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SYNTHESIS AND CRYSTAL STRUCTURE OF TWO Co(III) α-DIOXIMATES WITH THE FORMULA $[Co(DH)_2(PPh_3)(H_2O)]_2[EF_6]\cdot nH_2O$

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The $[Co(DH)_2(PPh_3)(H_2O)]_2[TiF_6]\cdot 2.5H_2O$ (**1**) and $Co(DH)_2(PPh_3)(H_2O)]_2[ZrF_6]\cdot 3.75H_2O$ (**2**) complexes have been obtained from the $CoEF_6\cdot 6H_2O$ - $2DH_2$ - PPh_3 system, where DH_2 is the dimethylglyoxime, E is Ti or Zr, and PPh_3 is triphenylphosphine. The structure and composition of these complexes have been elucidated by means of modern physical methods: element analysis, spectroscopy in UV-Vis, IR, NMR ^1H, ^{19}F, X-ray investigation. The Co(III) cation's coordination polyhedron consists of four nitrogen atoms of dimethylglyoxime monoanions, the phosphor atom of triphenylphosphine and the oxygen atom of the water molecule. In the equatorial plane of the complex cation octahedron, two DH^- monoanions are linked through intramolecular O–H···O hydrogen bonds. π-π interactions between the phenylic ring of PPh_3 and metalocycle have been revealed in the complex cations. In the crystal, the components of compounds **1** and **2** form a complicated system of hydrogen bonds.

1. Introduction

In *trans*-dioximates of cobalt(III) with the [CoX(DH)L] general formula, where X is the inorganic anion and L is the coordinated organic molecule, two dimethylglyoxime DH^- monoanions, each of them coordinated through two nitrogen atoms, form chelate metalocycles of five atoms. The monoanions DH^- are linked through O–H···O intramolecular hydrogen bonds which increase the stability of the $Co(DH)_2$ group. That is the reason why substitution reactions in the internal sphere of the complex occur mostly on the 1.6-coordinate, thus allowing the investigation of the coordination capacity in condition of competition of ligands linked with the central metal atom through various atoms. Depending on the donor properties displayed by the coordinated atom, phenomena connected with the mutual influence of the ligands placed in *trans*-position can also serve a subject of investigation. Introduction of ligands that have triphenylphosphine conjugated π-systems in the internal sphere of the complex leads to the complication of both the steric factors and the ligands reciprocal influence. In these complexes, the influence of the equatorial fragment upon the coordinated ligands in

the apical positions of the octahedron is practically constant, this making possible to observe the geometrical manifestation of the mutual influence of apically placed ligands.

So far, the synthesis of a series of cobalt [1–12], iron [13, 14], rhodium [15–17], and ruthenium dioximates [18, 19] with various dioximes has been performed: dimethylglyoxime [1, 3–8, 11–19], diphenylglyoxime [2, 19], 1.2-cyclohexanedionedioxime [10, 13] and α-furylglyoxime [9] with PPh_3 and its derivatives. The influence of radicals from the dioxime molecule upon the value of σ and π bond of triphenylphosphine has been disclosed. The oxidation state of the central atom in these complexes can be different, for example, Co^{+1} [11], Co^{+2} [12], Co^{+3} [1–10].

Previously, it has been established that when triphenylphosphine acts upon type $[Co(DioxH)_2(H_2O)X]$ cobalt(III) dioximates, where X is Cl, Br, I, SCN, non-electrolytes with formula $[Co(DioxH)_2(PPh_3)X]$ [3, 10] are specially formed. Structural data have confirmed a stronger trans influence of triphenylphosphine in proportion to water [7, 8].

Only one compound is registered in the Cambridge Structural Data Base (CSD) [20], where the axial positions are taken by a triphenylphosphine molecule and a water molecule having the formula of the complex cation $[Rh(DH)_2PPh_3H_2O]^+$ [17].

In the complexes that have one triphenylphosphine molecule and a chlorine ion on axial coordinates, the deviation of the metalocycle from the equatorial plane of the octahedral complex has been revealed [7]. This phenomenon might be generated by the steric complication caused by the placement of the triphenylphosphine ramified voluminous molecule [15].

Previously, two dioximates of Co(III) with triphenylphosphine and fluorurated anions – $[Co(NioxH)_2(PPh_3)_2]SiF_5$ and $[Co(NioxH)_2(PPh_3)_2]F$ have been obtained and investigated [21, 22]. In this work, we describe the synthesis method and the physicochemical and structural peculiarities of new dioximates $[Co(DH)_2(PPh_3)(H_2O)]_2[TiF_6]\cdot 2.5H_2O$ (**1**) and $[Co(DH)_2(PPh_3)(H_2O)]_2[ZrF_6]\cdot 3.75H_2O$ (**2**) that can serve construction blocks for obtaining compounds with dimeric structure when bridging ligands are substituted for the water coordinated molecules.

2. Experimental

2.1. Synthesis

*2.1.1. Synthesis of $[Co(DH)_2(PPh_3)(H_2O)]_2[TiF_6]\cdot 2.5H_2O$ (**1**).* We took 0.033 g (0.0001 mol) $CoTiF_6\cdot 6H_2O$ in 10 ml of methanol and added 0.023 g (0.0002 mol) of dimethylglyoxime in 20 ml of methanol and 0.026 g (0.0001 mol) triphenylphosphine in 20 ml of methanol. The mixture was heated for about 10 min in a water bath at 70ºC in a graphite crucible, then filtered and left for gradual evaporation at room temperature. Sedimentation of dark brown needle-shaped crystals occurs from this solution. Yield: 36%. The complex is soluble in alcohols, DMF, DMSO and less soluble in water.

Found, %: Co 8.59, C 46.28, H 4.91, N 8.18. Calc. for $C_{52}H_{67}Co_2F_6N_8O_{12.5}P_2Ti$, %: Co 8.76, C 46.41, H 5.02, N 8.33.

*2.1.2. Synthesis of $[Co(DH)_2(PPh_3)(H_2O)]_2[ZrF_6]\cdot 3.75H_2O$ (**2**)* has been obtained according to the same method with the exception that the cobalt salt has been $CoZrF_6\cdot 6H_2O$. Sedimentation of dark brown crystals occurs from the solution. Yield: 32%. The complex is soluble in alcohols, DMF, DMSO, and less soluble in water.

