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Isomerization of Binuclear Cadmium Carboxylate Complexes $[Cd_2L_2(O_2CR)_4]$

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Abstract—The binuclear cadmium complexes in which the metal atoms are linked by two chelate-bridging carboxylate anions, $[Cd_2L_2(\mu_2\text{-}(Piv)_2(\kappa^O,\kappa^{O'}\text{-}(Piv)_2]$ (L is 2,4-lutidine, phenanthridine, and 2,2'-bipyridine; and Piv is pivalate anion), and the complexes with the “Chinese lantern” structure in which the cadmium atoms are linked by four bridging carboxylate anions, $[Cd_2L_2(\mu_2\text{-}(Piv)_4]$ (L is 2,3-cyclododecenopyridine (Cdpy)) and $[Cd_2(L)_2(\mu_2\text{-}(PfAc))_4]$ (L is 1,10-phenanthroline, and PfAc is pentafluorophenylacetate anion), are considered. The two-bridge and four-bridge isomers of each binuclear $[Cd_2L_2(Piv)_4]$ complex with the monodentate and chelating N-donor ligands are calculated by the density functional theory using four different approximations. The stabilities of the isomers are compared and conclusions about the factors leading to the formation of complexes of this or another structure are made on the basis of the calculation data.

Keywords: cadmium, pivalic acid, pentafluorophenylacetic acid, X-ray structure analysis, N-donor ligands

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INTRODUCTION

The structures of carboxylates of cadmium and divalent 3*d* metals have many common features. The same monodentate and chelating pyridine derivatives often form complexes with the analogous structure in the case of 3*d* metals. For example, α-substituted pyridines form the binuclear complexes $[M_2L_2(\mu_2\text{-}O_2CR)_4]$ (M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II); L is α-substituted pyridine; and O_2CR is the monocarboxylic acid anion) of the “Chinese lantern” structure with four bridging carboxylate anions [1–7]. The chelating pyridine derivatives (2,2'-bipyridine (Bipy), 1,10-phenanthroline (Phen), and others) favor the stabilization of binuclear complexes with an analogous composition $[M_2L_2(O_2CR)_4]$ [8, 9] in which the metal atoms are bound only by two bridging carboxylate anions $[M_2L_2(\mu_2\text{-}(O_2CR)_2(\kappa^O,\kappa^{O'}\text{-}(O_2CR)_2]$. It should be mentioned that cadmium and 3*d* metals with the pyridine derivatives can form mononuclear complexes along with binuclear compounds [10–12], as well as compounds of different structures that are not considered in this work. Unlike 3*d* metals, cadmium ions with chelating ligands can form complexes of both structural types (two- [13–17] and four-bridge compounds [10, 18, 19]).

In the case of the cadmium complexes, this structural variativeness can indicate in favor of the easy isomerization of the two-bridge structure $[M_2L_2(\mu_2\text{-}(O_2CR)_2(\kappa^O,\kappa^{O'}\text{-}(O_2CR)_2]$ to the four-bridge structure $[M_2L_2(\mu_2\text{-}(O_2CR)_4]$, and vice versa. The ability to form structures of several types with the identical ligand composition can be fruitful, for example, for the development of methods for the targeted synthesis of carcass coordination polymers in which the isomerization of the binuclear fragment could result in structural phase transitions. Since one of two possible isomers will always be thermodynamically more stable, appropriate conditions should be determined for the isolation of a metastable isomer in the case of rather labile complexes of cadmium and divalent 3*d* metals, which is difficult to perform for one composition but can be fulfilled by the variation of ligands in the case of cadmium carboxylates.

The purpose of this work is to obtain an information about the structures of the isomers of the binuclear cadmium pivalate complexes with Bipy, 2,3-cyclododecenopyridine (Cdpy), and 2,4-lutidine (Lut) and of the pentafluorophenylacetate complex with Phen by calculations using the density functional theory (DFT). For the complexes with the “Chinese lantern” structure ($[M_2L_2(\mu_2\text{-}(O_2CR)_4]$), the structure of the hypothetical binuclear isomer of the same composition but with two bridging carboxylate anions ($[M_2L_2(\mu_2\text{-}(O_2CR)_2(\kappa^O,\kappa^{O'}\text{-}(O_2CR)_2]$) was calculated. The structure of the hypothetical isomer of the "Chinese lantern" type was calculated for the complexes with two bridging carboxylate anions. The stabilities of the isomers corresponding to each composition were compared using the quantum-chemical calculation results, and the conclusions about the factors leading to the formation of complexes of this or another structure were made. The main group of the considered carboxylates is presented by pivalates that make it possible to obtain the most part of the required types of binuclear structures and are also convenient starting objects for studying the chemistry of cadmium carboxylate complexes. The results obtained can directly be compared with the data accumulated on numerous analogous 3*d*-metal complexes [20–22]. The single pentafluorophenylacetate complex was considered, since for pivalate anions we failed to isolate a compound with the "Chinese lantern" type structure using chelating ligands.

EXPERIMENTAL

All procedures related to the synthesis of the new complex were carried out in air using ethanol (96%), acetonitrile (99.9%), $Cd(NO_3)_2 \cdot 4H_2O$ (99%, Acros organics), KOH (analytical grade), HPfAc (99%, Sigma-Aldrich), and 1,10-phenanthroline monohydrate ($Phen \cdot H_2O$, 99%, Alfa Aesar). Reagent KPfAc was synthesized in situ by the reaction of stoichiometric amounts of KOH and HPfAc in EtOH and MeCN. The IR spectrum of the compound was recorded on a Spectrum 65 FT-IR spectrophotometer (Perkin-Elmer) using the attenuated total internal reflection (ATR) method in a frequency range of 4000–400 cm^{-1}. Elemental analysis was carried out on a EuroEA 3000 CHNS analyzer (EuroVector).

