ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2021, Vol. 47, No. 8, pp. 551–559. © Pleiades Publishing, Ltd., 2021.
Russian Text © The Author(s), 2021, published in Koordinatsionnaya Khimiya, 2021, Vol. 47, No. 8, pp. 489–498.

Dedicated to the memory of Professor A.A. Pasynskii

Coordination of Hexahydro-1,3,5-Trimethyl-1,3,5-Triazine in Cadmium(II) and Cobalt(II) Carboxylate Complexes

M. A. Shmelev[a], *, Yu. K. Voronina[a], S. S. Chekurova[b], N. V. Gogoleva[a], T. M. Ivanova[a], O. I. Lyamina[a], E. V. Fatyushina[a], M. A. Kiskin[a], A. A. Sidorov[a], and I. L. Eremenko[a], [c]

[a] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia*
[b] *Mendeleev University of Chemical Technology of Russia, Moscow, Russia*
[c] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia*
**e-mail: shmelevma@yandex.ru*

Received March 19, 2021; revised March 30, 2021; accepted March 31, 2021

Abstract—The effect of bulky tridentate ligands on the geometry of carboxylate complexes was studied in relation to hexahydro-1,3,5-trimethyl-1,3,5-triazine (TACH). The reaction of $[Co_2Gd(NO_3)(Piv)_6(MeCN)_2]$ (Piv is the pivalic acid anion) with TACH gave the complex $[Co_2Gd(NO_3)(Piv)_6(TACH)_2]$ (**I**), in which the initial heterometallic moiety was retained and cobalt(II) ions coordinated the N-donor ligand to give a half-sandwich structure. The use of Cd(II) and Eu(III) pentafluorobenzoates in the reaction with TACH resulted in the isolation of only the homometallic complex $[Cd(Pfb)_2(TACH)_2]$ (**II**) (Pfb is pentafluorobenzoic acid anion). Owing to high coordination number of cadmium(II) ion in **II**, a sandwich complex with two TACH molecules coordinated to the same metal ion was obtained. The structure of new complexes was determined by X-ray diffraction (CIF file CCDC nos. 2062230 (**I**) and 2062229 (**II**)). It was shown that binding of an N-donor ligand to a metal ion induces a significant distortion of the metal coordination polyhedra and a conformational change of hexahydro-1,3,5-trimethyl-1,3,5-triazine.

Keywords: cadmium, cobalt, pivalic acid, hexahydro-1,3,5-trimethyl-1,3,5-triazine, pentafluorobenzoic acid, X-ray diffraction

DOI: 10.1134/S1070328421080078

INTRODUCTION

N-Donor ligands are widely used in coordination chemistry. Depending on the structural features and the coordination capacity, these ligands are used to design a specified environment of the metal centers. Among the large number of primary, secondary, and tertiary amines, mention should be made of 1,4,7-triazacyclononane (TACN), hexahydro-1,3,5-triazine, and their derivatives in which nitrogen atoms can occupy coordination sites of one triangular face of the metal environment [1–4].

Quite a few researchers have been engaged in the synthesis and studies of compounds of TACN and its derivatives. Numerous publications of top specialists in coordination, organometallic, physical, and organic chemistry are devoted to complexes of these ligand [5–7]. Facial coordination is preferable for macrocyclic 1,4,7-triazacyclononane. It can be avoided only if the coordination environment completely rules out this type of binding (e.g., a square geometry), or if some of the sites of the coordination polyhedron are strongly blocked by other ligands. Despite the unique character of TACN, the behavior of this ligand is trivial in some respect, i.e., the modes of coordination inherent in this ligand are limited. There are only two known sandwich cationic complexes with 1,4,7-trimethyl-1,4,7-triazacyclononane (L'): $[Na(L')_2](A)_2$ [8] and $[K(L')_2](A)_2$ [9] (A is tetrakis(3,5-bis(trifluoromethyl)phenyl)borate). No sandwich moieties with 1,4,7-triazacyclononane were obtained for rare earth elements; only half-sandwich complexes $[ScCl_3(L')]$, $[MCl_3(L')]$ (M = Sc, Y), are known from the literature [10, 11].

Although a large number of compounds have been obtained with TACN derivatives, probably, in some cases, diethylenetriamine or its derivatives, which are also capable of facial coordination to the metal, could be used instead.

There are other cyclic tridentate N-donor ligands that are also capable of facial tridentate chelating coordination, namely, hexahydro-1,3,5-triazine and its 1,3,5-derivatives. Among them, hexahydro-1,3,5-

trimethyl-1,3,5-triazine (TACH) and 1,3,5-tribenzylhexahydro-1,3,5-triazine were used most often. In our opinion, in quite a few cases, the use of hexahydro-1,3,5-triazines instead of 1,4,7-trimethyl-1,4,7-triazacyclononane would allow one to avoid steric hindrance and attain a much greater structural diversity of compounds.

The environment of the metal center can be completely composed of two coordinated TACH molecules thus giving cationic sandwich complexes. In the case of metals with large coordination numbers, these sandwich moieties can attach two or three more ligands with partial compensation of the positive charge (to give cationic complexes) or with full charge compensation (to give molecular complexes) [12–17].

Hexahydro-1,3,5-triazine derivatives are quite widely used in the coordination and organometallic chemistry, e.g., to increase the stability of compounds unstable to water or oxygen [14, 18]. As a rule, these ligands are coordinated to metal centers by all three nitrogen atoms to give half-sandwich moieties. Despite ready accessibility and low cost of hexahydro-1,3,5-triazines, there are only a few carboxylate complexes with the trimethyl-substituted derivative, TACH, in which it forms half-sandwich moieties. These are the mononuclear $[Ln(L)(OOCC(Ph)_3)_3]$ (Ln = La, Nd) and binuclear $[Ln_2(L)(OOCC(Ph)_3)_6]$ lanthanide complexes [2].

