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Three-coordinate silver(I) ions and tridentate ligands as complementary tectons in coordination polymer construction: a new example of semiregular 4.8^2 nets*

S. Z. Vatsadze,[a*] ***I. A. Vatsadze,***[b] ***M. A. Manaenkova,***[a] ***N. V. Zyk,***[a] ***A. V. Churakov,***[c] ***M. Yu. Antipin,***[d]
J. A. K. Howard,[e] ***and H. Lang***[f]

[a]*Chemistry Department, M. V. Lomonosov Moscow State University,*
1 Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (495) 939 8846. E-mail: szv@org.chem.msu.ru
[b]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (499) 135 5328. E-mail: vatsadze@yahoo.co.uk
[c]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (495) 954 1279. E-mail: churakov@igic.ras.ru
[d]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (499) 135 5085. E-mail: mishan@xray.ineos.ac.ru
[e]*Department of Chemistry, University of Durham,*
South Road, Durham DH1 3LE, UK.
[f]*Department of Inorganic Chemistry, Institute of Chemistry,*
*Chemnitz University of Technology, D-09111 Chemnitz, Germany***

The structures of the reaction products of silver nitrate with monoheterotopic tridentate ligands derived from *N*-alkyl-3,5-bis(3-pyridylmethylene)piperidin-4-one were studied. The aliphatic nitrogen atoms are involved in the coordination, all three nitrogen atoms of the ligands being coordinated to three different silver atoms. In turn, each silver atom is coordinated by two nitrogen atoms of the pyridine ring and one nitrogen atom of the piperidine ring of different ligands. The crystal structures of the complexes are different. Infinite ladder-like chains consisting of 16-membered metallamacrocycles as monomeric building blocks are present in the structure of the *N*-methyl derivative, whereas two-dimensional 4.8^2 nets consisting of 16- and 40-membered metallamacrocycles are observed in the crystal structure of the *N*-benzyl analog.

Key words: supramolecular chemistry, coordination polymers, silver(I), *exo*-dentate ligands, cross-conjugated dienones, three-coordinated nets, X-ray diffraction study.

Three-coordinated, or T-shaped, nets formed by metal ions and organic ligands have attracted attention not only from the esthetic viewpoint[1] but also as examples of the practical application of theoretical approaches to the description of the structures of solids.[1—4] There are one type of regular T-shaped nets[2] and three types of semiregular nets.[2] It was experimentally found that 4.8^2 nets are least abundant among semiregular nets (Fig. 1, *a*). This topology can be achieved in two ways. First, three-connected vertices can be combined with two-connected edges (Fig. 1, *b*). In this case, both combinations of a three-coordinate metal atom (vertex) and a bidentate ligand (edge) and combinations of a two-coordinate metal (edge) and a tridentate ligand (vertex) are possible. Only one structure of this type is known. In this structure, the erbium(III) ion serves as three-coordinate metal and 4,4´-bipyridine *N*,*N*´-dioxide acts as a bridging bidentate ligand.[5] An interaction between metal nitrate and the ligand gives rise to a two-dimensional net consisting of 44- and 88-membered metallamacrocycles (these macrocycles will be denoted as 44/88). Since in this case the

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** Technische Universität Chemnitz, Fakultät für Naturwissenschaften, Institut für Chemie, Lehrstuhl anorganische Chemie, Straße der Nationen 62, D-09111 Chemnitz, Germany.

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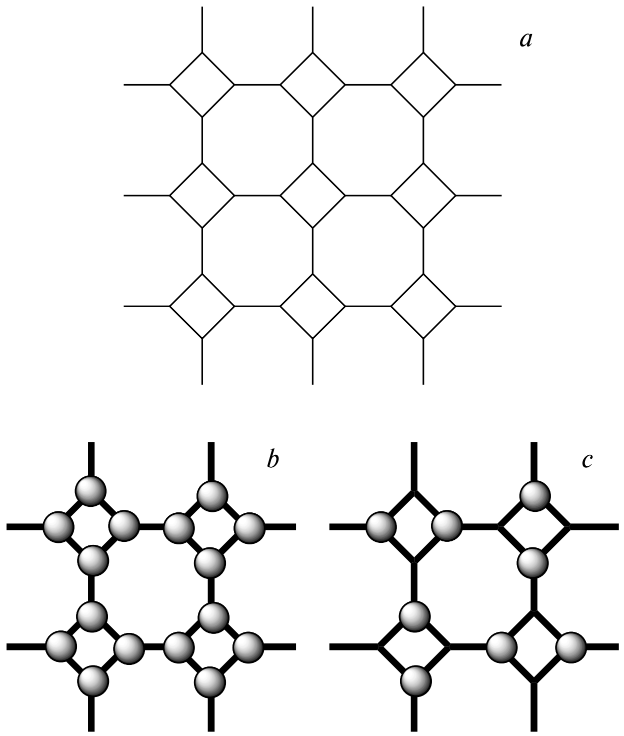