Synthesis of $[Cd_2(Phen)_2(\mu_2\text{-}(PfAc))_4]$. A solution of KPfAc (0.175 g, 0.649 mmol) in a mixture of EtOH (10 mL) and MeCN (10 mL) was poured to a solution of $Cd(NO_3)_2 \cdot 4H_2O$ (0.100 g, 0.325 mmol) in EtOH (15 mL). The reaction mixture was stirred on heating ($T = 70°C$) for 20 min. The formed white precipitate of KNO_3 was filtered off, and Phen (0.059 g, 0.325 mmol) was added to the filtrate. The resulting mixture was stirred at 70°C for 25 min, cooled down to room temperature, and kept with the slow evaporation of the solvent for 5 days. Precipitated colorless crystals suitable for XRD were separated from the mother liquor by decantation, washed with cold acetonitrile (5°C), and dried in air. The yield was 0.166 g (68.9% based on $Cd(NO_3)_2 \cdot 4H_2O$).

For $C_{56}H_{24}N_4O_8F_{20}Cd_2$

Anal. calcd., %	C, 45.3	H, 1.6	N, 3.8
Found, %	C, 45.4	H, 1.7	N, 3.6

IR (ATR), ν, cm^{-1}: 3675 w, 2971 w, 1635 s, 1590 m, 1571 m, 1519 m, 1497 s, 1427 m, 1415 m, 1378 s, 1346 m, 1313 m, 1265 w, 1223 w, 1210 w, 1201 m, 1096 w, 1089 w, 1046 m, 1008 s, 974 s, 917 s, 862 m, 849 s, 782 w, 775 m, 730 s, 722 m, 702 w, 636 m, 613 w, 581 w, 556 m, 552 w, 480 m.

XRD of a single crystal of $[Cd_2(Phen)_2(\mu_2\text{-}(PfAc))_4]$ was carried out on a Bruker Apex II diffractometer equipped with a CCD detector (MoK_α, $\lambda = 0.71073$ Å, graphite monochromator) [23]. A semiempirical absorption correction was applied for all compounds using the SADABS program [24]. 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 the organic ligands were generated geometrically and refined by the riding model. Calculations were performed using the SHELX program package [25] and OLEX 2 [26]. The geometry of the polyhedra of the metals was determined using the SHAPE 2.1 program [27, 28]. The crystallographic parameters and structure refinement details for $[Cd_2(Phen)_2(\mu_2\text{-}(PfAc))_4]$ at $T = 296(2)$ K are as follow: $C_{56}H_{24}N_4O_8F_{20}Cd_2$, $M_w = 1485.59$ g/mol, orthorhombic colorless crystals, 0.37 × 0.24 × 0.17 mm, space group $C2/c$, $a = 28.219(9)$, $b = 9.712(3)$, $c = 21.727(8)$ Å, $\beta = 112.37(2)°$, $V = 5507(3)$ Å^3, $Z = 4$, $\rho_{calc} = 1.792$ g cm^{-3}, $\mu = 0.900$ mm^{-1}, $1.73° \le \theta \le 25.00°$, segment of sphere $-0 \le h \le 21$, $0 \le k \le 23$, $-26 \le l \le 14$, 26994 measured reflections, 5386 independent reflections, 4581 reflections with $I > 2.0\sigma(I)$, $R_{int} = 0.1299$, GOOF = 1.027, R_1 ($I > 2\sigma(I)$) = 0.0483, wR_2 ($I > 2\sigma(I)$) = 0.1107, R_1 (all data) = 0.0573, wR_2 (all data) = 0.1212, $\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3} = –1.750/1.398.

The coordinates of atoms and other parameters of compound $[Cd_2(Phen)_2(\mu_2\text{-}(PfAc))_4]$ were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 2005752; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Calculation procedure. All calculations were performed using the GAUSSIAN 16 program [29]. The XSA data for the coordination compounds were used as the initial geometries. The structures of the complexes discussed were calculated by the full optimization without imposing symmetric restraints using the DFT method. The high stoichiometric nonrigidity of the complexes under study impelled to choose the approximation capable of correct reproducing the experimentally observed geometric characteristics. For this purpose, the calculations were performed using the B3LYP functional [29], which well recommended itself in the study of similar binuclear metal carboxylate complexes [20, 21, 30], and the extended Def2-TZVP basis set, which provided a reasonable compromise between the approximation level and calculation time and made it possible to use the effective core potential on cadmium atoms. Different schemes for taking into account dispersion interactions were used for modeling packing effects: the long-range corrections were included by the CAM-B3LYP functional [31], and Grimme's empirical D3BJ corrections were applied [32], including those in combination with CAM-B3LYP. The graphical images of the molecular structures were drawn using the ChemCraft program [33].

