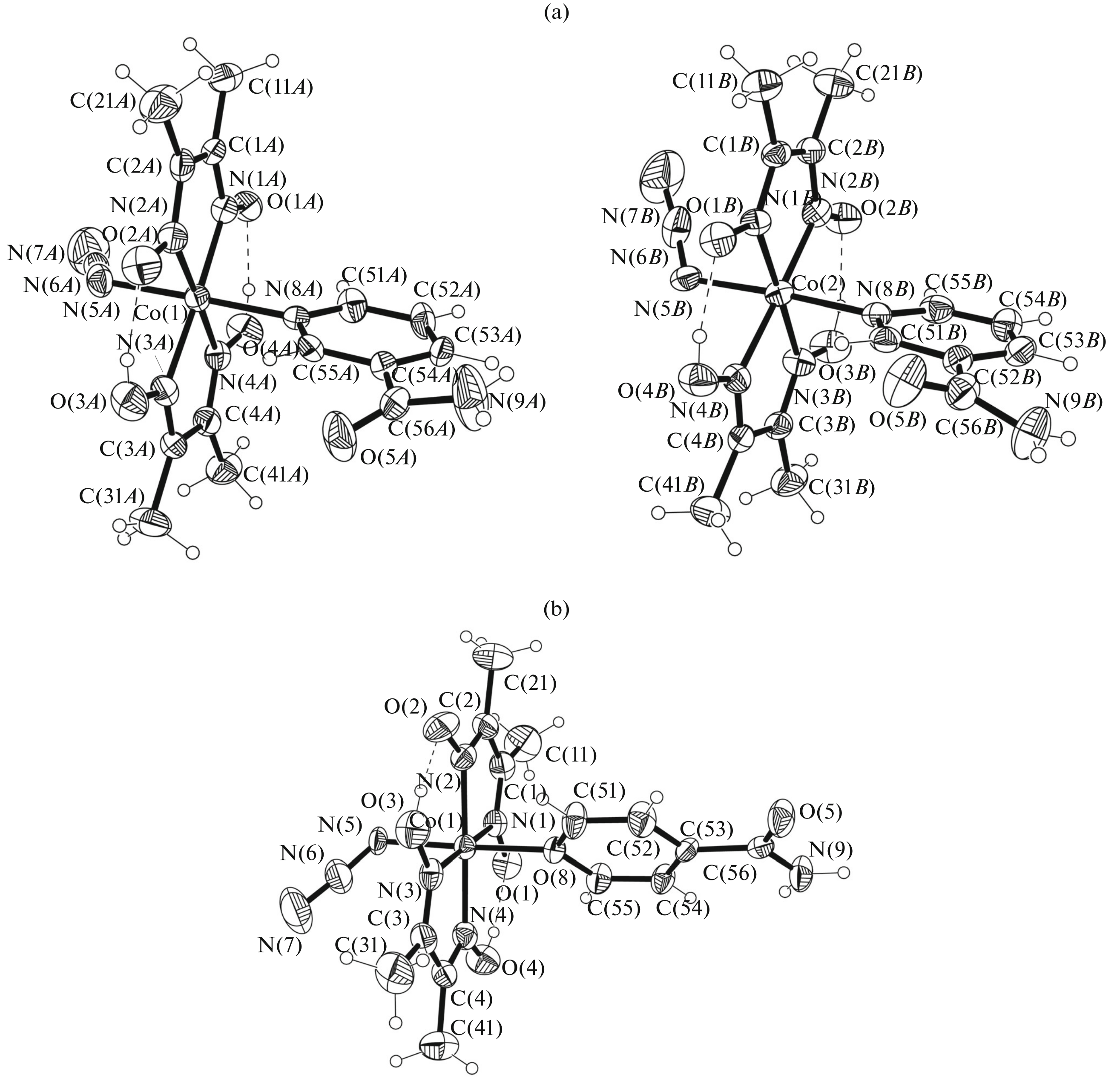


Fig. 3. (a) Structure of compound $NH_4[Co(SCN)_2(DmgH)_2] \cdot 3H_2O$ (**V**) with the notation of independent atoms of the complex anion and those randomly arranged at four positions of the NH_4^+ cation and water molecules and (b) the fragment of crystal packing of the components in compound **V**.

(Table 4, Fig. 3b). Supramolecular synthones $R_4^4(8)$, formed by the NH_4^+ cation (N(4)) via intermolecular hydrogen bonds with water molecules (O(1*w*) and O(2*w*)) joining, in turn, the complex anions into a 3D framework, can be emphasized in structure **V**.

The X-ray diffraction data showed that the reactions of $[Co(N_3)(DmgH)_2(SAM)]$ with Nia, INia, HINA, 4-PaoH, and Bipy (in a ratio of 1 : 1) gave molecular complexes **VI**, **VII**, **VIII**, **IX**, and **X**, respectively, and the independent part of the unit cells of the complexes contained one (**VII**, **IX**, and **X**) or two (**VI**


(a)

(b)

Fig. 4. Structures of molecular complexes (a) **VI**, (b) **VII**, (c) **VIII**, (d) **IX**, and (e) **X** with the notation of independent atoms (thermal ellipsoids are presented with 50% probability).

and **VIII**) crystallographically independent Co(III) complexes of the same composition (Fig. 4).

A usual octahedral coordination mode of the metal atoms is observed in complexes **VI–X** (Fig. 4). The equatorial plane of the complexes contains two $DmgH^-$ residues (**VIII** and **X**) or one neutral $DmgH_2$ and one doubly deprotonated residue Dmg^{2-} (**VI**, **VII**, and **IX**). The question about the specific dimethylglyoxime involved (neutral, mono- or bideprotonated) was predominantly answered on the basis of the geometric concepts: interatomic distances N–O (Table 3). However, these ligands are always coordinated via the bidentate chelating mode to form five-membered metallocycles. In this case, the apical positions of the Co(III) coordination polyhedron are occupied, on the one hand, by the inorganic anion N_3^-, and on the other hand, the *trans*-position of the latter is occupied by the additional organic ligands Nia, INia, HINA, 4-PaoH, or Bipy coordinated through the nitrogen atoms in compounds **VI**, **VII**,

