ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2022, Vol. 48, No. 6, pp. 333–343. © Pleiades Publishing, Ltd., 2022.
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# Pseudomacrocyclic Bis(dianilineglyoximato)cobalt(III) Complex Cations: Synthesis and Structures

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Received November 24, 2021; revised December 21, 2021; accepted December 22, 2021

**Abstract**—Four coordination compounds (one of which exists as two polymorphs) are synthesized from cobalt(II) chloride hexahydrate, dianilineglyoxime ($DAnH_2$), and various pyridyl ligands (L): $[Co(DAnH)_2(L^1)_2]Cl\cdot 2dmf$ (**I**), $[Co(DAnH)_2(L^2)_2]Cl\cdot H_2O$ (**II**), $[Co(DAnH)_2(L^3)_2]Cl$ (**III** and **IV**), and $[Co(DAnH)_2(L^4)_2]Cl$ (**V**) ($L^1$ and $L^2$ are 3-methylpyridine and 4-methylpyridine, respectively; $L^3$ is ethyl nicotinate; and $L^4$ is *N*,*N*-diethylnicotinamide). The reaction proceeds via the oxidation of a methanol solution containing $CoCl_2$, $DAnH_2$, and L in a molar ratio of 1 : 2 : 2 with oxygen. The compositions and structures of the compounds are determined by elemental analysis, IR spectroscopy, and X-ray diffraction (CIF files CCDC nos. 2122240–2122244, respectively). Compounds **I**–**V** are ionic and formed by centrosymmetric complex cations $[Co(DAnH)_2(L)_2]^+$ and anions $Cl^-$. The mononuclear complex cations with the coordination mode $CoN_6$ are octahedral. Two monodeprotonated ligands $DAnH^-$ coordinate to the metal ion via the bidentate chelating mode and are bound to each other by two hydrogen bonds O–H···O, and two ligands L supplement the coordination polyhedron of the central atom. The components in the crystals are mainly joined by intermolecular hydrogen bonds.

**Keywords:** cobalt(III) complexes, dianilineglyoxime, pyridine derivatives, IR spectra, X-ray diffraction

**DOI:** 10.1134/S1070328422060070

## INTRODUCTION

The beginning of studying transition metal dioximates is related to the first works of L.A. Chugaev [1, 2]. The complexes with diverse dioximes and dioximates can be used in both inorganic, organic, and analytical chemistry and biological, medical, and industrial chemistry [3–10]. The studies in recent decades were associated with the use of these compounds for hydrogen generation from water using visible light [11] primarily by the electrocatalytic method [12, 13] and then photochemically [14, 15]. The predominant part of the studies is related to symmetric dioximes/dioximates [3], although there are studies devoted to asymmetric dioximes [16–18]. In the recent time, serious attention was given to the polynuclear metal complexes due to their role in certain biological systems and potential use as multielectron redox catalysts [19]. Although the binuclear and trinuclear complexes with these ligands were mainly prepared by the coordination via the oxime oxygen atom [20–22], the polynuclear complexes based on dioximes can be synthesized using additional bridging ligands [23–27] and by the modification of dioximes condensing them with various organic molecules bearing additional donor centers [28, 29].

The exclusive stability and unique electronic properties of bis(dioximates) can be explained by their structure, which is stabilized by intramolecular hydrogen bonds leading to the formation of pseudomacrocycles [30–32].

We have previously synthesized the Ni(II), Zn(II), and Mn(II) complexes with dianilineglyoxime [27, 28]. The results of studying the reactions of the cobalt salts with this modified dioxime and various additional organic ligands based on the pyridine derivatives are presented in this work. Such pyridine derivatives as 3-methylpyridine and 4-methylpyridine ($L^1$ and $L^2$, respectively), ethyl nicotinate ($L^3$), and *N*,*N*-diethylnicotinamide ($L^4$) were used as additional ligands. These reactions gave four compounds (one of which exists as two polymorphs) that crystallized in space groups of different crystal systems: $[Co(DAnH)_2(L^1)_2]Cl\cdot 2dmf$ (**I**), $[Co(DAnH)_2(L^2)_2]Cl\cdot H_2O$ (**II**), $[Co(DAnH)_2(L^3)_2]Cl$ (**III** and **IV**), and $[Co(DAnH)_2(L^4)_2]Cl$ (**V**).

## EXPERIMENTAL

Commercial reagents and solvents (reagent grade) were used as received for the syntheses. Dianilineglyoxime was synthesized by the condensation of dichloroglyoxime with aniline using a described procedure [33].

**Synthesis of $[Co(DAnH)_2(L^1)_2]Cl·2dmf$ (I).** Dianilineglyoxime (0.54 g, 0.2 mol) was dissolved in dimethylformamide (dmf) (20 mL) to form solution 1. Cobalt(II) chloride hexahydrate (0.24 g, 0.1 mol) was dissolved in methanol (20 mL) (solution 2). Both solutions were mixed on stirring, after which the reaction mixture turned red. γ-Picoline (0.2 mL, 0.2 mol) was added in 10 min, and the color of the reaction mixture changed to dark brown. The air was bubbled through the solution for 2 h to oxidize cobalt. The solution was filtered and left to stay at room temperature for crystallization. After 20 days, dark brown cubic crystals suitable for X-ray diffraction (XRD) formed in the solution. The yield was 0.41 g (~43%).

For $C_{46}H_{54}N_{12}O_6ClCo$

| | | | | |
|---|---|---|---|---|
| Anal. calcd., % | C, 57.23 | H, 5.64 | N, 17.41 | Co, 6.10 |
| Found, % | C, 57.20 | H, 5.66 | N, 17.43 | Co, 6.09 |

IR (ν, $cm^{-1}$): 3391 s.br, 3226 s, 3198 s, 3147 s, 3095 s, 3020 m, 2956 m, 2936 sh, 1654 vs, 1608 sh, 1595 sh, 1572 vs, 1522 m, 1494 s, 1455 sh, 1445 m, 1418 m, 1390 s, 1355 vw, 1316 m, 1291 vw, 1248 s, 1227 s, 1178 w, 1156 vw, 1103 s, 1084 m, 1059 s, 1029 sh, 1001 w, 979 vw, 950 w, 915 m, 892 vw, 883 vw, 853 vw, 842 vw, 825 w, 803 m, 747 s, 698 w, 686 m, 662 m, 620 m, 535 m, 489 m, 419 w.