In this communication, we consider two important examples of TACH coordination in carboxylate complexes. In one case, TACH provides the formation of a half-sandwich moiety in the complex $[Co_2Gd(NO_3)(Piv)_6(TACH)_2]$ (**I**) with a stable heterometallic core, and in the other case, it gives a sandwich moiety composed of two monodentately coordinated triazine ligands in $[Cd(Pfb)_2(TACH)_2]$ (**II**).

EXPERIMENTAL

All operations related to the synthesis of new complexes were performed in air using commercial acetonitrile (99.9%) and TACH (97%, Sigma-Aldrich). The complexes $[\{Cd(Pfb)(H_2O)_4^+\}_n \cdot n(Pfb)]$ (Pfb is pentafluorobenzoate anion), $[Eu_2(Pfb)_6(H_2O)_8] \cdot 2H_2O$, and $[Co_2Gd(NO_3)(Piv)_6(MeCN)_2]$ (Piv is pivalate anion) were prepared by known procedures [19, 20]. IR spectra were measured on a Spectrum 65 FTIR spectrophotometer (PerkinElmer) by attenuated total reflectance (ATR) method in the 4000–400 cm^{-1} frequency range. Elemental analysis was performed on a EuroEA 3000 CHNS analyzer (EuroVector).

Synthesis of $[Co_2Gd(NO_3)(Piv)_6(TACH)_2]$ (I). TACH (0.036 g, 0.294 mmol) was added to a solution of $[Co_2Gd(NO_3)(Piv)_6(MeCN)_2]$ (0.150 g, 0.147 mmol) in 15 mL of MeCN (Co : TACH = 1 : 1), and the mixture was stirred for 20 min with heating up to 70°C. The resulting solution was kept at room temperature in a closed vial. The crystals formed after 7 days, which were suitable for X-ray diffraction, were separated from the mother liquor by decanting and washed with acetonitrile (T = ~5°C). The yield of **I** was 0.147 g (82.5% based on $[Co_2Gd(NO_3)(Piv)_6(MeCN)_2]$).

For $C_{42}H_{84}N_7O_{15}Co_2Gd$

Anal. calcd., %	C, 41.9	H, 7.2	N, 8.1
Found, %	C, 42.2	H, 7.5	N, 8.3

IR (ATR; ν, cm^{-1}): 3675 w, 2956 m, 2867 m, 2803 m, 1608 s, 1578 m, 1563 s, 1481 s, 1458 m, 1419 s, 1400 s, 1377 m, 1355 s, 1270 w, 1223 m, 1168 w, 1123 s, 1117 m, 1091 w, 1049 w, 1000 m, 981 w, 961 m, 930 m, 903 m, 840 m, 805 w, 791 m, 698 w, 612 s, 573 m, 549 m, 432 s, 443 s, 419 s, 403 s.

Synthesis of $[Cd(Pfb)_2(TACH)_2]$ (II). TACH (0.042 g, 0.322 mmol) was added to a solution of $[\{Cd(Pfb)(H_2O)_4^+\}_n \cdot n(Pfb)^-]$ (0.100 g, 0.166 mmol) in 7 mL of MeCN (Cd : L = 1 : 2). The reaction mixture was stirred for 15 min, and the resulting transparent solution was kept at 75°C in a closed vial. The colorless crystals formed after 10 days, which were suitable for X-ray diffraction, were separated from the mother liquor by decanting and washed with cold acetonitrile (T = ~5°C). The yield of **II** was 0.055 g (42.3% based on $[\{Cd(Pfb)(H_2O)_4^+\}_n \cdot n(Pfb)^-]$).

For $C_{26}H_{30}N_6O_4F_{10}Cd$

Anal. calcd., %	C, 39.4	H, 3.8	N, 10.6
Found, %	C, 39.3	H, 3.4	N, 10.8

IR (ATR; ν, cm^{-1}): 3298 w, 2804 w, 1705 w, 1625 w, 1555 m, 1351 s, 1470 c. 1400 m, 1372 s, 1350 s, 1298 m, 1163w, 1114 m, 990 m, 938 w, 841 m, 743 m, 526 m, 473 w, 439 w, 404 w.

Single crystal X-ray diffraction was carried out on a Bruker Apex II diffractometer equipped with a CCD array detector (MoK_α, λ = 0.71073 Å, graphite monochromator) [21]. The semiempirical absorption corrections were applied for all compounds using the SADABS program [22]. The structures were solved by direct methods and refined by full-matrix least squares in the anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms at the carbon atoms of organic ligands were generated geometrically and refined in the riding model. The calculations were carried out by the SHELX program package [23] using OLEX 2 software [24]. The geometry of metal polyhedra was determined using the SHAPE 2.1 program [25, 26]. The crystallographic data and structure refinement details for **I** and **II** are given in Table 1; selected bond lengths and bond angles are presented in Table 2.

