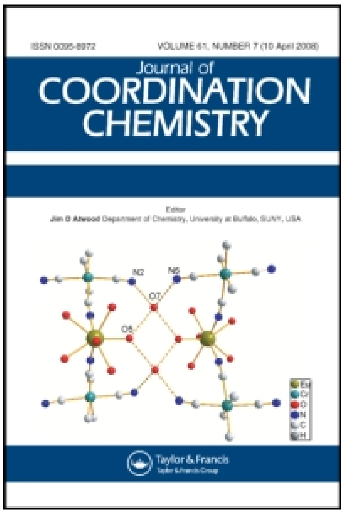

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The complexation of cadmium acetate and propionate by phenanthroline. Structure and properties of $[Cd(CH_3COO)_2(C_{12}H_8N_2)(H_2O)] \cdot H_2O$ and $[Cd(CH_3CH_2COO)_2(C_{12}H_8N_2)]_2 \cdot 2CH_3CH_2COOH$

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The complexation of cadmium acetate and propionate by phenanthroline. Structure and properties of $[Cd(CH_3COO)_2(C_{12}H_8N_2)(H_2O)]\cdot H_2O$ and $[Cd(CH_3CH_2COO)_2(C_{12}H_8N_2)]_2\cdot 2CH_3CH_2COOH$

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The coordination compounds $[Cd(CH_3COO\text{-}\kappa O^1,O^2)_2(\text{phenanthroline-}kN^1\ N^2)(H_2O)]\cdot H_2O$ (**1**) and $[Cd\{\mu\text{-}(CH_3CH_2COO\text{-}\kappa O^1,O^2)\}_2(\text{phenanthroline-}\kappa N^1,N^2)]_2\cdot 2CH_3CH_2COOH$ (**2**) were synthesized and characterized by elemental and thermal analysis and IR spectroscopy. Crystal and molecular structures of both compounds were determined. The complexes are air stable and fairly soluble in water. In both compounds the cadmium is seven-coordinate and contains chelating phenanthroline and two chelating carboxylate groups in the inner coordination sphere. The seventh coordinating oxygen belongs to water in **1** and to bridging carboxylate in **2**. All carboxylate groups are bonded unsymmetrically to the central atom. The coordination polyhedra can be described as distorted pentagonal bipyramid (compound **1**) and distorted capped tetragonal bipyramid (compound **2**). In the structure of **1** intermolecular O(water)–H $\cdots$ O (water/carboxylate) hydrogen bonds create a two-dimensional net along the crystallographic *a*0*c* plane. Each molecule of **2** is connected to two propionic acid molecules *via* hydrogen bonds. In both compounds exist π-stacking interactions.

Keywords: Acetate; Propionate; Cadmium; Phenanthroline; Conductivity; Crystal and molecular structure; Hydrogen bonding; Thermal decomposition

1. Introduction

The work presented here is a continuation of our studies on transition metal complexes with pyridine derivatives and carboxylates [1–6]. The compounds were characterized by chemical analysis, IR and VIS spectroscopy, molar conductivity, magnetic and thermal properties. The crystal and molecular structure of diaquadi(acetato-O)-*bis*(2,4′-bipyridyl) manganese(II) [1] and mono- and diaqua-di(acetato-O)*bis*(2,4′-bipyridyl) copper(II) [2] has been determined. Synthesis, properties and crystal structure of

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transition-metal(II) complexes with pyridine derivatives and carboxylates are extensively studied due to their structures [7–14] and applications, for example in heterogeneous catalysis [15, 16]. Thus, it is interesting to examine the influence of acetate and propionate anions on structure and properties of mixed ligand 1,10′-phenanthroline(phen) complexes of cadmium.

2. Experimental

2.1. *Chemicals and preparation of the complexes*

All chemicals were analytical grade. Propionic acid (Hprop) was obtained from Aldrich, and all other materials were from POCH-Gliwice. An aqueous solution of cadmium(II) propionate was obtained by dissolution of 22.5 mmol of $CdCO_3$ in 15 cm^3 of 3 mol dm^{-3} propionic acid. The suspension was stirred at 333 K and then filtered. The concentration of Cd in the resulting filtrate was determined by EDTA titration at pH 4. The cadmium(II) acetate solution was prepared by dissolution of anhydrous salt (12 mmol) in 19.2 cm^3 of water.

The complexes were prepared by reaction of cadmium(II) acetate or cadmium(II) propionate with phenanthroline. A solution of phen (12 mmol) in 96% v/v ethanol (20.8 cm^3) was added dropwise to water solutions containing appropriate Cd(II) carboxylates (12 mmol). The reaction mixtures were stirred at 333 K for 1 h and the colorless, clear solutions were left to stand. After five days the solid crystalline products were filtered off, washed with 40% v/v ethanol and ethanol-diethyl ether (1 : 1) mixture and dried at room temperature. Yield: 4.1116 g (76.7%) and 5.1815 g (84.2%), respectively, for acetate and propionate complex. For both compounds an additional crop of crystals suitable for X-ray single crystal diffraction measurements was obtained after a week from filtrate standing at ambient temperature. Yield: 1.1686 g (21.8%) and 0.8862 g (14.4%) respectively for acetate and propionate complex. For each compound, both isolated fractions of crystalline products were found to be identical by X-ray powder diffraction (XRPD). The complexes are air stable and fairly soluble in water. Anal. for complexes Calcd/Found (%): $[Cd(CH_3COO)_2(C_{12}H_8N_2)(H_2O)](H_2O)$ (**1**), Cd, 25.16/24.90; C, 43.02/43.92; H, 4.06/4.24; N, 6.27/6.20 and $[Cd(C_2H_5COO)_2(C_{12}H_8N_2)]_2(C_2H_5COOH)_2$ (**2**): Cd, 21.92/22.30; C, 49.18/50.11; H, 4.72/4.78; N, 5.46/5.50. IR (in KBr, cm^{-1}) for (**1**): 3350–3450 vs, 3011 sh, 2932 sh, 1685 w, 1620 sh, 1578 vs, 1560 sh, 1514 s, 1427 vs, 1410 s, 1344 m, 1225 w, 1144 m, 1101 m, 1049 m, 1018 m, 941 m, 851 s, 781 m, 729 s, 725 s, 679 s, 621 m, 509 vw, 473 vw, 421 w; for (**2**): 3049 w, 2976 w, 2941 w, 2879 vw, 1716 s, 1622 w, 1592 sh, 1560 s, 1516 s, 1427 vs, 1412 s, 1269 m, 1223 m, 1144 m, 1101 w, 1076 m, 1009 vw, 895 s, 856 vs, 812 m, 779 m, 729 s, 638 m, 502 w, 472 vw, 418 w.