RESULTS AND DISCUSSION

It has previously been shown that the binuclear complexes with the "Chinese lantern" structure $[M_2L_2(\mu_2\text{-(Piv)})_4]$ (Piv is the pivalic acid anion, and L is α-substituted pyridine) are formed in the reactions of Mn(II), Fe(II), Co(II), Ni(II), and Zn(II) pivalates with α-substituted pyridines [1–4, 22, 34–39]. Copper(II) forms analogous complexes and is characterized by similar dimeric complexes with the majority of other monodentate ligands [38, 40–47]. The reactions of cadmium pivalates with 2,4-lutidine and phenanthridine were shown to afford binuclear complexes of the same composition $[Cd_2(L)_2(Piv)_4]$ (L = 2,4-Lut, Phen) [10] but with different structures (Figs. 1a, 1b). The cadmium atoms in these compounds are bound only by two chelate-bridging carboxylate anions, and two other anions are bound to each cadmium atom via the chelate mode. The use of the more bulky ligand Cdpy in a similar reaction led to the formation of complex $[Cd_2(Cdpy)_2(\mu_2\text{-(Piv)})_4]$ in which all the four carboxylate anions were bridging (Fig. 1c) [10]. Evidently, the formation of this structure was favored by an increase in the volume of the substituent in the α-position of pyridine, which demonstrates the role of steric factors in assembling of the metal-carboxylate framework with this or another coordination mode of anions. However, the direct comparison of the coordination polyhedra of the metal centers and steric effects created by the N-donor ligands in the $[Cd_2(2,4\text{-Lut})_2(Piv)_4]$, $[Cd_2(Phen)_2(Piv)_4]$, and $[Cd_2(Cdpy)_2(\mu_2\text{-(Piv)})_4]$ complexes is insufficiently correct, because they are of different structures. We have previously reported the synthesis and structural study of the binuclear Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) pivalate complexes with Cdpy [38]. The maximum distortions of the geometry of the molecules with the "Chinese lantern" structure were observed for the nickel complex, and they are manifested as a significant deviation from the linear arrangement of the N donor atoms of the pyridine ligands and Ni atoms (NNiNi angle 151.67°). For other metal ions, the NMM angle varied in a range of 161.15°–168.35°. The steric hindrances created by the α-substituents of the coordinated pyridine fragments are indicated by the deviation of the pyridine fragment from symmetric coordination, in other words, by the difference between the angles formed by the metal atom, the nitrogen atom coordinated to the metal, and the nearest carbon atom of the pyridine cycle.

The binuclear cadmium pivalate complexes with Bipy and Phen have the expected two-bridge structures [21, 48]. The distinction of the structures of these coordination compounds from the complexes with 2,4-lutidine and phenanthridine is that they contain the chelate-bonded molecule of an N-donor base as the apical ligand $[Cd_2(Bipy)_2(\mu_2\text{-(Piv)})_2(\kappa^O,\kappa^{O'}\text{-(Piv)}_2]$ (Fig. 2a), due to which the coordination number of cadmium increases from 6 to 7.

The use of HPfAc and Phen gave the new complex $[Cd_2(Phen)_2(\mu_2\text{-(PfAc)})_4]$ in which the cadmium atoms are linked by four bridging anions PfAc (Cd...Cd 3.506(1) Å, Cd–O 2.219(3)–2.369(3) Å) (Fig. 2b). The cadmium atoms build up their environment to an octahedron by the coordination of two N atoms of the Phen molecule (Cd–N 2.394(3), 2.403(3) Å).

A few reports on the synthesis of the binuclear cadmium complexes with Bipy molecules and monocarboxylic acid anions characterized by the four-bridge structure are known [18, 49]. Only one of the known compounds is the molecular complex with monocarboxylic acid anions [18], whereas two others represent cations formed by the neutral zwitterionic carboxylate ligands (phosphorus-containing analogues of betaine), and the nitrate anion acts as the chelating ligand [49]. Thus, real structurally characterized compounds, which can be considered as reference points in analysis, correspond to each possible structure of the binuclear cadmium complexes with the monodentate or chelating ligand.

The ability of cadmium with chelating and monodentate pyridine derivatives to form complexes both with the "Chinese lantern" structure and containing the binuclear two-bridge fragment possibly indicates that the energy characteristics of these structures are fairly close and a relatively slight change in the ligand structure or crystallization conditions can result in the formation of different isomers.

Primarily we attempted to localize the structures corresponding to three possible isomers of the complex with Bipy. The calculations in the B3LYP approximation ignoring dispersion interactions allowed us to find the isomers with the binuclear two-bridge and four-bridge fragments (Fig. 3). The geometry optimization for the crystal structure with two chelate-bridging fragments gave the two-bridge isomer. The inclusion of long-range dispersion interactions into the scheme (CAM-B3LYP) made it possible to find the third isomer, which turned out to be 0.4 kcal/mol