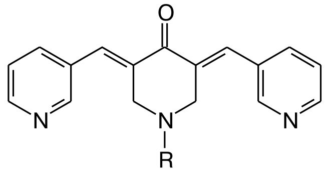
Fig. 1. (*a*) General view of the semiregular 4.8^2 network. (*b*) A combination of the three-coordinate metal ion (vertex) and the bidentate ligand (edge). (*c*) A combination of the complementary three-coordinate metal ion (vertex) and the tridentate ligand (vertex + edge).

ligand is neutral, the net exists as a polycation. To compensate the charge, each erbium(III) cation is bound to three counteranions.

The second approach to the construction of 4.8^2 nets is based on a combination of complementary three-connected vertices and three-connected edges (Fig. 1, *c*). In this case, metal serves as a vertex and a ligand acts as a vertex connected to three adjacent edges. Several examples of this type of nets were described in the literature.[6—9] Tridentate ligands capable of forming such nets with metal ions can contain three identical donor groups (homotritopic ligands), one group, which differs from the other two groups by the donor binding site (nature, the size, and the charge; monoheterotopic ligands), or three different donor centers (heterotritopic ligands). Only examples of the use of homotritopic ligands[7—9] and monoheterotopic ligands[6,8] were given in the literature. Nets containing sets of metallamacrocycles, such as 8/16,[9] 12/28,[8] 20/44,[6] and 32/64,[7] were documented. A knowledge of the size of the macrocyclic cavities in nets is of importance for an understanding of the interpenetration of the adjacent nets and for the control of this process.

In our laboratory, we have started research on cross-conjugated dienones, which are produced by the double crotonic condensation of cyclic ketones with heteroaromatic aldehydes, as *exo*-polydentate ligands.[10—12] Dienones have a number of advantages over the available ligands. First, these compounds allow the control of the angle between the directions of the donor electron pairs of the nitrogen atoms by varying the size and nature of the central ring. This parameter is of importance for the design of various metal—ligand combinations (cyclic dimers, cyclooligomers, infinite chains, *etc.*). Second, dienones are photosensitive materials.[11] This fact can be used for varying both the geometry and the degree of conjugation in the ligand molecules. Third, in the case of piperidin-4-one derivatives, the structures of the resulting complex products can be changed by varying the nature of the substituent at the aliphatic nitrogen atom. Fourth, the nitrogen atom in piperidin-4-one derivatives can be involved in the coordination to metal ions, thus increasing the denticity of the ligands to three. In this case, such ligands can be assigned to monoheterotopic ligands (identical substituents in aromatic fragments) or heterotritopic ligands (different substituents in aromatic fragments).

In the present study, we investigated the structures of the reaction products of silver nitrate with two related *N*-alkyl-3,5-bis(3-pyridylmethylene)piperidin-4-ones (**1a,b**),[11] which differ from each other by the nature of the substituent at the aliphatic nitrogen atom.



1a,b

R = Me (**1a**), CH_2Ph (**1b**)

It was found that the coordination polymer that is formed in the reaction of the *N*-methyl derivative has a ladder-like structure, whereas the reaction with the *N*-benzyl analog gives rise to 4.8^2 nets in the crystal.

Results and Discussion

The reactions of ligands **1a** and **1b** with silver nitrate were carried out under the same conditions by the slow diffusion of a solution of the Ag^+ salt in acetonitrile into a solution of the ligand in chloroform. In both cases, the reaction mixtures were protected from the light. Large yellow crystals of the following products suitable for X-ray diffraction grew in reaction vessels during 7—10 days (Table 1): the solvate with one water molecule $^1{}_\infty\{[AgNO_3(\mathbf{1a})]\cdot H_2O\}$* (**2a**) and the solvate with one

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* Hereinafter, we employ the nomenclature, which has been suggested in the study:[13] the sign ∞ in front of the formula signifies a polymeric complex, and the number in front of the infinity sign represents the dimensionality of the structure.

