ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2018, Vol. 44, No. 8, pp. 473–482. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © N.V. Gogoleva, A.A. Sidorov, Yu.V. Nelyubina, M.A. Shmelev, G.G. Aleksandrov, G.N. Kuznetsova, M.A. Kiskin, I.L. Eremenko, 2018, published in Koordinatsionnaya Khimiya, 2018, Vol. 44, No. 4, pp. 219–228.

Formation of Polynuclear Cadmium Pivalates in Exchange Reactions[1]

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Received September 5, 2017

Abstract—The exchange reaction of $CdCl_2 \cdot 2H_2O$ with KPiv affords cadmium(II) trimethyl acetate complexes ($K[Cd_6(Piv)_{12}Cl] \cdot 2MeCN$ (**I**), $[K_2Cd_3(Piv)_8(H_2O)_6]$ (**II**), and $[Cd(Piv)_2(H_2O)_2]$ (**III**) as a mixture with complex **II** and $[K_3Cd_2(Piv)_7(MeCN)_2]_n$ (**IV**) (HPiv is trimethylacetic acid). The exchange reaction of $CdSO_4 \cdot 8/3H_2O$ with $Ba(Piv)_2$ makes it possible to obtain complex **III** in a quantitative yield. Complex **III** can also be isolated by the recrystallization of $\{Cd(Piv)_2\}$ from water. The recrystallization of complex **III** or $\{Cd(Piv)_2\}$ from MeCN affords hexanuclear complex $[Cd_6(Piv)_{12}(MeCN)_2]$ (**V**), which transforms into complex **III** upon recrystallization from water. All new compounds are characterized by the data of single-crystal X-ray diffraction analysis (CIF files CCDC no. 1572202–1572206), IR spectroscopy, and C,H,N analysis.

Keywords: polynuclear cadmium(II) complexes, exchange reaction, X-ray diffraction analysis

DOI: 10.1134/S107032841808002X

INTRODUCTION

Among the works concerning the chemistry of metal carboxylates, a significant number of studies related to the use of pivalate complexes is worth of mentioning [1–8]. This is due to the fact that these complexes refer to compounds highly soluble in the majority of organic media, providing good prospects of their use in further chemical transformations as precursors for the diverse design of polynuclear structures including heterometallic molecules by the application of standard solution methods of synthesis and relative easiness of isolating new coordination compounds as single crystals for the subsequent structure determination by X-ray diffraction analysis. In fact, we have recently demonstrated some possibilities of the pivalate complexes containing only the metal ion and pivalate anion in the formation of new polynuclear compounds using these reactions with salts of other metals in the presence of inorganic or organic ligands [1]. The synthesis of the pivalate complexes of transition metals in the oxidation state +2 is mainly based on the exchange reactions of inorganic salts (chlorides, nitrates, oand sulfates) with the stoichiometric amount of potassium pivalate in an organic medium (EtOH, MeCN, and others) followed by the crystallization of the reaction product from various organic solvents. For example, the polymeric and discrete polynuclear molecular pivalates $[M(Piv)_2]_n$ (M = Fe, Co, Zn) [9–11]; $[M(Piv)_2(EtOH)]_n$ (M = Mn, Fe) [9]; $[Ni_9(OH)_6(Piv)_{12}(HPiv)_4]$ and $[Ni_6(Piv)_{12}]$ [10]; $[Cu_2(Piv)_4(HPiv)_2]$ and $[Cu_2(Piv)_4]_n$ [12, 13]; as well as $[M_4(OH)_2(Piv)_6(EtOH)_6]$ (M = Fe, Co, Ni) [9, 14, 15] were obtained. An alternative universal method for the synthesis of pivalate polynuclear molecules is the smelting of transition metal acetates with pivalic acid taken in excess (mp = 163.7°C) followed by the distillation of an acid excess and formation of the corresponding dipivalates $[M(Piv)_2]_n$ (M = Co, Zn) [10, 11] including the cadmium derivative $\{Cd(Piv)_2\}$, whose structure was not determined [16]. The carboxylate complexes synthesized using these procedures are reactive and react with both N,O-donating ligands of various nature and solvent molecules. The dissolution of $[M(Piv)_2]_n$ (M = Fe, Co) in EtOH (96%) is accompanied by the partial hydrolysis of the polymeric products to form hydroxopivalates $[M_4(OH)_2(Piv)_6(EtOH)_6]$ (M = Fe, Co, Ni) [9, 15]. It should be mentioned that a water impurity in solutions of organic solvents during complex formation often

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[1] The article is dedicated to memory of our colleague and friend I.B. Baranovskii.

[†] Deceased.

exerts no effect on the compositions of the isolated compounds, for example, the anhydrous carboxylate or nitratocarboxylate architectures are formed in the reactions affording the heteronuclear {M–Ln} complexes (M = Co, Ni, Cu, Zn; Ln = La, Eu, Gd, Tb, and others) [17–20].

The purpose of this work is to study the formation of new cadmium(II) pivalate complexes K[$Cd_6(Piv)_{12}Cl$] · 2MeCN (**I**), [$K_2Cd_3(Piv)_8(H_2O)_6$] (**II**), [$Cd(Piv)_2(H_2O)_2$] (**III**), [$K_3Cd_2(Piv)_7(MeCN)_2$]$_n$ (**IV**), and [$Cd_6(Piv)_{12}(MeCN)_2$] (**V**) in various exchange reactions and to investigate the influence of the synthesis conditions on the compositions and structures of the formed reaction products.