**Synthesis of $[Co(DAnH)_2(L^2)_2]Cl·H_2O$ (II)** was carried out according to a procedure similar to that for compound **I** using β-picoline instead of γ-picoline. Dark brown cubic crystals suitable for XRD formed in 16 days. The yield was 0.38 g (~45%).

For $C_{40}H_{42}N_{10}O_5ClCo$

| | | | | |
|---|---|---|---|---|
| Anal. calcd., % | C, 57.38 | H, 5.06 | N, 16.73 | Co, 7.04 |
| Found, % | C, 56.75 | H, 5.17 | N, 16.57 | Co, 6.95 |

IR (ν, $cm^{-1}$): 3360 s, 3220 s, 3143 w, 3083 s, 2996 s, 2952 m, 1657 sh, 1639 s, 1617 vs, 1570 vs, 1508 m, 1494 vs, 1441 s, 1380 m, 1345 w, 1310 m, 1244 s, 1229 m, 1214 s, 1081 sh, 1066 s, 1033 s, 1001 m, 973 vw, 953 vw, 936 vw, 916 w, 887 vw, 812 s, 787 sh, 749 s, 720 w, 691 s, 511–500 w.br.

**Synthesis of $[Co(DAnH)_2(L^3)_2]Cl$ (III)** was carried out according to a procedure similar to that for compound **I** using ethyl nicotinate instead of γ-picoline and without dmf. Dark brown cubic crystals suitable for XRD formed in 12 days. The yield was 0.43 g (~46%).

For $C_{44}H_{44}N_{10}O_8ClCo$

| | | | | |
|---|---|---|---|---|
| Anal. calcd., % | C, 56.50 | H, 4.74 | N, 14.98 | Co, 6.30 |
| Found, % | C, 56.47 | H, 4.81 | N, 14.91 | Co, 6.28 |

IR (ν, $cm^{-1}$): 3242 m, 3200 m, 3147 m, 3090 s, 3008 s, 2960 m, 1716 s, 1613 sh, 1571 vs, 1526 s, 1492 vs, 1445 s, 1391 w, 1367 m, 1337 m, 1313 sh, 1287 vs, 1246 sh, 1227 s, 1175 m, 1133 m, 1119 m, 1083 m, 1059 s, 1010 m, 949 m, 918 m, 891 m, 858 m, 824 w, 804 w, 791 w, 742 vs, 708 w, 686 s, 660 w, 625 m, 581 w, 569 w, 538 m, 490 s, 427 vw.

**Synthesis of $[Co(DAnH)_2(L^3)_2]Cl$ (IV)** was carried out according to a procedure similar to that for compound **III** using cobalt(II) thiocyanate trihydrate instead of cobalt(II) chloride. A brown precipitate formed on stirring and disappeared upon the addition of 3 droplets of concentrated HCl. The resulting solution was filtered and slowly evaporated in air. Dark brown cubic crystals suitable for XRD formed in 13 days. The yield was 0.38 g (~41%).

For $C_{44}H_{44}N_{10}O_8ClCo$

| | | | | |
|---|---|---|---|---|
| Anal. calcd., % | C, 56.50 | H, 4.74 | N, 14.98 | Co, 6.30 |
| Found, % | C, 56.58 | H, 4.83 | N, 14.99 | Co, 6.31 |

IR (ν, $cm^{-1}$): 3241 m, 3200 m, 3146 m, 3090 m, 3007 m, 2962 m, 1717 vs, 1614 m, 1574 vs, 1528 s, 1492 s, 1445 m, 1392 w, 1367 m, 1337 w, 1326 vw, 1285 vs, 1247 m, 1227 m, 1195 w, 1174 m, 1132 m, 1116 m, 1086 m, 1059 m, 1042 m, 1025 m, 1010 m, 950 m, 918 m, 891 m, 882 vw, 856 m, 838 vw, 824 w, 804 w, 790 w, 741 vs, 686 m, 659 w, 625 m, 581 w, 536 m, 514 w, 490 m, 441 vw, 427 vw, 415 vw.

**Synthesis of $[Co(DAnH)_2(L^4)_2]Cl$ (V)** was carried out according to a procedure similar to that for compound **III** using *N*,*N*-diethylnicotinamide (nicetamide) instead of ethyl nicotinate. Dark brown cubic crystals suitable for XRD formed in 10 days. The yield was 0.44 g (~44%).

For $C_{48}H_{54}N_{12}O_6ClCo$

| | | | | |
|---|---|---|---|---|
| Anal. calcd., % | C, 58.27 | H, 5.50 | N, 16.99 | Co, 5.96 |
| Found, % | C, 58.29 | H, 5.61 | N, 16.95 | Co, 5.97 |

IR (ν, $cm^{-1}$): 3412 m.br, 3230 m, 3190 m, 3134 m, 3086 m, 3059 w, 2987 s, 2948 m, 1634 vs, 1609 vs, 1591 vs, 1571 vs, 1523 m, 1491 s, 1471 s, 1454 sh, 1439 vs, 1430 m, 1383 m, 1363 m, 1347 m, 1314 m, 1291 m, 1240 m, 1220 m, 1203 sh, 1189 sh, 1174 sh, 1109 m, 1081 m, 1058 m, 1041 m, 1031 m, 983 vw, 959 w, 940 sh, 932 w, 913 w, 877 m, 823 m, 786 w, 762 w, 753 s, 728 m, 710 m, 693 s, 659 w, 618 w, 598 w, 577 w, 562 w, 526 m, 487 m.