Table 1. X-ray data collection and refinement statistics for compounds **2a** and **2b**

Parameter	**2a**	**2b**
Molecular formula	$C_{18}H_{20}Ag_1N_4O_{5.5}$	$C_{27}H_{25}Ag_1Cl_3N_5O_4$
M	488.25	697.74
Crystal dimensions/mm	0.20×0.10×0.10	0.10×0.10×0.05
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
a/Å	20.6397(8)	12.6176(6)
b/Å	10.0688(4)	11.3501(5)
c/Å	19.4947(8)	20.5011(10)
β/deg	90.946(1)	90.345(1)
V/Å^3	4050.8(3)	2935.9(2)
Z	8	4
d_{calc}/g cm^{-3}	1.601	1.579
μ/mm^{-1}	1.034	1.001
F(000)	1976	1408
Temperature/K	120(2)	110(2)
θ Scan range/deg	2.09—28.00	1.61—28.00
Number of measured reflections	14663	18233
Number of independent reflections (R_{int})	4872 (0.0323)	7076 (0.0573)
Number of variables	290	362
R_1 ($I \geq 2\sigma(I)$)	0.0544	0.0494
wR_2 (based on all reflections)	0.1843	0.1128
Goodness-of-fit on F^2	1.078	0.881
Residual electron density (max/min)/e Å^{-3}	2.244/–0.642	1.603/–0.459

chloroform molecule and one acetonitrile molecule $^{2}_{\infty}\{[AgNO_3(\mathbf{1b})]\ CHCl_3 \cdot CH_3CN\}$ (**2b**) in the case of ligands **1a** and **1b**, respectively. An analysis of the compositions of the powders obtained by drying the initially formed products showed that the molecules of solvation can easily be removed *in vacuo*.

According to the X-ray diffraction study, the aliphatic nitrogen atoms in crystalline products **2a** and **2b** (Fig. 2) are involved in the coordination, all three nitrogen atoms of the ligands being coordinated to three different silver ions. In turn, each silver ion is coordinated by two nitrogen atoms of the pyridine rings and one nitrogen atom of the piperidone fragment belonging to different ligands. Therefore, the formal requirements for the existence of T-shaped nets are met in the crystal structures of **2a** and **2b**. However, two-dimensional nets are observed only in prod-

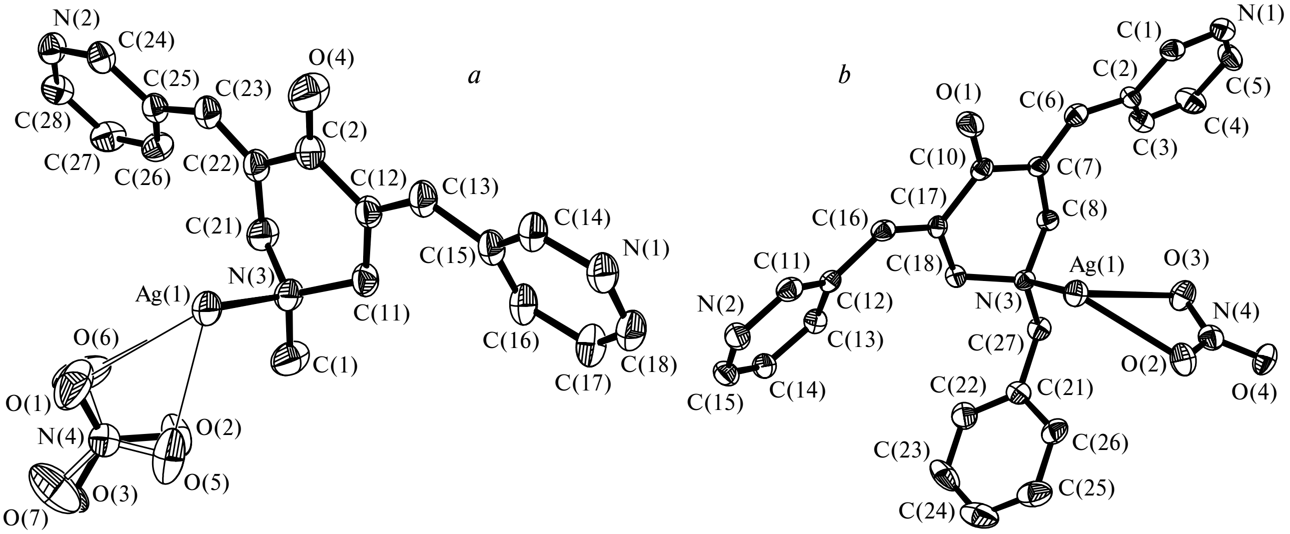

Fig. 2. Asymmetric fragments of complex **2a** (*a*) (water solvent molecules are omitted) and complex **2b** (*b*) (chloroform and acetonitrile solvent molecules are omitted).