2.2. *Crystal structure determination*

Colorless rectangular prism crystals of **1** and **2** were mounted on a KM-4-CCD automatic diffractometer equipped with a CCD detector. X-ray intensity data were collected with graphite monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) at 291.0(3) K, with ω scan mode. 20 and 33 seconds exposure times were used for **1** and **2**, respectively, and reflections inside the Ewald sphere were collected up to $2\theta = 50^\circ$. The unit cell parameters were determined from least-squares refinement of the setting angles of 9773 and 6833 strongest reflections, respectively, for **1** and **2**. Details concerning crystal data and refinement are given in table 1. Examination of reflections on two reference frames monitored after each 20 frames measured showed 46.19 and 17.23% loss of the intensity for **1** and **2**, respectively. During the data reduction decay correction coefficients were taken into account. Lorentz, polarization, and numerical absorption [17] corrections were applied. The structures were solved by direct methods and all non-hydrogen atoms refined anisotropically using full-matrix, least-squares technique on F^2. All hydrogen atoms were found from difference Fourier synthesis after four cycles of anisotropic refinement, and were refined as "riding" on the adjacent atom with individual isotropic displacement factor equal 1.2 times the value of equivalent displacement factor of the patent non-methyl carbon atoms and 1.5 times for patent methyl carbon atoms and oxygen atoms. The carbon bonded hydrogen atom positions were idealized after each cycle of refinement. The methyl groups were allowed to rotate about their local three-fold axis. The SHELXS-97 [18], SHELXL-97 [19] and SHELXTL [20] programs were used for all the calculations. Atomic scattering factors were those incorporated in the computer programs. Selected interatomic bond distances and angles are listed in table 2.

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

Compound	**1**	**2**
Empirical formula	$C_{16}H_{18}CdN_2O_6$	$C_{42}H_{48}Cd_2N_4O_{12}$
Formula weight	446.72	1025.64
Temperature (K)	291.0(3)	
Wavelength (Å)	λ(Mo-Kα) = 0.71073	
Crystal system, space group	Monoclinic, $P2_1/c$	
Unit cell and dimensions (Å, °)		
a	8.2593(9)	9.0420(6)
b	22.4360(11)	22.2822(16)
c	10.1718(6)	11.8252(10)
β	106.893(7)	109.726(7)
V (Å^3)	1803.6(2)	2242.7(3)
Z, Calcd density (Mg m^{-3})	4, 1.645	4, 1.519
Absorption coefficient (mm^{-1})	1.244	1.011
$F(000)$	896	1040
Crystal size (mm^3)	0.297 × 0.216 × 0.203	0.381 × 0.233 × 0.230
θ range for data collection	3.15 to 25.12°	3.30 to 25.15°
Index ranges	$-8 \le h \le 9$, $-26 \le k \le 26$, $-12 \le 1 \le 12$	$-10 \le h \le 10$, $-26 \le k \le 26$, $-14 \le 1 \le 13$
Reflections collected/unique	18633/3198 [$R_{(int)} = 0.0227$]	23155/3999 [$R_{(int)} = 0.0978$]
Completeness to $\theta = 25.1^\circ$(%)	99.9	99.8
Refinement method	Full-matrix least-squares on F^2	
Min. and max. transmission	0.730 and 0.775	0.751 and 0.792
Data/restraints/parameters	3198/0/228	3999/0/275
Goodness-of-fit on F^2	1.158	1.138
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0248$, $wR_2 = 0.0248$	$R_1 = 0.0441$, $wR_2 = 0.1050$
R indices (all data)	$R_1 = 0.0270$, $wR_2 = 0.0549$	$R_1 = 0.0463$, $wR_2 = 0.1068$
Largest diff. peak and hole (e Å^{-3})	0.405 and −0.373	0.694 and −0.764

Table 2. Selected bond distances (Å) and angles (°) for **1** and **2**.