EXPERIMENTAL

All procedures associated with the synthesis of new complexes were carried out in air using distilled water, hexane (reagent grade), acetonitrile (reagent grade), and ethanol (96%). The following reagents were used for the synthesis of new compounds: $CdSO_4 \cdot 8/3H_2O$ (≥98%, ACS reagent,), $CdCl_2 \cdot 2H_2O$ (≥98%, Sigma-Aldrich), KOH (analytical grade), and trimethylacetic acid (HPiv, ≥98%, Acros Organics). Potassium pivalate (KPiv) and $Ba(Piv)_2$ were prepared by the smelting of the stoichiometric amounts of KOH or $Ba(OH)_2$ and HPiv followed by washing the reaction product with hexane. Compound {$Cd(Piv)_2$} (probably, with a polymeric structure) was synthesized using a described procedure [16]. The IR spectra of the compounds were recorded on a Spectrum 65 FT-IR spectrophotometer (PerkinElmer) using the attenuated total reflectance method in a frequency range of 4000–400 cm^{-1}. Elemental analyses were carried out on a EuroEA 3000 CHNS analyzer (EuroVector).

Synthesis of K[$Cd_6(Piv)_{12}Cl$] · 2MeCN (I). Weighed samples of $CdCl_2 \cdot 2H_2O$ (1.00 g, 4.56 mmol) and KPiv (1.28 g, 9.13 mmol) were truturated in a mortar with several droplets of MeCN. The obtained solid product was poured with MeCN (50 mL) to dissolve the cadmium complex, the solution was filtered to remove a precipitate of KCl, the mother liquor was concentrated to a volume of 10 mL at 80°C, and the obtained solution was cooled to room temperature. Colorless crystals suitable for X-ray diffraction analysis were formed in 24 h and separated from the solution by decantation. The concentrating of the remained solution to a volume of 1–2 mL resulted in the isolation of an additional amount of the complex. The yield of compound **I** was 1.55 g (99%) based on the starting amount of $CdCl_2 \cdot 2H_2O$.

For $C_{64}H_{108}N_2O_{24}ClKCd_6$

Found, %	C, 37.61	H, 5.22	N, 1.40
Anal. calcd., %	C, 37.71	H, 5.34	N, 1.37

IR (ν,cm^{-1}): 3676 w, 3392 w, 3364 w, 2959 s, 2903 m, 1648 w, 1559 s, 1531 s, 1482 s, 1458 m, 1414 s, 1374 m, 1360 m, 1223 s, 1077 m, 1066 m, 1058 m, 1027 w, 939 w, 900 m, 807 m, 795 m, 604 s, 532 m, 491 w, 483 m, 468 w, 460 w, 432 w, 420 m, 411 s.

Synthesis of [$K_2Cd_3(Piv)_8(H_2O)_6$] (II). Method 1. Weighed samples of $CdCl_2 \cdot 2H_2O$ (1.00 g, 4.56 mmol) and KPiv (1.71 g, 12.16 mmol) were dissolved in water (50 mL). The obtained solution was stirred to the complete dissolution of the reagents and concentrated at 100°C to 25 mL. Then the solution was kept at ambient temperature in an open beaker for 48 h. The precipitated colorless crystals suitable for X-ray diffraction analysis were separated from the solution by decantation, washed with water (4°C), and dried in air. The yield of complex **II** was 0.55 g (27%) based on the starting amount of $CdCl_2 \cdot 2H_2O$.

For $C_{40}H_{842}O_{22}KCd_3$

Found, %	C, 37.00	H, 6.40
Anal. calcd., %	C, 36.05	H, 6.35

IR (ν, cm^{-1}): 3630 s, 3591 s, 3248 m, 2967 s, 2166 w, 1509 s, 1481 s, 1417 s, 1375 m, 1363 s, 1221 s, 1031 w, 905 s, 816 m, 725 s, 614 s, 528 m, 483 m, 455 m, 435 m, 422 m, 409 s.

Method 2. The synthesis was carried out similarly to the procedure indicated in method 1, except for the use of a different ratio of the reactants: $CdCl_2 \cdot 2H_2O$ (0.50 g, 2.28 mmol) and KPiv (0.64 g, 4.56 mmol). According to the X-ray diffraction data for several crystals, the reaction product is a mixture of complexes **II** and **III**. The yield of the reaction is difficult to determine.

Synthesis of [$Cd(Piv)_2(H_2O)_2$] (III). Method 1. A suspension (50 mL) containing $Ba(Piv)_2$ (1.32 g, 3.90 mmol) obtained *in situ* (reaction of $Ba(OH)_2$ and HPiv) was poured to a solution of $CdSO_4 \cdot 3/8H_2O$ (1.00 g, 1.30 mmol) in water (50 mL). The formed suspension was stirred on heating to 70–80°C for 1 h, cooled to ambient temperature, and kept for 24 h. The formed precipitate of $BaSO_4$ was filtered off, and mother liquor 1 was kept at ambient temperature in an open beaker. The first fraction of the crystals (suitable for X-ray diffraction analysis) taken from a solution (10 mL in volume) was decanted, and the crystals were washed with water (4°C) and dried in air. Mother liquor 2 was concentrated to a solution of 3–5 mL and kept at ambient temperature in an open beaker for 24 h. The formed colorless crystals were decanted, washed with cold water, and dried in a drying box over $CaCO_3$ to a constant weight. The yield of compound **III** was 1.35 g (98%, based on the starting amount of $CdSO_4 \cdot 3/8H_2O$).