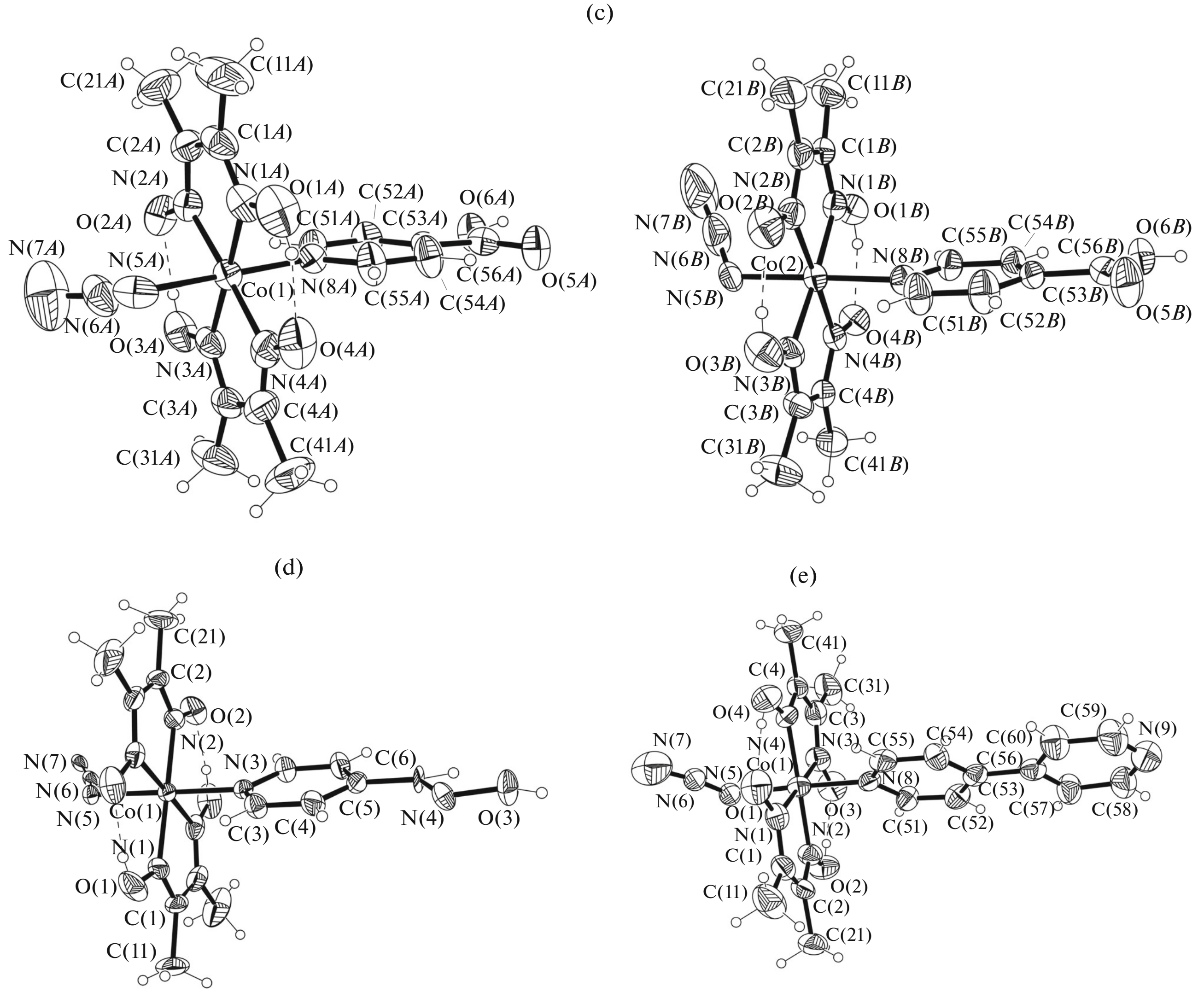


Fig. 4. (Contd.)

VIII, **IX**, and **X**, respectively. The dimethylglyoxime ligands (general formula $DmgH^-$) are joined by hydrogen bonds O–H···O (O···O 2.465(6)–2.553(4) Å Table 4, Fig. 4)) to form a 14-membered pseudo-macrocycle coordinated to the metal atom through the donor set of atoms N_4. In compound **VI**, for complex *A*, the Co–N(DmgH) distances range from 1.888(3) to 1.904(3) Å, the Co–N(N_3) distance is 1.977(4) Å, and Co–N(Nia) is 1.975(3) Å; for complex *B*, the Co–N(DmgH) distances lie in a range of 1.885(3)–1.907(4) Å, and Co–N(N_3) and Co–N(Nia) are in ranges of 1.960(4) and 1.975(4) Å, respectively. In complex **VII**, the Co–N(DmgH) distances range from 1.890(4) to 1.900(3) Å, Co–N(N_3) is 2.017(3) Å, and Co–N(INia) is 1.970(3) Å. In compound **VIII**, for complex *A*, (Co–N(DmgH) range from 1.881(4) to 1.897(4) Å, Co–N(N_3) is 2.024(5) Å, and Co–N(HINA) is 1.973(2) Å; for complex *B*, the Co–N(DmgH) distances range from 1.887(4) to 1.901(4) Å, Co–N(N_3) is 1.975(4) Å, and Co–N(HINA) is 1.971(4) Å. In complex **IX**, Co–N(DmgH) are 1.898(3) and 1.891(3) Å, Co–N(N_3) is 2.031(4) Å, and Co–N(4-PaoH) is 1.961(4) Å. In complex **X**, the Co–N(DmgH) distances are in a range of 1.889(6)–1.903(5) Å, Co–N(N_3) is 2.024(6) Å, and Co–N(Bipy) is 1.969(6) Å (Table 3), which is consistent with similar values in the Co(III) complexes with dioximes [24–26, 33–35].

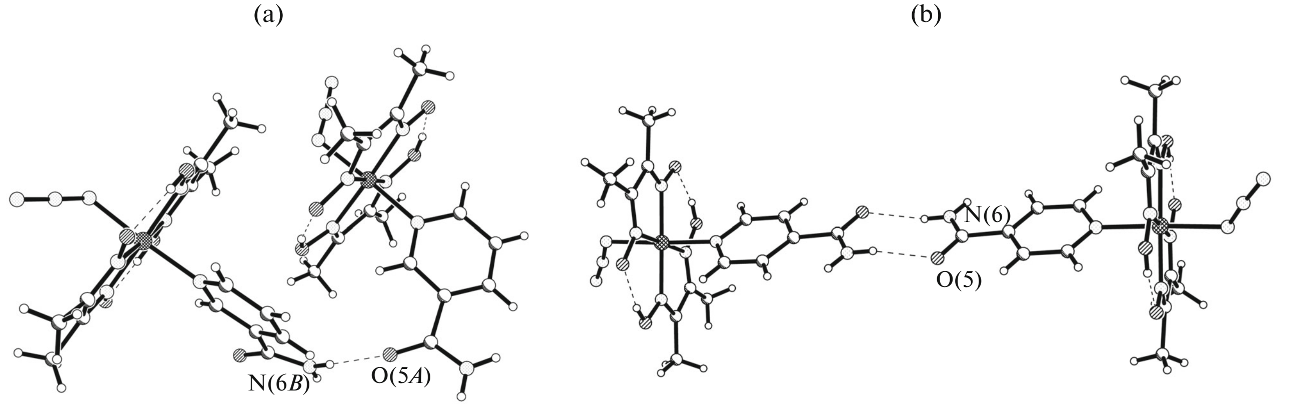


Fig. 5. Method of joining the complexes via the N–H···O hydrogen bond in (a) **VI** and (b) **VII**.

In crystals **VI** and **VII**, the molecular complexes are joined by intermolecular hydrogen bonds N–H···O and N–H···N (Table 4) in which the NH_2 groups of ligands Nia and INia act as proton donors. In **VI** only one intermolecular hydrogen bond joins two crystallographically independent complexes *A* and *B*, whereas in **VII** two complexes are joined by two centrosymmetric intermolecular hydrogen bonds N–H···O to form a supramolecular synthone $R_2^2(8)$ (Fig. 5).