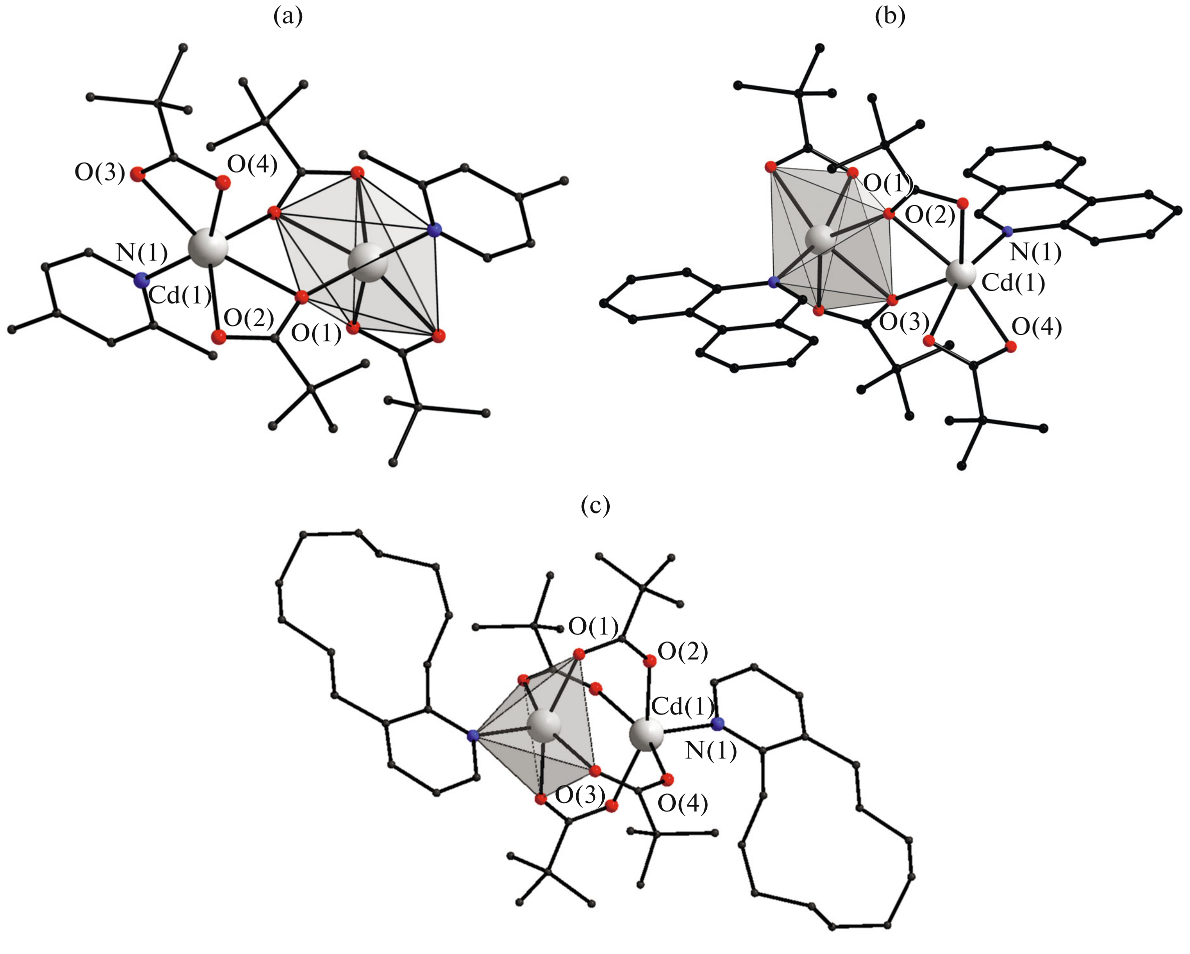


Fig. 1. Structures of complexes (a) $[Cd_2(2,4\text{-Lut})_2(Piv)_4]$, (b) $[Cd_2(Phen)_2(Piv)_4]$, and (c) $[Cd_2(Cdpy)_2(\mu_2\text{-}(Piv))_4]$. Hydrogen atoms are omitted.

lower in energy than the structure with the two-bridge fragment. The subsequent calculations including Grimme's D3BJ dispersion correction and its combination with CAM-B3LYP confirmed the possibility of three isomers to exist. The calculated difference in energies between the isomers with two bridging fragments does not exceed 0.8 kcal/mol (Fig. 3), which allows one to expect a barrier-free transition between them, for example, when packing the molecules in the crystal. According to the calculations, the "Chinese lantern" is the most favorable isomer, and the total energy of the structure corresponding to this isomer by 4–6 kcal/mol exceeds this characteristic for the experimentally observed chelate-bridging isomer. It can be assumed that the medium in which the reaction occurs exerts a substantial effect on the formation of the corresponding isomer.

The theoretical study of the complex with Lut using the B3LYP and CAM-B3LYP functionals showed the absence of stationary points corresponding to the chelate-bridging structure obtained by XRD (Fig. 4), and the optimization of its geometry results in the two-bridge isomer. The inclusion of Grimme's dispersion corrections (D3BJ) into the calculation scheme makes it possible to obtain the experimentally observed structure. As in the above considered complex with Bipy, the most favorable conformer of the isolated molecule of the complex is the structure of the "Chinese lantern" type stabilized by 2.4–3.9 kcal/mol, depending on the approximation used. Such an insignificant difference in energies can result in the formation of any isomer in the crystalline state.

The calculations of the complex with Cdpy of a similar composition show that the stationary points corresponding to chelate-bridging structures are stabilized only when Grimme's dispersion corrections are included, and the use of other approximations leads to the two-bridge structures (Fig. 5). In agreement with the XRD data, the structure of the "Chinese lantern" type corresponds to the ground state of this coordination compound and is by 2–6 kcal/mol more preferable than the isomers with two bridging ligands.