Compound	**1**	**2**
Cd(1)–O(4)	2.3170(18)	2.341(4)
Cd(1)–O(1)	2.3210(19)	2.532(3)
Cd(1)–N(1)	2.340(2)	2.369(3)
Cd(1)–N(2)	2.395(2)	2.337(3)
Cd(1)–O(2)	2.4843(19)	2.298(3)
Cd(1)–O(3)	2.5501(18)	2.505(3)
Cd(1)–O(5)	2.3039(18)	–
Cd(1)–O(4)#1	–	2.320(3)
O(1)–C(13)	1.262(3)	1.249(6)
C(13)–O(2)	1.243(3)	1.246(5)
O(3)–C(15)	1.250(3)	–
C(15)–O(4)	1.255(3)	–
O(3)–C(16)	–	1.230(5)
C(16)–O(4)	–	1.274(5)
Cd(1)–O(4)#1	–	2.320(3)
O(91)–C(91)	–	1.299(8)
C(91)–O(92)	–	1.180(9)
O(4)–Cd(1)–O(1)	87.12(6)	133.31(12)
O(4)–Cd(1)–N(1)	132.91(7)	137.24(11)
O(1)–Cd(1)–N(1)	136.15(7)	81.24(12)
O(4)–Cd(1)–N(2)	87.35(7)	104.17(12)
O(1)–Cd(1)–N(2)	98.85(8)	115.15(11)
N(1)–Cd(1)–N(2)	71.08(7)	71.19(10)
O(4)–Cd(1)–O(2)	138.47(6)	90.95(12)
O(1)–Cd(1)–O(2)	53.88(6)	53.18(11)
N(1)–Cd(1)–O(2)	82.45(7)	95.56(12)
N(2)–Cd(1)–O(2)	85.56(7)	164.53(11)
O(4)–Cd(1)–O(3)	52.94(6)	52.20(10)
O(1)–Cd(1)–O(3)	135.98(7)	143.85(12)
N(1)–Cd(1)–O(3)	87.85(7)	85.09(11)
N(2)–Cd(1)–O(3)	97.06(7)	91.36(12)
O(2)–Cd(1)–O(3)	168.56(6)	95.50(13)
O(5)–Cd(1)–O(4)	111.29(7)	–
O(4)#1–Cd(1)–O(4)	–	71.08(15)
O(5)–Cd(1)–O(1)	89.42(8)	–
O(4)#1–Cd(1)–O(1)	–	86.94(12)
O(5)–Cd(1)–N(1)	90.38(7)	–
O(4)#1–Cd(1)–N(1)	–	146.58(13)
O(5)–Cd(1)–N(2)	160.07(7)	–
O(4)#1–Cd(1)–N(2)	–	86.14(13)
O(5)–Cd(1)–O(2)	84.76(7)	–
O(4)#1–Cd(1)–O(2)	–	102.11(13)
O(5)–Cd(1)–O(3)	89.26(6)	–
O(4)#1–Cd(1)–O(3)	–	120.61(12)
C(13)–O(1)–Cd(1)	96.05(16)	87.3(3)
O(2)–C(13)–O(1)	121.1(2)	121.1(4)
C(13)–O(2)–Cd(1)	88.88(15)	98.4(3)
C(15)–O(3)–Cd(1)	87.49(15)	–
C(16)–O(3)–Cd(1)	–	91.9(3)
O(3)–C(15)–O(4)	120.9(2)	–
O(3)–C(16)–O(4)	–	117.3(4)
C(15)–O(4)–Cd(1)	98.31(15)	–
C(16)–O(4)–Cd(1)	–	98.6(3)
C(16)–O(4)–Cd(1)#1	–	147.3(3)
Cd(1)#1–O(4)–Cd(1)	–	108.92(15)
O(92)–C(91)–O(91)	–	122.7(7)

Symmetry transformations used to generate equivalent atoms:
#1 $-x, -y, -z$.

2.3. *Other measurements*

Elemental analyses were carried out using a Carbo–Erba C, H, N analyzer. Cadmium(II) concentrations were determined by complexometric titration with EDTA. IR spectra were recorded as KBr discs on a Shimadzu spectrometer over the range 4000–400 cm^{-1}. Thermal decomposition of complexes were studied by TG, DTA, DTG under static air conditions on a Q-1500 derivatograph over the temperature range 293–1273 K, at a heating rate of 5 and 10 $K\,min^{-1}$ for each compound. The sample masses were 100 mg and a standard material was α-Al_2O_3. The solid products of thermal decomposition were determined from derivatographic curves. The final products of decomposition were confirmed by XRPD using the Powder Diffraction File [21].

3. Results and discussion

A perspective view of mononuclear **1** and dinuclear **2** structures together with the atom numbering schemes are shown in figures 1 and 2; displacement ellipsoids are plotted with 50% probability. Compound **1** crystallizes as a monohydrate and **2** crystallizes as the propionic acid disolvate. All atoms in both compounds lie in general positions, but **2** has an internal inversion center and thus occupies two asymmetric units. The phenanthroline substituent in **1** shows symptoms of disorder, which manifest in relatively large values of orthogonalized atomic displacement parameters (oADPs) in the phen plane. This effect is also observed in **2**, but the enlargement of oADPs is distinctly smaller. Propionic acid in **2** shows signs of disorder, which exhibits in relatively large displacement ellipsoids, especially for the methyl group carbon atom. In both compounds the cadmium

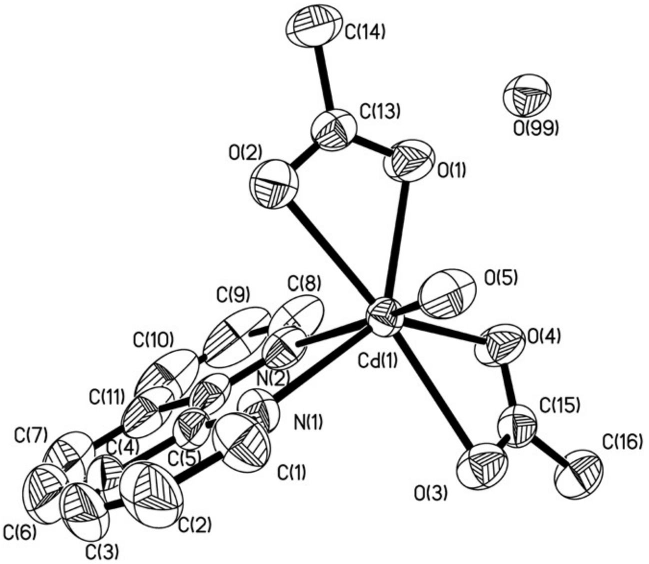


Figure 1. The molecular conformation of $[Cd(CH_3COO)_2(phenanthroline)(H_2O)] \cdot H_2O$ (**1**) with atom numbering, plotted with 50% probability of displacement ellipsoids. The hydrogen atoms are omitted for clarity.