In crystal **VI**, complexes *A* are bound by intermolecular hydrogen bonds N–H···O and N–H···N to both complexes *A* (of the same type) and complexes *B* (Table 4). Complexes *B* are bound by intermolecular hydrogen bonds N–H···O only to complexes *A* (Table 4). The fragment of the crystal structure of compound **VI** along the *x* axis is shown in Fig. 6a. An analysis of weak interactions showed that the structure was additionally stabilized by intermolecular hydrogen bonds C–H···O and C–H···N: C(53*A*)–H···O(2*B*) ($-x + 1/2, y + 1/2, -z + 3/2$) (C(53*A*)–O(2*B*) 3.400, H···O(2*B*) 2.54 Å, ∠CHO 150°), C(53*B*)–H···O(5*A*) (C(53*B*)–O(5*A*) 3.193, H···O(5*A*) 2.40 Å, ∠CHO 143°), C(41*B*)–H···N(5*A*) (C(41*B*)–N(5*A*) 3.441, H···N(5*A*) 2.56 Å, ∠CHO 153°), and C(41*B*)–H···N(7*A*) ($-x + 2, -y + 1, -z + 1$) (C(41*B*)–N(7*A*) 3.445, H···N(7*A*) 2.49 Å, ∠CHO 176°).

In **VII**, the centrosymmetric synthones from two complexes are bound to each other by intermolecular bonds hydrogen N–H···N (N(9)–H···N(7) ($x + 1, -y + 3/2, z + 1/2$) (Fig. 6b, Table 4). Figure 10 presents the fragment of the crystal structure of compound **VII** along the *x* axis additionally stabilized by weak intermolecular hydrogen bonds C–H···O: C(51)–H···O(2) ($-x + 1, -y + 2, -z + 1$) (C(51)–O(2) 3.134, H···O(2) 2.54 Å, ∠CHO 122°) and C(31)–H···O(1) ($x - 1, y, z$) (C(31)–O(1) 3.456, H···O(1) 2.51 Å, ∠CHO 170°).

In crystal **VIII**, the molecular complexes are joined to each other only by intermolecular hydrogen bonds involving crystallization water molecules (Table 4, Fig. 11). The O(1*w*) and O(2*w*) atoms via hydrogen bonds O–H···O and O–H···N bind both crystallographically independent complexes *A* and *B* and the one-type complexes to form the 3D structure (Table 4). The structure is stabilized by intermolecular hydrogen bonds C–H···O and C–H···N: C(51*A*)–H···O(2*A*) ($-x + 1, -y + 1, -z + 1$) (C(51*A*)–O(2*A*) 3.220, H···O(2*A*) 2.42 Å, ∠CHO 145°) and C(21*B*)–H···N(5*A*) ($x - 1, y, z$) (C(21*B*)–N(5*A*) 3.339, H···N(5*A*) 2.52 Å, ∠CHO 143°).

In **IX**, the molecular complexes are joined into chains by intermolecular hydrogen bonds O(3)–H(1)···N(6) and O(3)–H(1)···N(7) ($x, -y + 1/2, z + 1$) (Table 4, Fig. 6d). Dimethylformamide molecules are located between the chains in the crystal structure.

In crystal **X**, the mononuclear complexes are bound to each other by weak π···π interactions (distances 3.742 Å, Fig. 7) to form binuclear structural units joined by weak intermolecular hydrogen bonds C–H···O in which the oxime oxygen atoms always serve as acceptors: C(51)–H···O(1) ($-x + 3/2, y - 1/2, -z + 3/2$) (C(51)–O(1) 2.986, H···O(1) 2.27 Å, ∠CHO 133°), C(55)–H···O(2) ($-x + 3/2, y + 1/2, -z + 3/2$) (C(55)–O(2) 3.288, H···O(2) 2.52 Å, ∠CHO 140°), C(58)–H···O(3) ($x - 1/2, -y - 1/2, z - 1/2$) (C(58)–O(3) 3.400, H···O(3) 2.47 Å, ∠CHO 174°), and C(59)–H···O(4) ($x - 1/2, -y + 1/2, z - 1/2$) (C(59)–O(4) 3.355, H···O(4) 2.46 Å, ∠CHO 162°).

The stability of the equatorial fragment $Co(DmgH)_2$ and lability of some ligands arranged on the apical coordinate suggested an idea to use these complexes as “building blocks” in order to obtain polynuclear clusters or coordination polymers using the substitution of sulfanilamide molecules by biden-

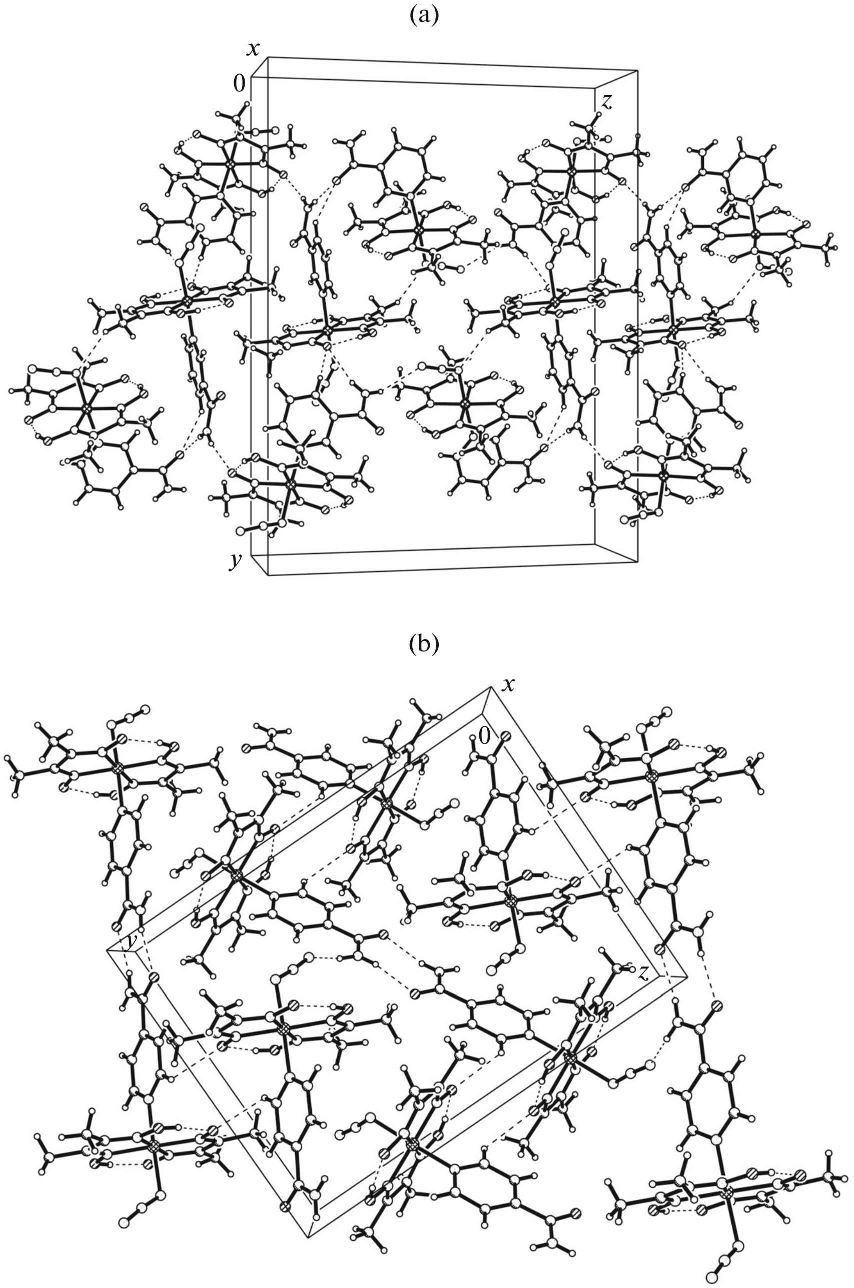


Fig. 6. Packing fragments for complexes *A* and *B* in (a) **VI**, (b) **VII**, (c) **VIII**, and (d) **IX**.

