Synthesis and molecular structure of the cobalt(II) chloride complex with bis(α-pyridyl)-substituted bispidinoaza-14-crown-4*

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The reaction of cobalt(II) chloride with bis(benzo)bispidinoaza-14-crown-4 (**L**) containing two α-pyridyl substituents affords complex $[Co(L)(H_2O)][CoCl_4]$ (**1**). The structure of complex **1** was determined by X-ray diffraction analysis. In structure **1**, molecule **L** is coordinated to the neutral Co(1) atoms as an *N*,*N*,*N*,*N*-tetradentate-chelating ligand. The tetrachlorocobaltate dianion acts as a counterion. The coordination polyhedron of the Co atom in complex **1** is an octahedron, and that of the Co(2) atom in the anion is a tetrahedron. The coordination polyhedra of the Co atoms in complex **1** are linked by the bridging chlorine atom. In the octahedron of the Co(1) atom, two five-membered and two six-membered nonplanar chelate metallocycles, which are conjugated with each other along the Co(1)—N(1) and Co(1)—N(2) bonds, undergo ring closure. All bond lengths of the Co(1) atom with the N atoms range from 2.098(4) to 2.228(5) Å, and the Co(2)—Cl bond lengths change from 2.233(2) to 2.331(2) Å. The longest Co(1)—Cl(4) bond (2.558(2) Å) is that with the metal ion. A molecule of complex **1** is stabilized by strong intramolecular hydrogen bonds involving the crown ether fragment.

Key words: cobalt(II) chloride, bis(α-pyridyl)bispidinoaza-14-crown ethers, coordination compound, X-ray diffraction analysis.

Considerable attention has been given during recent 10—15 years to the synthesis and study of the geometry (structure) and properties of coordination compounds, *viz*., transition metal ions with bispidine derivatives (3,7-diazabicyclo[3.3.1]nonane).[1] Researchers were especially interested in ligands of the first generation containing 2-pyridyl substituents in positions 2 and 4 of the bispidine ring. These substituents increase the dentate mode of the molecule from to three and four.[1—4] Lateral substituents, for instance, 3,4-diazacycloheptyl[5] or polypyridylmethyl,[6] were inserted to the nitrogen atoms of the amino groups of the bispidine ligands of the next generation, which made it possible to pre-organize the initial polydentate ligand.

In connection with the recent development[7—9] of the method for synthesis of the new group of bis(areno)aza-14-crowns-4-containing nitrogen heterocycles as subunits, it seems interesting to study the coordination ability of macrocycles, which contain the 14-crown-4 fragment in addition to the bispidine fragment and two α-pyridyl substituents.

In this work we present the results of the reaction of the polydentate ligand of the new type (**L**) with cobalt(II) chloride (Scheme 1). Complex **1** was synthesized by mixing hot solutions of **L** and cobalt(II) chloride (ratio $L : CoCl_2 \cdot 6H_2O = 1 : 2$) in acetone. The reaction mixture was stored at 20 °C for three days and then at −12 °C for one day. As a result, complex **1** was isolated from the solution as dark green crystals in 74% yield. The elemental analysis showed that this complex had the composition $[Co_2LCl_4H_2O]$.

Complex **1** was studied by X-ray diffraction analysis for unambiguous and detailed determination of its structure. It was found that complex **1** contained two cobalt atoms with different coordination environments, and the tetrachlorocobaltate dianion rather unexpectedly acts as a counterion (Fig. 1). In complex **1**, molecule **L** performs the structural function of the *N*,*N*,*N*,*N*-tetradentate ligand. This results in the formation of the environment of the Co(1) atom consisting of the five- and six-membered chelate metallocycles conjugated between each other along the Co(1)—N bonds. The coordination polyhedron (CP) of the Co(1) atom in the cation represents a slightly distorted octahedron. The Co(1) atom participates in coor-

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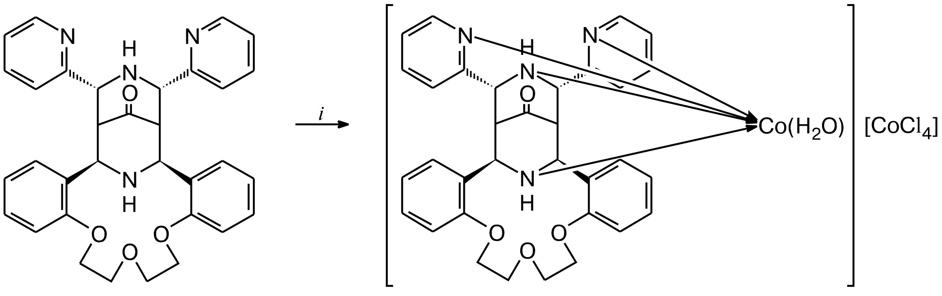
Scheme 1



L 1

i. $CoCl_2$, acetone, H_2O.