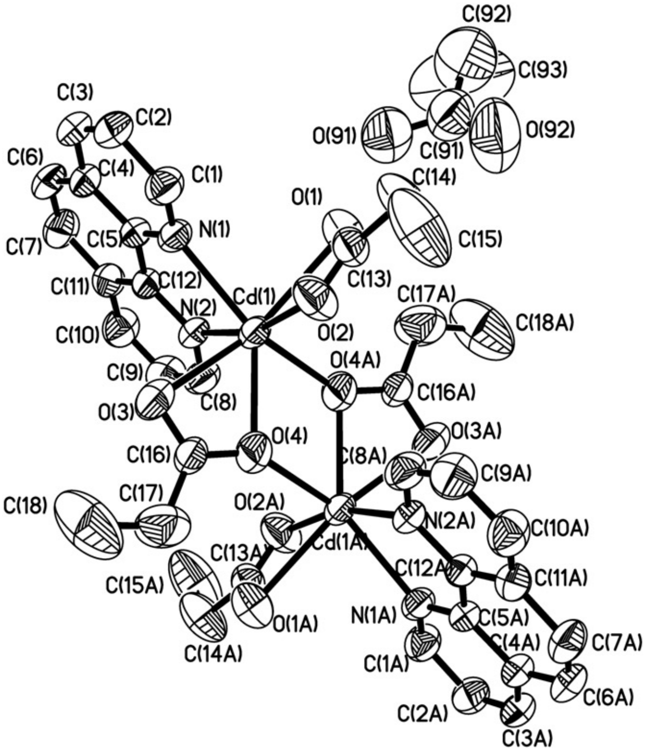


Figure 2. The molecular conformation of $[Cd(CH_3CH_2COO)_2(phenanthroline)]_2 \cdot 2CH_3CH_2COOH$ (**2**) with atom numbering, plotted with 50% probability of displacement ellipsoids. The hydrogen atoms and symmetry generated propionic acid molecule are omitted for clarity. The symmetry generated atoms are indicated by letter "A" after the atom number.

atoms are seven-coordinate and inner coordination spheres contain chelating phen molecule and two chelating carboxylate groups. In **1** the coordination is completed by oxygen atom of water molecule and in **2** by bridging oxygen atom of caboxylate group chelating the second nucleus of the complex. Thus, in **2**, two propionate groups are bidentate chelating and two tridentate chelating-bridging ones. All carboxylate groups are bonded unsymmetrically to cadmium atom. The coordination polyhedra can be described as distorted pentagonal bipyramidal [**1**, figure 3(a)] and distorted capped tetragonal bipyramidal [**2**, figure 3(b)] [22]. Considering chelating groups as monodentate groups coordinating via bisector of N–Cd–N or O–Cd–O angles, the coordination polyhedra can be described as disrupted tetrahedra [figure 3(c),(d)]. In **1** the distortion from ideal polyhedron is much larger than in **2** (the interaxis angles are 102.4(2), 103.6(2), 141.0(2), 126.0(2), 86.7(2), 100.7(2)° and 116.7(2), 107.9(2), 121.5(2), 117.2(2), 94.6(2), 96.8(2)°, respectively). The planar, within experimental error, phenanthroline molecules are inclined at 88.2(3), 86.6(2) (compound **1**) and 76.7(3), 86.8(3)° (compound **2**) to carboxylate groups indicated by O(1) and O(3) atoms, respectively. The cadmium atom deviates 0.108(2) and 0.052(3) Å from the phenanthroline least squares plane respectively for **1** and **2.** In **2** coordinating propionate ions are close to planarity (O(2)–C(13)–C(14)–C(15) and O(3)–C(16)–C(17)–C(18) torsion angles are 9.0(9) and −5.3(9)°) and the propionic acid molecule is bent (O(91)–C(91)–C(92)–C(93) torsion angle is −72(2)°.

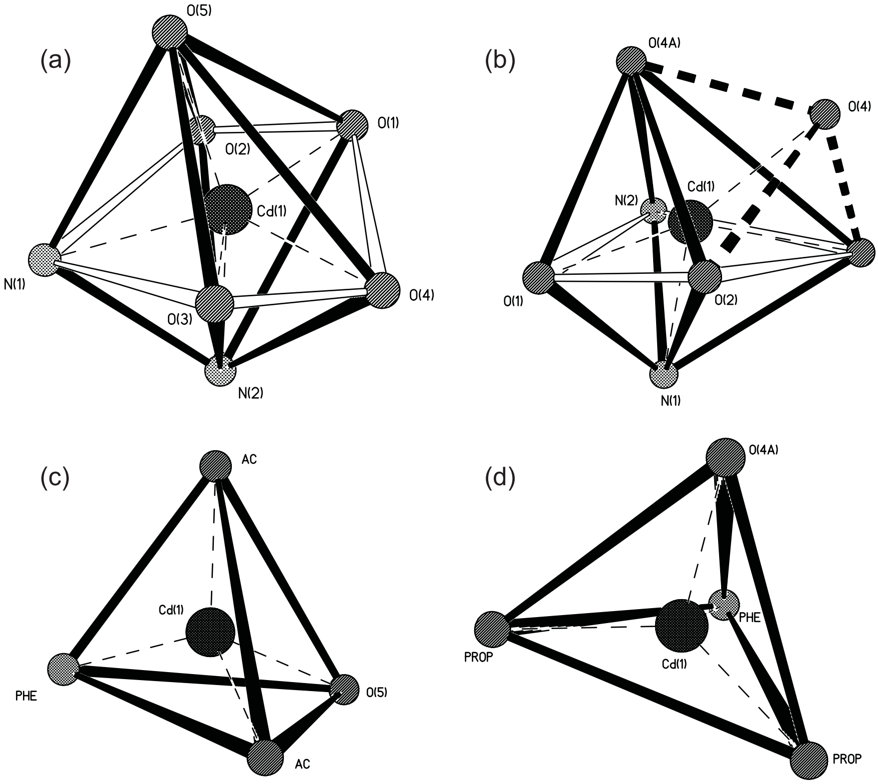


Figure 3. The cadmium coordination polyhedra. (a), (c) for **1** and (b), (d) for **2**. PHE, AC, PROP indicate respectively phenanthroline, acetate and propionate ligands (for exact description see text).