tate bridging ligands. The analysis of the CCDC data [37] shows that only the binuclear compounds have been prepared so far for Co(III) dioximates [43–47].

Both mono- and two polymorphous binuclear complexes **XI** and **XII** differed in both the symmetry and number of crystallization water molecules in the crystal were obtained by the reaction of the "building block" [Co(N_3)($DmgH)_2$(SAM)] with the bidentate Bipy ligand, which can be used as a bridging one depending on the stoichiometric ratio of the initial reactants. The symmetry center in compound **XI** lies on the C(7)–C(7*) bond of the bridging Bipy ligand (Fig. 8). In **XII**, both the Bipy ligand and metal atom are in the symmetry center (Fig. 9).

As a result, the octahedral coordination mode of the metal atoms is observed in binuclear molecular complexes **XI** and **XII**, as well as in mononuclear complex **X** with Bipy. However, the ligands having different charges lie in the equatorial plane of the metal environment in these compounds: complex *A* of com-

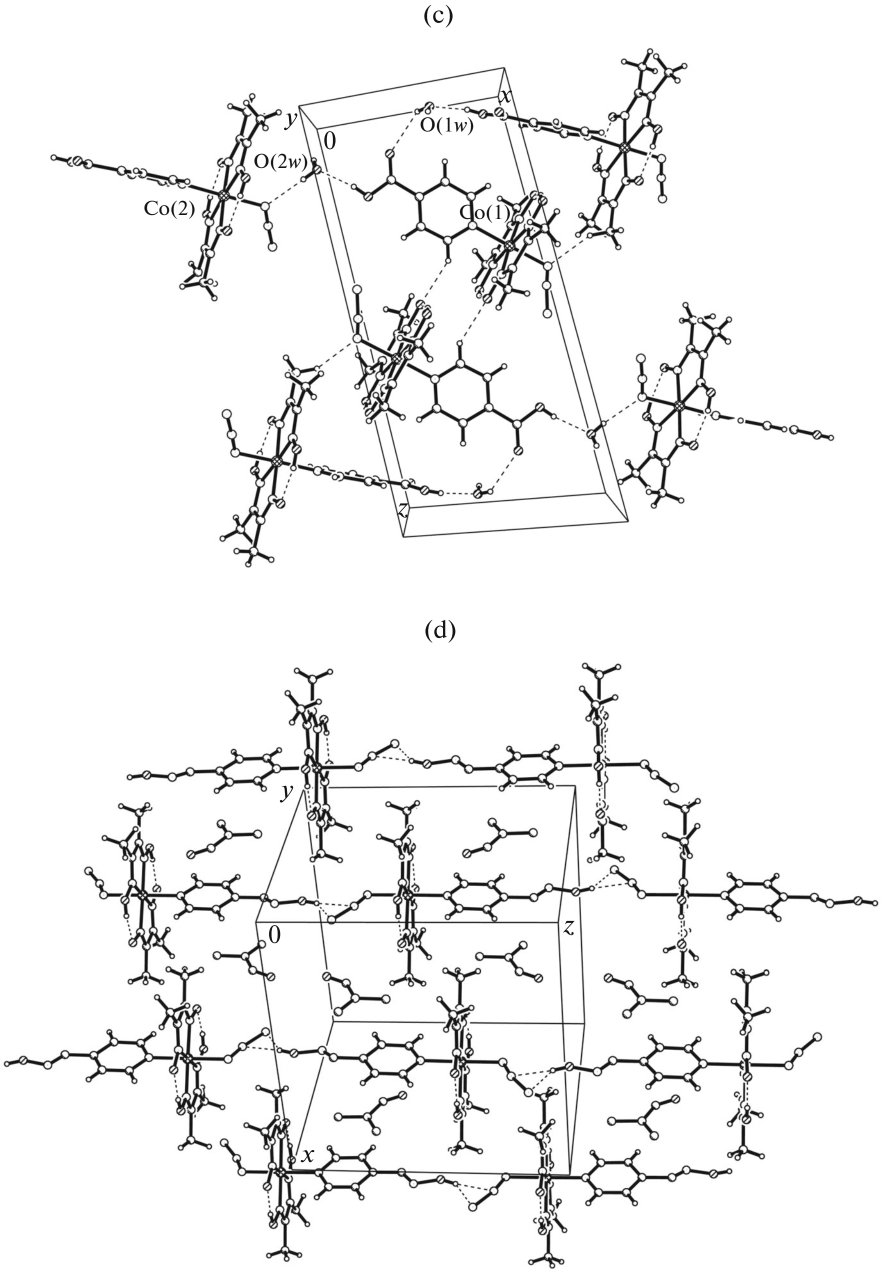


Fig. 6. (Contd.)

pound **XI** contains one neutral $DmgH_2$ and one doubly deprotonated residue Dmg^{2-} and both these ligands in *B* are monodeprotonated, whereas complex **XII** contains both residues $DmgH^-$. The type of the ligand present in the complex (neutral, mono- or bideprotonated dimethylglyoxime) was determined from the geometric concepts, namely, the symmetry of the environment and interatomic distances N–O (Table 3). The dimethylglyoxime ligands are always coordinated through the set of donor atoms N_2 via the chelating mode to form five-membered metallocycles, the apical coordinates of which contain the inorganic anion N_3^-, and Bipy coordinated through the nitrogen atoms is in the *trans*-position to the latter. The dimethylglyoxime ligands (general formula $DmgH^-$) are joined by hydrogen bonds O–H···O (O···O 2.481(5)–2.517(5) Å; Table 4, Figs. 8, 9) to form a pseudo-macrocycle. In **XI** (complexes *A* and *B*), the