For $C_{10}H_{22}O_6Cd$

Found, %	C, 34.10	H, 6.20
Anal. calcd., %	C, 34.25	H, 6.32

IR (ν, cm^{-1}): 3550 w, 3241 w, 2961 m, 2932 w, 2907 w, 2870 w, 2325 w, 1764 w, 1668 w, 1589 w, 1509 s, 1479 s, 1415 s, 1373 s, 1364 s, 1219 s, 1031 w, 937 w, 904 s, 815 s, 795 m, 611 s, 528 m, 488 w, 469 w, 457 w, 439 w, 425 m, 411 m, 405 m.

Method 2. A weighed sample of {Cd(Piv)$_2$} (0.50 g, 1.59 mmol) or [Cd$_6$(Piv)$_{12}$(MeCN)$_2$] (**V**) (0.50 g, 0.25 mmol) was dissolved in water (50 mL) and kept at ambient temperature on slow evaporating of water. The formed crystalline colorless precipitate was decanted, washed with cold water, and dried in a drying box over CaCO$_3$ to a constant weight. The yield of compound **III** was 0.51 g (96%, when {Cd(Piv)$_2$} was used) and 0.51 g (95.8%, when compound **V** was used).

For $C_{10}H_{22}O_6Cd$

Found, %	C, 34.20	H, 6.20
Anal. calcd., %	C, 34.25	H, 6.32

IR (ν, cm^{-1}): 3550 w, 3241 w, 2961 m, 2932 w, 2907 w, 2870 w, 2325 w, 1764 w, 1668 w, 1589 w, 1509 s, 1479 s, 1415 s, 1373 s, 1364 s, 1219 s, 1031 w, 937 w, 904 s, 815 s, 795 m, 611 s, 528 m, 488 w, 469 w, 457 w, 439 w, 425 m, 411 m, 405 m.

Synthesis of [K$_3$Cd$_2$(Piv)$_7$(MeCN)$_2$]$_n$ (IV). Method 1. A weighed sample of complex **II** (1.00 g, 0.75 mmol) was added with KPiv (0.26 g, 1.87 mmol) in MeCN (50 mL). The suspension was stirred on heating (80°C) for 1 h. The obtained solution was cooled and kept at ambient temperature for 24 h in an open beaker. The formed colorless crystals suitable for X-ray diffraction analysis were washed with MeCN (–5°C) and dried in air. The yield of compound **IV** was 1.82 g (84%, based on the starting amount of complex **II**).

Method 2. A weighed sample of complex **I** (1.00 g, 0.51 mmol) was added with KPiv (0.57 g, 4.06 mmol) in MeCN (50 mL), and the suspension was stirred on heating (80°C). The obtained solution was cooled and kept at ambient temperature in an open beaker. The crystals for X-ray diffraction analysis were sampled at the volume of mother liquor 1 equal to ~10 mL. The crystals were washed with MeCN (–5°C) and dried in air. Mother liquor 1 was concentrated to dryness and dissolved in MeCN (undissolved KCl was separated by filtration), and mother liquor 2 was kept at ambient temperature in an open beaker for 48 h. The formed finely crystalline precipitate was washed with MeCN (–5°C) and dried in air. The yield of complex **IV** was 2.08 g (81%, based on the starting amount of complex **I**).

For $C_{32}H_{69}O_{14}N_2K_3Cd_2$

Found, %	C, 33.61	H, 6.70	N, 2.62
Anal. calcd., %	C, 33.67	H, 6.64	N, 2.67

IR (ν, cm^{-1}): 3676 w, 3313 m, 2961 s, 2932 m, 2907 w, 2870 w, 1663 w, 1541 s, 1514 s, 1483 s, 1457 m, 1417 s, 1375 s, 1360 s, 1224 s, 1077 w, 1066 w, 1054 w, 1027 w, 936 w, 902 s, 803 m, 793 m, 753 w, 739 w, 605 s, 534 s, 485 w, 441 w, 425 w, 403 m.

Synthesis of [Cd$_6$(Piv)$_{12}$(MeCN)$_2$] (V). Method 1. A weighed sample of {Cd(Piv)$_2$} (0.50 g, 1.59 mmol) was dissolved in MeCN (50 mL) on heating (80°C) for 30 min, and then the solution was concentrated to a volume of 10 mL and cooled to ambient temperature. Large colorless crystals suitable for X-ray diffraction analysis were formed on slow cooling of the solution. The crystals were decanted from the solution and washed with MeCN (–5°C). The further concentrating of the mother liquor to a volume of 1–2 mL gave the final product with a yield close to quantitative. The yield of compound **V** was 0.52 g (99%, based on the starting amount of {Cd(Piv)$_2$}).

For $C_{64}H_{114}N_2O_{24}Cd_6$

Found, %	C, 38.90	H, 5.90	N, 1.51
Anal. calcd., %	C, 39.02	H, 5.83	N, 1.42

IR (ν, cm^{-1}): 3259 w, 2961 m, 2932 w, 2871 w, 2275 w, 1570 m, 1538 s, 1480 s, 1461 m, 1409 s, 1372 m, 1360 s, 1221 s, 1032 w, 938 w, 903 m, 890 w, 808 w, 786 w, 606 m, 531 m, 476 w, 466 w, 439 w, 430 w, 418 m, 410 m, 406 s.