Table 1. Crystallographic parameters and structure refinement details for **I** and **II**

Parameter	Value	
	I	**II**
M	1202.27	792.96
T, K	296(2)	296.15
System	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a Å	12.134(8)	10.5023(4)
b Å	23.002(14)	15.5799(6)
c Å	22.025(14)	20.8838(10)
α, deg	90	75.171(2)
β, deg	102.487(10)	85.547(2)
γ, deg	90	74.271(2)
V, Å^3	6002(7)	3179.5(2)
Z	4	4
ρ(calcd.), g/cm^3	1.331	1.657
μ, mm^{-1}	1.698	0.788
θ_{max}, deg	26.000	26.000
T_{min}/T_{max}	0.5874/0.7725	0.2893/0.3812
Number of measured reflections	23212	31483
Number of unique reflections	11115	12419
Number of reflections with $I > 2\sigma(I)$	8899	7249
R_{int}	0.0234	0.0416
Number of refined parameters	7066	8303
GOOF	1.020	0.966
R_1 ($I > 2\sigma(I)$)	0.0332	0.0690
wR_2 ($I > 2\sigma(I)$)	0.0892	0.2124
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	−0.806/0.626	−0.536/1.521

The atomic coordinates and other parameters for compounds **I** and **II** are deposited with the Cambridge Crystallographic Data Centre (CCDC) (nos. 2062230 (**I**) and 2062229 (**II**), respectively); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The reaction of the pre-synthesized heterometallic complex $[Co_2Gd(Piv)_6(NO_3)(MeCN)_2]$ [20] with TACH (Co : TACH = 1 : 1) in MeCN gave crystals of compound $[Co_2Gd(NO_3)(Piv)_6(TACH)_2]$ (**I**), in which the heterometallic moiety is retained and cobalt(II) ions coordinate the N-donor ligand molecule to give a half-sandwich structure. Upon the reaction of $[\{Cd(Pfb)(H_2O)_4^+\}_n \cdot n(Pfb)^-]$ and $[Eu_2(Pfb)_6(H_2O)_8]\cdot 2H_2O$ with TACH (Cd : Eu : TACH = 1 : 1 : 2) in MeCN, only the homometallic cadmium(II) complex $[Cd(Pfb)_2(TACH)_2]$ (**II**) was isolated. Note that a similar procedure was previously used to prepare a number of heterometallic Cd/Eu complexes with monodentate, bridging, and chelating N-donor ligands and substituted benzoic acid anions [27–32]. Compound **II** was also synthesized in the absence of lanthanide salts in the reaction mixture (see Experimental). Owing to the high coordination number of the cadmium(II) ion in **II**, a sandwich complex with two TACH molecules coordinated to one metal ion was formed.

The structures of compounds **I** and **II** were established by X-ay diffraction. Complex **I** crystallizes in the monoclinic space group $P2_1/c$. In the trinuclear $\{Co_2Gd\}$ core, the central Gd(III) ion is connected to each terminal cobalt(II) ion by three bridging Piv anions (Fig. 1a). In one coordinated pivalate anion, the *tert*-butyl group is disordered over two positions in ~1 : 1 ratio. The Gd environment is completed to a

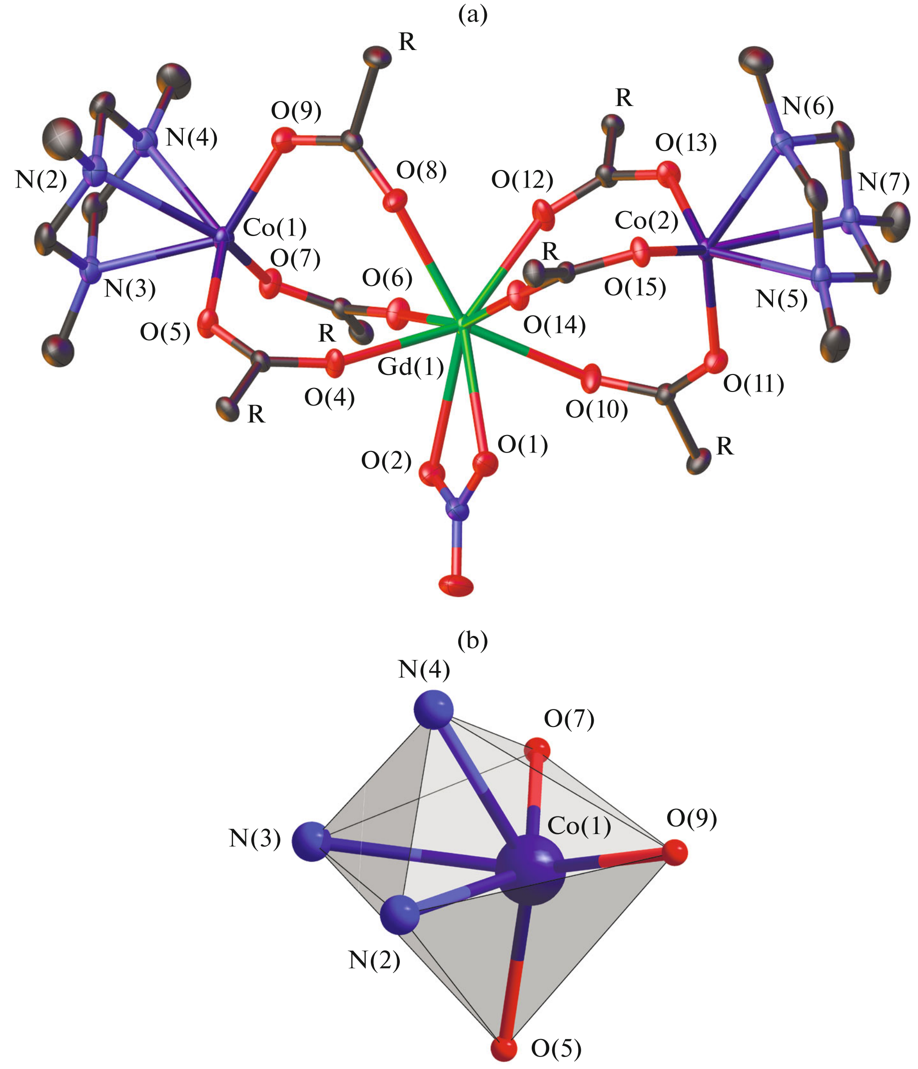

Fig. 1. (a) Molecular structure of **I** and (b) coordination polyhedron of Co(1) ion. R = $(CH_3)_3C$; in (a), the substituents at the carboxyl group and hydrogen atoms are omitted.