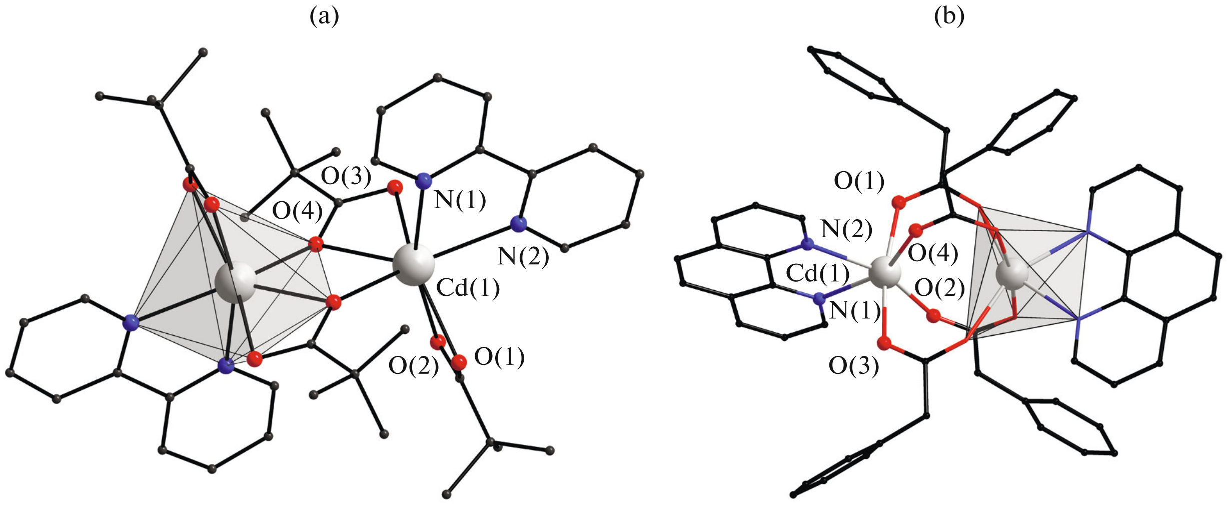


Fig. 2. Structures of complexes (a) $[Cd_2(Bipy)_2(\mu_2\text{-}(Piv)_2(\kappa^{O},\kappa^{O'}\text{-}(Piv)_2]$ and (b) $[Cd_2(Phen)_2(\mu_2\text{-}(PfAc))_4]$. Hydrogen and fluorine atoms (b) are omitted.

The $[Cd_2(Phen)_2(\mu_2\text{-}(PfAc))_4]$ complex was examined in conclusion. The XRD data show that this complex has the "Chinese lantern" structure in which the O atoms of the carboxyl groups are characterized by different lengths of the bonds with the metal ions and the Phen molecules are perpendicular to one another. The geometry optimization in different approximations is accompanied by a decrease in the angle between the Phen planes and the turn of the pentafluorophenyl group but retains the four-bridge structure of the dimer. The quantum-chemical study of the isomers in which only two ligands form bridges between the metal ions shows a dependence of their structures on the approximation used (Fig. 6). The B3LYP and CAM-B3LYP calculations expectedly resulted in the two-bridge structures, and the optimization in the B3LYP/Def2TZVP + GD3 approximation was accompanied by the transformation of the initial (two-bridge) geometry into the structure of the "Chinese lantern" type. The simultaneous use of two schemes for taking into account dispersion interactions (CAM-B3LYP/Def2TZVP + GD3) results in the structure in which one of the bridging carboxylate ligands is chelate-bridging (Fig. 6). Using this approximation, we found a fairly rare three-bridge isomer, whose insignificant destabilization relative to the structure with four bridging groups (1.2 kcal/mol) assumes the possibility of its presence in the reaction mixture. Similar structures were earlier found in the nickel compounds [50]. The second very interesting example is the cationic complex $[Zn_2(Piv)_3(Bipy)_2]^+$ isolated in the composition of the ionic compound $[Zn_2(Bipy)_2(Piv)_3][EuZn(Bipy)(NO_3)_3(Piv)_3]$ [51]. Thus, regardless of the approximation used, the conformer of the pentafluorophenylacetate complex with Phen of the "Chinese lantern" type is significantly more favorable (5.8–11.5 kcal/mol) than the two-bridge structures, which is consistent with the experiment. One of the probable reasons for a substantial difference in energies of the isomers of this compound compared to the above considered pivalate complexes with Lut and Cdpy is the hindered rotation of the planar aromatic substituents compared to a similar motion of the *tert*-butyl groups. It can be assumed that the systems based on aromatic ligands (unsubstituted, with donor substituents, with acceptor substituents, and condensed) will demonstrate a significant variety of structures, first, due to a high difference in the energy of the conformers (intramolecular interactions) and, second, because of a high probability of intermolecular interactions to occur.

The results of the performed quantum-chemical DFT study of the binuclear cadmium carboxylates with the monodentate and chelating N-donor ligands are well consistent with the experimental data indicating that different isomers exist and confirming the ability of the modern methods of quantum chemistry to correctly predict the structures and the possibility of synthesis of the considered types of carboxylate coordination systems. A comparatively small number of the cadmium complexes considered in this work made it possible to study them using four different approximations. An analysis of the results obtained by different calculation schemes showed that the best agreement of the calculated geometries of the binuclear cadmium carboxylate complexes with those found by XRD studies was obtained by a combination of CAM-B3LYP/Def2TZVP with empirical Grimme's GD3BJ corrections. This approximation can be recommended for the theoretical study of similar coordination compounds of this metal.