The compositions of compounds **I**–**V** were determined by elemental analysis and IR spectroscopy. The structures of compounds **I**–**V** were determined by single-crystal XRD. IR spectra were recorded on an FT-IR Perkin-Elmer Spectrum 100 instrument in Nujol in ranges of 4000–400 $cm^{-1}$ and 4000–650 $cm^{-1}$ (for the ATR mode).

**XRD.** Experimental data were obtained at a low temperature for compounds **I** and **II** and at room temperature for other compounds on Xcalibur E diffractometers ($MoK_\alpha$ radiation, $\lambda = 0.71073$ Å, graphite monochromator, ω scan mode). Unit cell parameters were refined with the full set of experimental data. The crystal structures were solved by direct methods and refined by least squares in the anisotropic full-matrix variant for non-hydrogen atoms (SHELX-97) [34]. Compound **II** crystallizes as a two-block non-merohedral twin, whose components were determined during data integration using the CrysAlis program and refined using the HKLF 5 procedure in the SHELXL program. The positions of some hydrogen atoms were calculated geometrically, and their Fourier syntheses were determined in part and isotropically refined by the rigid body model. The crystallographic data and experimental characteristics for compounds **I**–**V** are presented in Table 1. Selected interatomic distances and bond angles in the coordination polyhedra of compounds **I**–**V** are listed in Table 2. The geometric parameters of hydrogen bonds are given in Table 3.

The positional and thermal parameters for compounds **I**–**V** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2122240–2122244, respectively; deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

## RESULTS AND DISCUSSION

The reactions of the cobalt(II) salts with dianilineglyoxime and various additional pyridine derivatives in air afford four new compounds (one of which exists as two polymorphs) that crystallize in space groups of different crystal systems. The crystal structures were determined for five compounds: $[Co(DAnH)_2(L^1)_2]Cl\cdot 2dmf$ (**I**), $[Co(DAnH)_2(L^2)_2]Cl\cdot H_2O$ (**II**), $[Co(DAnH)_2(L^3)_2]Cl$ (**III** and **IV**), and $[Co(DAnH)_2(L^4)_2]Cl$ (**V**). All synthesized compounds are ionic and mainly formed by the complex cations $[Co(DAnH)_2L_2]^+$ and anions $Cl^-$. Crystallization molecules were found only in compounds **I** and **II**.

The IR spectra of the considered compounds exhibit many common absorption bands, since all the substances described contain the $[Co(DAnH)_2L_2]^+$ cation close in composition and structure (L is 3-methylpyridine, 4-methylpyridine, ethyl nicotinate, or *N*,*N*-diethylnicotinamide). The coordination polyhedra of Co(III) are octahedral in all compounds, and the differences in the contour of the spectra are mainly related to the nature of axial ligands and the presence of crystallization molecules of dmf (**I**) or water (**II**). A common group of absorption bands is observed in a range of 3400–2700 $cm^{-1}$: ~3242, ~3200, ~3146, ~3090, ~3008, and ~2960 $cm^{-1}$. They are assigned to different types of C–H stretching vibrations (aromatic rings, methyl and ethyl groups), ν(NH) stretching vibrations of dioxime, and possible overtones of some vibrations. The spectra of the considered compounds exhibit one of the most intense absorption bands of the spectrum: a broad complicated band in a range of 1615–1550 $cm^{-1}$, which is observed in the spectrum of dianilineglyoxime at 1595 $cm^{-1}$, also containing δ(NH) vibrations. The components of this complicated band are well resolved in the spectrum of complex **V** at 1609, 1591, and 1571 $cm^{-1}$. A particular band at 1634 $cm^{-1}$ refers to ν(C=N) of the oxime ligands [35]. The bands at 1609 and 1591 $cm^{-1}$ can be attributed to vibrations of the aromatic ring [35, 36], and the band at 1571 $cm^{-1}$ is assigned to δ(NH) vibrations [36]. The $\delta_{pl}$(C–H) vibrations of the 1-substituted benzene rings (five adjacent unsubstituted atoms) appear as three bands in ranges of 1181–1174, 1103–1089, and 1084–1001 $cm^{-1}$, and the $\delta_{nonpl}$(C–H) vibrations are observed as two very intense absorption bands in ranges of 753–742 and 693–686 $cm^{-1}$ [37]. The bands in ranges of 538–511 and 487–419 $cm^{-1}$ can be attributed to the ν(Co–N) vibrations [7].

The spectrum of complex **I** differs from the spectra of other compounds, because compound **I** contains both 4-methylpyridine (γ-picoline) as the coordinated ligand along the axial coordinate in the coordination polyhedron of the metal and crystallization molecules of dmf. As a result, the spectrum of compound **I** exhibits a strong band at 1654 $cm^{-1}$ caused by the ν(C=O) vibrations and absorption bands at 2960, 1455, and 1390 $cm^{-1}$ corresponding to $\nu_{as}(CH_3)$, $\delta_{as}(CH_3)$, and $\delta_s(CH_3)$, respectively [37]. The spectrum of compound **I** contains an absorption band at 1418 $cm^{-1}$ that corresponds to the $\delta_s(N–CH_3)$ vibrations and differs from vibrations of the $CH_3$ group linked with other atoms (C, O, P, S) [35]. The absorption band at 803 $cm^{-1}$ is also observed, which is characteristic of the $\delta_{nonpl}$(C–H) vibrations for the 4-substituted pyridine derivatives (two adjacent unsubstituted hydrogen atoms) [37]. The absorption band at 1316 $cm^{-1}$ is attributed to the ν(C–N) vibrations in amides [38]. It should be mentioned that no bands characteristic of dmf were observed when complex **I** was thoroughly washed with methanol and dried at 60°C after synthesis.