Found, %: Co 8.19, C 44.08, H 4.79, N 7.78. Calc. for $C_{52}H_{69.5}Co_2F_6N_8O_{13.75}P_2Zr$, %: Co 8.35, C 44.24, H 4.96, N 7.94.

2.2. X-ray crystallography

Experimental data for compounds **1** were obtained at 296 K using a BRUKER diffractometer (MoK_α radiation, graphite monochromator, ω scan mode). Experimental data for **2** were collected at low temperature with a KM4 CCD diffractometer using graphite-monochromated Mo-K_α radiation. Intensity data were corrected for the Lorentz and polarization effects and for absorption. The structures were solved by direct methods with the program SHELXS-97 [23] and refined by full-matrix least-squares method on F^2, with anisotropic displacement parameters for the non-hydrogen atoms, using the program SHELXL-97 [23]. One of the $[ZrF_6]^{2-}$ anions in **2** is disordered over two positions with the occupancies 0.45 and 0.55, other with occupancies 0.48 and 0.52. The orientations of anion $[TiF_6]^{2-}$ in **2** correlate well with the positions occupied by statistically disordered water molecules. The crystals of **1** and **2** exhibited inversion twinning. In structures **1** and **2** all H atoms, except the H atoms of water molecules, were placed in the calculated positions and given the isotropic displacement parameters equal to 1.2 × U_{eq}(C, O, N). The H atoms of the water molecules were not located. All H atoms were refined in the riding-model approximation. Crystal data and some further experimental and refinement details are given in Table 1.

Table 1. Crystal data and structure refinement for **1** and **2**.

Compound	1	2
Empirical formula	$C_{52}H_{67}Co_2F_6N_8O_{12.50}P_2Ti$	$C_{52}H_{73.50}Co_2F_6N_8O_{13.75}P_2Zr$
Formula weight	1345.84	1415.71
T, K	296(2)	100(2) K
Wavelength, Å	0.71073	0.71073
Crystal system, space group	monoclinic, $P2_1/c$	orthorhombic, $P2_12_12_1$
Unit cell dimensions		
a, Å	15.554(4)	15.5320(6)
b, Å	21.514(5)	21.5070(9)
c, Å	18.496(5)	36.822(1)
α, deg.	90	90
β, deg.	90.040(4)	90
γ, deg.	90	90
V, Å^3	6189(3)	12300.3(8)
Z, ρ(calc), Mg/m^3	4, 1.444	8, 1.529
μ, mm^{-1}	0.789	0.837
F(000)	2780	5836
Crystal size, mm	0.15 x 0.15 x 0.4	0.5 x 0.08 x 0.08
θ range for data collection, deg.	0.95 to 25.00	4.09 to 25.03
Limiting indices	$-18 \le h \le 18$, $-25 \le k \le 25$, $-21 \le l \le 21$	$-18 \le h \le 18$, $-24 \le k \le 25$, $-43 \le l \le 43$
Reflections collected / unique	53753 / 10887 [R(int) = 0.1036]	78912 / 21619 [R(int) = 0.1006]
Completeness to θ = 25.00, %	99.9	99.3
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10887 / 19 / 695	21619 / 66 / 1495
GOOD	1.068	
Final R indices (I>2σ(I))	$R1$ = 0.1638, $wR2$ = 0.4458	$R1$ = 0.0925, $wR2$ = 0.2278
R indices (all data)	$R1$ = 0.2073, $wR2$ = 0.4781	$R1$ = 0.1764, $wR2$ = 0.2678
Largest diff. peak and hole, e· Å^{-3}	1.707 and -1.431	0.996 and -1.026

Selected bond lengths and angles are given in Tables 2 and 3, while hydrogen-bond geometry is listed in Table 4. Crystallographic data for **1** and **2** have been deposited with the Cambridge Crystallographic Data Center, CCDC 787650 (**1**) and CCDC 787651 (**2**). Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or web: http://www.ccdc.cam.ac.uk).

Table 2. Selected bond lengths (Å) and angles (deg) for **1**.
a) complex cation

	A	B
Co–N(11)	1.90(1)	1.86(1)
Co–N(12)	1.72(1)	1.92(2)
Co–N(22)	1.98(1)	1.88(1)
Co–N(21)	1.87(1)	1.80(1)
Co–O(W)	1.95(2)	1.95(1)
Co–P(1)	2.272(4)	2.256(4)
P(1)–C(31)	1.81(1)	1.76(10)
P(1)–C(41)	1.817(8)	1.815(9)
P(1)–C(51)	1.82(1)	1.887(10)
O(11)–N(11)	1.43(2)	1.40(2)
O(12)–N(12)	1.41(2)	1.37(2)
O(21)–N(21)	1.38(2)	1.29(2)
O(22)–N(22)	1.27(2)	1.34(2)
N(11)–C(11)	1.17(2)	1.29(2)
N(12)–C(12)	1.27(3)	1.22(2)
N(21)–C(21)	1.24(2)	1.31(3)
N(22)–C(22)	1.28(3)	1.44(2)
C(11)–C(12)	1.39(3)	1.44(2)
C(11)–C(14)	1.52(3)	1.50(2)
C(12)–C(13)	1.55(4)	1.62(2)
C(21)–C(22)	1.43(3)	1.54(3)
C(21)–C(24)	1.44(3)	1.54(2)
C(22)–C(23)	1.55(3)	1.39(5)
	A	B
N(11)CoN(12)	79.0(5)	78.2(7)
N(11)CoN(21)	176.5(6)	176.6(6)
N(11)CoN(22)	98.3(7)	98.1(7)
N(12)CoN(21)	98.5(6)	100.4(6)
N(12)CoN(22)	174.6(6)	174.4(6)
N(21)CoN(22)	84.0(7)	83.0(7)
N(11)CoO(W)	86.6(6)	88.4(6)
N(12)CoO(W)	89.3(7)	88.1(9)
N(21)CoO(W)	91.1(6)	88.4(6)
N(22)CoO(W)	85.9(8)	87.7(9)
N(11)CoP(1)	91.2(4)	92.5(4)
N(12)CoP(1)	89.4(3)	86.5(5)
N(21)CoP(1)	91.1(4)	90.6(4)
N(22)CoP(1)	95.3(5)	97.8(4)
O(W)CoP(1)	177.6(5)	174.2(8)
C(31)P(1)C(41)	113.9(6)	113.5(6)
C(31)P(1)C(51)	97.9(6)	100.2(6)

