

**SQUEEZE FOR TREATING SEVERELY DISORDERED SOLVENT MOLECULES
IN THE REFINEMENT OF THE OTHERWISE ORDERED CRYSTAL STRUCTURES
OF $[\text{Cd}(\text{C}_{12}\text{H}_{10}\text{N}_4)(\text{C}_{15}\text{H}_9\text{O}_2)_2(\text{CH}_3\text{OH})] \cdot 0.5\text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$
AND $[\text{Cd}(\text{C}_{12}\text{H}_{10}\text{N}_4)_{1.5}(\text{C}_{15}\text{H}_9\text{O}_2)_2] \cdot \text{CH}_3\text{OH}^\bullet$**

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In the refinement of the crystal structure of $[\text{Cd}(\text{C}_{12}\text{H}_{10}\text{N}_4)(\text{C}_{15}\text{H}_9\text{O}_2)_2(\text{CH}_3\text{OH})] \cdot 0.5\text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$, the lattice water molecule was not located by difference Fourier synthesis but was instead deduced by using *SQUEEZE* owing to severe disorder of the water molecule in the otherwise ordered crystal structure. Similarly deduced were the two symmetry-independent methanol molecules in $[\text{Cd}(\text{C}_{12}\text{H}_{10}\text{N}_4)_{1.5}(\text{C}_{15}\text{H}_9\text{O}_2)_2] \cdot \text{CH}_3\text{OH}$. The first coordination polymer adopts a chain motif and the second a layer motif; for both, the *N*-heterocycle functions as a bridge to connect adjacent metal atoms. The solvent molecules are presumed to reside in voids, which are themselves connected into channels. The crystallographic program *Crystal Explorer* was used in the illustration of the channels. Crystal data $\text{C}_{44}\text{H}_{37}\text{N}_4\text{O}_{6.5}\text{Cd}$: $FW = 838.18$, monoclinic, $P2_1/n$, $a = 16.7871(4) \text{ \AA}$, $b = 26.5431(5) \text{ \AA}$, $c = 18.7034(5) \text{ \AA}$, $\beta = 111.915(3)^\circ$, $V = 7731.7(3) \text{ \AA}^3$. Crystal data for $\text{C}_{49}\text{H}_{38}\text{N}_6\text{O}_{5.5}\text{Cd}$: $FW = 911.25$, monoclinic, $P2_1/c$, $a = 11.0586(3) \text{ \AA}$, $b = 23.5007(6) \text{ \AA}$, $c = 17.3454(5) \text{ \AA}$, $\beta = 105.626(3)^\circ$, $V = 4341.2(2) \text{ \AA}^3$.

Keywords: solvent molecules; voids; *SQUEEZE*; *Crystal Explorer*

**SQUEEZE ЗА ТРЕТИРАЊЕ НА ИЗРАЗИТО НЕСРЕДЕНИТЕ МОЛЕКУЛИ
НА РАСТВОРУВАЧОТ ПРИ УТОЧНУВАЊЕ НА ИНАКУ СРЕДЕНИТЕ КРИСТАЛНИ
СТРУКТУРИ НА $[\text{Cd}(\text{C}_{12}\text{H}_{10}\text{N}_4)(\text{C}_{15}\text{H}_9\text{O}_2)_2(\text{CH}_3\text{OH})] \cdot 0.5\text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ И
 $[\text{Cd}(\text{C}_{12}\text{H}_{10}\text{N}_4)_{1.5}(\text{C}_{15}\text{H}_9\text{O}_2)_2] \cdot \text{CH}_3\text{OH}$**

Позицијата на молекулата на вода при уточнувањето на кристалната структура на $[\text{Cd}(\text{C}_{12}\text{H}_{10}\text{N}_4)(\text{C}_{15}\text{H}_9\text{O}_2)_2(\text{CH}_3\text{OH})] \cdot 0.5\text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ не е лоцирана со диферентната Фуријеова синтеза, туку е определена со помош на *SQUEEZE*, поради изразената несреденост на молекулата на вода во инаку средената кристална структура. На сличен начин се дефинирани и позициите на двете симетриски независни молекули на метанол во $[\text{Cd}(\text{C}_{12}\text{H}_{10}\text{N}_4)_{1.5}(\text{C}_{15}\text{H}_9\text{O}_2)_2] \cdot \text{CH}_3\text{OH}$. Првиот координационен полимер гради синцирест мотив, а вториот слоевит мотив, при што за обата *N*-хетеропрстенот игра улога на мост кој ги поврзува соседните метални атоми. Молекулите на растворувачите се сместени во празнините, формирајќи преку меѓусебно поврзување посебни канали. За илустрирање на каналите е користена кристалографската програма *Crystal Explorer*. Кристалографски податоци за $\text{C}_{44}\text{H}_{37}\text{N}_4\text{O}_{6.5}\text{Cd}$: $FW = 838.18$, моноклиничен, $P2_1/n$, $a = 16.7871(4) \text{ \AA}$, $b = 26.5431(5) \text{ \AA}$, $c = 18.7034(5) \text{ \AA}$, $\beta = 111.915(3)^\circ$, $V = 7731.7(3) \text{ \AA}^3$. Кристалографски податоци за $\text{C}_{49}\text{H}_{38}\text{N}_6\text{O}_{5.5}\text{Cd}$: $FW = 911.25$, моноклиничен, $P2_1/c$, $a = 11.0586(3) \text{ \AA}$, $b = 23.5007(6) \text{ \AA}$, $c = 17.3454(5) \text{ \AA}$, $\beta = 105.626(3)^\circ$, $V = 4341.2(2) \text{ \AA}^3$.