Compound **II** contains crystallization water molecules along with dianilineglyoxime-3-methylpyridine (β-picoline) and, hence, the IR spectrum exhibits absorption bands at 3360 and 1617 $cm^{-1}$ caused by the ν(OH) and δ(OH) vibrations, respectively, and bands

**Table 1.** Crystallographic data, experimental characteristics, and structure refinement parameters for compounds **I–V**

| Parameters | Value | | | | |
|---|---|---|---|---|---|
| | **I** | **II** | **III** | **IV** | **V** |
| Empirical formula | $C_{46}H_{54}N_{12}O_6ClCo$ | $C_{40}H_{42}N_{10}O_5ClCo$ | $C_{44}H_{44}N_{10}O_8ClCo$ | $C_{44}H_{44}N_{10}O_8ClCo$ | $C_{48}H_{54}N_{12}O_6ClCo$ |
| *FW* | 965.39 | 837.21 | 935.27 | 935.27 | 989.41 |
| Temperature, K | 160.2(5) | 160.0(1) | 293(2) | 293(2) | 293(2) |
| Crystal system | Triclinic | Monoclinic | Monoclinic | Trigonal | Monoclinic |
| Space group | $P\bar{1}$ | $P2/c$ | $I2/c$ | $R\bar{3}$ | $P2/n$ |
| $a$, Å | 9.2438(13) | 11.9552(8) | 13.0432(6) | 23.2162(12) | 9.0962(5) |
| $b$, Å | 10.9459(15) | 9.1175(5) | 16.0285(8) | 23.2162(12) | 12.6758(9) |
| $c$, Å | 12.2358(17) | 18.9469(14) | 22.7795(12) | 21.2789(12) | 20.5932(14) |
| $\alpha$, deg | 95.622(11) | 90 | 90 | 90 | 90 |
| $\beta$, deg | 105.473(12) | 105.503(8) | 102.944(5) | 90 | 91.417(5) |
| $\gamma$, deg | 102.045(12) | 90 | 90 | 120 | 90 |
| $V$, Å$^3$ | 1151.3(3) | 1990.1(2) | 4641.4(4) | 9932.6(12) | 2373.7(3) |
| $Z$ | 1 | 2 | 4 | 9 | 2 |
| $\rho_{calc}$, g/cm$^3$ | 1.392 | 1.397 | 1.338 | 1.407 | 1.384 |
| $\mu$, mm$^{-1}$ | 0.493 | 0.556 | 0.489 | 0.514 | 0.481 |
| $F(000)$ | 506 | 872 | 1944 | 4374 | 1036 |
| Crystal sizes, mm | 0.25 × 0.22 × 0.08 | 0.20 × 0.12 × 0.05 | 0.20 × 0.17 × 0.08 | 0.26 × 0.22 × 0.10 | 0.50 × 0.08 × 0.05 |
| Range of $\theta$, deg | 1.75–25.50 | 2.23–25.03 | 2.98–25.05 | 2.87–25.24 | 3.34–25.24 |
| Index ranges | $-11 \le h \le 19$,<br>$-13 \le k \le 13$,<br>$-13 \le l \le 14$ | $-14 \le h \le 14$,<br>$-10 \le k \le 10$,<br>$-21 \le l \le 22$ | $-11 \le h \le 15$,<br>$-18 \le k \le 19$,<br>$-27 \le l \le 24$ | $-18 \le h \le 27$,<br>$-24 \le k \le 23$,<br>$-16 \le l \le 25$ | $-7 \le h \le 10$,<br>$-15 \le k \le 9$,<br>$-24 \le l \le 44$ |
| Number of measured/ independent reflections ($R_{int}$) | 9967/4283 (0.0408) | 3443/3443 | 8067/4081(0.0622) | 6835/3995(0.0551) | 8569/4266(0.0415) |
| Number of reflections with $I > 2\sigma(I)$ | 3634 | 2510 | 2194 | 2034 | 2824 |
| Completeness, % | 100.0 ($\theta = 25.24°$) | 98.7 ($\theta = 25.03°$) | 99.5 ($\theta = 25.05°$) | 99.6 ($\theta = 25.24°$) | 99.3 ($\theta = 25.05°$) |
| Number of refined parameters | 290 | 262 | 292 | 289 | 312 |
| GOOF | 1.005 | 1.001 | 1.002 | 1.001 | 1.005 |
| $R$ factors ($I > 2\sigma(I)$) | $R_1 = 0.0533$,<br>$wR_2 = 0.1344$ | $R_1 = 0.0536$,<br>$wR_2 = 0.1135$ | $R_1 = 0.0704$,<br>$wR_2 = 0.1147$ | $R_1 = 0.0745$,<br>$wR_2 = 0.1149$ | $R_1 = 0.0566$,<br>$wR_2 = 0.1108$ |
| $R$ factors (for all data) | $R_1 = 0.0635$,<br>$wR_2 = 0.1443$ | $R_1 = 0.0849$,<br>$wR_2 = 0.1274$ | $R_1 = 0.1440$,<br>$wR_2 = 0.1370$ | $R_1 = 0.1544$,<br>$wR_2 = 0.1393$ | $R_1 = 0.0962$,<br>$wR_2 = 0.1286$ |
| $\Delta\rho_{max}/\Delta\rho_{min}$, e Å$^{-3}$ | 0.625/–0.479 | 0.520/–0.560 | 0.459/–0.311 | 0.561/–0.396 | 0.508/–0.322 |