dination of the N(1) nitrogen atom occupying the axial vertex in the CP. The second axial vertex is occupied by the bridging Cl(4) atom without steric hindrances, due to which the angle between the axial N(1)—Co(1)—Cl(4) bonds (176.6(2)°) is close to the ideal value of 180°. At the same time, the base of the octahedron, whose vertices are occupied by the N(2) atoms of the bispidine cycle, the N(3) and N(4) atoms of the pyridine cycle, and the O(5) atom of the water molecule, has substantial angular distortions. For instance, the opposite Co(1)—N(3) and Co(1)—N(4) bonds are appreciably bent, being tightened by the chelate metallocycles conjugated along the Co(1)—N(2) bonds: the angle between the Co(1)—N(3) and Co(1)—N(4) bonds is 151.1(2)°, which is nearly 30° smaller than the ideal value. However, the second pair of the opposite Co(1)—O(5) and Co(1)—N(2) bonds is bent to a lesser extent, and the angle between these bonds is 172.2(2)°. The intracyclic angles N—Co—N have the smallest values in the CP and considerably differ from 90° (77.1(2) and 78.4(2)°). Linear distortions in the octahedron are less pronounced, although almost all bonds are longer than the bonds usual for the cobalt atom in the octahedral environment.[10] For example, the axial Co(1)—N(1) bonds with the donor center of the azamacrocycle (2.228(5) Å) and, correspondingly, Co(1)—Cl(4) with the bridging chlorine atom (2.558(2) Å) are noticeably elongated. The Co—N (2.098(5)—2.130(5) Å) and Co—O (1.998(4) Å) equatorial bonds are elongated to a lesser extent.

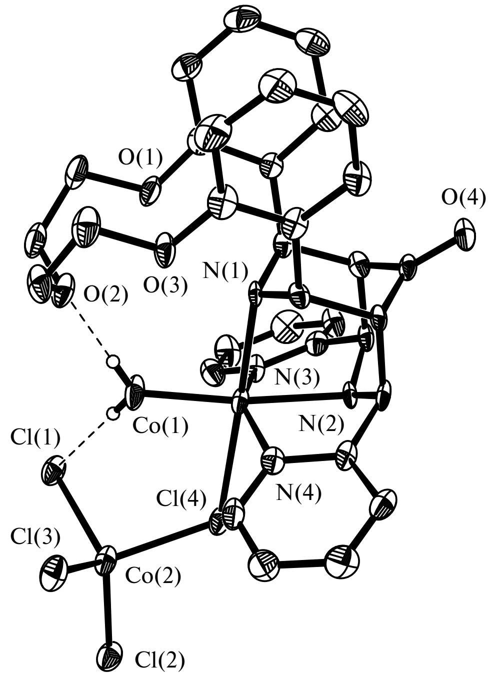


Fig. 1. Molecular structure of complex **1**. Only hydrogen atoms involved in hydrogen bonds (dashes) are shown. Non-hydrogen atoms are shown by ellipsoids of thermal vibrations with the 50% probability.

Intramolecular hydrogen bonds are significant for the stabilization of the polycyclic system of the coordination environment of the cobalt atom in complex **1** and the molecule as a whole. Among them the intramolecular hydrogen bond O(5)—H(1B)...O(2) is the strongest and most efficient (O(5)...O(2) 2.588(6) Å, H(1B)...O(2) 1.79 Å, angle O—H—O 179.8°). This intramolecular hydrogen bonds "pulls" the most remote O(2) oxygen atom of the macrocycle to the CP of the cobalt atom, due to which the deviation from the mean plane of the macrocycle of the O(2) atom (+1.036(5) Å towards the metal atom) noticeably exceeds the deviation of two other oxygen atoms from this plane (–0.185(5) for O(1) and –0.223(5) Å for O(3)). The addition of the N(1) atom to the cobalt atom also results in its substantial shift (by 1.366(5) Å) from the mean plane of the macrocycle (Δm = ±0.808 Å).

Thus, it was found that the first representative of the new type of ligands, *viz.*, aza-14-crown-4 **L**, can efficiently form coordination bonds with the cobalt cation through two sp^3-hybridized nitrogen atoms of the bispidine fragments involving two sp^2-hybridized nitrogen atoms of the pyridyl substituents. Three donor oxygen atoms of the crown ether moiety do not participate in the coordination