Bond valences were computed as $\nu_{ij} = \exp[(R_{ij} - d_{ij})/b]$ [23, 24], where R_{ij} is the bond-valence parameter (in the formal sense R_{ij} can be considered as a parameter equal to the idealized single-bond length between i and j atoms for given b) and b was taken as 0.37 Å [25, 26]. The $R_{\text{Cd–O}}$ and $R_{\text{Cd–N}}$ were taken as 1.8818, 2.043, respectively. The computed bond valences of the cadmium in **1** are $\nu_{\text{Cd(1)–O(1)}} = 0.305$, $\nu_{\text{Cd(1)–O(2)}} = 0.196$, $\nu_{\text{Cd(1)–O(3)}} = 0.164$, $\nu_{\text{Cd(1)–O(4)}} = 0.308$, $\nu_{\text{Cd(1)–O(5)}} = 0.320$, $\nu_{\text{Cd(1)–N(1)}} = 0.448$, $\nu_{\text{Cd(1)–N(2)}} = 0.386$ v.u. (valence units) and in **2** are $\nu_{\text{Cd(1)–O(1)}} = 0.173$, $\nu_{\text{Cd(1)–O(2)}} = 0.328$, $\nu_{\text{Cd(1)–O(3)}} = 0.186$, $\nu_{\text{Cd(1)–O(4)}} = 0.289$, $\nu_{\text{Cd(1)–O(4)}\#(-x,-y,-z)} = 0.306$, $\nu_{\text{Cd(1)–N(1)}} = 0.414$, $\nu_{\text{Cd(1)–N(2)}} = 0.452$ v.u. Thus, the computed valence of Cd(1) is 2.13 and 2.14 v.u. for **1** and **2**. In both compounds the computed valence of Cd is slightly larger than the formal oxidation state of the cadmium, but only violation of the valence-sum rule by more than 0.25 – 0.30 v.u. [27] unambiguously indicates mistakes in interpretation of the structure by omission or addition of weak hydrogen bonds, showing that bonds are strained from crystallographic constraints that prevent the bonds from attaining their ideal lengths [28]. However, for both compounds, the existing small deviation of valence sum rule can be explained by constraints imposed by chelating phenanthroline and carboxylate groups. Larger value for **2** arises from tridentate carboxylate group, restraining coordination geometry more than bidentate carboxylate group. According to calculated bond valences, the weakest are Cd–O chelating bonds (one from each pair). The second Cd–O bond from each chelating carboxylate group, bridging Cd–O bond (**2**) and Cd–O(water) bond are almost one and half times stronger and the strongest are Cd–N bonds. In both compounds the phenanthroline molecules are bonded almost two times stronger than carboxylate ions.

In the structure of **1** intramolecular O(water)–H···O(water/carboxylate) hydrogen bonds (table 3) create a two-dimensional network along crystallographic *a*0*c* plane with $R_2^2(8)R_5^5(16)[C_3^3(8)C_2^2(6)]$ pattern [29]. Each molecule of **2** is connected to two propionic acid molecules creating a $D_2^2(9)$ pattern [29]. In both structures C–H···O short contacts (table 3) can be considered as weak hydrogen bonds [30, 31]. In both compounds exist π-stacking interactions (table 4, figures 4 and 5) [32] which provide additional stabilization to the crystalline networks.

The IR spectra exhibit absorptions typical for 1,10-phenanthroline coordinating in chelating mode [33–35]. Characteristic bands corresponding to the ν(CN), ν(CC) and

Table 3. Hydrogen-bonds for **1** and **2** (distances in Å, angles in °).

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
1				
O(5)–H(5O)···O(4)#1	0.91	1.79	2.691(3)	170.4
O(5)–H(5P)···O(99)#1	0.89	1.93	2.782(3)	158.4
O(99)–H(99O)···O(1)	0.88	1.89	2.764(3)	170.6
O(99)–H(99P)···O(3)#2	0.89	1.99	2.852(3)	162.5
C(2)–H(2)···O(2)#3	0.93	2.44	3.216(4)	140.7
C(3)–H(3)···O(99)#4	0.93	2.52	3.373(4)	152.6
2				
O(91)–H(91)···O(1)	0.82	1.81	2.598(6)	160.8
C(3)–H(3)···O(3)#5	0.93	2.49	3.284(5)	144.1

Symmetry transformations used to generate equivalent atoms:
#1 $x, -y+1/2, z+1/2$, #2 $x-1, -y+1/2, z-1/2$, #3 $-x, -y, -z+1$, #4 $-x, y-1/2, -z+1/2$, #5 $-x+1, -y, -z+1$.

Table 4. Stacking interactions (distances in Å and angles in °). Cg(1), Cg(2), Cg(3) indicates the centroids of aromatic rings (*R*) containing N(1), N(2), C(6) atoms, respectively, α is a dihedral angle between planes *I* and *J*, β is an angle between Cg(*I*)–Cg(*J*) vector and normal to plane *I* and d_p is a perpendicular distance of Cg(I) on ring *J* plane.