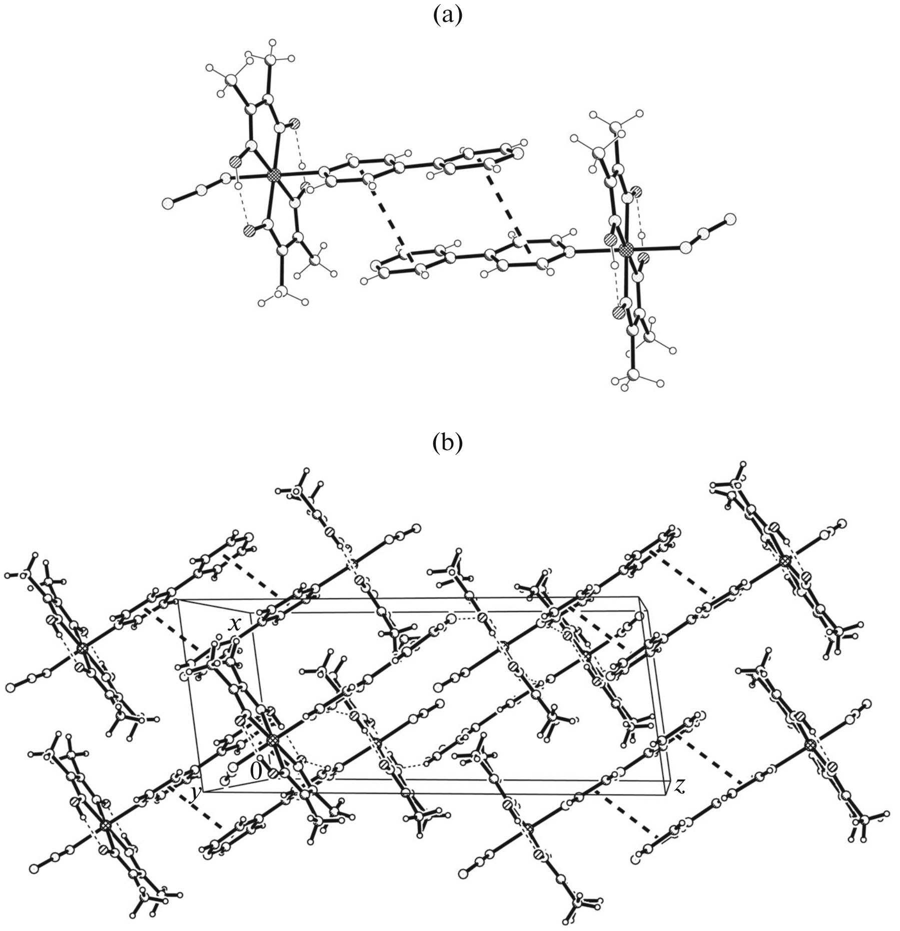


Fig. 7. (a) Formation of dimeric structural units and (b) the crystal structure fragment in **X**.

Table 5. Calculated and experimental bond lengths Co–N_{azide} and Co–second axial ligand L_{axial} in compounds **I–X**

Complex	Theoretical values, Å		Experimental values, Å	
	R (Co–L_{axial})	*R* (Co–N_{azide})	*R* (Co–L_{axial})	*R* (Co–N_{azide})
I	2.09	1.92	2.014(3)	1.963(4)
II	2.03	1.94	1.973	1.950
III	2.66	1.92	2.311	2.014
IV	2.54	1.92		
V	2.45		2.2920(8)	
VI	2.03	1.94	1.975(3)/1.975(4)	1.977(4)/1.960(4)
VII	2.04	1.94	1.970(3)	2.017(3)
VIII	2.04	1.94	1.973(3)/1.971(4)	2.024(5)/1.975(4)
IX	2.03	1.94	1.961(4)	2.031(4)
X	2.03	1.94	1.969(6)	2.024(6)

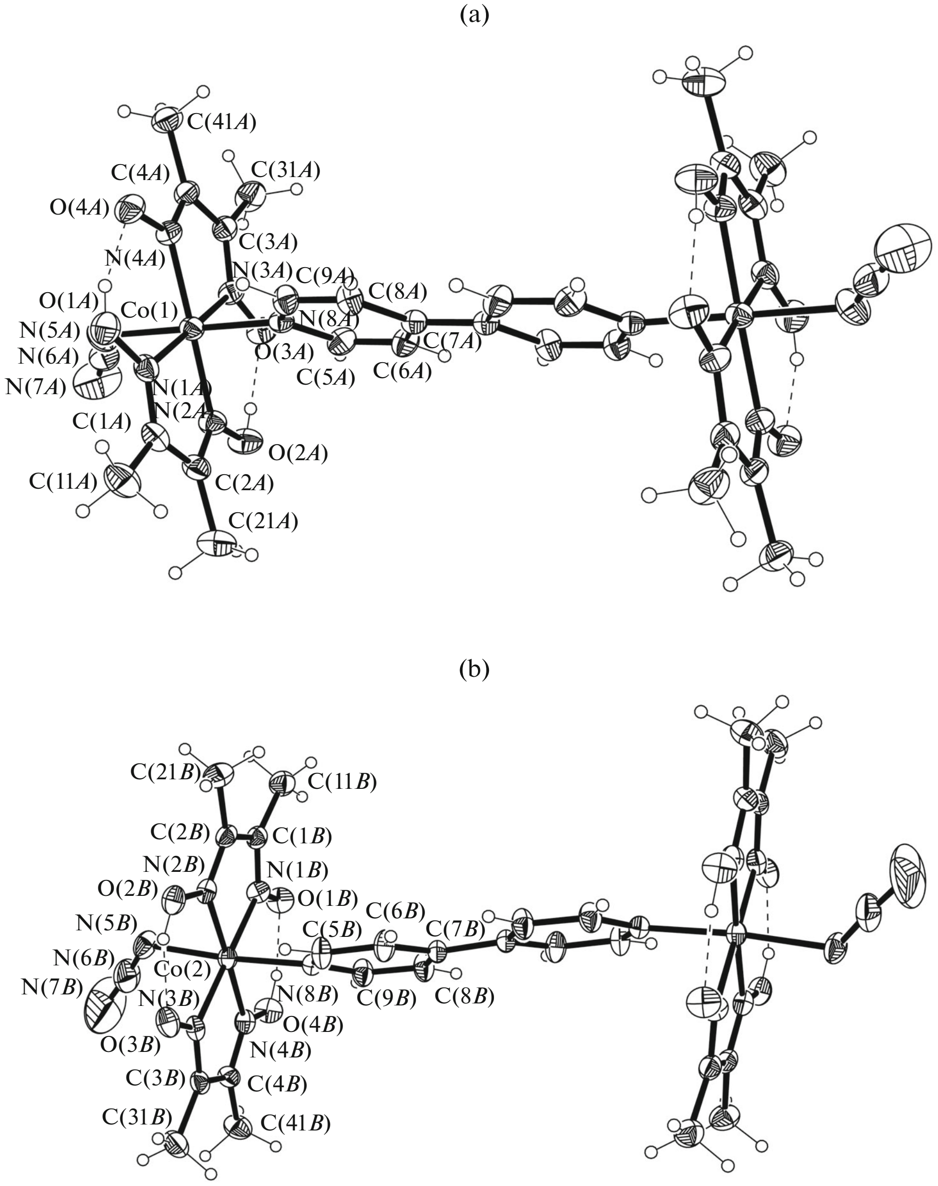


Fig. 8. Binuclear Co(III) complexes (a) *A* and (b) *B* bearing the bipyridine bridging ligand in **XI** with the notation of independent atoms (thermal ellipsoids are presented with 30% probability).