**Table 2.** Interatomic distances ($d$) and bond angles ($\omega$) in the coordination polyhedra of compounds **I–V***

| Bond | $d$, Å | | | | |
|---|---|---|---|---|---|
| | **I** | **II** | **III** | **IV** | **V** |
| Co(1)–N(1) | 1.895(2) | 1.905(3) | 1.895(3) | 1.894(3) | 1.893(2) |
| Co(1)–N(2) | 1.909(2) | 1.892(3) | 1.896(3) | 1.901(3) | 1.902(2) |
| Co(1)–N(5) | 1.967(2) | 1.967(3) | 1.961(3) | 1.977(4) | 1.972(3) |
| **Angle** | $\omega$, deg | | | | |
| | **I** | **II** | **III** | **IV** | **V** |
| N(1)Co(1)N(2) | 81.52(9) | 81.7(1) | 81.5(1) | 81.8(2) | 81.38(10) |
| N(1)Co(1)N(5) | 91.25(9) | 89.6(1) | 89.3(1) | 90.6(1) | 90.41(11) |
| N(1)Co(1)N(2)$^{\#1}$ | 98.48(9) | 98.3(1) | 98.5(1) | 98.2(2) | 98.62(10) |
| N(1)Co(1)N(5)$^{\#1}$ | 88.75(9) | 90.4(1) | 90.7(2) | 89.4(2) | 89.59(11) |
| N(2)Co(1)N(5) | 91.06(9) | 89.7(1) | 90.1(1) | 90.4(2) | 89.57(11) |
| N(2)Co(1)N(5)$^{\#1}$ | 88.94(9) | 90.3(1) | 89.9(1) | 89.6(2) | 90.43(11) |

Symmetry codes: $^{\#1}$ $-x + 1, -y + 1, -z + 1$ (**I**, **II**, **III**); $^{\#1}$ $-x + 5/3, -y + 4/3, -z + 4/3$ (**IV**); $^{\#1}$ $-x + 2, -y, -z + 1$ (**V**).

at 2952, 1465, and 1380 cm$^{-1}$ characteristic of the $\nu_{as}(CH_3)$, $\delta_{as}(CH_3)$, and $\delta_s(CH_3)$ vibrations, respectively, in 3-methylpyridine. Strong absorption bands at 812 and 749 cm$^{-1}$ assigned to the $\delta_{nonpl}$(CH) vibrations for the aromatic ring in the 3-substituted pyridine derivatives also appear in the spectrum: for the isolated unsubstituted hydrogen atom and for three adjacent unsubstituted hydrogen atoms, respectively [35].

Compounds **III** and **IV** have the same molecular structures and, therefore, the IR spectra are nearly identical. The $\nu$(C=O) vibrations of ethyl nicotinate appear as a strong band at 1716 cm$^{-1}$, whereas the $\nu$(C–O–C) vibrations appear as a stronger band at 1287 cm$^{-1}$ and a band at 1119 cm$^{-1}$ [35, 37]. The $\delta_{nonpl}$(C–H) vibrations of the heterocyclic ring appear at 891 cm$^{-1}$ for the single hydrogen atom and at 804 cm$^{-1}$ for three adjacent unsubstituted hydrogen atoms.

Compound **V** contains *N*,*N*-diethylnicotinamide that appears in the IR spectrum as the following characteristic absorption bands (cm$^{-1}$): 1634 $\nu$(C=O), 1471 $\delta_{as}(CH_3)$, 1383 $\delta_s(CH_3)$, and 1314 $\nu$(C–N) [36]. The absorption bands at 877 and 823 cm$^{-1}$ are also observed, which are characteristic of the $\delta_{as}$(C–H) vibrations, for three adjacent unsubstituted hydrogen atoms and for the isolated unsubstituted hydrogen atom, respectively [37].

Compound **I** crystallizes in the space group $P\overline{1}$ of the triclinic crystal system. Compounds **II**, **III**, and **V** crystallize in the space groups of the monoclinic crystal system, and compound **IV** crystallizes in $P\overline{3}$ (Table 1). In all centrosymmetric complex cations of compounds **I–V**, the coordination polyhedron of the cobalt atom is an octahedron formed by the donor atoms $N_6$: four nitrogen atoms belong to two coplanar bidentate dioximate monoanions arranged in the equatorial plane, and two nitrogen atoms belong to the pyridine derivatives that exist in the *trans*-axial positions (Figs. 1a–1e). The coplanar arrangement of the central fragments of the chelate ligands and metallic center is maintained by the pair of strong intramolecular hydrogen bonds O(1)–H···O(2) (Table 3). As a result, pseudomacrocycles of 14 atoms with four alternating five-membered chelate and six-membered cycles stabilized by hydrogen bonds are formed around the metal. The interatomic distances in the coordination polyhedra of the metal (Co–N(oxime) 1.892(4)–1.909(9), Co–N(py) 1.958(3)–1.973(3) Å (Table 2)) are consistent with the data for the structures of similar compounds [39–48]. The structure of the complex cation is more frequently stabilized additionally by weak intramolecular hydrogen bonds C–H···O in which the C(3) or C(7) atoms of the pyridine fragments act as donors and O(1) or O(2) of the oxime fragments are involved as acceptors (Table 3). Compound **I** exhibits a weak intramolecular hydrogen bond C–H···O between the phenyl rings and oxime oxygen atoms. The aromatic fragments of the bulky dioximate ligands are arranged relative to each other in a different way: in compounds **II**, **IV**, and **V** the angle between the corresponding planes is 62.3°, 70.9°, and 63.1°, whereas in compounds **I** and **III** this angle is 101.8° and 128.1°, respectively.

In compounds **I–V**, the complex cations and anions are joined by hydrogen bonds N–H···Cl formed by the donor NH groups of the organic ligands with the external chloride anions. The chains of alternating components can be distinguished in the structures of compounds **I–III** and **V**, whereas compound **IV** consists of the layers (Figs. 2–6). Since the coordi-

