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The authors congratulate Academician I.L. Eremenko on his 70th birthday

Unexpected Participation of the Carbonate Anion in the Assembly of Hexanuclear Cadmium(II) Trimethylacetate Complex

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Abstract—A new unusual molecular complex $[Cd_6(CO_3)(Piv)_{10}(Phen)_2]$ (**I**) was prepared by the reaction of cadmium(II) trimethylacetate, $Cd(Piv)_2 \cdot 2H_2O$, and 1,10-phenanthroline (Phen) in 2 : 1 ratio in acetonitrile in air. Six cadmium atoms form a trigonal prismatic metal core and are connected to the carbonate anion located inside it. The structure of complex **I** was derived from X-ray diffraction data (CIF file CCDC no. 1912223).

Key words: cadmium(II), trimethylacetate, carboxylate complexes, polynuclear metal core, X-ray diffraction

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INTRODUCTION

The structure of homometal cadmium(II) complexes with monocarboxylic acid anions and aromatic chelating ligands, 2,2'-bipyridine and 1,10-phenanthroline (Phen), has been studied for quite a number of compounds. For example, mono-, bi-, and trinuclear complexes with N-donor ligands in terminal positions have been reported [2–7]. The structure of cadmium(II) complexes of this type is similar to the structures of Mn(II), Fe(II), Co(II), and Zn(II) complexes, which usually have smaller coordination numbers (C.N.) (from 4 to 6 for 3*d* metals versus typical C.N. of 7–8 for cadmium).

For cobalt(II), unsymmetrical binuclear molecular pivalate complexes $[Co_2L(Piv)_4]$ (L = 2,2'-bipyridine, 2,2'-dipyridylamine) with M : L ratio of 2 : 1 were previously obtained [8]. Among known cadmium(II) carboxylates, there are no compounds with similar structure, although the structural moiety composed of metal centers connected by two bridging and one chelating bridging carboxylate anion, present in these compounds, is also present in the trinuclear linear molecular complexes [7]. The Cd : Phen ratio in this case is 3 : 2. Similar binuclear moieties were found in coordination polymers based on dicarboxylic acid anions [9, 10], with the Cd : Phen ratio being also 3 : 2.

In this paper, we report an unusual result obtained in attempted synthesis of cadmium(II) pivalate complex with 1,10-phenanthroline ($Cd(Piv)_2$: Phen = 2 : 1) in acetonitrile solution in air, namely, the formation of the hexanuclear molecular complex $[Cd_6(CO_3)(Piv)_{10}(Phen)_2]$ (**I**) containing a μ_6-carbonate anion.

EXPERIMENTAL

All operations related to the synthesis of complex **I** were performed in air using reagent grade acetonitrile. Compound **I** was synthesized from commercially available 1,10-phenanthroline monohydrate (99%, Chempur) and $Cd(Piv)_2 \cdot 2H_2O$ prepared by a reported procedure [11].

Synthesis of $[Cd_6(\mu_6\text{-}CO_3\text{-}\kappa^8O,O,O',O',O',O'',O'',\text{-}O'')(\mu\text{-Piv-}\kappa^3O,O,O')_8(\mu\text{-Piv-}\kappa^2O,O')_2(Phen)_2]$ (I). Phen (0.051 g, 0.29 mmol) was added to a solution of $Cd(Piv)_2 \cdot 2H_2O$ (0.2 g, 0.57 mmol) in acetonitrile (15 mL). The reaction mixture was stirred for 5 min at 20°C. The resulting colorless solution was left an air at 20°C for slow evaporation. The colorless crystals suitable for X-ray diffraction that formed after 14 days were separated from the mother liquor by decantation, washed with cold acetonitrile ($T \approx$ 5°C), and dried in air. An unknown white-colored finely crystalline product was formed in parallel; therefore, it was impossible to calculate the yield and carry out elemental

analysis of complex **I** or to characterize the complex by other methods.

