COORDINATION POLYMER WITH A STAIRCASE MOLECULAR ARCHITECTURE: CONNECTING BINUCLEAR Zn(II) BIS-CHELATE PLATFORMS WITH BRIDGING 4,4′-BIPYRIDYL

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A new tetraketone ligand with two separated β-diketone functions was prepared, 1,3-[CO-CH$_2$-CO-C(CH$_3$)$_2$OCH$_3$]$_2$Ph (H$_2$L$^{i\text{PrOMe}}$). The title coordination polymer, [Zn$_2$(L$^{i\text{PrOMe}}$)$_2$(DMSO)$_2$(bipy)]$_n$ (DMSO = dimethylsulfoxide; bipy = 4,4′-bipyridyl), formed as the only crystalline product upon interaction of Zn(II) acetate, H$_2$L$^{i\text{PrOMe}}$ and bipy in 1:1:1 to 1:1:5 molar ratios in DMSO as a solvent. A single crystal XRD study of the compound revealed a staircase polymeric architecture of the complex. The architecture is based on binuclear ′Zn$_2$(L$^{i\text{PrOMe}}$)$_2$′ platforms where each Zn(II) cation is chealted by two β-diketonate groups of two L$^{i\text{PrOMe}}$ ligands in the equatorial plane, while each L$^{i\text{PrOMe}}$ ligand chelates two Zn(II) cations. The coordination environment of each Zn(II) is completed to a distorted octahedron by an O-atom of a terminal DMSO and an N-atom of bridging bipy ligands. The resulting staircase polymeric ribbons are packed in a self-inclusion mode as would be expected for van der Waals interactions. Most fragments of the molecule were found to be disordered over two equally populated orientations that was interpreted as evidence of a modulated structure. In addition, several fragments reveal additional minor disordering and high thermal motion.

K e y w o r d s : crystal engineering, crystal packing, wheel-and-axle, ladder-and-platform, tetraketone, β-diketonate, dimethylsulfoxide, modulated structure.

INTRODUCTION

The design of ″wheel-and-axle″ and ″ladder-and-platform″ molecular geometries proved to be very useful for creating porous architectures in crystals [1]. According to this strategy, new host molecules are created as combinations of bulky or flat fragments (″wheels″ or ″platforms″, respectively) and rod-like connectors (″spacers″). Due to their specific shape, such molecules tend to create voids as they pack in the crystal structure. The voids are filled with guest solvent molecules and potentially may be evacuated to create micropores in the materials. Our recent studies were concentrated on coordination polymers with the geometry of ″molecular ladders″ [2 — 5]. In order to create larger platforms, we aimed at the synthesis of tetraketones with two separated β-diketonate functions that were able to form binuclear metal complexes (Fig. 1). With doubly deprotonated H$_2$L^{Ph} tetraketone as a ligand, Zn(II) as a metal center, 4,4′-bipyridyl (bipy) as a spacer and dimethylsulfoxide (DMSO) as a terminal ligand, both double ″humming-top″ and double-strand ladder-and-platform geometries were obtained (Fig. 2) [5]. However, the third alternative shown in Fig. 2, the ″staircase″ geometry could not be isolated.
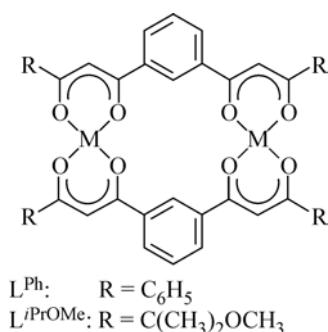
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Fig. 1. Molecular structure of ML$_2$ platform

L^{Ph}: R = C$_6$H$_5$
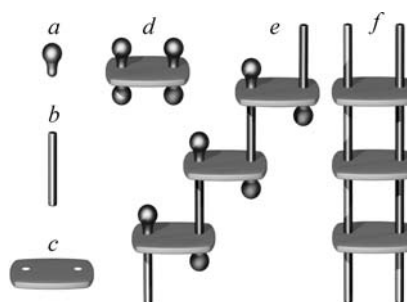L^{iPrOMe}: R = C(CH$_3$)$_2$OCH$_3$