**Table 3.** Geometric parameters of intra- and intermolecular hydrogen bonds in the structures of compounds **I**–**V**

| Contact D–H···A | Distance, Å | | | Angle DHA, deg | Coordinates of atoms A |
|---|---|---|---|---|---|
| | (D–H) | (H···A) | (D···A) | | |
| **I** | | | | | |
| N(3)–H···Cl(1) | 0.88 | 2.62 | 3.112(2) | 117 | $x, y, z$ |
| N(4)–H···Cl(1) | 0.88 | 2.38 | 3.157(2) | 147 | $x, y, z$ |
| O(1)–H···O(2) | 0.84 | 1.71 | 2.521(3) | 160 | $-x + 1, -y + 1, -z + 1$ |
| C(3)–H···O(2) | 0.95 | 2.55 | 3.224(3) | 128 | $-x + 1, -y + 1, -z + 1$ |
| C(7)–H···O(2) | 0.95 | 2.52 | 3.257(3) | 135 | $x, y, z$ |
| C(26)–H···N(2) | 0.95 | 2.68 | 3.200(3) | 115 | $x, y, z$ |
| C(2*D*)–H(2)···Cl(1) | 0.98 | 2.91 | 3.818(4) | 154 | $x, y + 1, z$ |
| C(2*D*)–H···O(1) | 0.98 | 2.50 | 3.351(5) | 145 | $-x + 1, -y + 1, -z + 1$ |
| C(5*D*)–H···Cl(1) | 0.98 | 2.84 | 3.569(8) | 132 | $x, y + 1, z$ |
| **II** | | | | | |
| N(3)–H···Cl(1) | 0.88 | 2.43 | 3.241(4) | 153 | $x, y, z$ |
| N(4)–H···Cl(1) | 0.88 | 2.34 | 3.205(3) | 170 | $x, y, z$ |
| C(3)–H···O(1) | 0.95 | 2.54 | 3.218(5) | 129 | $x, y, z$ |
| C(3)–H···O(2) | 0.95 | 2.57 | 3.277(5) | 132 | $-x + 1, -y + 1, -z + 1$ |
| C(7)–H···O(2) | 0.95 | 2.52 | 3.222(5) | 130 | $x, y, z$ |
| O(1*w*)–H(1)···O(1) | 0.87 | 2.35 | 3.033(3) | 136 | $x, y, z$ |
| **III** | | | | | |
| N(3)–H···Cl(1) | 0.86 | 2.36 | 3.212(4) | 174 | $x, y, z$ |
| N(4)–H···Cl(1) | 0.86 | 2.33 | 3.179(4) | 168 | $x, y, z$ |
| O(1)–H···O(2) | 1.05 | 1.47 | 2.498(4) | 166 | $-x + 1, -y + 1, -z + 1$ |
| C(3)–H···O(2) | 0.93 | 2.49 | 3.187(5) | 132 | $-x + 1, -y + 1, -z + 1$ |
| C(7)–H···O(1) | 0.93 | 2.57 | 3.259(6) | 131 | $-x + 1, -y + 1, -z + 1$ |
| **IV** | | | | | |
| N(3)–H···Cl(1) | 0.67 | 2.62 | 3.213(4) | 149 | $x, y, z$ |
| N(4)–H···Cl(1) | 0.87 | 2.66 | 3.267(4) | 128 | $x, y, z$ |
| O(1)–H···O(2) | 1.13 | 1.38 | 2.490(4) | 166 | $-x + 5/3, -y + 4/3, -z + 4/3$ |
| C(3)–H···O(2) | 0.93 | 2.54 | 3.217(6) | 130 | $-x + 5/3, -y + 4/3, -z + 4/3$ |
| C(7)–H···O(1) | 0.93 | 2.59 | 3.231(6) | 127 | $-x + 5/3, -y + 4/3, -z + 4/3$ |
| C(7)–H···O(2) | 0.93 | 2.58 | 3.297(6) | 134 | $x, y, z$ |
| C(10)–H···Cl(3) | 0.96 | 2.94 | 3.815(11) | 152 | $x, y, z$ |
| C(10)–H···Cl(4) | 0.96 | 2.86 | 3.745(9) | 155 | $x, y, z$ |
| C(22)–H···Cl(4) | 0.93 | 2.93 | 3.69(7) | 141 | $x - 2/3, y - 1/3, -z + 1/3$ |
| **V** | | | | | |
| N(3)–H···Cl(1) | 0.86 | 2.44 | 3.286(3) | 170 | $x, y, z$ |
| N(4)–H···Cl(1) | 0.86 | 2.24 | 3.100(3) | 173 | $x, y, z$ |
| O(1)–H···O(2) | 0.85 | 1.65 | 2.481(3) | 164 | $-x + 2, -y, -z + 1$ |
| C(3)–H···O(2) | 0.93 | 2.44 | 3.183(4) | 137 | $-x + 2, -y, -z + 1$ |
| C(7)–H···O(2) | 0.93 | 2.48 | 3.230(4) | 137 | $x, y, z$ |
| C(10)–H···O(1) | 0.96 | 2.64 | 3.254(4) | 122 | $-x + 5/2, y - 1/2, -z + 1/2$ |