Method 2. A weighed sample of compound **III** (0.50 g, 1.59 mmol) was dissolved in MeCN (25 mL) on heating (80°C) for 30 mL, and the solution was cooled to ambient temperature and kept in an open beaker. Crystals suitable for X-ray diffraction analysis were formed from a solution of 10 mL. The further concentrating of the solution resulted in the formation of a colorless finely crystalline product. The reaction product was decanted, washed with MeCN (–5°C), and dried in air. The yield of compound **V** was 0.44 g (94%, based on the starting amount of compound **III**).

For $C_{64}H_{114}Cd_6N_2O_{24}$

Found, %	C, 39.08	H, 5.80	N, 1.50
Anal. calcd., %	C, 39.02	H, 5.83	N, 1.42

IR (ν, cm^{-1}): 3259 w, 2961 m, 2932 w, 2871 w, 2275 w, 1570 m, 1538 s, 1480 s, 1461 m, 1409 s, 1372 m, 1360 s, 1221 s, 1032 w, 938 w, 903 m, 890 w, 808 w, 786 w, 606 m, 531 m, 476 w, 466 w, 439 w, 430 w, 418 m, 410 m, 406 s.

X-ray diffraction analyses for single crystals of compounds **I**, **II**, **IV**, and **V** were carried out on a Bruker SMART APEXII diffractometer, and the analysis for compound **III** was conducted on a Bruker APEXII DUO diffractometer (CCD detector, MoK_α, λ = 0.71073 Å, graphite monochromator) [21]. A semiempirical absorption correction was applied for all compounds [22]. The structures were solved by a direct method and refined by full-matrix least squares in the

Table 1. Crystallographic parameters and refinement details for the structures of compounds **I**–**V**

Parameter	Value				
	I	**II**	**III**	**IV**	**V**
FW	2038.47	1332.47	350.67	1132.06	1969.97
T, K	153(2)	150(2)	120(2)	153(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$C2/m$	$C2/c$	$P2_1/n$	$C2/c$	$P\bar{1}$
Crystal size, mm	0.43 × 0.13 × 0.08	0.34 × 0.25 × 0.18	0.35 × 0.05 × 0.01	0.34 × 0.13 × 0.09	0.29 × 0.23 × 0.09
a, Å	25.497(2)	18.7966(8)	5.633(2)	24.480(3)	11.0045(14)
b, Å	14.1449(10)	16.9853(7)	24.703(7)	21.887(2)	14.1286(7)
c, Å	13.1698(9)	19.3618(9)	10.360(3)	22.498(2)	15.3952(8)
α, deg	90	90	90	90	112.2810(10)
β, deg	116.0148(10)	110.8440(6)	91.387(6)	111.449(2)	103.268(2)
γ, deg	90.00	90	90	90	96.875(2)
V, Å^3	4268.4(5)	5777.0(4)	1441.1(7)	11 220(2)	2098.2(3)
Z	2	4	4	8	1
$\rho_{\rm calc}$, g/cm^3	1.586	1.532	1.616	1.340	1.559
μ, mm^{-1}	1.613	1.306	1.528	1.034	1.559
F(000)	2044	2728	712	4656	992
Range of data collection over θ, deg	1.69–29.55	2.23–29.69	0.82–26.98	1.29–29.22	1.95–29.62
Ranges of reflection indices	$-25 \le h \le 35$, $-19 \le k \le 19$, $-18 \le l \le 17$	$-26 \le h \le 26$, $-23 \le k \le 23$, $-23 \le l \le 26$	$-7 \le h \le 7$, $-31 \le k \le 31$, $-13 \le l \le 13$	$-20 \le h \le 33$, $-26 \le k \le 30$, $-29 \le l \le 30$	$-15 \le h \le 15$, $-19 \le k \le 21$, $-18 \le l \le 21$
Number of measured reflections	16809	32268	19121	34594	24051
Number of independent reflections ($R_{\rm int}$)	6129 (0.043)	8138 (0.047)	3136 (0.075)	14 927 (0.072)	11 531 (0.030)
Number of reflections with $I > 2\sigma(I)$	4849	7209	2762	8388	9973
Refinement variables	254	339	160	544	433
GOOF	1.00	1.00	1.48	0.99	1.00
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.056$, $wR_2 = 0.159$	$R_1 = 0.029$, $wR_2 = 0.080$	$R_1 = 0.071$, $wR_2 = 0.202$	$R_1 = 0.061$, $wR_2 = 0.139$	$R_1 = 0.049$, $wR_2 = 0.151$
R factors for all reflections	$R_1 = 0.072$, $wR_2 = 0.179$	$R_1 = 0.034$, $wR_2 = 0.083$	$R_1 = 0.078$, $wR_2 = 0.208$	$R_1 = 0.122$, $wR_2 = 0.174$	$R_1 = 0.054$, $wR_2 = 0.156$
Residual electron density (min/max), e/Å^3	–1.640/3.340	–1.108/1.285	–2.172/3.375	–0.809/1.262	–3.015/2.697

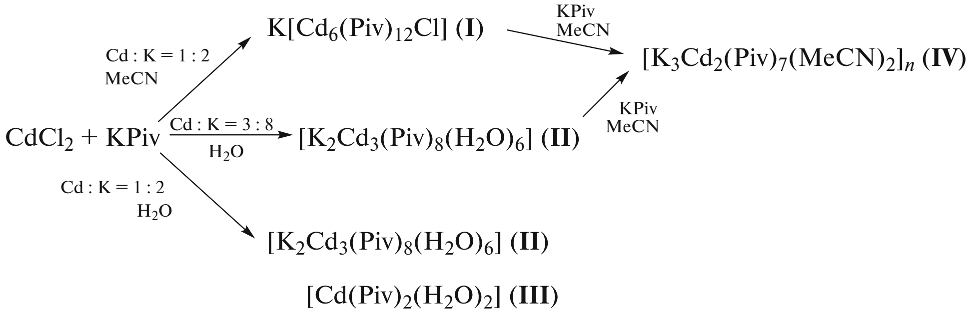
anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms at the carbon atoms of the organic ligands were generated geometrically and refined in the riding model. The hydrogen atoms of the hydrate molecules in crystals of compounds **II**, **III**, and **IV** were revealed from the difference Fourier syntheses and refined in the isotropic approximation in the framework of the riding model. The calculations were performed using the SHELX-97 and SHELX-2014 program packages [23]. The crystallographic parameters and structure refinement details are presented in Table 1.