For $C_{75}H_{106}N_4O_{23}Cd_6$

Anal. calcd., % C, 42.82 H, 5.04 N, 2.66

Single-crystal X-ray diffraction study of compound **I** was carried out on a Bruker Apex II diffractometer (CCD array detector, MoK_α, $\lambda = 0.71073$ Å, graphite monochromator) [12]. Semiempirical absorption corrections were applied [13]. The structure of **I** was solved by direct methods and refined in the full-matrix 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 using the SHELX-2014/6 program package [14]. Crystallographic parameters and structure refinement details: $C_{81}H_{115}Cd_6N_7O_{23}$, M = 2229.19 g/mol, crystal size 0.34 × 0.30 × 0.26 mm, colorless crystal, T = 150(2) K, monoclinic system, space group $P2_1/n$, a = 16.9654(12), b = 30.488(2), c = 18.4769(11) Å, $\beta = 95.829(2)°$, V = 9507.5(11) Å^3, Z = 4, ρ = 1.557 g/cm^3, μ = 1.387 mm^{-1}, θ = 1.84°–26.40°, $-21 \le h \le 21$, $-37 \le k \le 38$, $-22 \le l \le 23$, total of 87838 reflections, 19450 unique reflections, 16929 reflections with $I \ge 2\sigma(I)$, R_{int} = 0.0296, T_{min}/T_{max} = 0.672/0.725, S = 1.027, R_1 = 0.0340, wR_2 = 0.0643 (for all data), R_1 = 0.0263, wR_2 = 0.0600 (for $I \ge 2\sigma(I)$), $\Delta\rho_{min}/\Delta\rho_{max}$ = –0.606/1.171, e Å^{-3}.

The full set of X-ray diffraction parameters for **I** is deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 1912223; deposit@ccdc.cam. ac.uk; http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The reaction of $Cd(Piv)_2 \cdot 2H_2O$ with a deficient amount of Phen in MeCN (Cd : Phen = 2 : 1) and subsequent repeated recrystallization with slow evaporation of the reaction solution at room temperature in air resulted in isolation of several prismatic colorless crystals. A previously unknown hexanuclear molecular complex **I** (Fig. 1) with Cd : Phen = 3 : 1 was thus obtained. The metal atoms are located at the vertices of a distorted trigonal prism (the dihedral angle between the planes of the triangular faces is 16.24(2)°, the Cd...Cd distances within the triangular moieties are in the range of 3.736(2)–3.908(2) Å, and the Cd...Cd distances between the triangular moieties are 3.700(2)–4.687(2) Å), the cavity of which accommodates the carbonate anion coordinated by six metal atoms (Fig. 1b). The CO_3^{2-} dianion lies in the plane almost perpendicular to the quadrangular face of the Cd_6 metal core, formed by the Cd(1), Cd(2), Cd(3), and Cd(4) ions (the dihedral angle is 88.61(7)°). The O(1M) oxygen atom binds the Cd(5) and Cd(6) metal centers (Cd(5)–O, 2.342(2); Cd(6)–O, 2.383(2) Å). Each of the two other remaining oxygen atoms of CO_3^{2-} bind three cadmium atoms of each of the triangular faces of the metal core (Cd(1)–O(2M), 2.270(2); Cd(2)–O(2M), 2.393(2); Cd(6)–O(2M), 2.487(2); Cd(3)–O(3M), 2.256(2); Cd(4)–O(3M), 2.361(2); Cd(5)–O(3M), 2.536(2) Å). The metal centers of the triangular faces of the metal core are connected in pairs by one bridging (Cd–O 2.215(2)–2.255(2) Å) and two chelating bridging pivalate anions, which close the chelate ring at the Cd(2), Cd(4), Cd(5), and Cd(6) atoms (Cd–O, 2.307(2)–2.526(2) Å). The Cd(1), Cd(2), Cd(3), and Cd(4) environments are completed to octahedron ($Cd(1)O_6$), pentagonal bipyramid ($Cd(2)O_7$, $Cd(4)O_7$), and one-cap trigonal prism ($Cd(3)O_7$) via coordination by the chelating pivalate anion; each anion performing the μ-bridging function binds in pairs the cadmium atoms of different triangular moieties of the metal core (Cd–O, 2.242(2)–2.544(2) Å). The Cd(5) and Cd(6) atoms coordinate additionally two N atoms of the chelating Phen molecules, thus completing their environments (CdO_5N_2) to one-cap octahedra (Cd–N 2.325(2)–2.368(2) Å). The aromatic rings of the Phen molecules are located one above another in nearly parallel planes (the dihedral angle is 11.35(4)°), which gives rise to π-stacking interactions (the shortest distance between the carbon atoms of the aromatic rings is 3.316(3) Å).