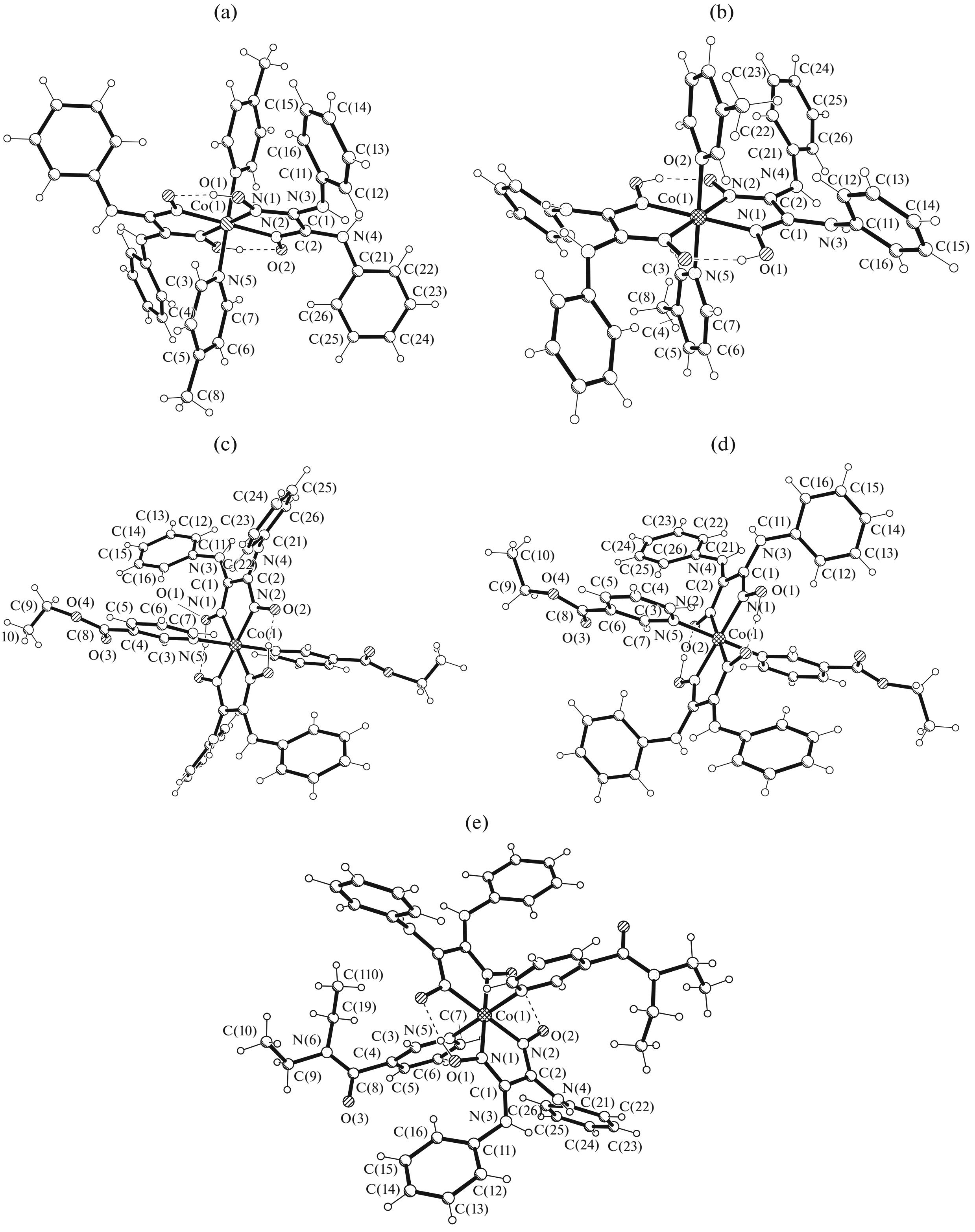

**Fig. 1.** Structures of the complex cations in compounds **I**–**V** (a–e) with notation of crystallographically independent atoms.

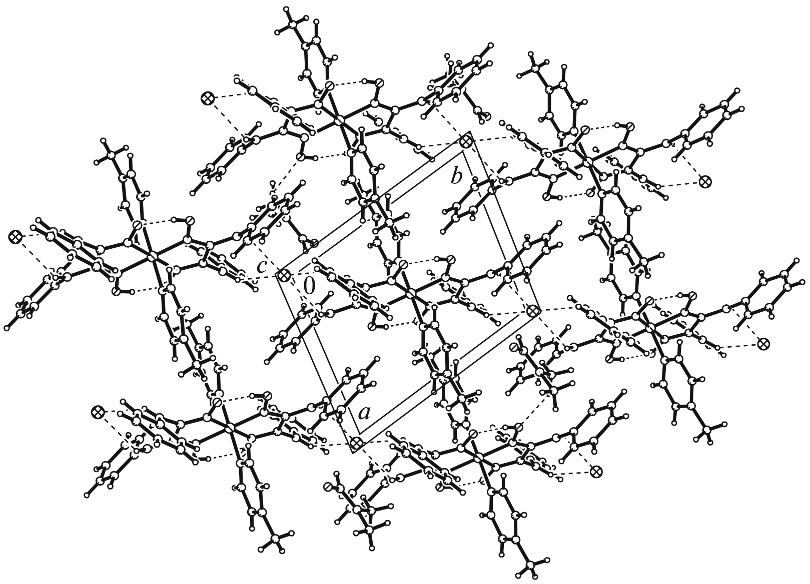

**Fig. 2.** Fragment of the crystal structure of compound **I** with chains of the alternating Co(III) complex cations and chloride anions and bonded dmf molecules.

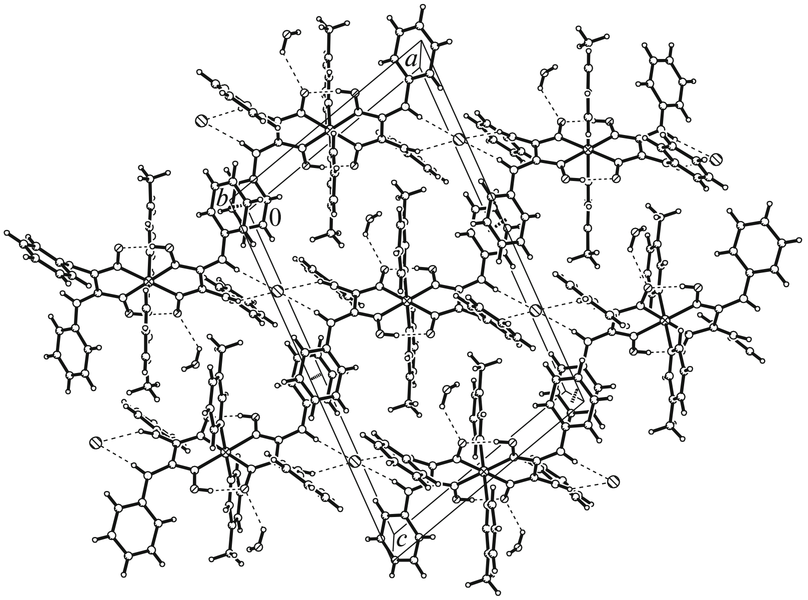

**Fig. 3.** Joining into layers of chains with the alternating Co(III) complex cations and anions in compound **II** and molecules of water of crystallization localized in the cavities.