The structural data for compounds **I**–**V** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC no. 1572202–1572206, respectively; http://www.ccdc.cam.ac.uk/).

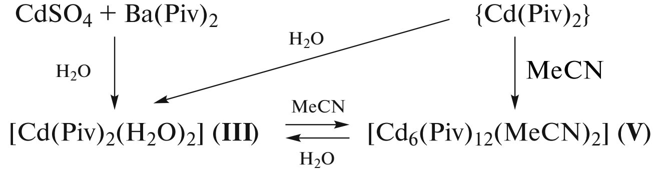
RESULTS AND DISCUSSION

Acetonitrile, being a relatively labile ligand in spite of the donor properties, was chosen as an organic solvent for the synthesis of cadmium(II) pivalates in aqueous and organic media. Acetonitrile can be replaced by other N-donating ligands (for example, pyridine). In addition, acetonitrile, unlike nonpolar solvents, dissolves cadmium salts, which is necessary for exchange reactions.

The results of the studies show that the products of various composition and structure can be isolated depending on the choice of the medium of the exchange reaction between $CdCl_2 \cdot 2H_2O$ and KPiv. The reaction of $CdCl_2 \cdot 2H_2O$ and KPiv in a molar ratio of 1 : 2 in MeCN affords complex **I** (Scheme 1). A mixture of complexes **II** and **III** is formed at the same ratio of the reactants in water (Scheme 1). The use of the molar ratio $CdCl_2$: KPiv = 3 : 8 makes it possible to obtain complex **II** in an almost quantitative yield. Compound **III** was not isolated in the pure state in this reaction, because a mixture of products was formed at the ratio $CdCl_2$: KPiv = 1 : 2. The replacement of KPiv by $Ba(Piv)_2$ and of $CdCl_2 \cdot 2H_2O$ by $CdSO_4 \cdot 8/3H_2O$ made it possible to solve the problem, because an aqueous solution giving only the crystals of compound **III** in an quantitative yield was obtained after a precipitate of $BaSO_4$ was separated (Scheme 2). The recrystallization of $\{Cd(Piv)_2\}$ from water also results in the quantitative formation of monomer **III** (Scheme 2).



Scheme 1.



Scheme 2.

It should be mentioned that the reactions of complexes **I**–**III** with the corresponding amounts of KPiv in MeCN afford coordination polymer **IV**, whose composition corresponds to the formula $[K_3Cd_2(Piv)_7(MeCN)_2]_n$ (Scheme 1).

The recrystallization of $\{Cd(Piv)_2\}$ or compound **III** from MeCN gives new molecular complex **V**, which reversibly transforms into complex **III** on dissolving in H_2O (Scheme 2).

The processes of formation of cadmium(II) pivalates (from $CdCl_2$ and KPiv), which make it possible to obtain {K–Cd} compounds **I**, **II**, and **IV** in yields close to quantitative, are shown in Scheme 1. However, pure complexes **III** and **V** could not be isolated using this scheme. Scheme 2 illustrates the syntheses

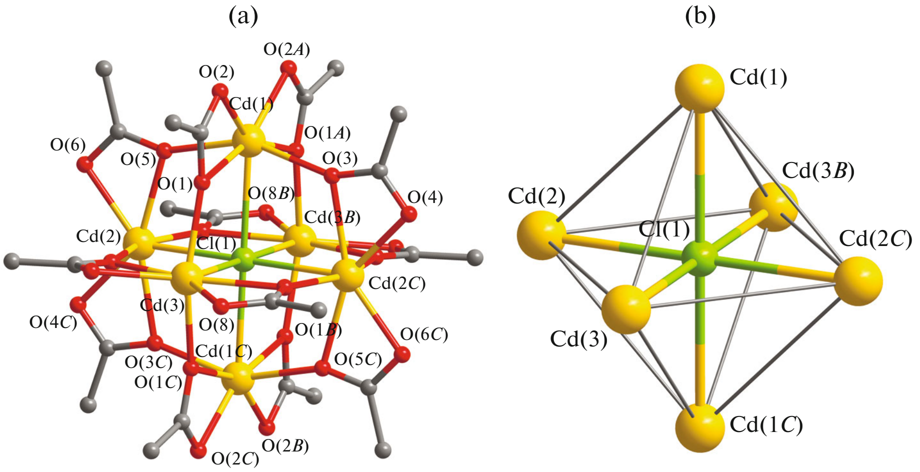


Fig. 1. (a) Structure of the molecule and (b) $\{Cd_6Cl\}$ fragment of complex **I** (hydrogen atoms and *tert*-butyl groups are omitted). Symmetry codes: (*A*) *x*, –*y*, *z*; (*B*) –*x*, –*y*, 1 – *z*; (*C*) –*x*, *y*, 1 – *z*.

of pure complexes **III** and **V** and their mutual transformations that provide their formation in a nearly quantitative yield without using high-temperature processes.