Co–N(DmgH) distances are in the following ranges: 1.885(4)–1.907(4) Å; Co–N(N_3) 1.966(5) and 1.963(4) Å, Co–N(Bipy) 1.970(4) and 1.984(3) Å. In **XII** (complexes *A* and *B*), the Co–N(DmgH) distances are in the following ranges: 1.883(3)–1.898(3) Å; Co–N(N_3) 1.916(6) and 2.017(6) Å, Co–N(Bipy) 2.081(4) and 1.935(3) Å.

In crystal **XI**, molecular binuclear complexes *A* and *B* are joined with each other into chains by intermolecular hydrogen bonds involving crystallization water molecules (Table 4, Fig. 10). The O(1*w*) atom binds crystallographically independent complexes *A* and *B* via intermolecular hydrogen bonds: O(1*w*)–H(1)···N(5*A*), O(1*w*)–H(1)···N(6*A*), and O(1*w*)–H(2)···O(1*B*). The structure is additionally stabilized by intermolecular hydrogen bonds C–H···O: C(31*w*)–H···O(2*A*) (*x*, *y*, *z* – 1) (C(31*B*)–O(2*A*) 3.507, H···O(2*A*) 2.59 Å, ∠CHO 159°), C(31*B*)–H···O(3*A*) (C(31*B*)–O(3*A*) 3.350, H···O(3*A*) 2.47 Å, ∠CHO 153°), and C(8*A*)–H···O(2*B*) (–*x* + 1, –*y*, –*z*) (C(8*A*)–O(2*B*) 3.407, H···O(2*B*) 2.54 Å, ∠CHO 155°).

In crystal **XII**, molecular binuclear complexes *A* and *B* are joined into chains by intermolecular hydro-

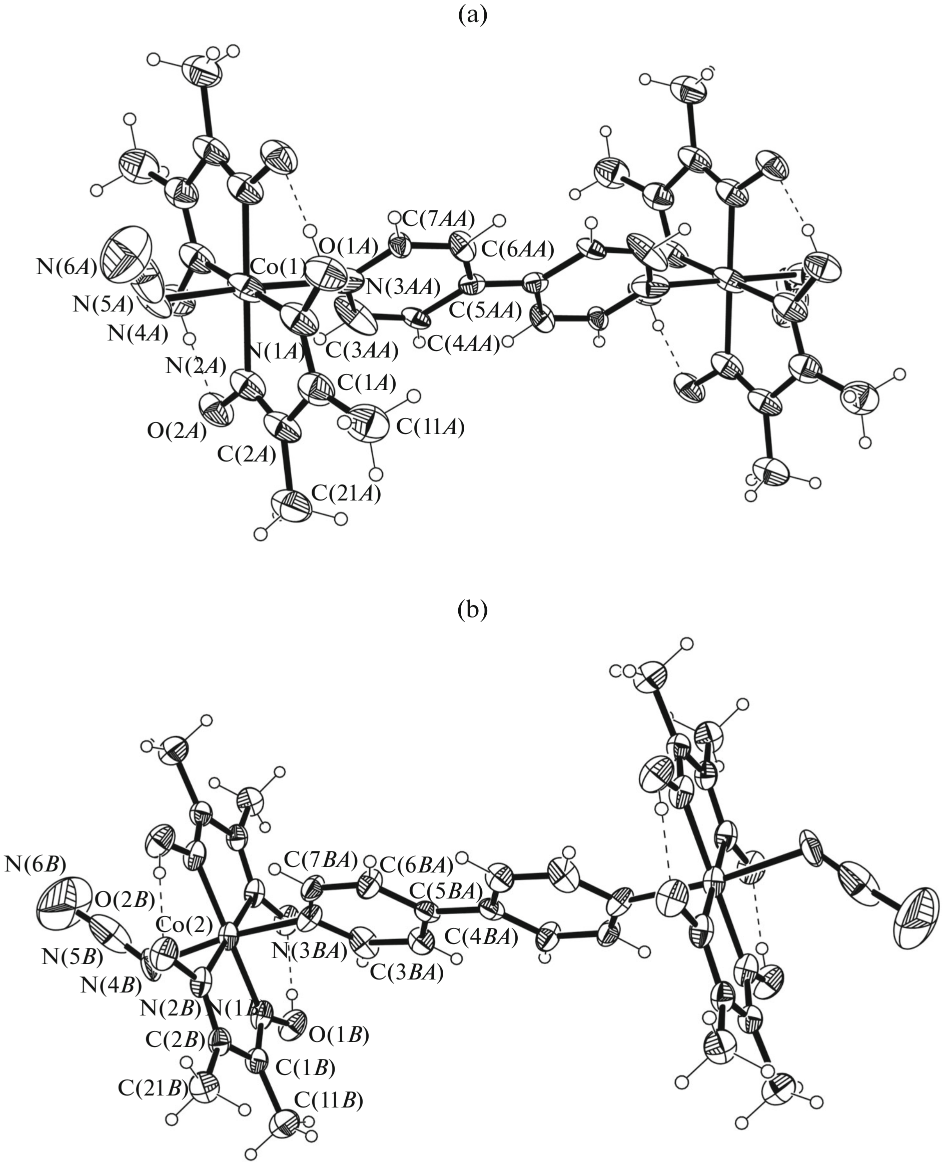


Fig. 9. Symmetric binuclear Co(III) complexes (a) *A* and (b) *B* bearing the bipyridine bridging ligand in **XII** with the notation of independent atoms (thermal ellipsoids are presented with 30% probability).

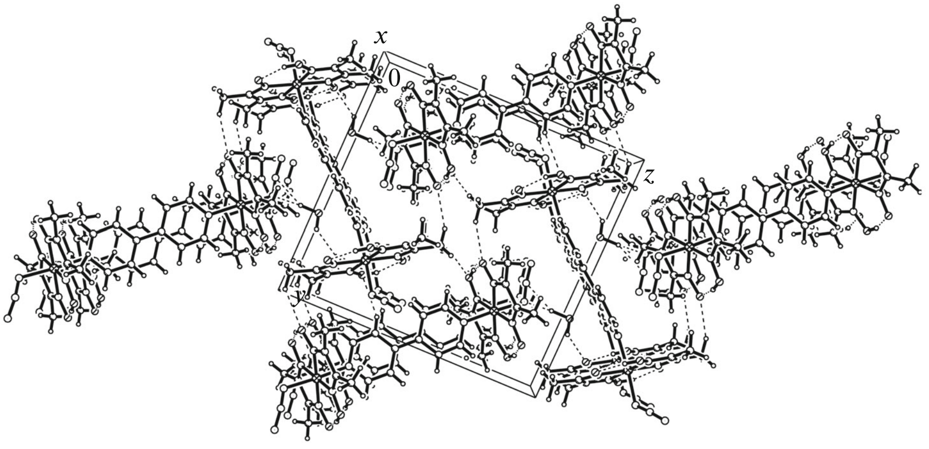


Fig. 10. Packing fragments of complexes *A* and *B* in **XI**.