nated ligands in compounds **I**–**V** are not too rich in functional groups capable of forming strong intermolecular hydrogen bonds, only weak various interactions, except for N–H···Cl, were observed in these crystals. In compound **II**, the chains are joined into layers by weak π···π interactions between the parallel aromatic rings of the adjacent complex cations (centroid···centroid distances are 3.910 Å) (Fig. 3). In compound **III**, the chains are stabilized by weak π···π interactions (centroid···centroid distances are 4.325 Å, and the angle between the planes of the corresponding aromatic rings is 6.1°). In compound **IV**, the complex cations and anions are additionally stabilized by weak hydrogen bonds C–H···Cl (Table 3), whereas in **V** the C–H···O hydrogen bonds between the complex cations join chains of the alternating cations and anions into a layer (Fig. 6). The packing of the components in compound **I** revealed the same weak hydrogen bonds C–H···O and C–H···Cl for dmf molecules in compound **I**, and in compound **II** the out-of-sphere water

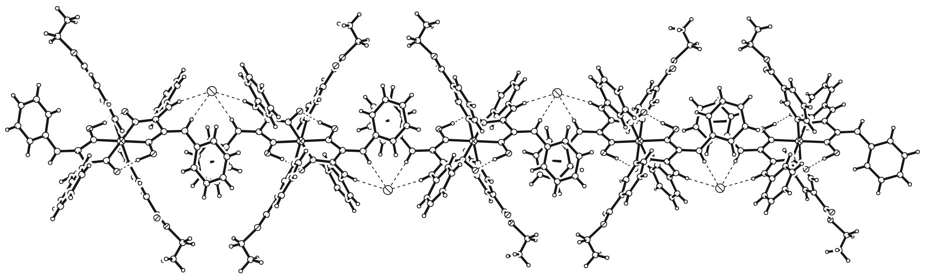

**Fig. 4.** Formation of chains with the alternating complex cations and chloride anions stabilized by weak π···π interactions in compound **III**.

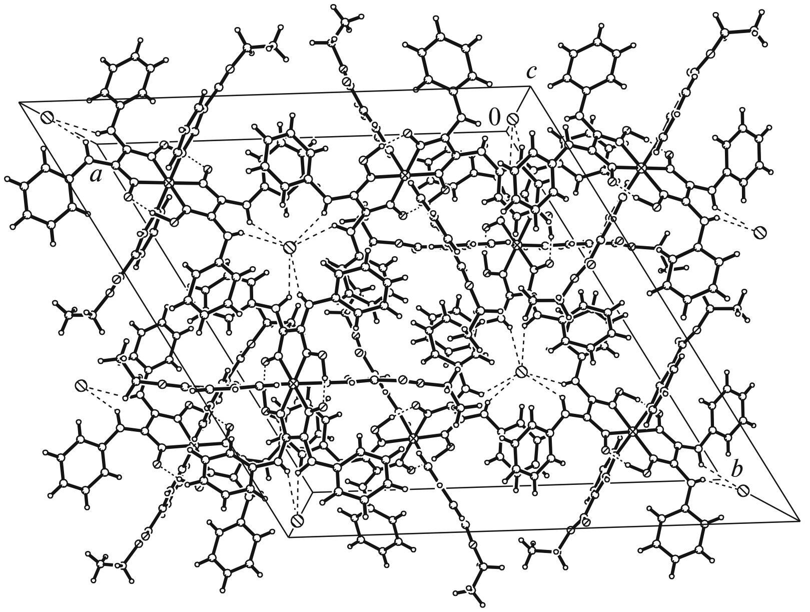

**Fig. 5.** Formation of a layer of the Co(III) complex cations and chloride anions in compound **IV**.

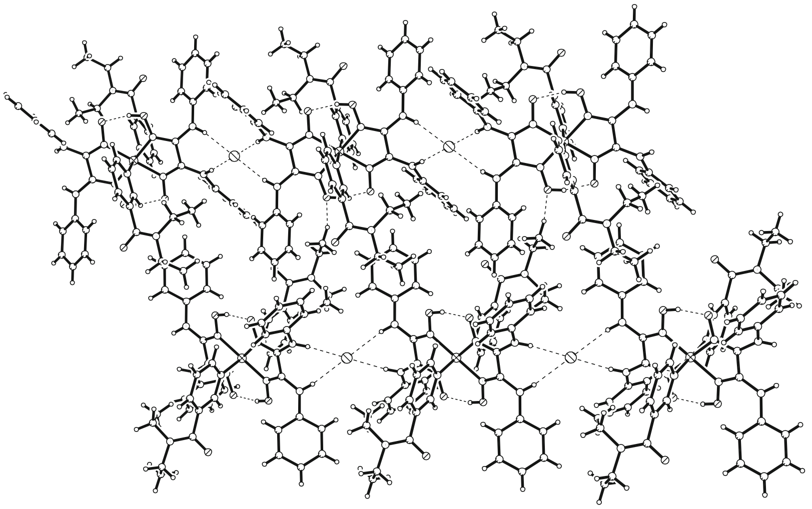

**Fig. 6.** Formation of a layer of chains with the alternating Co(III) complex cations and chloride anions in compound **V**.

molecules are joined with the main components by hydrogen bonds O(*w*)–H···O.

The components are well packed in the crystal, and only in compound **I** the volume of cavities occupies 23.5% of the total unit cell volume upon the removal of dmf molecules. The cavity volume in compound **II** is 7.2% after the removal of the water molecules, and for compounds **III–V** containing no crystallization molecules this volume ranges from 0 to 6.0%.

## FUNDING

This work was carried out in terms of state assignments (projects nos. 20.80009.5007.28 (“Development of New Multifunctional Materials and Efficient Technologies for Agriculture, Medicine, and Technology and Educational System Based on s- and d-Metal Complexes with Polydentate Ligands”) and 20.80009.5007.15 “Implementation of Crystal Engineering and X-ray Crystallography for Design and Creation of Hybrid Organic/Inorganic Materials with Advanced Physical and Biologically Active Functions”) of the National Agency for Research and Development of Republic of Moldova.

## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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*Translated by E. Yablonskaya*