In complex **I**, the hexanuclear anion in which the metal atoms occupy vertices of the octahedron have the symmetry C_{2h} (Fig. 1). The hexanuclear metal framework (the Cd···Cd distance over the edges of the Gd$_6$ octahedron is 3.900–4.038 Å) is centered by the chlorine atom (Cd–Cl 2.7858(5)–2.8612(6) Å). Twelve carboxylate groups in the $[Cd_6(Piv)_{12}Cl]^-$ anion perform the chelate-bridging function in such a way that each metal atom is linked with two chelate groups (Cd–O 2.270(4)–2.446(4) Å) and supplements the coordination number of Cd to 7 (CdO_6Cl) by the coordination of two O atoms of two carboxylate groups (Cd–O 2.294(4)–2.343(4) Å) bound to the adjacent metal atoms. The K^+ ion disordered over two positions forms K–O ionic bonds (2.764(5), 2.853(7) Å) with $[Cd_6(Piv)_{12}Cl]^-$.

The structure of the $[Cd_6(Piv)_{12}Cl]^-$ anion in compound **I** is similar to the structure of the known hexanuclear anions of manganese(II), cobalt(II), and nickel(II) [24, 25].

In crystal **II**, the twofold axis passes through the central Cd(1) atom (Fig. 2). The coordination environments of the cadmium atoms are different. The central Cd(1) atom coordinates eight oxygen atoms of four chelate carboxylate anions (Cd–O 2.3526(14)–2.4624(14) Å), and each peripheral Cd(2) atom coordinates seven O atoms of two chelate carboxylate anions (Cd–O 2.342(2)–2.397(2) Å) and three water molecules (Cd–O 2.309(2)–2.3899(14) Å). The coordination polyhedra of the cadmium atoms Cd(1)O_8 and Cd(2)O_7 are the triangular dodecahedron and pentagonal bipyramid, respectively. The mononuclear $\{Cd(Piv)_4\}$ and $\{Cd(Piv)_2(H_2O)_3\}$ fragments are connected to each other by two K^+ ions forming ionic bonds with the O atoms of the carboxylate groups (K–O 2.704(2)–2.855(2) Å). Joining of the adjacent $\{K_2Cd_3\}$ fragments by hydrogen bonds between the H atoms of the coordinated water molecules and the O atoms of the carboxylate groups (O···O 2.729–2.916 Å, angles O–H···O 150°–173°) is also observed in the crystal.

The formation of a molecular complex in the presence of an alkaline metal is unusual. The formation of the stable molecular complexes was observed for transition 3*d* metals but in the presence of blocking ligands (NEt_3, Py, 2,2'-Bipy, and others can act as blocking ligands) [26–28]. However, only high-dimensional structures are formed in the absence of a blocking ligand [29, 30]. Many polymers are known for cadmium in which the mononuclear anionic fragments $\{Cd(O_2CR)_x\}^{2-x}$ ($x = 3, 4$) are linked by alkaline metal atoms into the polymeric structure [31–37]. In the majority of the known examples, dicarboxylic acids act as carboxylate-containing ligands and alkaline metal ions bind chains or layers into a 2D or 3D structure. Complex **II** is the first example for the molecular carboxylate K–Cd compound. Water molecules preventing polymer formation are the blocking ligands in this example.

Complex **III** is mononuclear (Fig. 3). The Cd(1) atom coordinates two chelate carboxylate anions (Cd–O 2.254(6)–2.394(6) Å) and two water molecules (Cd–O 2.226(8), 2.255(8) Å). The coordination polyhedron CdO_6 is a distorted trigonal antiprism. In

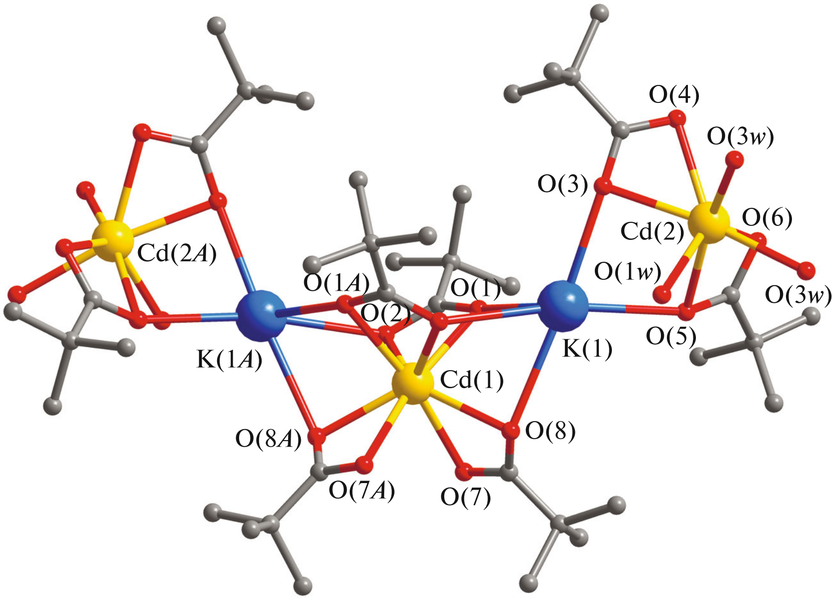


Fig. 2. Structure of complex **II** (hydrogen atoms are omitted). Symmetry code: (*A*) $-x, y, 1/2 - z$.

the crystal, the H atoms of the water molecules are involved in hydrogen bonds with the O atoms of the adjacent molecules of the complex (O···O 2.654–2.807 Å, angle O–H···O 161°–175°) to form a layered structure.