It is known that decarboxylation of carboxylic acids requires special conditions (high temperature [15], irradiation [16], or the presence of a catalyst [17]). Conduction of the reaction similar to that for the synthesis of **I** under argon resulted in crystallization of the previously described binuclear complex $[Cd_2(Piv)_4(Phen)_2]$ (**II**) [1], which was identified by powder and single crystal X-ray diffraction. Compound **II** contains Cd atoms and Phen molecules in 1 : 1 ratio, contrary to the 2 : 1 molar ratio introduced into the reaction. An example of formation of a polynuclear metal core of a carboxylate complex involving carbonate anion may be promising for the synthesis of polynuclear cadmium carboxylate complexes. However, it is necessary to create conditions that prevent the formation of insoluble inorganic carbonates. Probably, in the case of complex **I**, such conditions may by generated by adding organic ligands with hydrophobic substituents and by using low concentrations of the carbonate anion present in the solution. Conduction of the reaction in pure carbon dioxide did not give any carbonate complexes. For Cd : Phen ratios of 3 : 1 and 2 : 1, only crystals of the above-noted binuclear complex **II** were isolated [1]. Apparently, potassium hydroxide used for the synthesis of the initial $Cd(Piv)_2 \cdot 2H_2O$ could serve as the source of carbonate ions, since KOH always contains some carbonate impurity. Thus, the preparation of the hexanuclear complex **I**

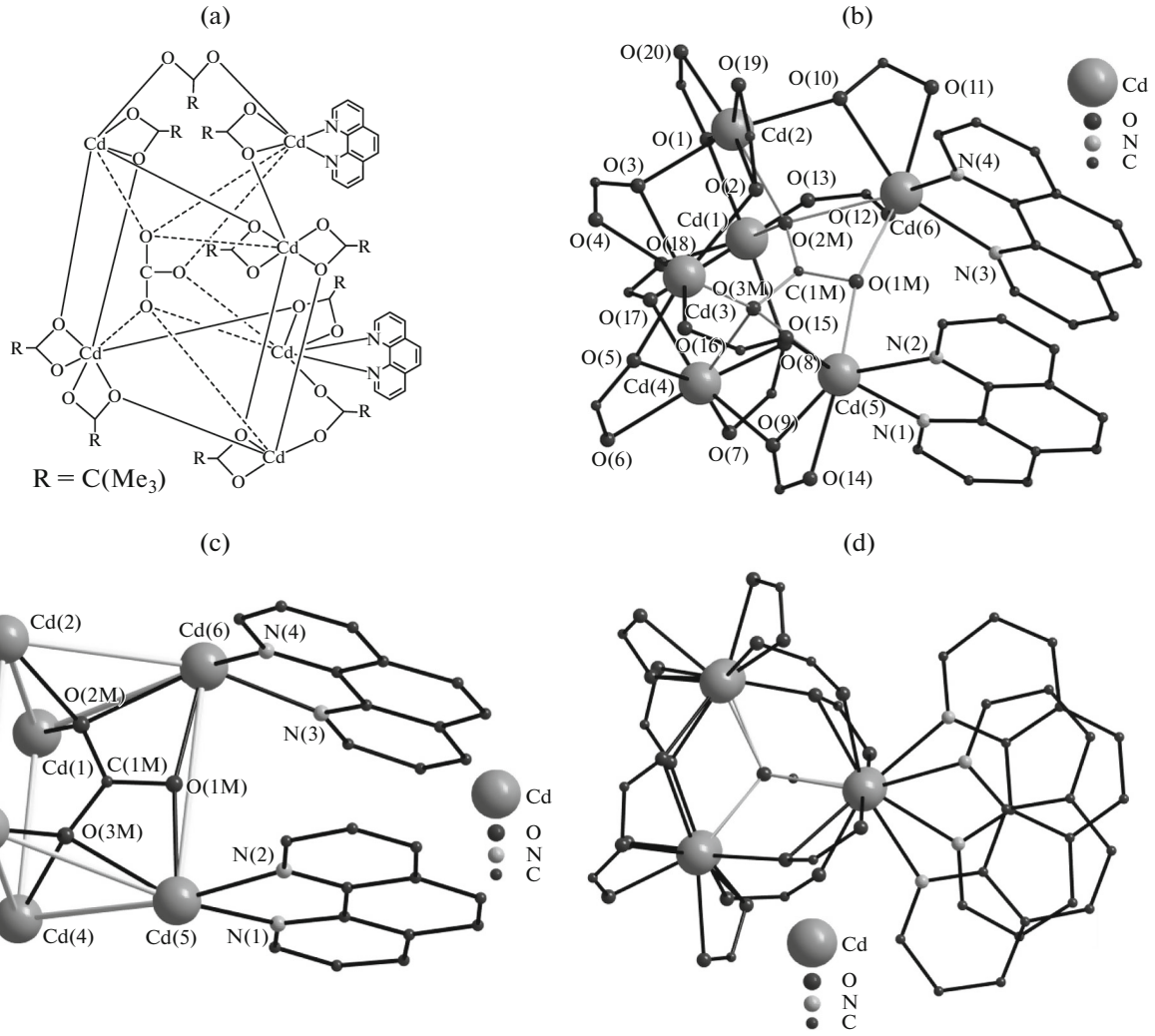

Fig. 1. (a) Schematic view and (b, c, d) structure of the molecule of complex **I**. (c) Light gray color marks the metal core edges of **I**; (a) dashed line marks the bonds between CO_3 and metal centers; (b, d) *tert*-butyl substituents and (c) Piv anions are not shown for clarity.