Fig. 2. Three types of molecular geometries based on a combination of terminal ligand (a), bridging ligand (b) and binuclear platform (c): double humming-top geometry (d), staircase geometry (e), and double-strand ladder-and-platform geometry (f)

As a next step in our ongoing research, we prepared a new tetraketone, H$_2$L^{iPrOMe}, and attempted to isolate coordination polymers of the ligand with the same set of the other components. Surprisingly, the only crystalline product formed with various ratios of the reagents was found to be a polymer with the staircase molecular geometry. This communication describes the synthesis and crystal structure of the compound.

EXPERIMENTAL

The ligand H$_2$L^{iPrOMe} (1,3-bis[4-methyl-4-methoxypentanedione-1,3]phenylene, see Fig. 1) was prepared in three steps as described previously for H$_2$L^{Ph} [5]. (1) Diketone 1,3-[CO—C≡C——C(CH$_3$)$_2$OCH$_3$]$_2$Ph was prepared from 1,3-(COCl)$_2$Ph and HC≡C—C(CH$_3$)$_2$OCH$_3$ by the method of catalytic acylation using CuCl as a catalyst [6, 7]. (2) Diaminodivinyldiketone 1,3-[CO—CH=C(NH$_2$)—C(CH$_3$)$_2$OCH$_3$]$_2$Ph was synthesized by bubbling gaseous ammonia in the stirred solution of diketone (1) (8.2 g, 0.025 mol) in methanol (100 ml) at 22—40 °C for 3 hours (nucleophilic ammonia addition [8]). The diaminodivinyldiketone was isolated as an undistillable liquid (yield 6.8 g, 79.5 %) that crystallized with difficulty from CH$_2$Cl$_2$ (m.p. 140—142 °C). Found, %: C 66.43; H 7.79; N 7.70. Calculated for C$_{20}$H$_{28}$N$_2$O$_4$ (M = 360.4), %: C 66.64; H 7.83; N 7.77. (3) H$_2$L^{iPrOMe} was prepared by the hydrolysis of (2) (7.3 g, 0.02 mol) as described in [9]. The tetraketone was isolated as a solid (yield 5.9 g, 82.5 %) and recrystallized from hexane (m.p. 84—85 °C). Found, %: C 66.05; H 7.15. Calculated for C$_{20}$H$_{26}$O$_6$ (M = 362.4), %: C 66.27; H 7.23.

The title coordination polymer, [Zn$_2$(L^{iPrOMe})$_2$(DMSO)$_2$(bipy)]$_n$, was prepared from Zn(CH$_3$COO)$_2$·2H$_2$O (44 mg, 0.2 mmol), H$_2$L^{iPrOMe} (73 mg, 0.2 mmol), bipy (39 mg, 0.25 mmol) and DMSO as a solvent (4 g). The mixture was heated up to ~140 °C until a clear transparent solution was formed which was then cooled at the rate of 0.1 °C/min down to room temperature. Using this procedure, white prismatic crystals of relatively poor quality but suitable in size were obtained. Due to the low solubility of the compound, the yield was close to quantitative. Variation in the molar ratio of the reagents Zn:L^{iPrOMe}:bipy from 1:1:1 to 1:1:5 yielded the same and the only solid product that was the title coordination polymer.

Single crystals of the title compound were studied on a Bruker CCD X-ray diffractometers (a SMART 1K instrument was used to determine room temperature unit cell parameters and a Kappa APEX II was used to collect a full set of data at 100 K) equipped with MoK_α radiation and graphite monochromators. The data collection was set to cover a complete Ewald sphere for high redundancy, to the resolution of 0.8 Å (2θ to ~52°). A multiscan spherical absorption correction (SADABS) was applied to the final dataset.