Table 2. Selected bond lengths (*d*) and bond angles (ω) in compounds **2a** and **2b**

2a*		**2b****	
Parameter	Value	Parameter	Value
Bond	*d*/Å	Bond	*d*/Å
Ag(1)—N(2)$^{\#1}$	2.248(4)	Ag(1)—N(3)	2.291(3)
Ag(1)—N(1)$^{\#2}$	2.290(4)	Ag(1)—N(2)#1	2.310(3)
Ag(1)—N(3)	2.422(4)	Ag(1)—N(1)#2	2.414(3)
Ag(1)—O(1)	2.72(3)	Ag(1)—O(2)	2.507(3)
Ag(1)—O(2)	2.61(2)	Ag(1)—O(3)	2.868(3)
Ag(1)—O(5)	2.80(2)	O(1)—C(10)	1.213(5)
Ag(1)—O(6)	2.69(3)	C(10)—C(7)	1.490(5)
O(4)—C(2)	1.213(7)	C(10)—C(17)	1.495(5)
C(2)—C(12)	1.491(7)	C(6)—C(7)	1.333(5)
C(2)—C(22)	1.513(6)	C(16)—C(17)	1.327(5)
C(12)—C(13)	1.343(6)	C(7)—C(8)	1.507(5)
C(22)—C(23)	1.349(7)	C(17)—C(18)	1.508(5)
C(11)—C(12)	1.503(7)		
C(21)—C(22)	1.495(7)		
Angle	ω/deg	Angle	ω/deg
N(2)$^{\#1}$—Ag(1)—N(1)$^{\#2}$	128.24(15)	N(3)—Ag(1)—N(2)$^{\#1}$	133.33(11)
N(2)$^{\#1}$—Ag(1)—N(3)	119.50(14)	N(3)—Ag(1)—N(1)$^{\#2}$	124.84(11)
N(1)$^{\#2}$—Ag(1)—N(3)	98.28(14)	N(2)$^{\#1}$—Ag(1)—N(1)$^{\#2}$	88.82(11)
C(1)—N(3)—C(21)	108.8(4)	C(18)—N(3)—C(8)	109.0(3)
C(1)—N(3)—C(11)	108.1(4)	C(18)—N(3)—C(27)	109.9(3)
C(21)—N(3)—C(11)	109.4(4)	C(8)—N(3)—C(27)	108.5(3)
C(1)—N(3)—Ag(1)	113.7(4)	C(18)—N(3)—Ag(1)	109.4(2)
C(21)—N(3)—Ag(1)	108.3(3)	C(8)—N(3)—Ag(1)	105.4(2)
C(11)—N(3)—Ag(1)	108.3(3)	C(27)—N(3)—Ag(1)	114.5(2)
C(14)—N(1)—C(18)	118.0(4)	C(1)—N(1)—C(5)	116.8(4)
C(14)—N(1)—Ag(1)$^{\#2}$	123.8(4)	C(1)—N(1)—Ag(1)$^{\#2}$	117.5(3)
C(18)—N(1)—Ag(1)$^{\#2}$	118.2(3)	C(5)—N(1)—Ag(1)$^{\#2}$	125.3(3)
C(24)—N(2)—C(28)	116.9(4)	C(11)—N(2)—C(15)	117.3(4)
C(24)—N(2)—Ag(1)$^{\#1}$	120.8(3)	C(11)—N(2)—Ag(1)$^{\#3}$	113.8(3)
C(28)—N(2)—Ag(1)$^{\#1}$	122.0(3)	C(15)—N(2)—Ag(1)$^{\#3}$	121.5(3)

* The symmetry codes for **2a**: #1 $-x + 1/2$, $-y + 3/2$, $-z$; #2 $-x + 1$, y, $-z + 1/2$.

* The symmetry codes for **2b**: #1 $-x + 1$, $y + 1/2$, $-z + 3/2$; #2 $-x + 1$, $-y + 1$, $-z + 1$; #3 $-x + 1$, $y - 1/2$, $-z + 3/2$.

uct **2b** (*vide infra*). Selected bond lengths and bond angles for compounds **2a** and **2b** are given in Table 2.