C(41)P(1)C(51)	102.5(5)	99.4(6)
C(31)P(1)Co	109.0(4)	111.8(5)
C(41)P(1)Co	109.6(4)	110.1(4)
C(51)P(1)Co	123.6(4)	121.2(4)
C(11)N(11)O(11)	121.6(13)	119.9(13)
C(11)N(11)Co	119.2(12)	118.7(13)
O(11)N(11)Co	119.0(10)	121.3(12)
C(12)N(12)O(12)	115.5(17)	120.1(17)
C(12)N(12)Co	118.1(15)	118.4(13)
O(12)N(12)Co	126.3(8)	120.8(12)
C(21)N(21)O(21)	120.2(13)	117.7(13)
C(21)N(21)Co	116.3(14)	117.2(11)
O(21)N(21)Co	123.0(9)	124.3(11)
C(22)N(22)O(22)	134.6(14)	113.3(12)
C(22)N(22)Co	105.9(14)	120.5(10)
O(22)N(22)Co	119.0(12)	126.2(12)
N(11)C(11)C(12)	109(2)	111.2(15)
N(11)C(11)C(14)	123.3(19)	127.3(16)
C(12)C(11)C(14)	128(2)	121.4(16)
N(12)C(12)C(11)	115(3)	113.3(17)
N(12)C(12)C(13)	123(2)	125.4(17)
C(11)C(12)C(13)	122(2)	121.2(15)
N(21)C(21)C(22)	112.5(17)	114.2(13)
N(21)C(21)C(24)	123.6(18)	117(2)
C(22)C(21)C(24)	123.4(19)	128(2)
N(22)C(22)C(21)	121.2(18)	104.1(15)
N(22)C(22)C(23)	110.0(18)	130(2)
C(21)C(22)C(23)	128.8(19)	119.8(17)
C(32)C(31)P(1)	120.6(9)	120.0(8)
C(36)C(31)P(1)	119.3(9)	119.7(8)
C(42)C(41)P(1)	122.4(5)	116.8(6)
C(46)C(41)P(1)	117.6(5)	123.2(6)
C(52)C(51)P(1)	115.8(7)	117.0(7)
C(56)C(51)P(1)	124.2(7)	122.8(7)

b) anion

Ti(1)–F(1)	1.84(1)	F(1)Ti(1)F(3)	94(1)	F(2)Ti(1)F(6)	88.0(8)
Ti(1)–F(2)	1.98(2)	F(1)Ti(1)F(4)	97(2)	F(3)Ti(1)F(4)	99(2)
Ti(1)–F(3)	1.67(3)	F(1)Ti(1)F(5)	86(1)	F(3)i(1)F(5)	83(2)
Ti(1)–F(4)	1.89(2)	F(1)Ti(1)F(6)	175(1)	F(3)Ti(1)F(6)	91(2)
Ti(1)–F(5)	1.88(2)	F(2)Ti(1)F(3)	170(2)	F(4)Ti(1)F(5)	176(2)
Ti(1)–F(6)	1.81(1)	F(2)Ti(1)F(4)	90(1)	F(4)Ti(1)F(6)	84(2)
F(1)Ti(1)F(2)	86.8(9)	F(2)Ti(1)F(5)	87.6(9)	F(5)Ti(1)F(6)	92(1)

Table 3. Selected bond lengths (Å) and angles (deg) for **2**.
a) complex cation

Bond	A	B	C	D
Co–N(11)	1.90(1)	1.89(1)	1.85(1)	1.83(1)
Co–N(12)	1.85(1)	1.82(2)	1.92(1)	1.92(1)
Co–N(21)	1.89(1)	1.90(1)	1.85(1)	1.90(1)
Co–N(22)	1.86(1)	1.89(1)	1.90(1)	1.91(1)