A solution of the structure could be obtained in several monoclinic unit cells and space groups but all exhibited massive disorder and poorly behaved thermal parameters. An examination of the frames indicated a number of weak diffraction peaks that could not be indexed. This was true for all the crys-

tals that were screened. A more detailed examination of a large number of frames with the program Cell_now indicated a possible multiply-twinned primitive monoclinic unit cell. The data were integrated in the metrically monoclinic cell, solved in $P1$ and refined until all non-hydrogen atoms were located. A symmetry checking program, PLATON, indicated the correct space group to be $P2_1/c$. Refinement in this space group progressed slowly until the disordered fragments were all located. Initially the site occupation factors of the disordered fragments were refined independently. As pairs of alternate orientations appeared to be equal (within 3 %), the populations of the alternate orientations were set to be equal for the final cycles of the refinement. Several possible twin laws, suggested by the programs Cell_now and Rotax were found to be ineffective in improving the residuals. This observation taken together with the large-scale 50:50 disorder initially suggested the possibility of a missed larger unit cell. Since many weak diffraction peaks that indexed as half-integral in h (as would be expected for a doubled a axis) had been observed, several enlarged unit cells, particularly those with a doubled a axis were reexamined and rejected. The observed disorder and extra diffraction peaks are consistent with a modulated structure [10].

In order to ensure the stability of the refinement and the reasonableness of the final solution, a number of constraints and restraints were imposed on the positional and thermal parameters of the atoms. All hydrogen atoms were included in calculated positions with isotropic thermal parameters defined as a multiple of an average thermal parameter for the attached carbon. The geometry of some chemically equivalent fragments was restrained to be similar in bond distances and bond angles. Finally, the thermal parameters of adjacent atoms were restrained to a certain degree of similarity in order to account for rigid body motion of large disordered fragments.

One of major orientations of the asymmetric part of the structure is shown in Fig. 3a and the superposition of the two major orientations is illustrated in Fig. 3b. In addition to the main disorder, a minor disorder was resolved for the Zn1 atom (15.6(5) %), one of $CC(CH_3)_2OCH_3$ fragments (18.5(5) %), sulfur

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Parameters of the crystal structure and XRD experiments for $[Zn_2(L^{iPrOMe})_2(DMSO)_2(bipy)]_n$

Temperature, K	100	293
Formula	$C_{54}H_{68}N_2O_{14}S_2Zn_2$	$C_{54}H_{68}N_2O_{14}S_2Zn_2$
M	1164.0	1164.0
Crystal system, space group	monoclinic, $P2_1/c$	monoclinic
a, Å	8.1946(5)	8.249(3)
b, Å	22.915(1)	23.091(7)
c, Å	29.598(2)	29.961(8)
β, deg.	105.65(1)	105.61(3)
V, Å³; Z	5351.8(5), 4	5496(3), 4
Calculated density, g/cm³	1.445	1.407
Reflections used in unit cell refinement	5318	382
Crystal dimensions, mm	0.3×0.08×0.03	0.4×0.1×0.05
Crystal color, shape	white prism	white prism
Reflections collected	61846	–
Reflections unique, R_{int}	10863, 0.080	–
Reflections observed ($I_{hkl} > 2\sigma$)	6347	–
Parameters	1156	–
R_1, wR_2 (observed reflections)	0.070, 0.174	–
GOOF	1.026	–
Residual peak and hole, e/Å³	+1.18 and –0.98	–
CCDC deposition number	624038	–

Selected bond lengths d, Å *and valent angles* ω, deg. *in the structure studied (for numeration scheme see* Fig. 3*a)*

Bond	d	Angle	ω
Zn1—O1A	2.060(4)	O1A—Zn1—O3A	90.4(2)
Zn1—O3A	2.043(4)	O1C—Zn1—O3C	87.4(2)
Zn1—O1C	2.098(4)	O1A—Zn1—O1C	95.3(2)
Zn1—O3C	2.088(4)	O3A—Zn1—O3C	86.9(1)
Zn1—O1E	2.109(8)	O1A—Zn1—O1E	85.5(3)
Zn1—N7E	2.191(4)	O1A—Zn1—N7E	90.5(2)
Zn2—O4A	2.062(3)	O4A—Zn2—O6A	88.9(1)
Zn2—O6A	2.082(3)	O4C—Zn2—O6C	89.4(1)
Zn2—O4C	2.056(3)	O4A—Zn2—O4C	87.3(1)
Zn2—O6C	2.062(3)	O6A—Zn2—O6C	94.2(1)
Zn2—O1G	2.182(9)	O6A—Zn2—O1G	85.7(3)
Zn2—N8E′	2.169(4)	O6A—Zn2—N8E′	91.9(1)

atoms of both DMSO ligands (5.4(4) and 3.7(3) %), while the residual peaks (max 1.18 e/Å^3) indicated still unresolved disorder in the peripheral regions of the polymer.