In the structure of **2a**, the distances between the pyridine nitrogen atoms and the silver atom have similar values (Ag(1)—N(2B), 2.248(4) Å; Ag(1)—N(1A), 2.290(4) Å). The Ag(1)—N(3) distance for the aliphatic nitrogen atom is substantially longer (2.422(4) Å). The coordination polyhedron of the silver ion can be described as a distorted triangle (N(3)—Ag(1)—N(1A), 98.3(1)°; N(3)—Ag(1)—N(2B), 119.5(1)°; N(1A)—Ag(1)—N(2B), 128.2(1)°). The deviation of the silver atom from the mean plane passing through the donor nitrogen atoms (0.495(2) Å) is caused by the additional coordination of the disordered bidentate nitrate anion (Ag—O distances are in a range of 2.61(2)—2.80(2) Å).

In complex **2b**, the distance between one of the pyridine nitrogen atoms and the silver atom is nearly equal to the distance between the metal atoms and the aliphatic nitrogen atom (Ag(1)—N(2B), 2.310(3) Å; (Ag(1)—N(3), 2.291(3) Å), whereas the Ag(1)—N(1A) distance between another pyridine nitrogen atom and the metal atom is substantially longer (2.414(3) Å). The coordination polyhedron of the silver ion can also be described as a distorted triangle (N(3)—Ag(1)—N(1A), 124.8(1)°; N(3)—Ag(1)—N(2B), 133.3(1)°; N(1A)—Ag(1)—N(2B), 88.8(1)°). As in the structure of compound **2a**, the deviation of the silver atom from the mean plane passing through three donor nitrogen atoms (0.468(2) Å) in **2b** is attributed to the additional coordination by the bidentate nitrate anion (Ag(1)—O(2), 2.507(3) Å; Ag(1)—O(3), 2.868(3) Å).

In the case of *N*-methyl ligand **1a**, interactions between the complementary constituents give rise to polymeric structures in the crystals of product **2a** (Fig. 3).