R(*I*)···*R*(*J*)	Cg···Cg	α	β	d_p
1				
Cg(I) Cg(J)	Cg–Cg	Alpha	Beta	CgI_perp
Cg(1)···Cg(1)#1	4.1673	0.02	29.40	3.631
Cg(2)···Cg(3)#2	3.6874	1.45	21.03	3.453
Cg(3)···Cg(2)#2	3.6874	1.45	20.54	3.442
2				
Cg(1)···Cg(1)#1	3.7569	0.02	22.76	3.464
Cg(1)···Cg(3)#1	3.7990	0.25	24.29	3.468
Cg(3)···Cg(1)#1	3.7990	0.25	24.09	3.463
Cg(2)···Cg(3)#3	3.7348	0.67	16.38	3.589
Cg(3)···Cg(2)#3	3.7348	0.67	16.04	3.583

Symmetry equivalent used to generate rings: #1 $-x+1, -y, -z+1$,
#2 $-x, -y, -z$, #3 $-x, -y, -z+1$.

γ(CH) modes of phen appear at 1622 (1620), 1592, 1560 (1560), 1516 (1514) and 729 (729) cm^{-1}, respectively (values for **1** are in parentheses and for **2** without brackets). The ring breathing frequencies for the phen is masked by wagging vibration of the CH$_3$ group of acetate or propionate. For **2** a broad strong intensity band centered at 1716 cm^{-1} originating from stretching ν(CO) frequencies of the uncoordinated propionic acid is observed. The location of this band is in agreement with literature

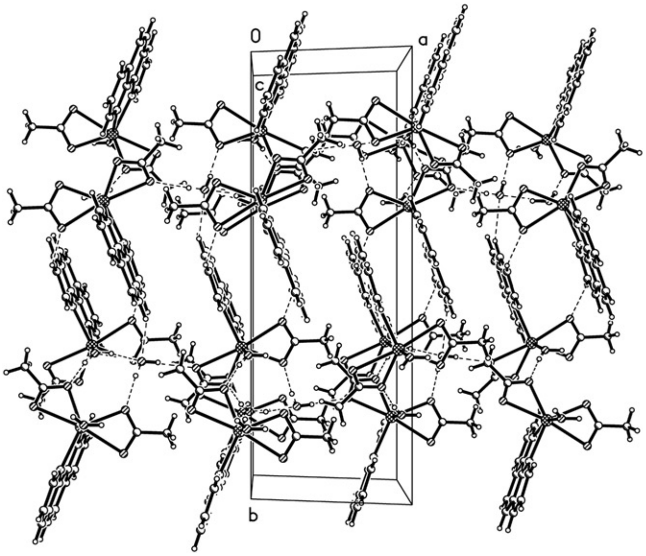


Figure 4. A part of molecular packing of **1** showing π-stacking interactions. Intermolecular hydrogen bonds are indicated by dashed lines.

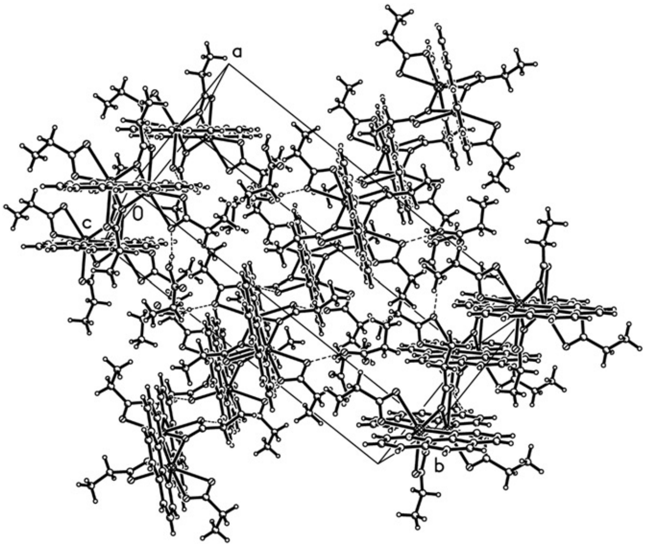
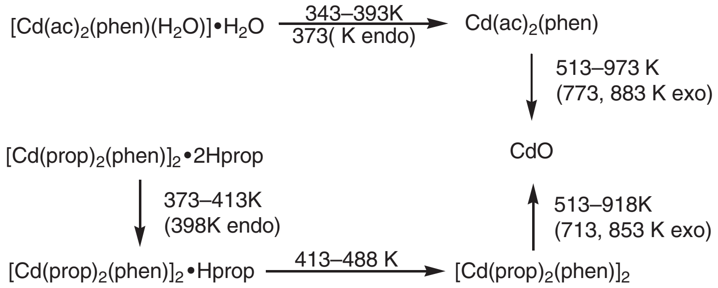


Figure 5. A part of molecular packing of **2** showing π-stacking interactions. Intermolecular hydrogen bonds are indicated by dashed lines.

values [36], confirming the presence of propionic acid. The symmetric ν_s(COO) stretching vibration of coordinated acetate and propionate ions are at 1410 and 1412 cm^{-1}, respectively, however, asymmetric ν_{as}(COO) stretching vibrations [37, 38] overlap with absorption bands of phen and are not easily identified. A strong and broad band in the water stretching region (3350–3450 cm^{-1}) is observed for **1**.

Thermal decomposition of **1** and **2** is gradual (for details see Supplemental Material). Changing the heating rate does not change the shape of the curves, however, the extrema of differential curves are slightly better formed. The general scheme of thermal decomposition is as follows:



Without brackets – temperature range; in brackets – DTA peaks (ac – acetate, prop – propionate).