dodecahedron with triangular faces (GdO_8) by chelation of a nitrate anion. Each cobalt(II) ion coordinates a κ^3-bound TACH molecule, thus completing its environment to a highly distorted octahedron (CoN_3O_3, Table 2, Fig. 1b). All N–Co bonds are considerably longer than the average Co–N coordination bond, and one of these bonds is elongated compared with the other two bonds (Co(1)–N(2), 2.455(4); Co(1)–N(3), 2.307(4); Co(1)–N(4), 2.329(4); Co(2)–N(5), 2.297(3); Co(2)–N(6), 2.267(4); Co(2)–N(7), 2.427(3) Å). The coordinated TACH molecule is in the chair conformation, and geometry of the hexahydro-1,3,5-triazine moiety is slightly distorted upon coordination to the cobalt(II) ion (Table 3).

As compared with the previously synthesized $\{Co_2Ln(Piv)_6(NO_3)(L)_2\}$ complexes with monodentate and chelating ligands (L), the coordination of the bulky TACH molecule to cobalt(II) leads to elongation of the Co–Ln bonds and increase in the CoLnCo angle in the $\{Co_2Ln\}$ trinuclear metal core (L = TACH; Co(1)–Gd(1), 4.143(2); Co(2)–Gd(1), 4.173(3) Å; CoGdCo, 144.21(2)°; L = MeCN [20], Co...Ln, 3.987(1) Å; CoLnCo, 136.39(1)°; L is pyridine [33]; Co...Ln, 4.034(6) Å; CoLnCo, 137.85°; L is quinoline [34]; Co...Ln, 4.031(3) Å; CoLnCo, 137.83°; L = 2,4,4,5,5-pentamethyl-2-imidazolin-1-oxyl 3-oxide [35]; Co...Ln, 3.970(1) Å; CoLnCo, 142.19°).

The crystal packing of complex **I** is additionally stabilized by C–H...O contacts between the H atoms of *tert*-butyl groups and the O atoms of the Piv anions to form a supramolecular layer (Table 4).

Complex **II** crystallizes in the triclinic space group $P\bar{1}$. The independent part of the unit cell contains two structurally similar molecules $[Cd(Pfb)_2(TACH)_2]$

Table 2. Selected bond lengths (Å) and angles (deg) for complexes **I** and **II**

I		**II**	
Bond	*d*, Å	Bond	*d*, Å
Co(1)–N(2)	2.455(4)	Cd(1A)–N(1A)	2.452(5)
Co(1)–N(3)	2.307(4)	Cd(1A)–N(2A)	2.690(5)
Co(1)–N(4)	2.329(4)	Cd(1A)–N(3A)	2.666(5)
Co(1)–O(5)	1.953(3)	Cd(1A)–N(4A)	2.467(5)
Co(1)–O(7)	1.963(3)	Cd(1A)–N(5A)	2.700(5)
Co(1)–O(9)	1.954(4)	Cd(1A)–N(6A)	2.634(6)
Co(2)–N(5)	2.297(3)	Cd(1A)–O(1A)	2.311(5)
Co(2)–N(6)	2.267(3)	Cd(1A)–O(3A)	2.297(6)
Co(2)–N(7)	2.427(3)	Cd(1B)–N(7)	2.441(5)
Co(2)–O(11)	1.971(3)	Cd(1B)–N(8)	2.672(6)
Co(2)–O(13)	1.964(3)	Cd(1B)–N(10)	2.690(6)
Co(2)–O(15)	1.968(3)	Cd(1B)–N(11)	2.463(5)
Gd(1)–O(1)	2.518(3)	Cd(1B)–N(12)	2.647(6)
Gd(1)–O(2)	2.525(4)	Cd(1B)–N(13)	2.700(7)
Gd(1)–O(4)	2.297(3)	Cd(1B)–O(1B)	2.323(6)
Gd(1)–O(6)	2.292(3)	Cd(1B)–O(3B)	2.311(6)
Gd(1)–O(8)	2.296(3)	Angle	ω, deg
Gd(1)–O(10)	2.284(3)	N(1A)Cd(1A)N(2A)	53.8(2)
Gd(1)–O(12)	2.327(3)	N(1A)Cd(1A)N(3A)	53.7(2)
Gd(1)–O(14)	2.277(3)	N(3A)Cd(1A)N(2A)	51.3(2)
Angle	ω, deg	N(1A)Cd(1A)O(1A)	90.5(2)
N(2)Co(1)N(4)	57.1(1)	N(2A)Cd(1A)O(1A)	144.1(2)
N(4)Co(1)O(7)	88.8(2)	N(3A)Cd(1A)O(1A)	107.4(2)
O(5)Co(1)O(7)	114.4(1)	N(3A)Cd(1A)O(3A)	125.4(2)
O(5)Co(1)N(2)	86.9(1)	N(2A)Cd(1A)O(3A)	74.4(2)
N(3)Co(1)O(9)	137.9(2)	N(1A) Cd(1A)O(3A)	92.6(2)
O(7)Co(1)O(9)	113.5(2)	N(4A)Cd(1A)O(1A)	85.1(2)
O(5)Co(1)O(9)	111.1(2)	N(5A)Cd(1A)O(1A)	131.4(2)
N(4)Co(1)O(9)	85.9(2)	N(6A)Cd(1A)O(1A)	85.0(2)
N(2)Co(1)O(9)	86.6(2)	N(1A)Cd(1A)N(4A)	169.4(2)
N(3)Co(1)N(4)	57.8(2)	N(1A)Cd(1A)N(5A)	134.6(2)
N(3)Co(1)N(2)	57.1(2)	O(1A)Cd(1A)O(3A)	115.3(2)
N(3)Co(1)O(5)	82.3(2)	N(7)Cd(1B)N(8)	53.7(2)
N(3)Co(1)O(7)	88.3(2)	N(7)Cd(1B)N(10)	53.6(2)
N(6)Co(2)N(7)	57.8(1)	N(8)Cd(1B)N(10)	51.5(2)
N(7)Co(2)O(11)	88.6(1)	O(3B)Cd(1B)N(7)	92.5(2)
O(11)Co(2)O(15)	113.9(1)	O(3B)Cd(1B)N(8)	125.4(2)
N(6)Co(2)O(15)	87.7(1)	O(3B)Cd(1B)N(10)	74.2(2)
O(13)Co(2)O(15)	118.0(1)	O(3B)Cd(1B)N(11)	80.7(2)
N(6)Co(2)O(13)	89.9(1)	O(3B)Cd(1B)N(12)	129.3(2)
N(7)Co(2)O(13)	87.3(1)	O(3B)Cd(1B)N(13)	84.3(2)
O(13)Co(2)O(11)	103.6(1)	O(3B)Cd(1B)O(1B)	115.8(2)
N(5)Co(2)O(11)	91.6(1)	N(11)Cd(1B)N(12)	54.4(2)
N(5)Co(2)O(13)	141.6(1)	N(11)Cd(1B)N(13)	53.5(2)
N(5)Co(2)N(6)	59.5(2)	N(12)Cd(1B)N(13)	51.7(2)