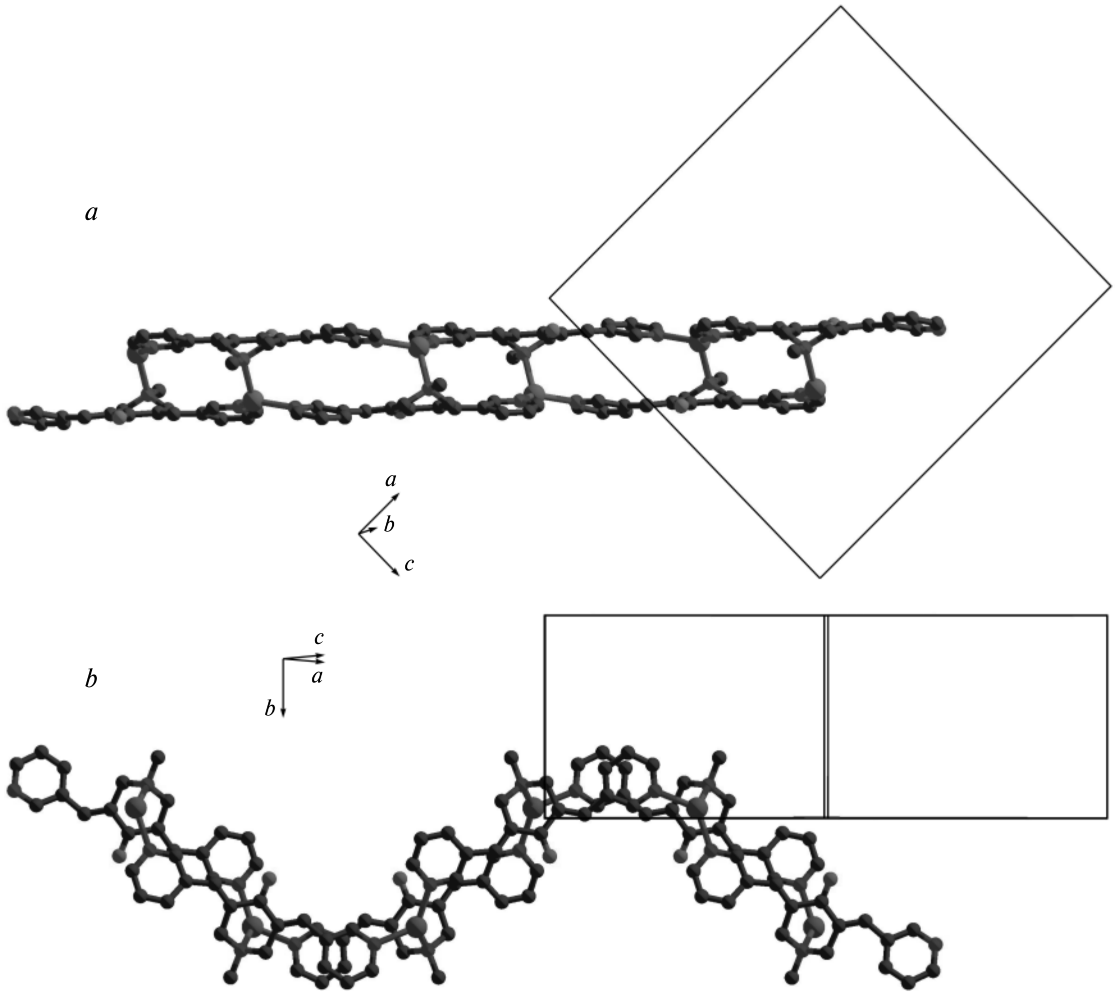

Fig. 3. Fragments of the crystal structure of complex **2a**: (*a*) the view of the double chain along the crystallographic *b* axis; (*b*) the top view of the double chain. The hydrogen atoms and the water solvent molecules are omitted.

These structures can topologically be assigned to ladder-like structures (Fig. 3, *a*).

The mutual arrangement of the zigzag double chains in the crystal structure of **2a** gives rise to infinite channels running along the crystallographic *c* axis (Fig. 4). The channels are occupied by disordered water solvent molecules. Apparently, these channels (provided that the integrity of the structure is retained upon the removal

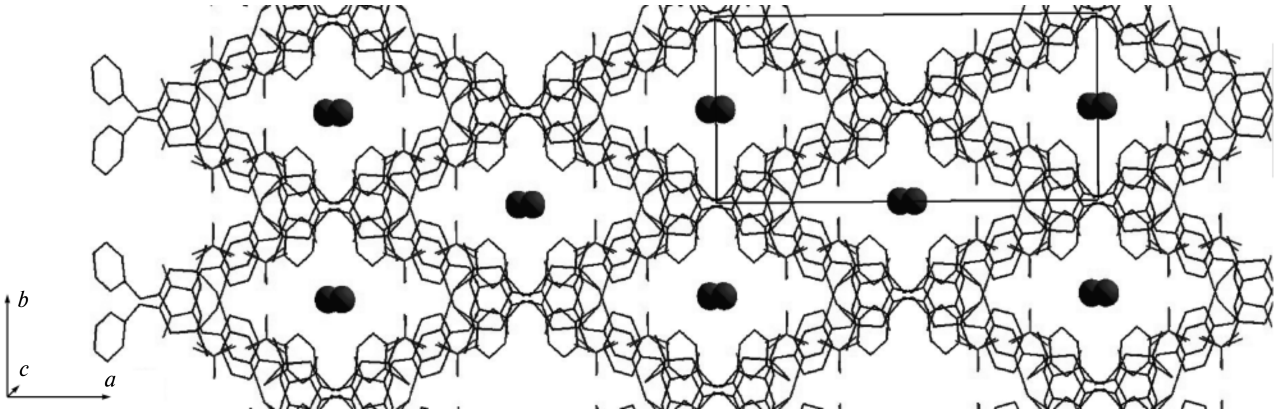

Fig. 4. Crystal structure of **2a** projected along the crystallographic *c* axis. The oxygen atoms of the water solvent molecules are represented as spheres. The hydrogen atoms are omitted.

of water molecules) can be filled with other guest molecules.

In the case of *N*-benzyl ligand **1b**, a two-dimensional network structure is observed in the crystals of product **2b** (Fig. 5). In the crystal structure, the layers are arranged one above another in an —AA— fashion. There are one chloroform solvent molecule and one acetonitrile solvent molecule per silver atom. The solvent molecules are located between the layers of the complex molecules.

The topological analysis of bonding between the Ag centers showed that 4.8^2 nets of the second type are present in the crystal structure of **2b** (see Fig. 1, *c*), and metallamacrocycles of dimensions 16/40 are formed.