Co–O(W)	2.002(9)	2.000(9)	1.96(1)	1.985(9)
Co–P(1)	2.261(4)	2.261(4)	2.260(4)	2.270(4)
P(1)–C(31)	1.83(2)	1.85(2)	1.81(1)	1.79(2)
P(1)–C(41)	1.80(2)	1.83(1)	1.79(1)	1.85(1)
P(1)–C(51)	1.81(1)	1.88(2)	1.86(1)	1.78(2)
O(11)–N(11)	1.39(2)	1.33(2)	1.34(2)	1.37(1)
O(12)–N(12)	1.38(1)	1.45(2)	1.38(2)	1.36(1)
O(21)–N(21)	1.33(2)	1.30(2)	1.36(1)	1.31(1)
O(22)–N(22)	1.35(2)	1.33(1)	1.30(2)	1.42(1)
N(11)–C(11)	1.29(2)	1.28(2)	1.39(2)	1.34(2)
N(12)–C(12)	1.34(2)	1.34(2)	1.29(2)	1.22(2)
N(21)–C(21)	1.30(2)	1.32(2)	1.33(2)	1.35(2)
N(22)–C(22)	1.36(2)	1.27(2)	1.29(2)	1.24(2)
C(11)–C(12)	1.40(2)	1.45(2)	1.44(2)	1.52(2)
C(11)–C(14)	1.57(2)	1.65(2)	1.43(2)	1.41(2)
C(12)–C(13)	1.41(2)	1.41(2)	1.52(2)	1.54(2)
C(21)–C(22)	1.48(2)	1.48(2)	1.49(2)	1.52(2)
C(21)–C(24)	1.49(2)	1.54(2)	1.52(2)	1.35(2)
C(22)–C(23)	1.52(2)	1.59(2)	1.45(2)	1.48(2)
Angle	A	B	C	D
N(11)CoN(12)	81.5(6)	79.6(6)	81.0(6)	81.2(5)
N(11)CoN(21)	172.9(6)	173.6(5)	174.6(5)	174.9(5)
N(11)CoN(22)	96.9(7)	96.7(6)	97.6(6)	100.5(6)
N(12)CoN(21)	98.4(5)	99.3(6)	99.5(6)	98.7(5)
N(12)CoN(22)	176.4(5)	174.5(5)	176.3(5)	175.7(5)
N(21)CoN(22)	82.8(6)	84.0(6)	81.6(6)	79.2(5)
N(11)CoO(W)	88.9(5)	89.0(5)	88.5(6)	87.3(4)
N(12)CoO(W)	87.8(5)	87.4(5)	87.7(5)	89.0(4)
N(21)CoO(W)	84.0(5)	84.7(4)	86.1(5)	87.6(4)
N(22)CoO(W)	89.0(5)	88.5(5)	88.9(5)	87.1(4)
N(11)CoP(1)	98.6(4)	98.2(4)	98.2(4)	98.2(4)
N(12)CoP(1)	91.7(4)	93.0(3)	92.8(4)	91.3(3)
N(21)CoP(1)	88.5(4)	88.1(3)	87.2(4)	86.9(3)
N(22)CoP(1)	91.7(4)	91.5(4)	90.7(4)	92.4(3)
O(W)CoP(1)	172.3(3)	172.8(3)	173.2(4)	174.5(3)
C(41)P(1)C(31)	111.4(7)	100.3(7)	112.6(7)	101.1(6)
C(51)P(1)C(31)	100.1(7)	113.1(7)	102.5(6)	111.2(6)
C(41)P(1)C(51)	100.6(8)	102.7(7)	101.8(6)	102.9(7)
C(31)P(1)Co	109.0(5)	109.6(4)	108.8(4)	110.3(4)
C(41)P(1)Co	111.6(5)	121.1(4)	109.7(4)	122.0(5)
C(51)P(1)Co	123.3(5)	109.8(4)	121.3(5)	108.9(5)
C(11)N(11)O(11)	124(1)	122(1)	119(1)	114(1)
C(11)N(11)Co	114(1)	114(1)	117(1)	120(1)
O(11)N(11)Co	121.9(10)	123(1)	123.2(10)	125.9(10)
C(12)N(12)O(12)	118(1)	115(1)	123(1)	119(1)
C(12)N(12)Co	117.6(10)	122(1)	117(1)	117(1)
O(12)N(12)Co	123.9(9)	121.7(9)	118.7(9)	122.7(9)
C(21)N(21)O(21)	119(1)	124(1)	117(1)	120(1)
C(21)N(21)Co	116.8(10)	114.8(9)	118.2(9)	117(1)
O(21)N(21)Co	124.6(10)	121(1)	123.6(10)	121.7(9)
C(22)N(22)O(22)	115(1)	122(1)	120(2)	120(1)
C(22)N(22)Co	117(1)	112.4(10)	117(1)	122(1)

O(22)N(22)Co	127.6(10)	125.5(9)	123(1)	117.2(9)
N(11)C(11)C(12)	117(2)	119(2)	111(2)	106(1)
N(11)C(11)C(14)	121(2)	121(2)	122(2)	128(2)
C(12)C(11)C(14)	122(2)	120(2)	126(2)	125(2)
N(12)C(12)C(11)	110(1)	104(2)	113(2)	115(1)
N(12)C(12)C(13)	122(1)	126(2)	122(2)	126(2)
C(11)C(12)C(13)	128(1)	130(2)	124(2)	119(1)
N(21)C(21)C(22)	113(1)	110(1)	109(1)	111(1)
N(21)C(21)C(24)	125(1)	122(1)	125(1)	126(1)
C(24)C(21)C(22)	122(1)	127(2)	126(2)	123(1)
N(22)C(22)C(21)	110(1)	118(2)	113(2)	110(1)
N(22)C(22)C(23)	124(1)	122(1)	127(1)	129(1)
C(21)C(22)C(23)	126(1)	120(1)	119(2)	121(1)
C(32)C(31)P(1)	115(1)	120(1)	122(1)	131(1)
C(36)C(31)P(1)	131(1)	120(1)	117.6(10)	116.1(10)
C(42)C(41)P(1)	120(1)	115.2(9)	124(1)	113(1)
C(46)C(41)P(1)	121(1)	126.9(10)	118.7(10)	126(1)
C(52)C(51)P(1)	123(1)	123(1)	111(1)	121(1)
C(56)C(51)P(1)	120(1)	113(1)	128(1)	125(1)

b) anion

Bond	Zr(1), A	Zr(1), B	Zr(2A), C	Zr(2A), D	Zr(2B), C	Zr(2B), D
Zr–F(1)	1.962(9)		2.05(1)		1.99(1)	
Zr–F(2)	2.046(8)		1.79(2)	1.95(3)	2.00(2)	1.73(3)
Zr–F(3)	2.10(2)	1.91(2)	2.10(2)	2.02(1)	1.98(2)	2.25(1)
Zr–F(4)	2.01(2)	1.95(2)	2.44(3)	2.41(3)	1.95(3)	1.77(3)
Zr–F(5)	1.93(2)	2.07(2)	2.20(3)	2.02(5)	1.73(3)	2.63(5)
Zr–F(6)	2.00(2)	1.99(1)	1.56(2)	1.84(2)	2.01(2)	2.26(2)
Angle	Zr(1), A	Zr(1), B	Zr(2A), C	Zr(2A), D	Zr(2B), C	Zr(2B), D
F(1)ZrF(2)	172.0(4)		91.6(8)	87.4(11)	87.9(7)	96(1)
F(1)ZrF(3)	91.2(7)	94.5(6)	144.9(7)	174.7(6)	173.3(7)	147.6(6)
F(1)ZrF(4)	86.0(6)	89.4(5)	77.6(7)	80.0(8)	92.0(9)	99.8(10)
F(1)ZrF(5)	93.0(6)	80.3(6)	87.7(9)	92.0(18)	104.9(10)	77(1)
F(1)ZrF(6)	96.4(6)	91.5(5)	91.0(7)	95.4(7)	80.9(5)	85.3(6)
F(2)ZrF(3)	94.1(7)	93.0(6)	95.5(8)	87.8(11)	95.5(8)	86(1)
F(2)ZrF(4)	87.8(5)	87.5(5)	135.3(10)	79(1)	167.5(10)	106(2)
F(2)ZrF(5)	82.0(6)	92.1(6)	59.6(10)	93(2)	65(1)	79(2)
F(2)ZrF(6)	90.0(6)	91.4(5)	97.9(9)	177(1)	102.5(8)	143(1)
F(3)ZrF(4)	91.1(8)	90.4(7)	71.9(8)	96.9(8)	86.0(10)	110.8(10)
F(3)Zr(5)	175.4(9)	174.3(7)	68.9(9)	91(2)	82(1)	71(1)
F(3)ZrF(6)	85.8(8)	91.4(7)	103.5(9)	89.4(7)	92.6(7)	74.2(6)
F(4)ZrF(5)	91.2(8)	87.3(8)	76.6(11)	169(2)	103(1)	175(2)
F(4)ZrF(6)	176.1(8)	178.0(7)	86.0(9)	102.3(9)	89.8(10)	111(1)
F(5)ZrF(6)	91.8(8)	91.0(7)	162.4(11)	86(2)	166(1)	65(1)