Table 3. Geometric characteristics of the uncoordinated TACH molecule [36] and TACH molecule in complexes **I** and **II**

Bond/angle	TACH [36]	$[Co_2Gd(NO_3)(Piv)_6(TACH)_2]$ (**I**)	$[Cd(Pfb)_2(TACH)_2]$ |(**II**)
C–N, Å	1.451(1)–1.473(1)	1.410(6)–1.446(7)	1.435(14)–1.469(14)
CNC, deg	109.0–112.4	109.5–111.4	109.0–110.8
NCN, deg	110.4–111.8	103.5–106.7	104.9–108.2

Table 4. Geometric characteristics of the C–H...F and C–H...O contacts in the crystals of compounds **I** and **II**

Hydrogen bond	Distance, Å			DHA angle, deg
	D–H	H...A	D...A	
		I		
C(38)–H(38A)...O(15)	0.97	2.59	2.938(6)	101
C(38)–H(38B)...O(3)	0.97	2.56	3.499(7)	164
		II		
C(15B)–H(15D)...O(2B)	0.97	2.35	3.128(11)	137
C(17A)–H(17A)...O(2A)	0.97	2.35	3.123(11)	136
C(18B)–H(18F)...O(4A)	0.96	2.56	3.517(12)	177
C(20A)–H(20A)...O(4B)	0.96	2.54	3.498(14)	173
C(20A)–H(20C)...F(5A)	0.96	2.53	3.471(12)	168
C(22A)–H(22B)...O(4B)	0.97	2.49	3.430(11)	162
C(22B)–H(22D)...O(4A)	0.97	2.45	3.379(12)	161
C(25B)–H(25F)...F(6B)	0.96	2.54	3.285(13)	135

(**II**). The cadmium(II) ion coordinates two κ^3-bound TACH molecules to give a sandwich structure (Fig. 2), in which its environment is completed to a distorted dodecahedron with triangular faces via monodentate coordination of two Pfb anions (Fig. 2b, CdN_6O_2). Virtually all N–Cd bonds in compound **II** are noticeably longer than the average Cd–N coordination bond, while the Cd–O bond lengths are usual. The TACH molecule in **II** occurs in a chair conformation, and the geometry of the hexahydro-1,3,5-triazine moiety is slightly distorted upon coordination to cadmium(II) (Table 3).

The crystal packing of complex **II** is additionally stabilized by the C–H...F and C–H...O contacts between the H atoms of the coordinated TACH molecules, fluorine atoms of the pentafluorophenyl substituents, and carboxyl O atoms (Fig. 3, Table 4) and by stacking interactions between two pentafluorobenzoate anions of neighboring molecules (the distance between the centers of the interacting moieties and the angle between the planes are 3.825 Å and 0.00°, respectively).

From the structural standpoint, it is of interest to note a conformational change of hexahydro-1,3,5-trimethyl-1,3,5-triazine within the metal coordination sphere compared to the free molecule. Earlier, it was found that the TACH molecule occurs as the monoaxial conformer in the crystal [36] and in the gas phase [37] and as a mixture of diaxial and monoaxial conformers in solution. The all-equatorial conformer was not detected. According to quantum chemical calculations, the barrier for monoaxial to all-equatorial transition is 20 kJ/mol [36]. This conformational behavior is attributable to repulsion of the nitrogen lone pairs (LPs) of electrons and the anomeic effect [38–42].