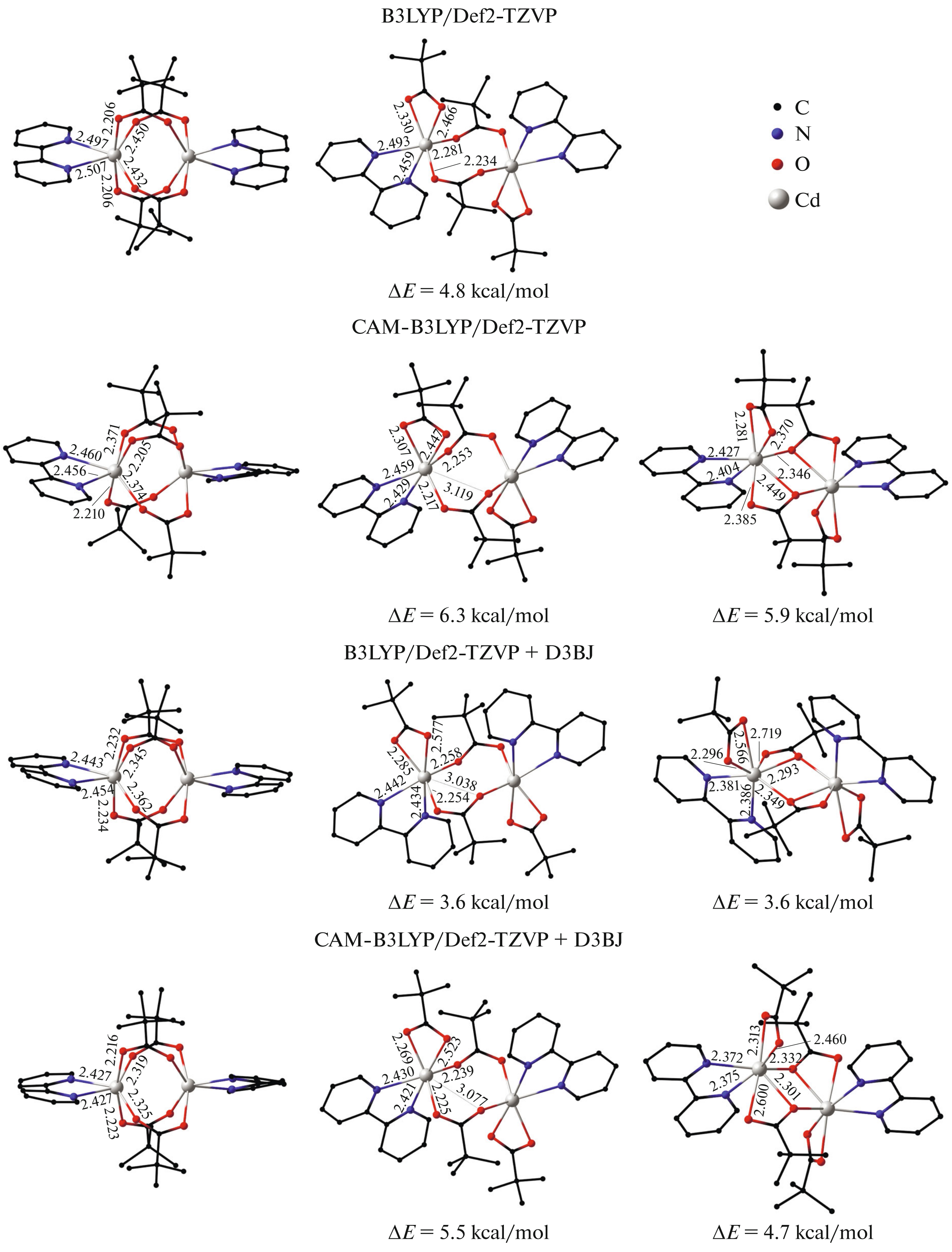
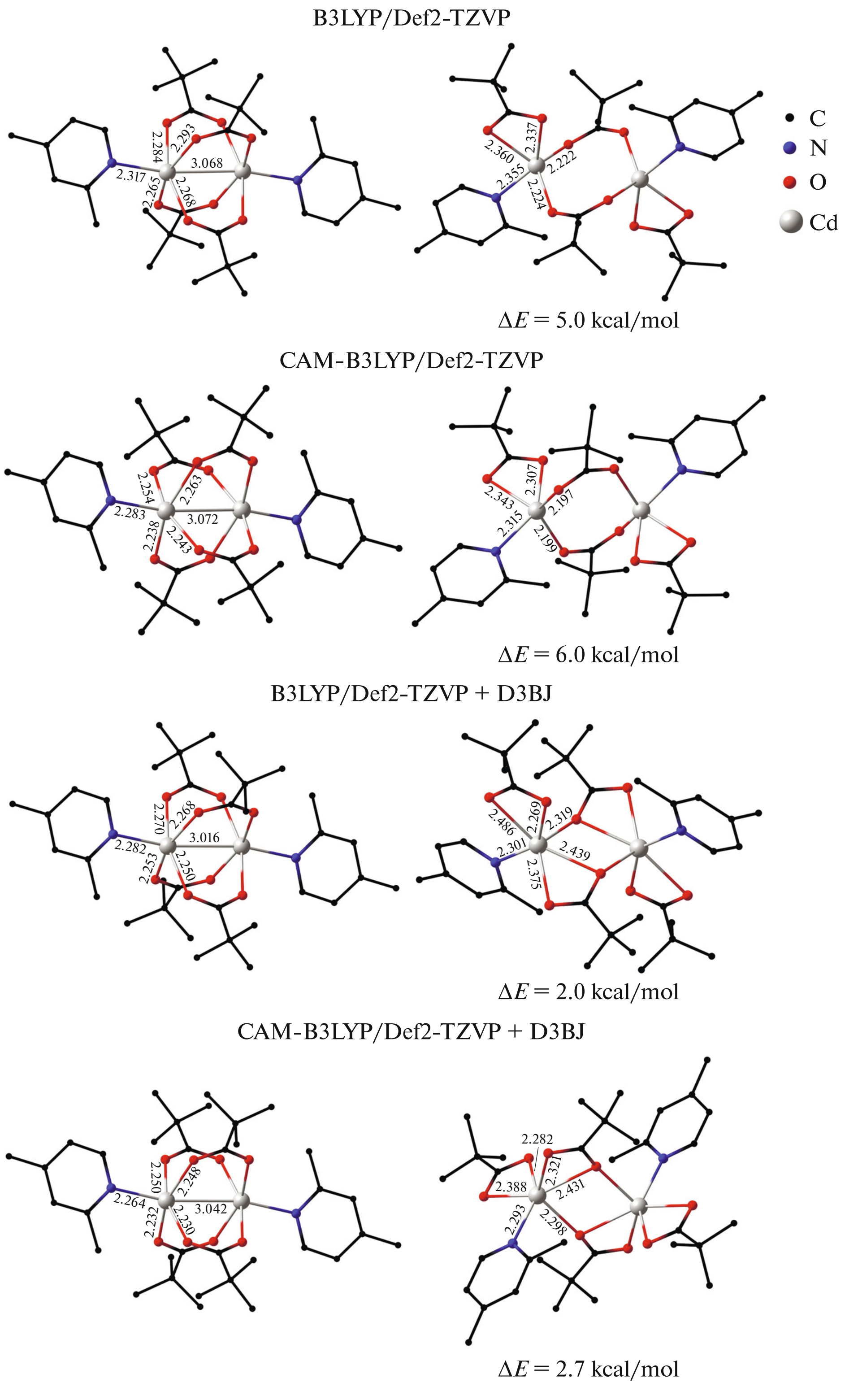