Table 4. Intramolecular hydrogen bond distances (Å) and angles (deg) for **1** and **2**.

1					
D–H	d(D–H)	d(H···A)	∠DHA	d(D···A)	A
O(11A)–H(1)	0.82	1.59	164	2.385	O(22A)
O(12A)–H(1)	0.82	1.63	159	2.417	O(21A)
O(11B)–H(1)	0.82	1.64	162	2.435	O(22B0)

O(12B)–H(1)	0.82	1.81	162	2.596	O(21B)
2					
D–H	d(D–H)	d(H···A)	∠DHA	d(D···A)	A
O(12A)–H(1)	0.82	1.73	161	2.516	O(21A)
O(22A)–H(1)	0.82	1.72	159	2.503	O(11A)
O(12B)–H(10	0.82	1.65	159	2.433	O(21B)
O(22B)–H(1)	0.82	1.69	161	2.483	O(11B)
O(12C)–H(1)	0.82	1.63	166	2.432	O(21C)
O(22C)–H(1)	0.82	1.67	162	2.460	O(11C)
O(12D)–H(1)	0.82	1.72	161	2.505	O(21D)
O(22D)–H(1)	0.82	1.70	165	2.503	O(11D)

The UV spectra of the samples ($4.5 \cdot 10^{-5}$ mol/L) were registered using a Perkin Elmer Lambda 25 spectrometer.

The infrared spectra were recorded using a Perkin-Elmer FT-IR Spectrometer "Spectrum 100" in the region 4000-400 cm^{-1}.

^{1}H and ^{19}F NMR spectra were recorded using an AVANCE II 300 (BRUKER) spectrometer.

3. Results and discussion

The interaction of salts $CoEF_6 \cdot 6H_2O$ (E = Ti(IV), Zr(IV)) with dimethylglyoxime and triphenylphosphine in the molar proportion of 1:2:1 (aqua-methanolic medium), the $[Co(DH)_2(PPh_3)(H_2O)]_2[TiF_6] \cdot 2.5H_2O$ (**1**) and $[Co(DH)_2(PPh_3)(H_2O)]_2[ZrF_6] \cdot 3.75H_2O$ (**2**) complexes have been obtained, where DH_2 is dimethylglyoxime and PPh_3 is triphenylphosphine. Two bonds are present in the UV spectra of complexes: the first one at ~258 nm characterizes the change transfer from the cobalt atom to the chelate cycle and corresponds to the stable group $Co(DH)_2$, while the second one at ~336 nm reveals the presence of a triphenylphosphine molecule in the complex. The absorption band in IR spectra in a region of 1240–1245 cm^{-1} (ν(N-O)) shows the coordination of dimethylglyoxime anions. One can also talk about the coordination of PPh_3 molecules after changes of absorption frequencies ν(PC), δ(CPC) and others. The absorption bands in a region of 1580–1590 cm^{-1} (ν(CC)+δ(CCH)) confirm the presence of triphenylphosphine in the complex. At PPh_3 coordination, the absorption bands values from 1480, 1430, 855, 749, 690, 513, and 420 cm^{-1} increase, while those from 1090 and 1030 cm^{-1} decrease. These data represent one more proof of triphenylphosphine coordination to metal.

The NMR ^{1}H spectra of these complexes have shown that at coordination the CH_3 groups of dimethylglyoxime undergo a shift towards the weak field approximately by 0.4 ppm from 1.9 ppm at 2.39 (**1**) and 2.40 (**2**) ppm. The formation of *trans*-dioximates is interpreted by those four equivalent methyl groups that produce a single signal, while in the case of *cis*-dioximates, due to low symmetry, more signals should appear for

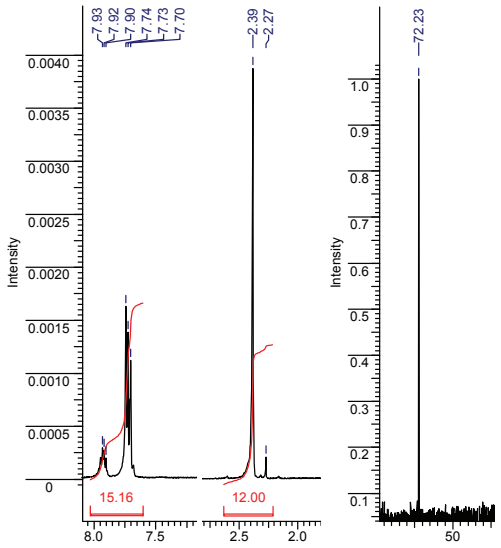

Fig. 1. NMR ^{1}H and ^{19}F spectra of complex $[Co(DH)_2(PPh_3)(H_2O)]_2[TiF_6] \cdot 2.5H_2O$.

these groups. Signals of coordinated triphenylphosphine also undergo a slight shift towards the weak field and are characterized by multiplets in the 7.65-8.00 ppm region. At integration of protonic spectrum signals (Fig. 1), one can see that DH^-:PPh_3 proportion is 2:1, this demonstrating the occupation of a single axial position by the neutral ligand PPh_3, the other position being taken by the solvent molecules. In an aqueous solution of Co(III) dioximates, one can often observe the tendency of time substitution of axial ligands for water molecules even at room temperature. Repeated registration (one day interval) of NMR ^1H spectra for **1** and **2** compounds showed no change that could confirm this substitution. In this case, we can speak about a higher stability in relation to previously studied dioximates [24].