Analysis of the data on TACH geometry in the crystals of various compounds present in the CCDC demonstrated [43] that upon introduction of this ligand to the metal coordination sphere, the monoaxial conformation is retained only in the case of coordination to one nitrogen atom, while binding to two or three nitrogen atoms is accompanied by a change in the nitrogen atom pyramidalization, with the ring conformation being transformed to all-equatorial one. In this case, LPs of all three N atoms are accessible for metal coordination, and the energy benefit from the complex formation exceeds the energy expenditure for the conformational change of one or several rings. A similar transition occurs in complexes **I** and **II** we prepared (Fig. 4).

For detailed conformational analysis of these compounds, it is convenient to use the CNCg angle, where C is the methyl carbon atom, Cg is the ring centroid.

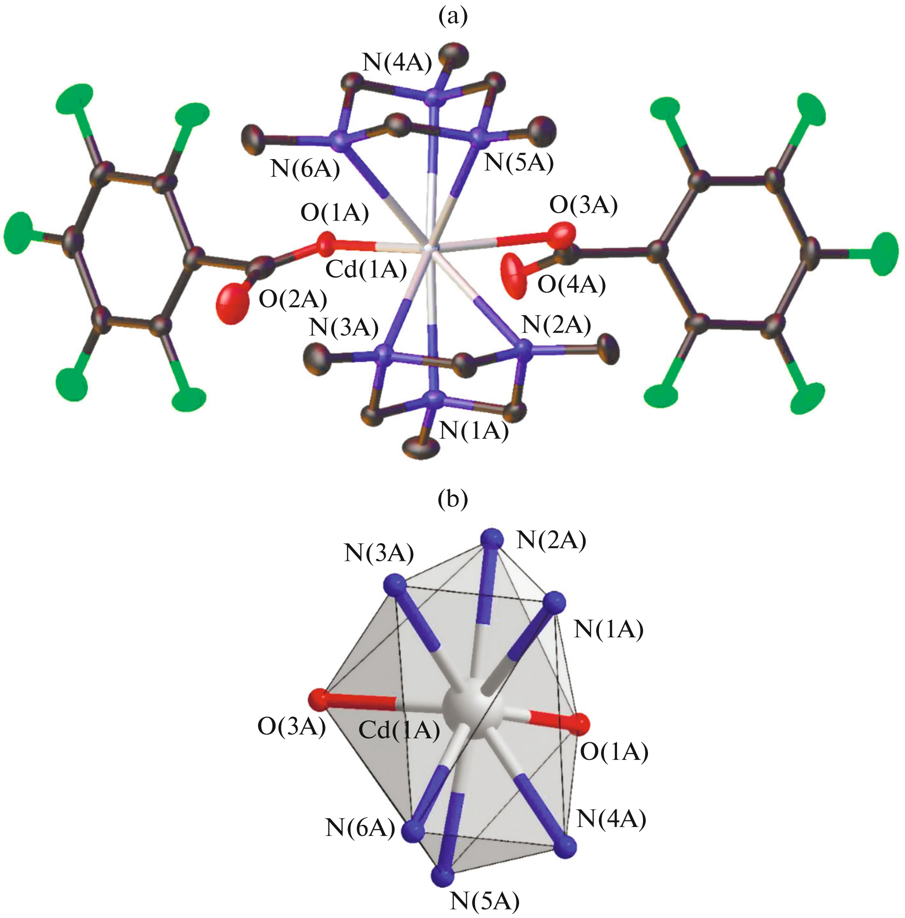

Fig. 2. (a) Molecular structure of **II** and (b) coordination polyhedron of Cd(II) ion; in (a), hydrogen atoms are omitted.

In the diagram, it can be seen that all angles present in the three-coordinated molecules are in the 160°–170° range, while in the singly coordinated molecules, one-third of angles are 90°–110°, which corresponds to a monoaxial conformation of all rings. The most interesting situation is observed for doubly coordinated

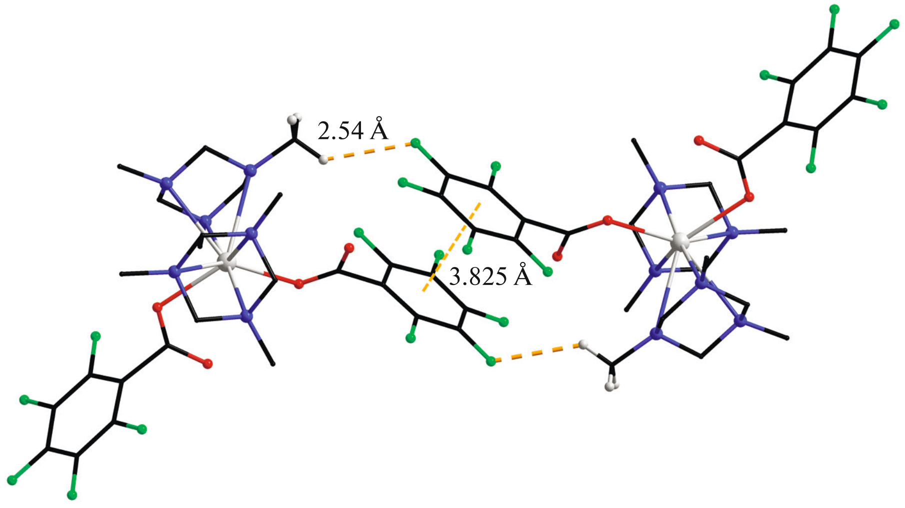

Fig. 3. Fragment of the crystal packing of complex **II**. Hydrogen atoms are omitted.