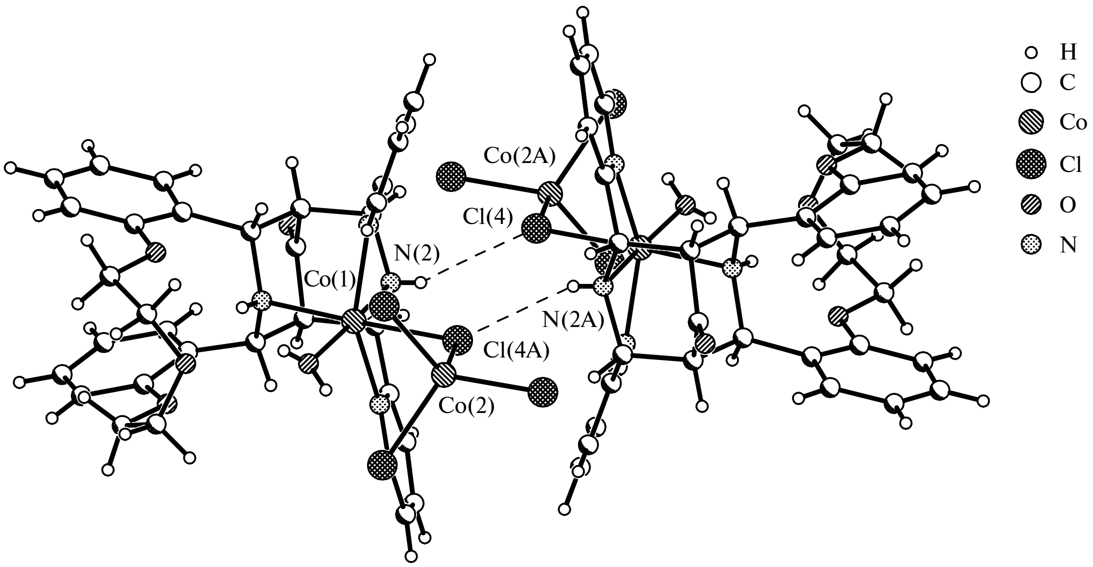


Fig. 2. Centrosymmetric dimers in structure **1**. Hydrogen bonds are shown by dashes.

of the cobalt cation but stabilizes the complex due to intramolecular hydrogen bonds.

In crystals the neighboring molecules form centrosymmetric dimers due to hydrogen bonds N—H...Cl (Fig. 2).

Experimental

The initial (16*R**,18*R**,20*S**,22*S**)-18,20-dipyridin-2-yl-6,7,9,10,17,18,19,20,21,22-decahydro-16*H*-16,22-epimino-17,21-methanodibenzo[*h*,*q*][1,4,7,13]trioxazacyclooctadecin-24-one (**L**) was synthesized using a known procedure.[9] Elemental analyses to C, H, N, and Cl were carried out on a Vario EL Cube analyzer (Elementar) at the NIOPIK State Scientific Center. The Co content was determined by energy dispersive analysis on a FEI Quanta 200 3D scanning electron microscope.

Complex [Co(L)(H_2O)][$CoCl_4$] (1). A weighed sample of the ligand (0.030 g, 0.06 mmol) was dissolved in acetone (15 mL) on heating and filtered through the paper filter. A solution of $CoCl_2 \cdot 6H_2O$ (0.026 g, 0.11 mmol) in acetone (5 mL) was prepared similarly. Hot solutions were mixed with stirring and kept at room temperature for 3 days, and then the reaction mixture with crystals formed was kept for 1 day more at −12 °C. The crystals of the complex were filtered off, washed with a minimum amount of acetone, and dried under reduced pressure to a constant weight. Product **1** was obtained as dark green crystals in a yield of 0.033 g (74%). A single crystal for X-ray diffraction analysis was selected from the isolated crystals. The remained crystals were powdered and dried *in vacuo*. Found (%): C, 47.87; H, 3.85; N, 6.63; Cl, 17.05; Co, 13.80. $C_{33}H_{34}Cl_4Co_2N_4O_5$. Calculated (%): C, 47.95; H, 4.12; N, 6.78; Cl, 17.19; Co, 14.27.

The X-ray diffraction study of compound **1** was performed on a Bruker SMART APEX II automated diffractometer at 150 K (Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator). The crystals of **1** ($C_{33}H_{34}Cl_4Co_2N_4O_5$, M = 826.30) are monoclinic, space group $C2/c$, a = 29.476(3) Å, b = 10.4664(11) Å, c = 27.144(3) Å, β = 113.962(2)°, V = 7652.5(14) Å^3, Z = 8, d_{calc} = 1.434 g cm^{-3}, μ(Mo$K\alpha$) = 1.189 mm^{-1}, F(000) = 3376. Intensities of 14 295 reflections (of which 6818 reflections were independent, R_{int} = 0.0894) were measured by the ω scan mode in the range $2.09° < \theta < 25.24°$ ($-35 \le h \le 30$, $-12 \le k \le 9$, $-22 \le l \le 32$). An absorption correction was implied on the basis of measurements of equivalent reflection intensities. The structure was solved by a direct method; all non-hydrogen atoms were refined by full-matrix anisotropic least squares for F^2 (SHELXTL).[11] All hydrogen atoms were placed in the calculated positions and refined using the riding model. The final values of the R factors were R_1 = 0.0771 for 3979 reflections with $I > 2\sigma(I)$ and wR_2 = 0.1535 over the whole data array using 433 refinement parameters. The goodness-of-fit was 1.001, and the minimum and maximum values of the different electron density were −1.015 and 0.953 e Å^{-3}, respectively. The structure contains large voids (~560 Å^3); however, they are not occupied by any solvate molecules, which is indicated by the low value of residual peaks (lower than 1 e Å^{-3}), and they are localized near the cobalt atoms rather than in the intermolecular space. The full set of crystallographic data for compound **1** was deposited with the Cambridge Crystallographic Data Centre (CCDC 806052).

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