A singlet is observed in the NMR ^{19}F spectra at 72.23 ppm ($\delta[TiF_6]^{2-}$) (**1**) and -14.23 ppm ($\delta[ZrF_6]^{2-}$) (**2**). The appearance of a single signal proves the high stability of these polyfluorurated anions preserving the octahedral configuration EF_6 intact.

The crystalline structure of compounds **1** and **2** has been revealed through an X-ray investigation. In the asymmetric part of the unit cell of **1**, there are two crystallographically independent complex cations $[Co(DH)_2(PPh_3)(H_2O)]^+$, an anion $[TiF_6]^{2-}$ and water molecules that statistically occupy three positions. Four complex cations have been revealed for crystal **2,** which are crystallographically independent and have a similar composition to that of Co(III) cations from **1**, two $[ZrF_6]^{2-}$ anions, both with a disorder degree and statistically positioned water molecules. The coordination polyhedron shaped as a distorted octahedron of Co(III) cation in **1** and **2** consists of four nitrogen atoms that belong to two remainders of the coordinated dimethylglyoxime anion, a phosphorus atom from the triphenylphosphine molecule, and one oxygen atom of a coordinated water molecule. The independent complex cations A and B (**1**) and A, B, C, and D (**2**) are shown in Figs. 2 and 3, respectively. The bond distances Co–N are within an interval of 1.72(1)–1.92(2) Å for **1** and 1.83(2)–1.92(1) Å for **2** (Tables 2, 3) and are in full agreement with those established for cobalt(III) dioximates [1-12]. The equatorial plane of the octahedron in the complex cation consists of those two DH^- anions linked through O–H···O intramolecular hydrogen bonds. The parameters of these hydrogen bonds are given in Table 4. The interatomic distances Co–P and Co–O(W) in **1** are 2.272(4), 2.256(4) and 1.95(2), 1.95(2) Å for A and B cations, respectively, while in **2** these distances are within intervals 2.260(4)–2.270(4), 1.96(1)–1.999(9) Å for A–D cations. These values are in full agreement with Co–P and Co–O(W) distances from various dioximates of Co(III) that contain coordinated molecules of PPh_3 and water [1–12, 24–27]. It is worth noting that Co–P distances found in **1** and **2** are approximately 0.1 Å smaller than those revealed in the compounds with two PPh_3 molecules [19, 20]. For each of the complex cations of Co(III) from **1** and **2,** we found the π-π type interaction between an aromatic ring of the PPh_3 coordinated molecule and one of metalocycles, the distances between their centers being 3.854 and 3.922 Å in **1** and within 3.591–3.874 Å in **2**. Previously, this interaction type has been observed in Co(III) dioximates with PPh_3 [1–12]. The difference between NO interatomic distances of complex cations from **1** and **2** (Table 2, 3) shows the diverse way of deprotonation of dimethylglyoxime ligands from **1** and **2**. Thus, more correct cations formulae would be $[CoD(DH_2)(PPh_3)(H_2O)]^+$ and $[Co(DH)_2(PPh_3)(H_2O)]^+$ in **1** and **2,** respectively.

In octahedral anions $[TiF_6]^{2-}$ and $[ZrF_6]^{2-}$, the Ti–F and Zr–F distances are, on average, 1.85(2) and 1.96(3) Å, thus corresponding to those found for these anions [28, 29]. Here, it is worth noting that if the CSD [20] includes only five dioximates of cobalt with $[ZrF_6]^{2-}$ anion previously studied by us in [29–31], then there are no such dioximates with the $[TiF_6]^{2-}$ anion. Compound **1** is the first dioximate of Co(III) which contains the $[TiF_6]^{2-}$ anion in the external sphere.

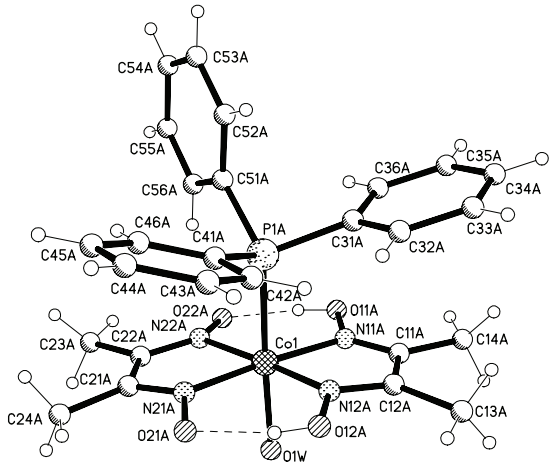

Fig. 2a. Structure of complex cation A from **1**.

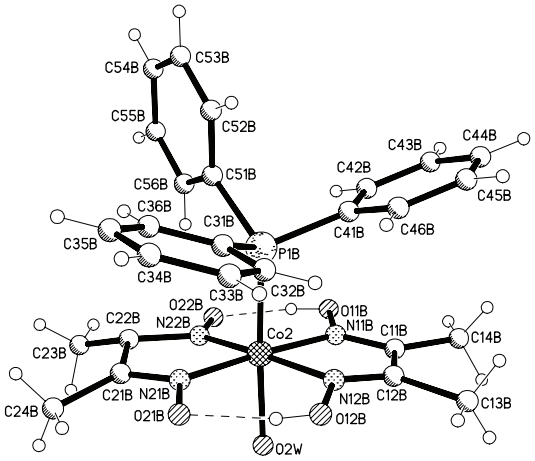

Fig. 2b. Structure of complex cation B from **1**.