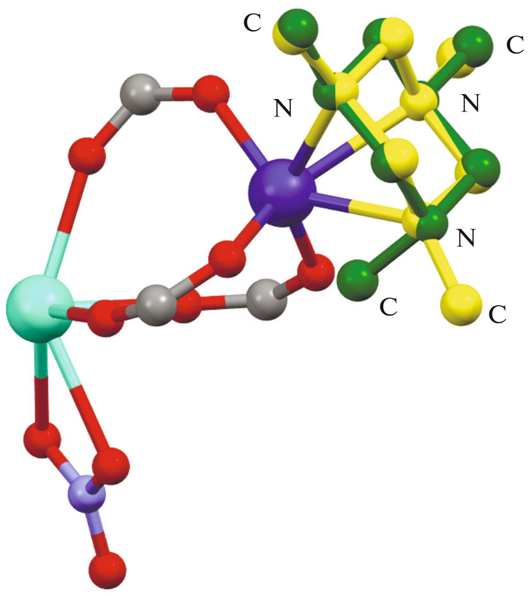

Fig. 4. Superposition of free TACH molecule (green) and TACH molecule in complex **II** (yellow).

molecules: there are altogether eight such structures in the CCDC; four of them exist in the fully equatorial conformation, while three exist in a quite unusual diaxial conformation. Comparison of the structures of these complexes showed that the equatorial structure is formed if the TACH molecule is chelated to one ion, while the diaxial structure is observed in the case of bridging coordination to two different metal ions (Fig. 5).

One more structure present in the CCDC (YOLCOU) is formed by co-crystallization of TACH with perfluorinated trimercury anti-crown ((o-$C_6F_4Hg)_3$). In the crystals of this compound, the heterocycle also has an all-equatorial conformation, but formally TACH is not coordinated to mercury, although these atoms are located strictly one above the other, since the Hg...N distances in this compound are 2.85–2.94 Å, which considerably exceeds the average length of the Hg–N coordination bond (2.5 Å). Apparently, non-covalent interaction of nitrogen LPs with mercury atoms takes place in this case; this requires that these atoms be accessible, like the formation of coordination bonds [44].

Thus, we isolated the half-sandwich heterometallic complex $[Co_2Gd(NO_3)(Piv)_6(TACH)_2]$ (**I**) and the sandwich homometallic complex $[Cd(Pfb)_2(TACH)]$ (**II**). Owing to large coordination number of cadmium(II) ion in **II**, we were able to obtain a sandwich complex with two TACH molecules coordinated to one metal ion. The coordination of κ^3-TACH molecules to cobalt(II) and cadmium(II) ions results in a considerable distortion of the metal coordination environment and a conformational change of 1,3,5-trimethyl-1,3,5-triazacyclohexane. These effects were observed for complexes **I** and **II**.

ACKNOWLEDGMENTS

X-ray diffraction, IR spectroscopy, and C,H,N,S analysis were performed using the equipment of the Center for Collective Use of the Physical Investigation methods of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, within the state assignment for the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, in the field of fundamental scientific research.

FUNDING

This study was supported by the Ministry of the Education and Science of the Russian Federation within the state assignment for Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences.