Fig. 3. Geometric and energy characteristics of the isomers of the $[Cd_2(Bipy)_2(\mu_2\text{-}(Piv)_2(\kappa^O,\kappa^{O'}\text{-}(Piv)_2]$ complex calculated using different approximations. Here and in Figs. 4–6, hydrogen atoms are omitted. The energy of the isomers presented in the left row is accepted to be zero.


B3LYP/Def2-TZVP

ΔE = 5.0 kcal/mol

CAM-B3LYP/Def2-TZVP

ΔE = 6.0 kcal/mol

B3LYP/Def2-TZVP + D3BJ

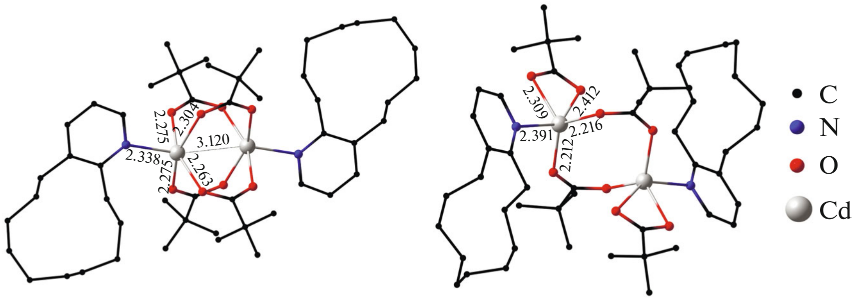
ΔE = 2.0 kcal/mol

CAM-B3LYP/Def2-TZVP + D3BJ

ΔE = 2.7 kcal/mol

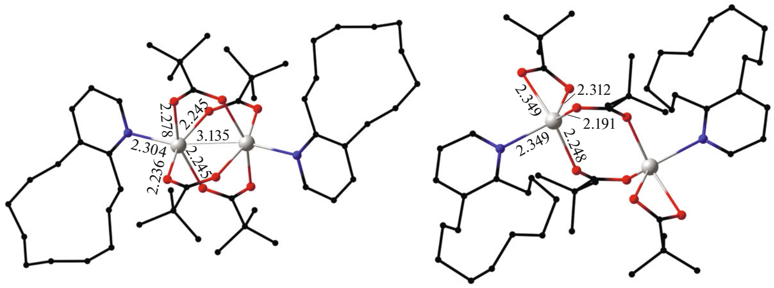
Fig. 4. Geometric and energy characteristics of the isomers of the $[Cd_2(2,4\text{-Lut})_2(Piv)_4]$ complex calculated using different approximations.