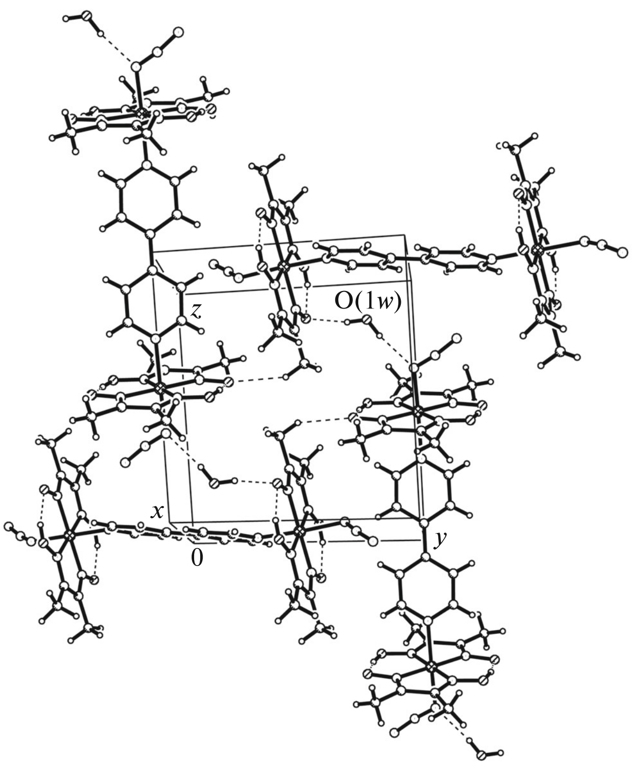


Fig. 11. Formation of chains of alternating complexes *A* and *B* in **XII** by water molecules and their joining via weak C–H···O interactions.

gen bonds involving crystallization water molecules (Table 4, Fig. 11): O(1*w*)–H(1)···N(4*A*) and O(1*w*)–H(2)···O(2*B*). Structure **XII**, as **XI**, is stabilized by weak intermolecular hydrogen bonds C–H···O: C(21*B*)–H···O(2*A*) (C(21*B*)–O(2*A*) 3.270, H···O(2*A*) 2.42 Å, ∠CHO 148°) and C(4*B*)–H···O(1*w*) (C(4*B*)–O(1*w*) (x + 1, y, z – 1) (C(4*B*)–O(1*w*) 3.243, H···O(2*B*) 2.55 Å, ∠CHO 132°).

The calculated bond lengths Co–N_{azide} and Co–second axial ligand in the optimized molecular structures of compounds **I–X** are presented in Table 5. The comparative analysis of the theoretical and experimental data presented in Table 5 proves a good correlation between them for the bond lengths of the cobalt atom with elements coordinating with them on the apical axis.

The competitive ability of various functional groups to coordination with the complexing agent $[Co(N_3)(DmgH_2)_2]$ can be evaluated from the Co–ligand bond energy (E_b), which was calculated as the difference between the total energy of ligand L and complexing agent $[Co(N_3)(DmgH_2)_2]$ and the energy of complex $[Co(N_3)(DmgH_2)_2(L)]$: $E_b = (E_L + E_{Co(N3)(DH2)2}) - E_{Co(N3)(DH2)2\text{-}L}$. The calculation results are presented in Table 6.

Table 6. Energies of Co–L bonds*

Ligand	E_b, au	E_b, kcal/mol
Sbu (L^1)	0.0678	42.54
Spa (L^2)	0.0566	35.52
Sde (L^3)	0.0552	34.64
Sd (L^4)	0.0548	34.39
Sda (L^5)	0.0492	30.87
4-PaoH	0.0925	58.04
Bipy	0.0871	54.66
Nia	0.0821	51.52
Py	0.0800	50.20
INia	0.0770	48.32
HINA	0.0751	47.13
Thio	0.0576	36.14
PPh_3	0.0446	27.99

* Designation of sulfanilamide ligands L^i corresponds to Scheme 1.

Table 7. Energy gain Δ*E* (kcal/mol) in the substitution of sulfanilamide ligands L^i by a ligand-substituent*

Complex	Substitution reaction	Δ*E* (kcal/mol)
II	$[Co(N_3)(DmgH)_2L^4] + Py \rightarrow [Co(N_3)(DmgH)_2(Py)] + L^4$	−15.30
III	$[Co(N_3)(DmgH)_2L^4] + PPh_3 \rightarrow [Co(N_3)(DmgH)_2(PPh_3)] + L^4$	+6.4
IV	$[Co(N_3)(DmgH)_2L_3] + Thio \rightarrow [Co(N_3)(DmgH)_2(Thio)] + L^3$	−1.76
	$[Co(N_3)(DmgH)_2L^2] + Thio \rightarrow [Co(N_3)(DmgH)_2(Thio)] + L^2$	−1.07
VI	$[Co(N_3)(DmgH)_2L^4] + Nia \rightarrow [Co(N_3)(DmgH)_2(Nia)] + L^4$	−16.56
	$[Co(N_3)(DmgH)_2L^5] + Nia \rightarrow [Co(N_3)(DmgH)_2(Nia)] + L^5$	−22.97
VII	$[Co(N_3)(DmgH)_2L^4] + INia \rightarrow [Co(N_3)(DmgH)_2(INia)] + L^4$	−13.61
	$[Co(N_3)(DmgH)_2L^5] + INia \rightarrow [Co(N_3)(DmgH)_2(INia)] + L^5$	−20.02
VIII	$[Co(N_3)(DmgH)_2L^4] + HINA \rightarrow [Co(N_3)(DmgH)_2(HINA)] + L^4$	−12.49
IX	$[Co(N_3)(DmgH)_2L^4] + 4\text{-}PaoH \rightarrow [Co(N_3)(DmgH)_2(4\text{-}PaoH)] + L^4$	−23.22
X	$[Co(N_3)(DmgH)_2L^1] + Bipy \rightarrow [Co(N_3)(DmgH)_2(Bipy)] + L^1$	−9.22
XI	$2[Co(N_3)(DmgH)_2L^1] + Bipy \rightarrow [(Co(N_3)(DmgH)_2)_2(Bipy)] + 2L^1$	−14.18

* Roman numerals in the left column correspond to the numeration of the obtained compounds.

Since coordination compounds **X–XII** were synthesized using the substitution of sulfanilamide molecules in the "building block" $[Co(N_3)(DmgH)_2(SAM)]$ by the bidentate heterofunctional ligands, we estimated the energy gain for these reactions (Δ*E*), which was calculated as the difference in the energies of the reactants and products: $\Delta E = \Sigma E_{\text{product}} - \Sigma E_{\text{reactant}}$ (Table 7). The obtained results indicate the exothermic character of the substitution reactions.

ACKNOWLEDGMENTS

The authors are grateful to V.N. Shafranskii for the sulfanilamide derivatives kindly presented for the study.

This work was supported by the Supreme Council for Science and Technical Development of the Academy of Sciences of Moldova, project no. 14.518.02.04 A IAP ASM.