Compound **1** loses two molecules of water in the temperature range 343–393 K (mass loss Calcd 8.06%, found 8.0%) with an endothermic peak in DTA curve at 373 K corresponding to dehydration. Decreasing the heating rate does not lead to splitting of the DTG peak originating from inner and the outer coordination sphere water, as was previously observed for another compound containing the same amount of water in both coordination spheres [39]. Complex **2** is thermally stable up to 373 K, where decomposition starts by successive release of uncoordinated propionic acid. In the first stage one mole of propionic acid is split off and in the second stage another molecule of propionic acid is lost. Its corresponding to two mass losses in the temperature range 373–413 K (Calcd 7.22%, found 7.0%) and 413–488 K (Calcd 7.22%, found 7.0%). An endothermic effect at 398 K appears on the DTA curve. The intermediates $Cd(ac)_2(phen)$ or $[Cd(prop)_2(phen)]_2$ begin to decompose at 513 K and create CdO via two stages. However the poorly resolved on TG curves decomposition stages can be separated on the basis of DTG curve, the mass losses (29.0, 34.0 for **1** and 29.5, 31.5 for **2**) cannot be attributed to the masses of the ligands. This, together with partial overlapping of peaks on derivative curves, suggests that decomposition of carboxylate ligands accompany decomposition of phenanthroline molecules. The very strong and broad exothermic effects on DTA curve (at 773, 883 K for **1** and 713, 853 K for **2**) are associated with decomposition of organic ligands. Total decomposition of **1** ends at 973 K (CdO Calcd 28.74%, found 29.0%) and of **2** at 918 K (CdO Calcd 25.04%, found 25.0%). In general, the thermal degradation steps are similar to those for other cadmium complexes containing carboxylates and N-donor cyclic ligands [40–42].

The title complexes show rare coordination of cadmium. Among 4366 known structures of cadmium complexes [43], 180 compounds contain phenanthroline, but there is only one mononuclear seven-coordinate compound containing two chelating carboxylates [44], and an analogous dinuclear compound cannot be found. Usage of acrylic ($C_3H_4O_2$) acid instead of propionic acid ($C_3H_6O_2$) leads to a mononuclear

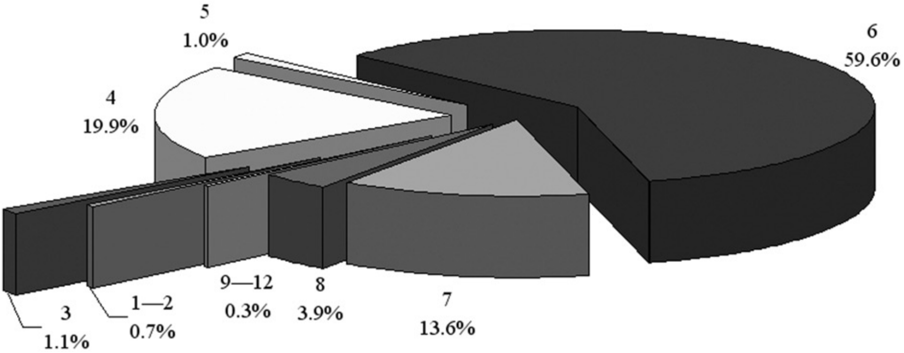


Figure 6. Percentage participation of cadmium coordination compounds with different coordination numbers (according to [43]).

complex [44], confirming the novelty of **2**. Generally seven-coordination is uncommon for cadmium (figure 6) and only four compounds similar to dinuclear **2** (containing chelating organic ligand, two bidentate chelating and two tridentate chelating-bridging carboxylate groups in the inner coordination sphere) can be found [45–47]. Five compounds with structural similarity to **1** with inner coordination sphere containing chelating organic ligand, two bidentate chelating carboxylates and water have been reported [44, 48–51].

Supplementary data

Tables of crystal data and structure refinement, anisotropic displacement coefficients, atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms, H-atom coordinates and isotropic displacement parameters, bond lengths and interbond angles have been deposited with the Cambridge Crystallographic Data Centre under Nos. CCDC643434 and CCDC643433, respectively, for **1** and **2**.

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References

[1] T.J. Bartczak, D. Czakis-Sulikowska, J. Kałużna. *J. Coord. Chem.*, **46**, 193 (1998).
[2] R. Kruszyński, A. Adamczyk, J. Radwańska-Doczekalska, T.J. Bartczak. *J. Coord. Chem.*, **55**, 1209 (2002).
[3] D. Czakis-Sulikowska, A. Czylkowska, A. Malinowska. *J. Therm. Anal. Calorim.*, **67**, 667 (2002) and references therein.
[4] D. Czakis-Sulikowska, A. Czylkowska. *J. Therm. Anal. Calorim.*, **71**, 395 (2002).