B3LYP/Def2-TZVP



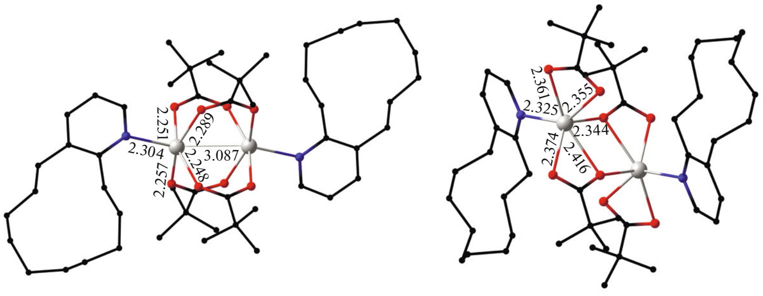
$\Delta E = 5.0$ kcal/mol

CAM-B3LYP/Def2-TZVP



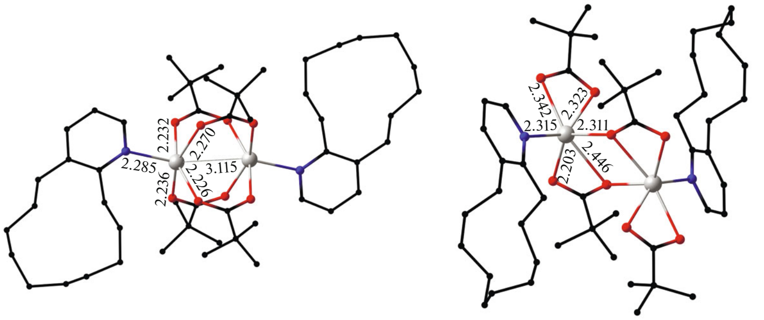
$\Delta E = 6.0$ kcal/mol

B3LYP/Def2-TZVP + D3BJ



$\Delta E = 2.0$ kcal/mol

CAM-B3LYP/Def2-TZVP + D3BJ



$\Delta E = 2.7$ kcal/mol

Fig. 5. Geometric and energy characteristics of the isomers of the $[Cd_2(Cdpy)_2(\mu_2\text{-}(Piv))_4]$ complex calculated using different approximations.

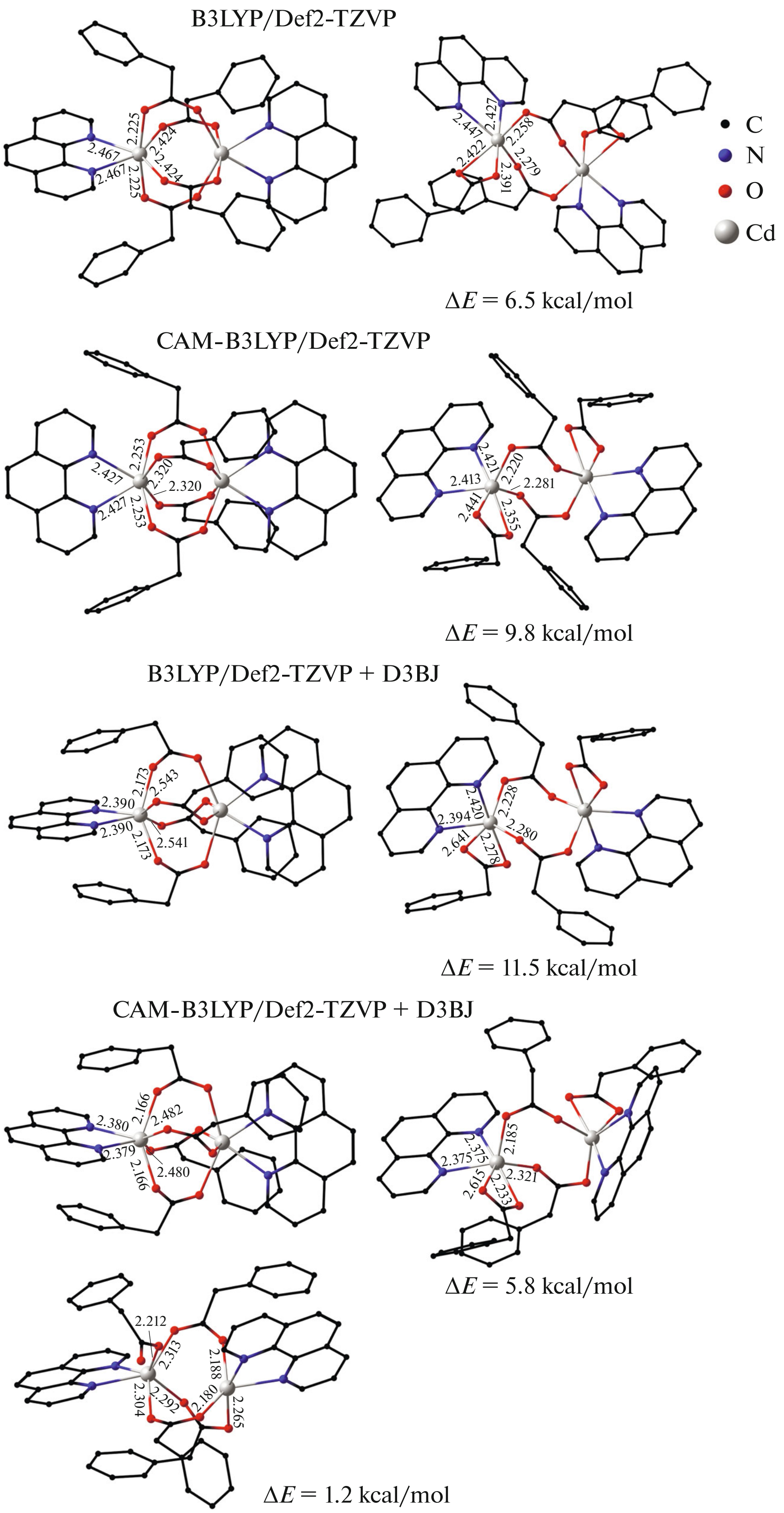


Fig. 6. Geometric and energy characteristics of the isomers of the $[Cd_2(Phen)_2(\mu_2\text{-}(PfAc))_4]$ complex calculated using different approximations. Fluorine atoms are omitted for clarity.

ACKNOWLEDGMENTS

The XRD of ([$Cd_2(Phen)_2(\mu_2\text{-}(PfAc))_4$]), IR spectroscopy, and elemental analyses of the complexes were carried out on the equipment of the Center for Collective Use "Physical Methods of Investigation" at the Kurnakov Institute of General and Inorganic Chemistry (Russian Academy of Sciences) in terms of the state assignment of the Kurnakov Institute of General and Inorganic Chemistry (Russian Academy of Sciences) in the area of basic research.

FUNDING

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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