The topology of the structures of products **2a** and **2b** is schematically represented in Fig. 6, which shows that the structural motifs are formed by different combinations of the 16-membered metallamacrocyclic fragments $[AgL]_2$. Apparently, the aggregate growth in solution occurs with the involvement of these building blocks. This mechanism should also involve solvent molecules in the crystal growth step. Investigations aimed at elucidating the mechanism of formation of coordination polymers in solution are presently underway.

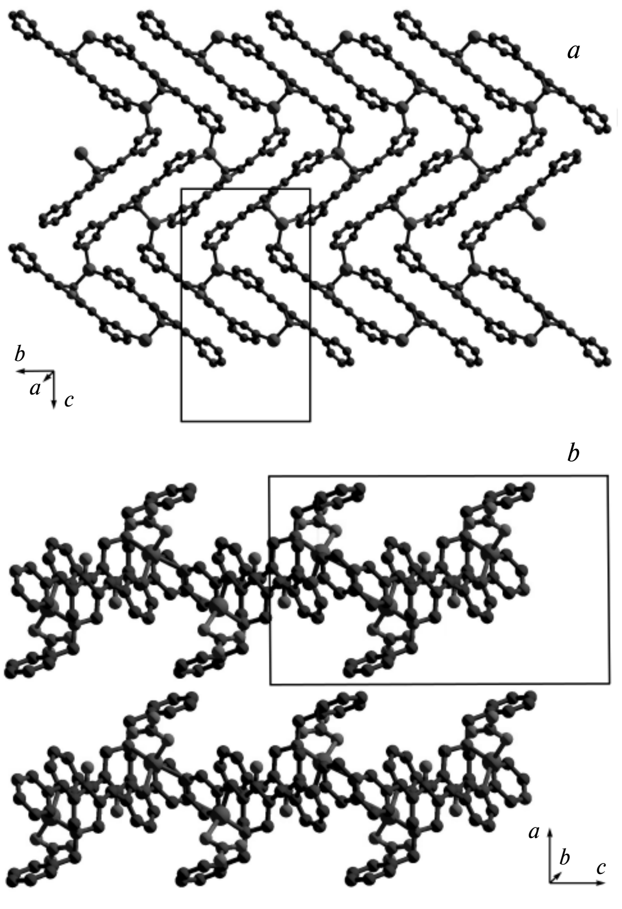

Fig. 5. Crystal structure of complex **2b**: (*a*) a two-dimensional network viewed along the crystallographic *a* axis (nitrate anions and the benzyl groups are omitted); (*b*) the —AA— fragment of the layered structure of **2b** viewed along the crystallographic *b* axis. The hydrogen atoms and the chloroform and acetonitrile solvent molecules are omitted.

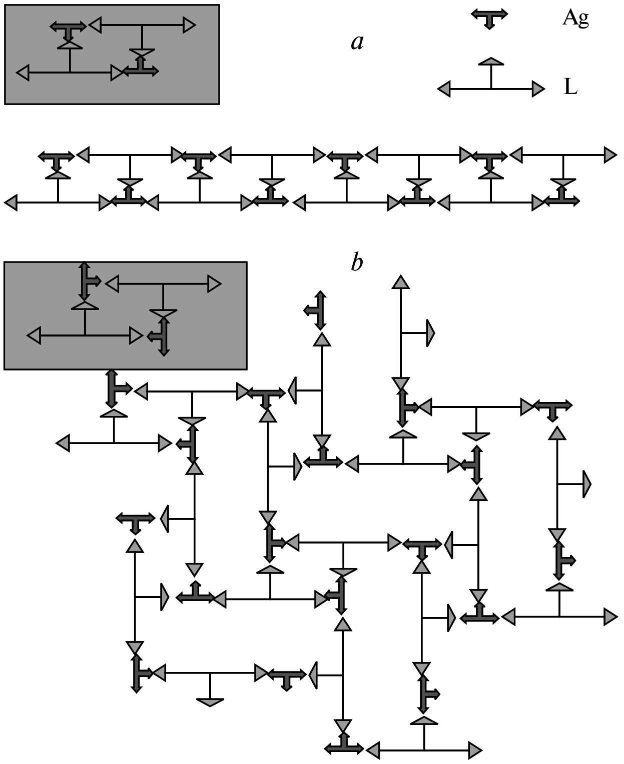

Fig. 6. Schematic representation of the formation of the structural motifs in the crystal structures of complexes **2a** (*a*) and **2b** (*b*) from the [2+2]-metallamacrocyclic intermediate.