The parameters of the crystal structure and XRD experiments are summarized in Table 1. Structural information for the 100 K experiment was deposited with Cambridge Structural Database (www. ccdc.cam.ac.uk) in form of a CIF file (CCDC deposition number 624038) and is freely available upon request via www. ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

As determined in the single crystal XRD study, the title compound is a 1D coordination polymer with the stoichiometry $[Zn_2(L^{iPrOMe})_2(DMSO)_2(bipy)]_n$ (Fig. 3). The basic structural element of the molecule — ″platform″ — is a neutral binuclear complex, as shown in Fig. 1, composed of two Zn(II) cations and two doubly deprotonated tetraketone ligands. Each Zn(II) cation is chelated by two β-diketonate functions of the two ligands and each ligand chelates two Zn(II) cations. The central part of the platform which includes bis-chelate fragments and phenylene rings is relatively flat and also less mobile, while peripheral methoxy-*iso*-propyl groups create bulkiness on the rim of the platform and display an increased thermal motion and disordering. Further, each Zn(II) cation is axially coordinated by one O-atom of a terminal DMSO ligand and one N-atom of a bridging bipy. Two DMSO liagnds are on the opposite sides of the platform, as are the bipy bridges.

Coordination environment of each Zn(II) is a distorted octahedron (Fig. 3, Table 2). Average length is 2.069(7) Å for the equatorial coordination bonds Zn—O(L^{iPrOMe}) (statistics for 8 bonds), 2.17(2) Å for the axial bonds Zn—O(DMSO) (4 bonds), and 2.18(1) Å for the axial bonds Zn—N(bipy) (2 bonds). Average and maximal deviations of coordination angles from ideal are 3.0° and 6.8°, respectively (40 angles). Average bonds and angles of the chelating β-diketonate fragments are the following: 1.28(2) Å for C=O (13 bonds); 1.42(1) Å for C—C (18 bonds); 124(1)° for O—C—C (18 angles); 125.6(9)° for C—C—C (10 angles). The chelating rings appear to be not ideally planar but this observation may be misleading because of the possibility of unresolved positions for some atoms of the disordered fragments. Dihedral angles between two β-diketonate fragments connected to the same Zn(II) atom cannot be defined without ambiguity arising from various equally populated orientations but, most probably, are 8.5° (Zn1, A and C orientations), 17.5° (Zn1, B and D), 22.2° (Zn2, A and C) and 14.0° (Zn2, B and D). Overall, both the Zn(II) coordination polyhedron and the geometry of bis-chelate fragments display many similarities to those observed in simpler metal(II) bis-(β-diketonate) analogs [11—21] but with a higher degree of distortion.
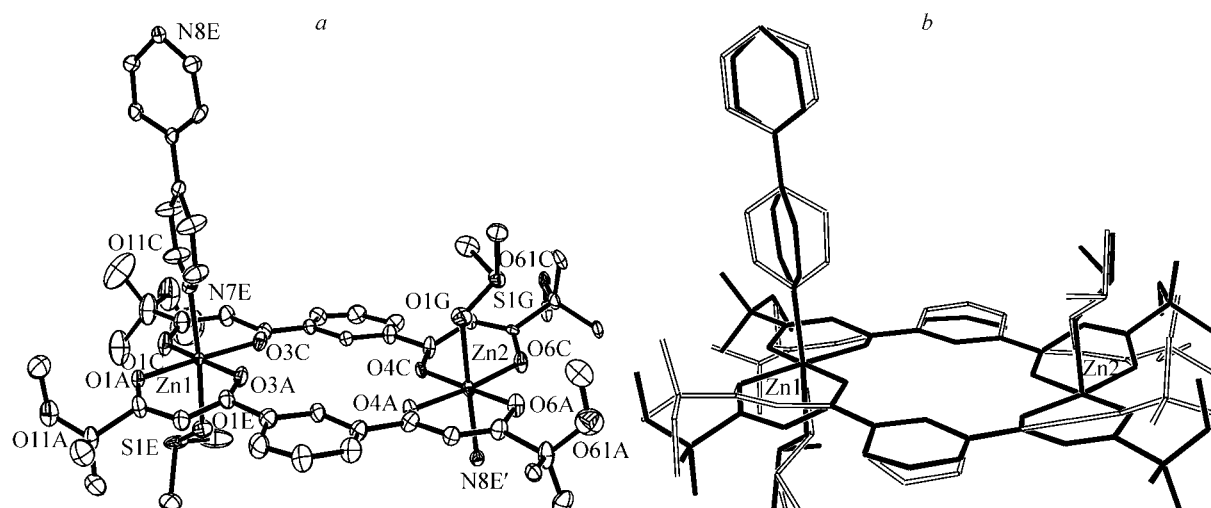
Fig. 3. ORTEP drawing for a major orientation of the asymmetric part (complemented with a symmetry gener-ated N8E' atom) of the structure studied (*a*) and a superposition of two major orientations (one outlined with black and another with white sticks) (*b*). H-atoms and minor orientations are not shown. Selected distances and angles are listed in Table 2