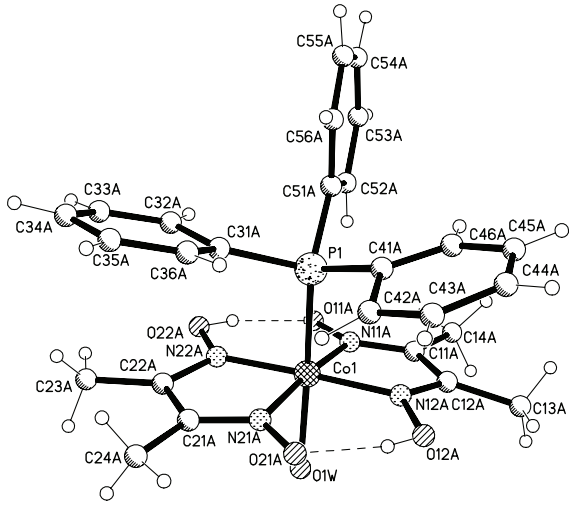

Fig. 3a. Structure of complex cation A from **2**.

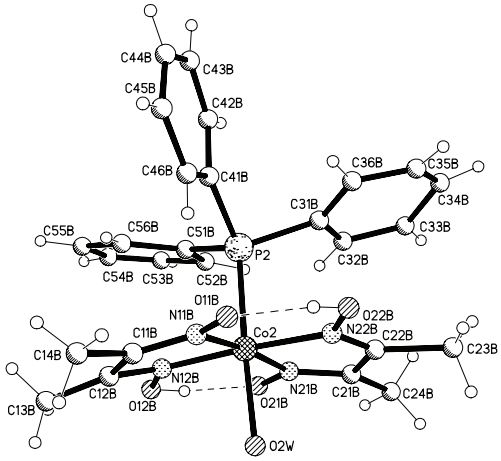

Fig. 3b. Structure of complex cation B from **2**.

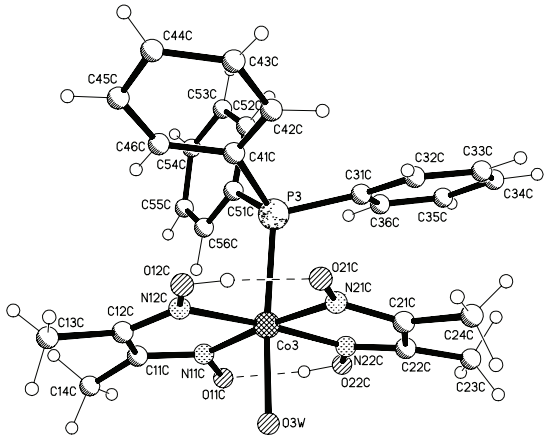

Fig. 3c. Structure of complex cation C from **2**.

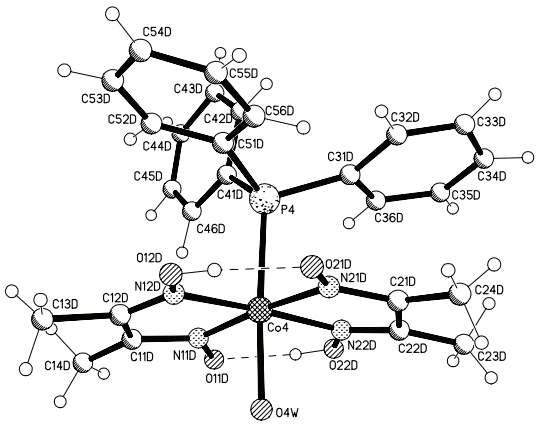

Fig. 3d. Structure of complex cation D from **2**.

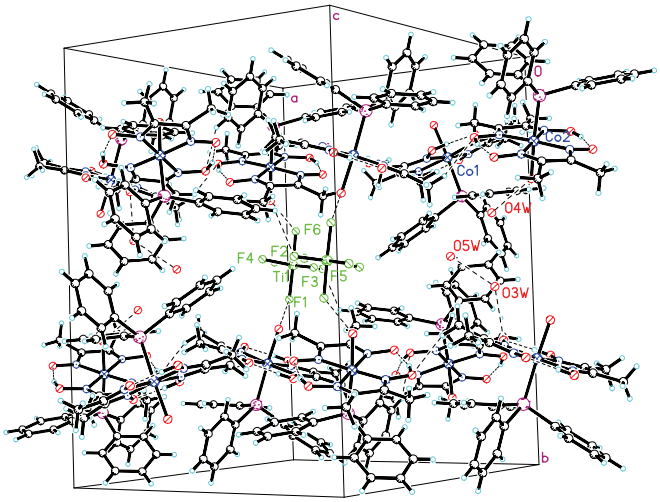

Fig. 4a. A fragment from the crystalline structure of compound **1**.

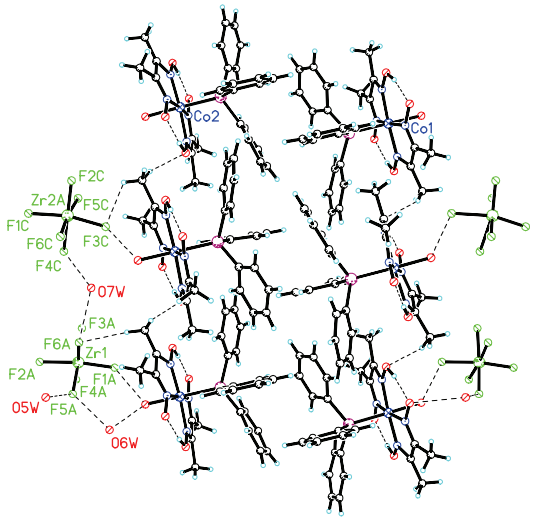

Fig. 4b. A fragment from the crystalline structure of compound **2**.

Since the positions of hydrogen atoms from coordinated and non-coordinated water molecules have not been localized for **1** and **2**, and the fluor atoms from $[ZrF_6]^{2-}$ anions statistically occupy several positions, only the donor-acceptor parameters from crystals are indicative of the O(W)–H···F hydrogen bridges. Figures 4a and 4b show fragments from crystalline structures of compounds **1** and **2**. It is marked out that the complex cations and the anions are linked both through electrostatic interactions and by hydrogen bonds of the O(W)–H···F and C–H···F types. Solvation water molecules also participate in the formation of the hydrogen bond system.