To summarize, we synthesized and structurally characterized the previously unknown reaction products of silver nitrate with related monoheterotopic ligands derived from 3,5-bis(3-pyridylmethylene)piperidin-4-one. In both products, the aliphatic nitrogen atoms are involved in the coordination, all three nitrogen atoms of the ligands being coordinated to three different silver ions. In turn, each silver ion is coordinated by two nitrogen atoms of the pyridine ring and one nitrogen atom of the piperidine ring belonging to different ligands. The crystal structures of the complexes are different. In the structure of the *N*-methyl derivative, there are infinite ladder-type chains consisting of 16-membered metallamacrocycles as monomeric building blocks, whereas two-dimensional 4.8^2-type nets consisting of 16- and 40-membered metallamacrocycles are present in the crystal structure of the *N*-benzyl derivative.

Experimental

The IR absorption spectra were recorded on a Bruker instrument in KBr pellets. The elemental analysis was performed on a Carlo Erba ER-20 instrument. Ligands **1a** and **1b** were synthesized according to a procedure described earlier.[11]

Synthesis of silver complexes with dienones (general procedure). Acetonitrile (3 mL) was added dropwise to a solution of the ligand (0.036 mmol) in dichloromethane (5 mL) (**1a**, 0.0104 g) or chloroform (**1b**, 0.0132 g) until the mixture was separated into two phases. Then a solution of an equivalent amount of silver nitrate (0.036 mmol, 0.0061 g) in acetonitrile (5 mL) was added dropwise to the two-phase system. The resulting three-phase system was closed to protect from the light and kept over a period of time sufficient for the formation of crystalline products (generally for 3—7 days). The latter were separated by filtration and washed with chloroform, dichloromethane, and a small amount of acetonitrile. To achieve an agreement between the analytical and spectroscopic data, the samples were dried at room temperature using a water-jet vacuum pump.

Reaction of silver(I) nitrate with *N*-methyl-3,5-bis[(*E*)-(3-pyridyl)methylidene]piperidin-4-one (1a). The reaction afforded yellow single crystals of **2a** with the composition $[(\mathbf{1a})\cdot(AgNO_3)\cdot(H_2O)]$ (X-ray diffraction data). The drying *in vacuo* gave a powder with m.p. 194—196 °C (with decomp.). IR, ν/cm^{-1}: 1673 m (C=O), 1615 s (C=C), 1384 s (NO_3). Found (%): C, 46.71; H, 3.32; N, 11.66. $[(C_{18}N_3H_{17}O)(AgNO_3)]$. Calculated (%): C, 46.87; H, 3.71; N, 12.15.

Complex of silver(I) nitrate with *N*-benzyl-3,5-bis[(*E*)-(3-pyridyl)methylidene]piperidin-4-one (2b). The reaction afforded yellow single crystals of **2b** with the composition $[(\mathbf{1b})\cdot(AgNO_3)\cdot(CHCl_3)\cdot(CH_3CN)]$ (X-ray diffraction data). The drying *in vacuo* gave a powder with m.p. 176—177 °C (with decomp.). IR, ν/cm^{-1}: 1673 m (C=O), 1621 s (C=C), 1384 m (NO_3). Found (%): C, 53.44; H, 3.68; N, 10.21. $[(C_{24}H_{21}N_3O)(AgNO_3)]$. Calculated (%): C, 53.65; H, 3.94; N, 10.43.

X-ray diffraction study. The experimental X-ray diffraction intensities for compounds **2a** and **2b** were measured on an automated Bruker SMART diffractometer using graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å). Absorption corrections were applied based on the intensities of equivalent reflections.[14] The structures were solved by direct methods (SHELX-86).[15] All nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method based on F^2 (SHELXL-97).[16] In the structure of **2a**, the nitrate anion is disordered over two positions with occupancies of 0.54/0.46. One of the water solvent molecules is also disordered over two equivalent positions in the vicinity of the crystallographic inversion center. In both structures, all hydrogen atoms were positioned geometrically and refined using a riding model. The high residual electron density for the structure of **2a** is attributed, on the one hand, to a poor quality of the crystals and, on the other hand, to the presence of a large number of disordered fragments. The X-ray data collection and refinement statistics for compounds **2a** and **2b** are given in Table 1.

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