Several complexes $[Cd(O_2CR)_2(H_2O)_2]$ have been structurally characterized to the present time. 4-Nitrobenzoate [38], 3-phenyl acrylate [38], *para*-chlorobenzoate [39], 4-methyl benzoate [40], and crotonate [41] have similar mononuclear structures. Cadmium acetate has the same composition but represents a chain polymer [42] built of mononuclear fragments, which are structural analogs of the listed above mononuclear diaquadicarboxylate complexes, but one of the O atoms of one chelate cycle is bridging. The head-to-tail binding provides chain formation. Probably, the longer Cd–O bond compared to a similar bond in the case of 3*d* metals makes it possible to form a polymeric structure for the acetate. A larger substituent at the carboxy group results in the shielding of the metal center and formation of the mononuclear diaquadicarboxylate complexes. However, in the case of cad-

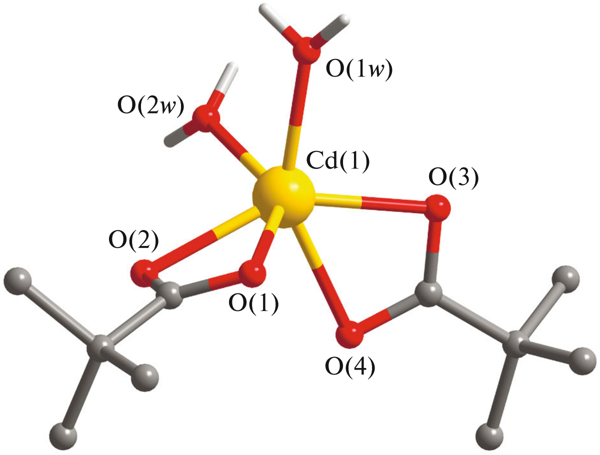


Fig. 3. Structure of complex **III** (hydrogen atoms at the carbon atoms are omitted).

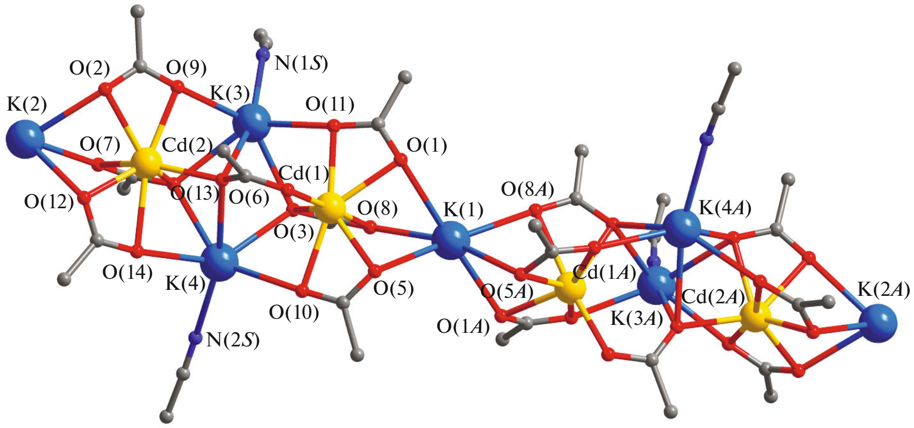


Fig. 4. Structure of complex **IV** (hydrogen atoms and *tert*-butyl groups are omitted). Symmetry code: (*A*) –*x*, *y*, 3/2 – *z*.

mium(II) 2-hydroxybenzoate, the same monomers are bound according to the head-to-head type [43], leading to the formation of a symmetric binuclear complex in which the Cd atoms are bound by two chelate-bridging groups. These structures are more characteristic of the cadmium carboxylate complexes with the chelating N-donating ligands [44–48]. Evidently, a reason for the formation of this binuclear structure is its stabilization by intramolecular hydrogen bonds.

The twofold axis in complex **IV** passes through the K(1) atom (Fig. 4). This complex can formally be presented as an ionic polymer in which the $\{Cd(Piv)_3\}$ fragments are linked by the bridging carboxylate group and the chain is additionally stabilized by the potassium ions incorporated between the Cd-containing fragments. Each cadmium atom coordinates seven O atoms of three chelate (Cd–O 2.289(4)–2.509(4) Å) and one bridging (Cd–O 2.242(4), 2.297(4) Å) carboxylate groups. The coordination polyhedron $Cd(1)O_7$ is a pentagonal bipyramid, and $Cd(2)O_7$ is a one-cap trigonal prism. The Cd(1) and Cd(1*A*) cadmium atoms (–*x*, *y*, –*z* + 3/2) are linked through one potassium ion, and Cd(1) and Cd(2) are bound through the carboxylate group and two potassium atoms.

As mentioned above, in the presence of an alkaline metal, cadmium(II) carboxylates form polymeric products, which is observed for complex **IV**, where the MeCN molecules coordinated by the K^+ ions probably block the formation of a structure of a higher dimensionality.