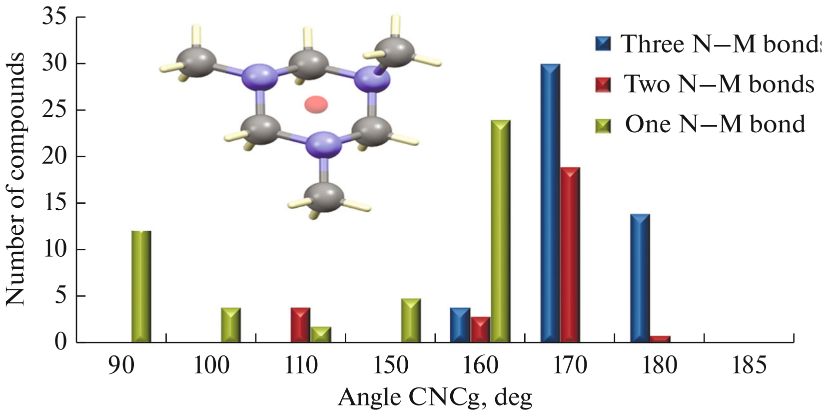

Fig. 5. Histogram of distribution of CNCg angles in TACH molecules coordinated in the mono-, bi-, and tridentate fashion.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Kohn, R.D., Coxon, A.G.N., Chunawat, S., et al., *Polyhedron*, 2020, vol. 185, p. 114572.
2. Vinogradov, A.A., Lyssenko, K.A., Ananyev, I.V., et al., *Russ. J. Coord. Chem.*, 2020, vol. 65, p. 308. https://doi.org/10.1134/S1070328420050097
3. Levin, N. and Codesido, N.O., Marcolongo, J.P., et al., *Inorg. Chem.*, 2018, vol. 57, p. 12270.
4. Zhang, C.-X., Fang, D.-W., Wang, J.-L., et al., *Inorg. Chim. Acta*, 2020, vol. 507, p. 119599.
5. Gordon, J.B., Vilbert, A.C., Siegler, M.A., et al., *J. Am. Chem. Soc.*, 2019, vol. 141, p. 3641.
6. Yang, L., He, X., and Dinca, M., *J. Am. Chem. Soc.*, 2019, vol. 141, p. 10475.
7. Levin, N., Codesido, N.O., Marcolongo, J.P., et al., *Dalton Trans.*, 2019, vol. 48, p. 6767.
8. Everett, M., Jolleys, A., Levason, W., et al., *Chem. Commun.*, 2014, vol. 50, p. 5843.
9. Dyke, J., Levason, W., Light, M.E., et al., *Dalton Trans.*, 2015, vol. 44, p. 13853.
10. Curnock, E., Levason, W., Light, M.E., et al., *Dalton Trans.*, 2018, vol. 47, p. 6059.
11. Hajela, S., Schaefer, W.P., and Bercaw, J.E., *J. Organomet. Chem.*, 1997, vol. 532, p. 45.
12. Hulsmann, M., Neumann, B., Stammler, H.-G., and Mitzel, N.W., *Eur. J. Inorg. Chem.*, 2012, p. 4200.
13. Kohn, R.D., Pan, Z., Kociok-Kohn, G., and Mahon, M.F., *Dalton Trans.*, 2002, p. 2344.
14. Nieland, A., Lamm, J.-H., Mix, A., et al., *Z. Anorg. Allg. Chem.*, 2014, vol. 640, p. 2484.
15. Krieck, S., Gorls, H., and Westerhausen, M., *J. Am. Chem. Soc.*, 2010, vol. 132, p. 12492.
16. Kamps, I., Neumann, B., Stammler, H.-G., and Mitzel, N.W., *Organometallics*, 2010, vol. 29, p. 4746.
17. Kohn, R.D., Seifert, G., Pan, Zh., et al., *Angew. Chem., Int. Ed.*, 2003, vol. 42, p. 793.
18. Venugopal, A., Kamps, I., Bojer, D., et al., *Dalton Trans.*, 2009, p. 5755.
19. Shmelev, M.A., Gogoleva, N.V., Kuznetsova, G.N., et al., *Russ. J. Coord. Chem.*, 2020, vol. 46, no. 8, p. 557. https://doi.org/10.1134/S1070328420080060
20. Kiskin, M., Zorina-Tikhonova, E., Kolotilov, S., et al., *Eur. J. Inorg. Chem.*, 2018, no. 12, p. 1356.
21. *SMART (control) and SAINT (integration) Software. Version 5.0*, Madison: Bruker AXS Inc., 1997.
22. Sheldrick, G.M., *SADABS*, Madison: Bruker AXS Inc., 1997.
23. Sheldrick, G.M., *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, vol. 71, p. 3.
24. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., et al., *J. Appl. Crystallogr.*, 2009, vol. 42, p. 339.
25. Alvarez, S. and Llunell, M., *Dalton Trans.*, 2000, no. 19, p. 3288.
26. Casanova, D., Llunell, M., Alemany, P., et al., *Chem.-Eur. J.*, 2005, vol. 11, p. 1479.
27. Shmelev, M.A., Gogoleva, N.V., Sidorov, A.A., et al., *Russ. J. Coord. Chem.*, 2020, vol. 46, no. 1, p. 1. https://doi.org/10.1134/S1070328420010078
28. Shmelev, M.A., Gogoleva, N.V., Sidorov, A.A., et al., *Russ. J. Coord. Chem.*, 2020, vol. 46, no. 7, p. 493. https://doi.org/10.1134/S1070328420070076
29. Shmelev, M.A., Kiskin, M.A., Voronina, J.K., et al., *Materials*, 2020, vol. 13, no. 24, p. 5689.
30. Shmelev, M.A., Gogoleva, N.V., Sidorov, A.A., et al., *Inorg. Chim. Acta*, 2021, vol. 515, p. 120050.
31. Shmelev, M.A., Gogoleva, N.V., Sidorov, A.A., et al., *Chem. Select.*, 2020, vol. 5, p. 8475.
32. Shmelev, M.A., Kuznetsova, G.N., Dolgushin, F.M., et al., *Russ. J. Coord. Chem.*, 2021, vol. 47, no. 2, p. 127.
33. Sap'yanik, A.A., Lutsenko, I.A., Kiskin, M.A., et al., *Russ. Chem. Bull.*, 2016, vol. 65, p. 2601.
34. Cui, Y., Chen, G., Ren, J., et al., *Inorg. Chem.*, 2000, vol. 39, p. 4165.
35. Fursova, E.Yu., Kuznetsova, O.V., Ovcharenko, V.I., et al., *Russ. Chem. Bull.*, 2007, p. 1742.
36. Sicking, C., Mix, A., Neumann, B., et al., *Dalton Trans.*, 2012, vol. 41, p. 104.
37. Zverev, V.G., Kuznetsov, V.V., Rykov, A.N., et al., *Russ. J. Phys. Chem. A*, 2007, vol. 81, p. 1639.
38. Jones, R.A.Y., Katritzkya, A.R., and Snarey, M., *J. Chem. Soc. B*, 1970, p. 135.
39. Bushweller, C.H., Lourandos, M.Z., and Brunelle, J.A., *J. Am. Chem. Soc.*, 1974, vol. 96, p. 1591.
40. Hutchins, R.O., Kopp, L.D., and Eliel, E.L., *J. Am. Chem. Soc.*, 1968, vol. 90, p. 7174.
41. Harris, N.J. and Lammertsma, K., *J. Am. Chem. Soc.*, 1997, vol. 119, p. 6583.
42. Jewett, J.G., Breeyear, J.J., Brown, J.H., and Bushweller, C.H., *J. Am. Chem. Soc.*, 2000, vol. 122, p. 308.
43. Groom, C.R., Bruno, I.J., Lightfoot, M.P., and Ward, S.C., *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.*, 2016, vol. 72, p. 171.
44. Tugashov, K.I., Gribanyov, D.A., Dolgushin, F.M., et al., *Organometallics*, 2019, vol. 38, no. 15, p. 2910.

Translated by Z. Svitanko