REFERENCES

1. Chugaev, L.A., *Zh. Rus. Fiz.-Khim. Obshch.*, 1905, vol. 37, no. 2, p. 243.
2. Chugaev, L.A., *Izbrannye trudy* (Selected Works), Chernyaev, I.I., Ed., Moscow: Izd-vo AN SSSR, vol. 1, 1954.
3. Rockenbaur, A., Eyor, M., Kwielinsci, M., and Tyrlik, S., *Inorg. Chim. Acta*, 1982, vol. 58, p. 237.
4. Matkovskii, K.L. and Bologa, O.A., *Globus Nauki*, 2006, vol. 6, p. 34.
5. Voloshin, Ya.Z., Varzatskii, O.A., and Bubnov, Yu.N., *Izv. Akad. Nauk, Ser. Khim.*, 2007, no. 4, p. 555.
6. Voloshin, Y.Z., Belov, A.S., Vologzhanina, A.V., et al., *Dalton Trans.*, 2012, vol. 41, p. 6078.
7. Bourosh, P.N., Coropcheanu, E.B., Ciloci, A.A., et al., *Russ. J. Coord. Chem.*, 2013, vol. 39, no. 11, p. 777.
8. Thomas, T.W. and Underhill, A.E., *Chem. Commun.*, 1969, vol. 13, p. 725.
9. Schrauzer, G.M. and Windgassen, K.I., *J. Am. Chem. Soc.*, 1967, vol. 89, p. 1999.
10. Bowman, K., Gaughan, A.P., and Dori, Z., *J. Am. Chem. Soc.*, 1972, vol. 94, p. 727.
11. Ablov, A.V., Simonov, Yu.A., Malinovskii, S.T., et al., *Dokl. Akad. Nauk SSSR*, 1975, vol. 221, no. 3, p. 605.
12. Coropcheanu, E.B., Rija, A.P., Lozan, V.I., et al., *Russ. J. Coord. Chem.*, 2012, vol. 38, no. 8, p. 545.
13. Rija, A., Coropceanu, E., Bologa, O., et al., *Russ. J. Inorg. Chem.*, 2013, vol. 58, no. 4, p. 440.
14. Bourosh, P., Coropceanu, E., Rija, A., et al., *J. Mol. Struct.*, 2011, vol. 998, p. 198.
15. Ozol, L.D., Botoshanskii, M.M., Bulgak, I.I., et al., *Zh. Neorg. Khim.*, 1980, vol. 25, no. 4, p. 1137.
16. Ablov, A.V., Samus', N.M., Konunova, G.A., and Khoroshun, I.V., *Zh. Neorg. Khim.*, 1974, vol. 19, no. 10, p. 2788.
17. Ablov, A.V., Samus', N.M., and Luk'yanets, T.S., *Zh. Neorg. Khim.*, 1975, vol. 20, no. 10, p. 2763.
18. Samus', N.M., Damaskina, O.N., and Luk'yanets, T.S., in *Reaktsii zameshcheniya v koordinatsionnykh soedineniyakh kobal'ta* (Substitution Reactions in Cobalt Coordination Compounds), Chisinau: Shtiintsa, 1979.
19. Gupta, B.D., Yamuna, R., and Mandal, D., *Organometallics*, 2006, vol. 25, no. 3, p. 706.
20. Gupta, B., Yamuna, R., and Singh, V., *Organometallics*, 2003, vol. 22, p. 226.
21. Gilaberte, J.M., López, C., Alvarez, S., et al., L, *New J. Chem.*, 1993, vol. 17, p. 193.
22. Gupta, B., Tiwari, U., Barclay, T., and Cordes, W., *J. Organomet. Chem.*, 2001, vol. 629, p. 83.

23. Mandal, D., Chadha, P., Laskar, M., et al., *Tetrahedron Lett.*, 2007, vol. 48, p. 2377.
24. Coropceanu, E.B., Rija, A.P., Shafranskii, V.N., et al., *J. Struct. Chem.*, 2007, vol. 48, p. 1110.
25. Simonov, Yu.A., Mazus, M.D., Popa, I.A., et al., *Zh. Strukt. Khim.*, 1990, vol. 31, p. 77.
26. Simonov, Yu.A., Mazus, M.D., Popa, I.A., et al., *Zh. Strukt. Khim.*, 1989, vol. 30, p. 155.
27. Clemente, D.A. and Marzotto, A., *Acta Crystallogr., Sect. B: Struct. Sci.*, 2004, vol. 60, p. 287.
28. Marques, L., Lang, E.S., Fenner, H., and Castellano, E.E., *Z. Anorg. Allg. Chem.*, 2005, vol. 631, p. 745.
29. Manzoni de Oliveira, G., Baraldi, A., de Lourenco Marques, L., et al., *Inorg. Chim. Acta*, 2008, vol. 361, p. 132.
30. Bellu, S., Hure, E., Trape, M., et al., *Polyhedron*, 2005, vol. 24, p. 501.
31. Blasco, F., Ortiz, R., Perello, L., et al., *J. Inorg. Biochem.*, 1994, vol. 53, p. 117.
32. Torre, M.H., Facchin, G., Kremer, E., et al., *J. Inorg. Biochem.*, 2003, vol. 94, p. 200.
33. Mel'nik, E., Bourosh, P., Rizha, A., et al., *Russ. J. Coord. Chem.*, 2012, vol. 38, no. 9, p. 646.
34. Ponnuswamy, M.N. and Trotter, J., *Acta Crystallogr., Sect. C: Cryst. Struct. Communs.*, 1983, vol. 39, p. 726.
35. Nelson, J.H., Takach, N.E., Bresciani-Pahor, N., et al., *Acta Crystallogr., Sect. C: Cryst. Sttuct. Communs.*, 1984, vol. 40, p. 742.
36. Samus', I.D. and Belov, N.V., *Dokl. Akad. Nauk SSSR*, 1970, vol. 193, no. 2, p. 333.
37. Allen, F.H., *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, vol. 58, p. 38.
38. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, no. 1, p. 112.
39. Granovsky, A.A., http://classic.chem.msu.su/gran/gamess/index.html
40. Rassolov, V.A., Pople, J.A., Ratner, M.A., and Windus, T.L., *J. Chem. Phys.*, 1998, vol. 109, p. 1223.
41. Ditchfield, R., Hehre, W.J., and Pople, J.A., *J. Chem. Phys.*, 1971, vol. 54, p. 724.
42. Dreos, R., Randaccio, L., Siega, P., et al., *Inorg. Chim. Acta*, 2010, vol. 363, p. 2113.
43. Englert, U. and Strahle, J., *Gazz. Chim. Ital.*, 1988, vol. 118, p. 845.
44. Gupta, B.D., Vijaikanth, V., and Singh, V., *Organometallics*, 2004, vol. 23, p. 2069.
45. Vijaikanth, V., Gupta, B.D., Mandal, D., and Shekhar, S., *Organometallics*, 2005, vol. 24, p. 4454.
46. Kumar, S. and Seidel, R.W., *Inorg. Chem. Commun.*, 2013, vol. 27, p. 1.
47. Xu-Feng Liu, Ying-Xin Zhang, and Jing Yan, *Transition Met. Chem.*, 2015, vol. 40, no. 3, p. 305.

Translated by E. Yablonskaya