Topologically the studied coordination polymer belongs to the staircase type of architecture as shown schematically in Fig. 2*e*. The 'Zn$_2$(L^{iPrOMe})$_2$' platforms are connected to each other by bipy bridging ligands with a Zn—Zn separation of 11.5 Å to form zig-zag polymeric chains propagating by means of the 2$_1$ symmetry element (Fig. 4). The packing of the chains in the crystal is defined by van der Waals forces as almost no other obvious intermolecular interactions could be found. The only ex-ception is a weak C—H...O interaction indicated by a rather short distance of 3.39 Å between one of methoxy O-atoms and a C-atom of bipy from adjacent ribbon, with its H-atom directed on the O-atom. It should be noted that methoxy oxygens and acidic C—H groups of the chelates could form strong hydrogen bonds and, in fact, the bonds exist but as intramolecular interactions (for most orientations
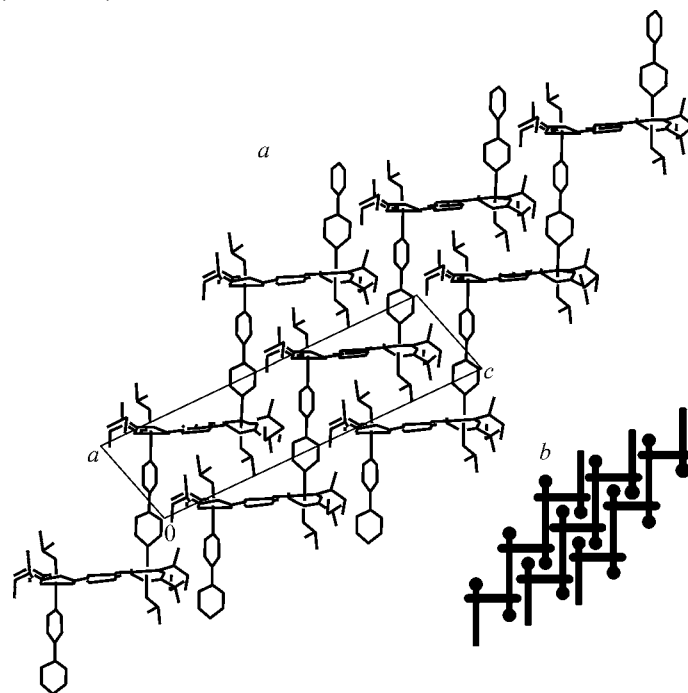

Fig. 4. Fragment of the crystal packing of the structure studied. Projection along *b* axis (half-wide of the unit cell; only one major orientation is shown; H-atoms are omitted) (*a*) and schematic illustration explaining the mode of packing and mutual alignment of the polymeric molecules in the layer (*b*)

the C...O distances vary within 2.70—2.79 Å). The chains appear to be self-complementary; they align parallel and form a densely packed layer as shown in Fig. 4a and illustrated schematically in Fig. 4b. The layers stack along b direction leaving no voids of molecular size.