4. Conclusions

The interaction of $CoEF_6 \cdot 6H_2O$ with DH_2 (dimethylglyoxime) and PPh_3 (triphenylphosphine), where E is Ti or Zr, in approximately the same synthetic conditions resulted in two novel complex complexes of the compositions $[Co(DH)_2(PPh_3)(H_2O)]_2[TiF_6] \cdot 2.5H_2O$ (**1**) and $Co(DH)_2(PPh_3)(H_2O)]_2[ZrF_6] \cdot 3.75H_2O$ (**2**). Both compounds represent ionic complexes. The fluorine-containing anion $[TiF_6]^{2-}$·and $[ZrF_6]^{2-}$, like $[AlF_6]^{3-}$, $[SiF_6]^{2-}$, $[SiF_5]^-$, F^-, and $[BF_4]^-$, is not involved in the inner coordination sphere of a Co(III) dioximate.

Acknowledgements

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References

[1] G.N. Schrauzer and G. Kratel, Chem. Ber., 102, 7, 2392, (1969).
[2] A.V. Ablov, A.M. Goldman, and O.A. Bologa, Zh. Neorg. Khim., 16, 6, 1763, (1971).
[3] A.V. Ablov, A.M. Goldman, O.A. Bologa, Yu.A. Simonov, and M.M. Botoshansky, Zh. Neorg. Khim., 16, 8, 2187, (1971).
[4] L.G. Marzilli and J.G. Salerno, L.A. Epps, Inorg. Chem., 11, 9, 2050, (1972).
[5] A.V. Ablov, M.M. Botoshansky, Yu.A. Simonov, T.I. Malinovsky, A.M. Goldman, and O.A. Bologa, Dokl. Akad. Nauk SSSR, 206, 4, 863, (1972).

[6] S. Bruckner and L. Randaccio, J. Chem. Soc. Dalton Trans., 10, 1017, (1974).
[7] M.M. Botoshansky, Yu.A. Simonov, T.I. Malinovsky, and M.A. Simonov, Kristallografyia, 20, 63, (1975).
[8] A.I. Shkurpelo, Yu.A. Simonov, O.A. Bologa, and T.I. Malinovskii, Dokl. Akad. Nauk SSSR, 248, 5, 1120, (1979).
[9] M.M. Botoshansky, Yu.A. Simonov, and O.A. Bologa, Zh. Struct. Khim., 22, 5, 132, (1981).
[10] Yu.A. Simonov, P.N. Bourosh, O.A. Bologa, M.D. Mazus, and N.V. Gerbeleu, Zh. Struct. Khim., 40, 1, 85, (1999).
[11] M.C. Datta, C.R. Saha, and D. Sen, J. Appl. Chem. Biotechn., 27, 2, 383, (1977).
[12] T. Yamaguchi and T. Tsumura, Chem. Lett., 2, 4, 409, (1973).
[13] V.N. Zubarev, V.N. Shofransky, and A.M. Goldman, Zh. Neorg. Khim., 22, 4, 1026, (1977).
[14] K.I. Turta, V.E. Zubareva, V.N. Shofransky, I.I. Bulgak, D.G. Batir, B.V. Timokhin, and V.I. Dmitriev, Koord. Khim., 13, 5, 634, (1987).
[15] F.A. Cotton and J.G. Norman, J. Am. Chem. Soc., 93, 1, 80, (1971).
[16] M. Moszner, F. Asaro, S. Geremia, G. Pellizer, and C. Tavagnacco, Inorg. Chim. Acta, 261, 2, 161, (1997).
[17] J. Galinkina, C. Wagner, E. Rusanov, K. Merzweiler, H. Schmidt, and D. Steinborn, Z. Anorg. Allg. Chem., 628, 2375, (2002).
[18] A.M. Bond and M. Khalifa, Australian J. Chem., 41, 9, 1389, (1988).
[19] A. Das, S.M. Peng, and S. Bhattacharya, Polyhedron, 20, 3-4, 327, (2001).
[20] F.H. Allen, Acta Cryst., B 58, 380, (2002).
[21] Yu.A. Simonov, N.V. Gerbeleu, M. Gdaniec, P.N. Bourosh, E.B. Coropceanu, and O.A. Bologa, Koord. Khim., 27, 5, 368, (2001).
[22] S.T. Malinovsky, E.B. Coropceanu, V.E. Zavodnik, and O.A. Bologa, Kristallografyia, 47, 1, 58, (2002).
[23] M. Sheldrick, Acta Crystallogr., Sect. A, 64, 112, (2008).
[24] E. Coropceanu, N. Gerbeleu, O. Bologa, and G. Cernei, Analele stiintifice ale USM, 312, (2000).
[25] M.W. Attia, E. Zangrando, L. Randaccio, and C. Lopez, Acta Crystallogr., Sect. C: Cryst. Struct. Commun., 43, 1521, (1987).
[26] U. Englert, G. Heger, E. Kummerle, and R. Wang, Z. Kristallogr., 214, 7, (1999).
[27] Zhi-Y. Dong, X.-W. Liu, X.-Q. Wang, R.-J. Wang, and G.-Q. Shen, Acta Crystallogr., Sect.E: Struct. Rep. Online, 59, m260, (2003).
[28] S. Noro and S. Kitagawa, Stud. Surf. Sci. Catal., 141, 363, (2002).
[29] A.P. Rija, E.B. Koropchanu, O.A. Bologa, S.T. Malinovsky, and M. Gdaniec, Zh. Strukt. Khim., [in Russian], 48, 1197, (2007).
[30] E.B. Koropchanu, A.P. Rija, V.N. Shofransky, O.A. Bologa, M. Gdaniec, and S.T. Malinovsky, Zh. Strukt. Khim. [in Russian], 48, 1175, (2007).
[31] S.T. Malinovsky, E.B. Koropchanu, O.A. Bologa, A.N. Rija, and M. Gdaniec, Zh. Strukt. Khim., [in Russian], 48, 548, (2007).