The inversion center in complex **V** lies at the geometric center of the distorted cycle (Cd···Cd 3.441, 3.572, 3.674 Å) formed by six cadmium atoms (Fig. 5a). The metal atoms over the perimeter of the Cd_6 hexagon are bound by two bridging (Cd–O 2.156(3), 2.223(4) Å) and eight chelate-bridging (Cd–O 2.190(3)–2.440(3) Å) carboxylate groups. The formation of the metal framework is additionally contributed by two carboxylate groups, each of which binds four metal atoms (Cd–O 2.313(3)–2.376(3) Å), arranged at different sides of the Cd_6 plane (Fig. 5b). The coordination polyhedron of the Cd(1) atom (CdO_6N) is completed to the coordination number equal to 7 due to the coordination of the N atom of the MeCN molecule (2.376(5) Å) and corresponds to a pentagonal bipyramid. The coordination polyhedra CdO_6 of the Cd(2) and Cd(3) atoms are distorted octahedra.

Thus, we found simple methods for the formation of cadmium dipivalates **III** and **V**, providing the quantitative yield of the product when the reaction of cadmium sulfate with barium pivalate is used. Owing to amphiphilicity, any compound can be used for subsequent syntheses in water or organic media. The exchange reaction of cadmium chloride with potassium pivalate does not allow the efficient synthesis of cadmium dipivalate because of the formation of stable cadmium–potassium compounds in both water and an organic solvent. It is most likely that the procedure using cadmium sulfate and barium carboxylate is universal and can be used for the synthesis of pivalates and other compounds as well. Its advantages are the quantitative yield of cadmium carboxylate, stoichiometric consumption of the reagents, and mild synthesis conditions.

ACKNOWLEDGMENTS

Spectral and X-ray diffraction studies were carried out on the equipment of the Center for Collective

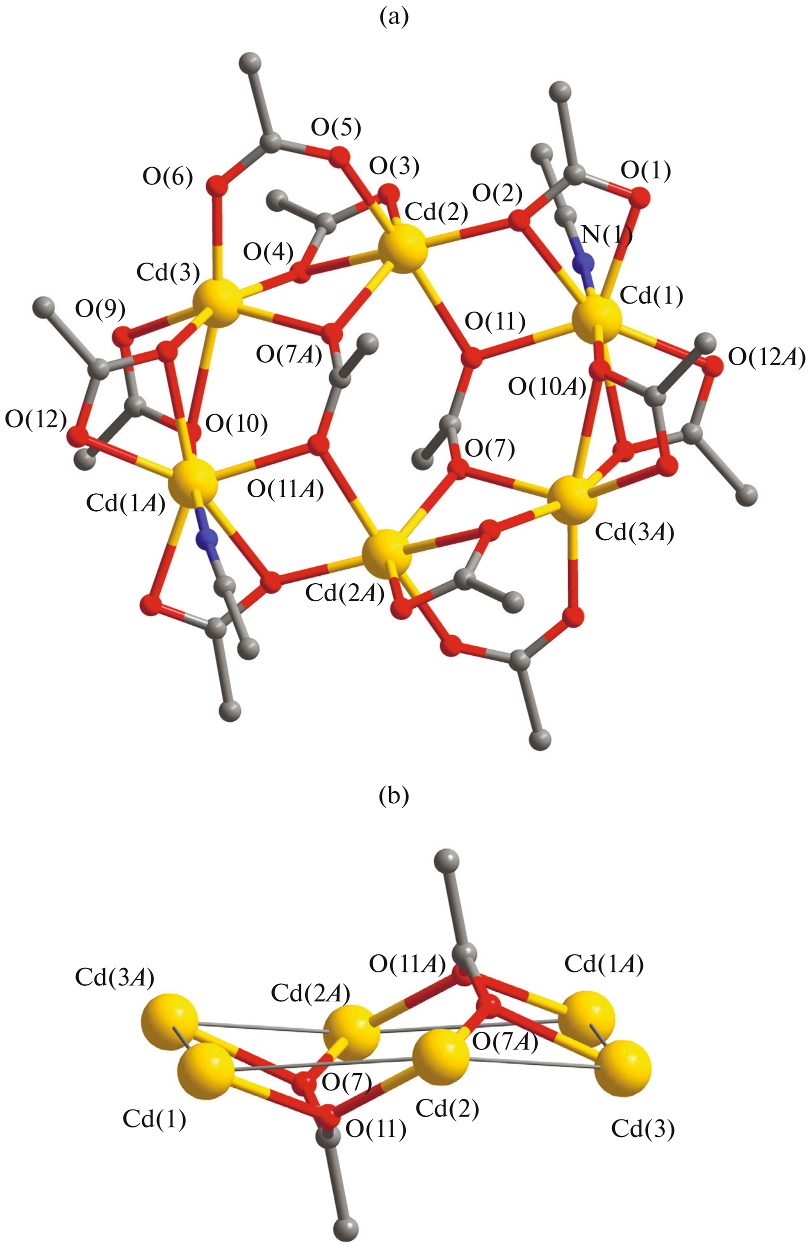


Fig. 5. (a) Structure of the molecule and (b) $\{Cd_6(\mu_4\text{-}Piv)_2\}$ fragment of complex **V** (hydrogen atoms and *tert*-butyl groups are omitted). Symmetry code: (*A*) $1 - x$, $1 - y$, $1 - z$.

Use at the Kurnakov Institute of General and Inorganic Chemistry (Russian Academy of Sciences) and the X-ray Structural Centre at the Nesmeyanov Institute of Organoelement Compounds (Russian Academy of Sciences).

A.A. Sidorov and N.V. Gogoleva acknowledge support from the Russian Foundation for Basic Research (project no. 17-03-00743). M.A. Kiskin and M.A. Shmelev acknowledge support from the Russian Science Foundation (project no. 16-13-10537).

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Translated by E. Yablonskaya