[5] D. Czakis-Sulikowska, J. Radwańska-Doczekalska, M. Markiewicz. *Polish J. Chem.*, **77**, 1255 (2003).
[6] D. Czakis-Sulikowska, A. Malinowska, M. Markiewicz. *Polish J. Chem.*, **77**, 1363 (2003).
[7] J. Moncol, M. Mudra, P. Lonnecke, M. Koman, M. Melnik. *J. Coord. Chem.*, **57**, 1065 (2004).
[8] J.R. Su, D.J. Xu. *J. Coord. Chem.*, **58**, 629 (2005).
[9] A.D. Burrows, R.W. Harrington, M.F. Mahon, S.J. Teat. *Cryst. Growth Des.*, **4**, 813 (2004).
[10] A. Morsali, X.M. Chen. *J. Coord. Chem.*, **57**, 1233 (2004).
[11] W.J. Evans, J.C. Brady, J.W. Ziller. *J. Am. Chem. Soc.*, **123**, 7711 (2001).
[12] C. Ma, W. Wang, X. Zhang, C. Chen, Q. Liu, H. Zhu, D. Liao, L. Li. *Eur. J. Inorg. Chem.*, 3522 (2004).
[13] Y. Zheng, J. Lin, Z. Kong. *Polyhedron*, **19**, 2111 (2003).
[14] F. Bentiss, P. Roussel, M. Drache, P. Conflant, M. Lagrenee, J.P. Wignacourt. *J. Mol. Struct.*, **707**, 63 (2004).
[15] S. Wang, D.B. Mitzi, C.A. Field, A. Guloy. *J. Am. Chem. Soc.*, **117**, 5297 (1995).
[16] P.J. Hagrman, D. Hagrman, J. Zubieta. *Angew. Chem. Int. Ed.*, **38**, 2638 (1999).
[17] X-RED. *Version 1.18. STOE & Cie GmbH, Darmstadt*, Germany (1999).
[18] G.M. Sheldrick. *Acta Cryst.*, **A46**, 467 (1990).
[19] G.M. Sheldrick. *SHELXL*-97: *Program for the Refinement of Crystal Structures*, University of Gottingen, Germany (1997).
[20] G.M. Sheldrick. *SHELXTL: release 4.1 for Siemens Crystallographic Research Systems* (1990).
[21] Powder Diffraction File International Center of Diffraction Data, 12 Campus Boulevard, Newton Square, PA, USA (2003).
[22] D.L. Kepert. In *Progress in Inorganic Chemistry*, S.J. Lippard (Ed.), John Wiley & Sons, New York, Vol. 25 (1979).
[23] W.H. Zachariasen. *J. Less-Common Metals*, **62**, 1 (1978).
[24] I.D. Brown. *Acta Cryst.*, **B53**, 381 (1997).
[25] I.D. Brown. *Acta Cryst.*, **B48**, 553 (1992).
[26] M. O'Keeffe, N.E. Brese. *Acta Cryst.*, **B47**, 192 (1997).
[27] G.J. Palenik. *Inorg. Chem.*, **42**, 2725 (2003).
[28] T.R. Wagner, M. O'Keeffe. *J. Solid State Chem.*, **73**, 211 (1998).
[29] J. Berbstein, R.E. Davis, L. Shimoni, N.-L. Chang. *Angew Chem. Int. Ed. Eng.*, **34**, 1555 (1995).
[30] R. Taylor, O. Kennard. *J. Am. Chem. Soc.*, **104**, 5063 (1982).
[31] G.R. Desiraju, T. Steiner. *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, Oxford (1999).
[32] C.A. Hunter, J.K.M. Sanders. *J. Am. Chem. Soc.*, **112**, 5525 (1990).
[33] S.B. Halligudi, N.H. Khan, R.I. Kureshy, E. Suresh, K. Venkasubramanian. *J. Mol. Catal. A: Chem.*, **124**, 147 (1997).
[34] R. Carballo, B. Covelo, S. Balboa, A. Casteiòeiras, J. Niclós. *Z. Anorg. Allg. Chem.*, **627**, 948 (2001).
[35] B. Machura, R. Kruszynski, M. Jaworska, J. Klak, J. Mrozinski. *Polyhedron*, **25**, 2537 (2006).
[36] K. Nakamoto. *Infrared and Raman Spectra and Coordination Chemistry*, John Wiley and Sons, New York (1997).
[37] A.B.P. Lever, D. Ogden. *J. Chem. Soc. A*, **0**, 2041 (1967).
[38] G.B. Deacon, R.I. Phillips. *Coord. Chem. Rev.*, **33**, 227 (1980).
[39] S.-S. Yun, S.K. Kang, H.-R. Suh, H.-S. Suh, E.K. Lee, J.-K. Kim, C.-H. Kim. *Bull. Korean Chem. Soc.*, **26**, 1197 (2005).
[40] D. Czakis-Sulikowska, A. Malinowska, M. Markiewicz. *J. Therm. Anal. Calorim.*, **60**, 151 (2000).
[41] D. Czakis-Sulikowska, A. Czylkowska, A. Malinowska. *J. Therm. Anal. Calorim.*, **65**, 505 (2001).
[42] D. Czakis-Sulikowska, A. Czylkowska, J. Radwańska-Doczekalska, R. Grodzki, E. Wojciechowska. *J. Therm. Anal. Calorim.*, **90**, 557 (2007).
[43] F.H. Allen. *Acta Cryst.*, **B58**, 380 (2002); CSD v 5.25 including three updates: 01-2007, 05-2007, 08-2007.
[44] T.-J. Cai, W.-J. Jiang, Z.-S. Peng, Y.-F. Long, Q. Deng. *Z. Kristallogr. New Cryst. Struct.*, **221**, 421 (2006).
[45] G. Givaja, A.J. Blake, C. Wilson, M. Schroder, J.B. Love. *Chem. Commun.*, 4423 (2005).
[46] C.-S. Liu, X.-S. Shi, J.-R. Li, J.-J. Wang, X.-H. Bu. *Cryst. Growth Des.*, **6**, 656 (2006).
[47] J.T. Mague, J.L. Krinsky. *Inorg. Chem.*, **40**, 1962 (2001).
[48] B.-S. Zhang, X.-R. Zeng, X.-N. Fang, C.-F. Huang. *Z. Kristallogr. New Cryst. Struct.*, **220**, 141 (2005).
[49] L.-G. Zhu, M.-L. Hu. *Acta Cryst.*, **E62**, m653 (2006).
[50] S.-L. Li, T.C.W. Mak. *Aust. J. Chem.*, **50**, 79 (1997).
[51] Y.-Q. Cheng, X.-Q. Cai, M.-L. Hu. *Z. Kristallogr. New Cryst. Struct.*, **220**, 390 (2005).