It should be mentioned that the crystal structure is not simple and reveals certain problems in packing bulky polymeric molecules in the 3D space. The first indications of this complexity are seen in the enhanced thermal parameters and minor disordering of peripheral molecular fragments. These factors reflect an imperfect fit of the polymeric molecules in the overall crystal packing. Another indication is the major fifty-fifty disordering of most fragments that was interpreted as a modulated structure [10]. Apparently, simple translation does not provide sufficient packing efficiency and there is a high probability to have slightly different molecular geometry in adjacent unit cells. This modulation appears to arise from significant steric interactions between adjacent chains, primarily between the $C(CH_3)_2OCH_3$ groups.

The mode of packing demonstrated in Fig. 4 may be considered as interdigitation of the spatially self-complementary molecules where pockets (indentations) of one molecule are filled with fragments (prominences) of another. In this case, the structure would be stable when the accommodated fragments have an appropriate geometry and size [22]. Otherwise, a significant geometrical mismatch between the indentations and prominences will create a potential for the inclusion of a guest component. In a study by Clegg et al. [23], a similar coordination polymer was reported, $[Cu_2(L^{tBu})_2(azpy)]_n \cdot 2n(THF)$ (L^{tBu} is similar to the ligands shown in Fig. 1 with R = tert-butyl; azpy = = 4,4′-trans-azopyridyl; THF = tetrahydrofuran), but without terminal ligands (five-coordinated Cu(II) centers), the compound crystallizing as a solvate with two moles of guest solvent. A similar situation was observed in $[Cu_2(L^{tBu})_2(xbp)]_n \cdot 2.2n(THF)$ (xbp = 4,4′-(1,3-xylylene)-bis(3,5-dimethylpyrazolyl)) [24]. In one more study, two staircase coordination polymers based on trinuclear platforms were reported [25]; a similar ″zipper-like″ interdigitation of polymeric molecules was observed but included guest species were found in both cases. In another coordination polymer reported by Kawata et al. [26], $\{[Cu(bpm)_{1.5}(suc)_{0.5}](ClO_4)(H_2O)_2\}_n$ (bpm = 2,2′-bipyrimidyl; suc = succinate), the packing of staircase polymeric molecules is controlled by π—π stacking interactions of side aromatic fragments and by hydrogen bonding with ClO_4^- counterions and water molecules included in the crystal structure. Finally, staircase architectures were reported based on a binuclear Mn(II) complex [27] and Cu(II) complex [28] but in these two cases the packing is altered by extensive hydrogen bonding with the included species. As may be concluded from the above comparison, a mismatch is observed in most cases and the imperfect packing is accommodated by including solvent in the voids. In contrast, in the compound of our study, the packing problem is resolved with a type of self-inclusion [29] accompanied by small adjustments as described in a modulated structure. The formation of the observed successful packing motif may explain the persistence of the title compound which forms instead of expected double-strand ladder-and-platform geometry (Fig. 2f).

Along with our previous reports [5, 30], the present study demonstrates the use of bis-(β-diketonate) ligands in the design of coordination polymers with a desired architecture, where the set of potential final geometries is reduced to few basic motifs by an appropriate choice of components. The bipy ligand has been widely used for similar purposes [31] but bridging ligands with β-diketonate functions were applied much less frequently (see refs 12—37 in our previous paper [5]). There have been a few studies utilizing ligands combining both β-diketonate and N-donor functions [32—35]. The creation of new bridging ligands incorporating β-diketonate functions and their assembly with metal centers may develop into a new major direction of crystal engineering.

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