evidently requires finding a method for introducing the appropriate amount of carbonate anions into the reaction solution. The attempts to synthesize complex **I** from freshly precipitated cadmium carbonate via its dissolution in the presence of trimethylacetic acid and Phen (Cd : Phen molar ratios of 3 : 1, 2 : 1, and 1 : 1) allowed the synthesis of only the known hexanuclear cadmium pivalate $[Cd_6(MeCN)_2(Piv)_{12}]$ [18] and $[Cd_2(Piv)_4(Phen)_2]$ (**II**) [1].

Note that there are few known polynuclear compounds in which a carbonate anion binds six or more metal atoms. These are mainly molecular or ionic island complexes of high nuclearity, for example, $\{Cu_{20}[\mu_9\text{-}CO_3][\mu_3\text{-}HO]_{24}[\mu_2\text{-}OOCMe\text{-}k^2O,O']_6\text{-}[H_2NC_3H_7]_{10}[H_2O]_6\text{-}(OOCMe)_8\} \cdot 8H_2O$ [19], $\{Zn_{8}\text{-}Cu_{12}[\mu_{10}\text{-}CO_3][\mu_3\text{-}HO]_{24}[\mu_2\text{-}OOCMe\text{-}k^2O,O']_{12}[H_2O]_{12}\}\text{-}(OOCMe)_2 \cdot HOOCMe$ [19], $\{Cd_{10}[\mu_6\text{-}CO_3][\mu_5\text{-}ClO_4]_2[\mu_3\text{-}C_{10}H_8N_3O\text{-}k^2N,N',k^3O]_6[\mu_3\text{-}C_{10}H_7N_3O\text{-}k^2N,N',k^3O]_4\} \cdot \{Cd_{10}[\mu_8\text{-}CO_3][\mu_5\text{-}ClO_4][\mu_4\text{-}ClO_4\text{-}k^4O,O',O'']][\mu_3\text{-}C_{10}H_8N_3O\text{-}k^2N,N',k^3O]_6[\mu_3\text{-}C_{10}H_7N_3O\text{-}k^2N,N',k^3O]_4\}(ClO_4)_4 \cdot x CH_3OH \cdot 11H_2O$ ($C_{10}H_8N_3O$ = 2-((imidazol-2-yl)methyleneamino)phenol anion) [20]. There are also coordination polymers constructed by linked polynuclear metal frameworks [21]. A distinctive feature of the obtained molecular compounds is that the polynuclear complex contains only one carbonate anion, which forms 6 to 9 bonds with metal atoms.

It should be noted that cadmium carboxylates tend to form polynuclear compounds in which metal atoms are linked by chelating bridging carboxylate anions. We prepared the hexanuclear molecular $[Cd_6\text{-}(MeCN)_2(Piv)_{12}]$ and cationic $[Cd_6Cl(Piv)_{12}]^+$ complexes [18]. In the former complex, apart from two μ_4-

pivalate-anions, the other ten anions occupy chelating bridging positions, whereas in the highly symmetrical cationic complex, the metal core is centered by the μ_6-chloride anion and all 12 carboxylate anions are chelating bridging ligands. In the hexanuclear complex **I**, all carboxylate anions are also chelating bridging ligands. However, unlike **I**, the neutral $[Cd_6(MeCN)_2(Piv)_{12}]$ and cationic $[Cd_6Cl(Piv)_{12}]^+$ complexes are not only unstable in the presence of chelating ligands, but are also easily destroyed by monodentate pyridine derivatives. The isolation of compound **I** shows that determining the conditions for the formation of these compounds opens up new routes towards stable polynuclear transition metal carboxylate complexes due to the presence of additional ligands, which stabilize the metal core framework (for example, carbonate, phosphate, or sulfate) and form insoluble products with cadmium in nonaqueous media. However, the formation of the crystal of $[Cd_6(Phen)_2(\mu_6\text{-}CO_3)(Piv)_{10}]$ attests to the possibility of preparing these compounds.

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