Клучни зборови: молекули на растворувачот; *SQUEEZE*; *Crystal Explorer*

[•] Dedicated to Academician Gligor Jovanovski on the occasion of his 70th birthday.

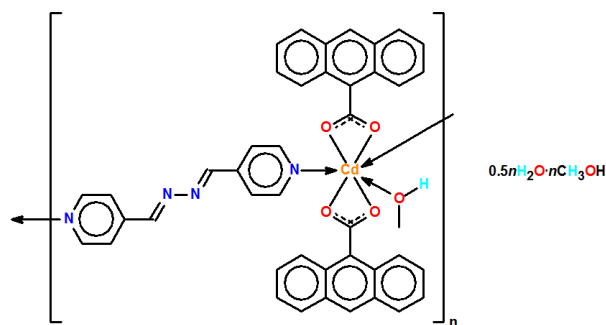
1. INTRODUCTION

In some crystal structure analyses of small molecules, residual peaks in the difference Fourier map that will not yield to refinement are usually suspected to be solvent molecules if the peaks are positioned away from the otherwise ordered part of the structure. If no other chemical analyses can be performed on the compounds for a variety of reasons, then an educated guess of the nature and number of the solvent molecules can be made with the *SQUEEZE* procedure of the *PLATON* suite under such circumstances. This calculates the contribution of disordered solvent molecules, assumed to exist in voids, in the refinement of the ordered part of the crystal structure by extracting information on the electron density from a correctly-phased model of the ordered part [1, 2]. According to *PLATON*, voids are those spaces in a crystal structure that can accommodate a sphere of 1.2 Å radius, but the voids themselves should not overlap with the Van der Waals spheres of the ordered atoms. After the application of the *SQUEEZE* procedure, no additional parameters in the subsequent refinement should be necessary if the voids have no more residual electron density. A recent report presented cases of using the procedure on a range of crystal structures [3].

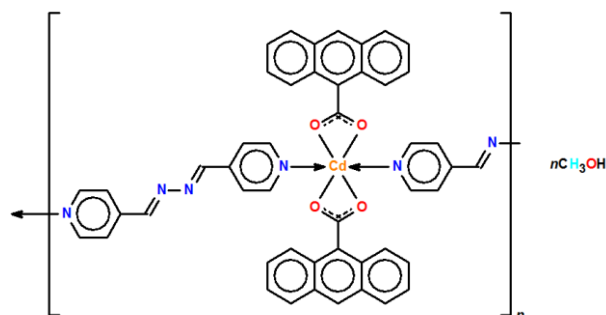
In this study, cadmium nitrate, anthracene-9-carboxylic acid and a 4,4'-bipyridine-like *N*-heterocycle when reacted in methanol medium yielded two types of prismatic crystals, one being light yellow and the other being dark yellow. It was impractical to separate the two manually owing to the small quantity of crystals synthesized; consequently, no further chemical measurements could be performed on the mixture. Other compounds were not found in the medium.

4-[(1*E*)-[(*E*)-2-(Pyridine-4-ylmethylidene)hydrazine-1-ylidene]methyl]pyridine itself exists as a flat, centrosymmetric molecule [4, 5] whose two aromatic donor sites are each capable of binding to a metal center to generate a chain motif, as exemplified by the cadmium nitrate adduct [6]. The present study was initiated to explore other adducts of cadmium bis(anthracene-9-carboxylate) as the compound forms adducts with other *N*-heterocyclic ligands: for example, the 2,2'-bipyridine and 1,10-phenanthroline adducts are both water-bridged dimers. The 4,4'-bipyridine adduct adopts a ribbon structure; two carboxylate-chelated cadmium atoms are each bridged through two other carboxylate anion to a central cadmium atom, and the three-metal entity is linked to adjacent three-metal entities to generate a ribbon [7]; the adducts exhibit luminescence. The crystal structures of two cadmi-

um bis(anthracene-9-carboxylate) adducts of the Schiff base ligand (**I** and **II**) are reported here together along with a description of how the solvent molecules are identified by the use of *SQUEEZE*.



I



II

2. SYNTHESIS

4-[(1*E*)-[(*E*)-2-(Pyridine-4-ylmethylidene)hydrazine-1-ylidene]methyl]pyridine was synthesized from the condensation pyridine-4-carboxaldehyde with hydrazine [4, 5]. The Schiff base (0.001 mol), cadmium nitrate (0.001 mol) and anthracene-9-carboxylic acid (0.002 mmol) were loaded into a convection tube along with several drops of triethylamine; the tube was filled with methanol kept at 333 K. Crystals were collected from the side arm after several days; one type has a light yellow and the other a dark yellow color. Although the two types of crystals could be distinguished when viewed under a microscope, their manual separation was not carried out; it was not practical to scale up the synthesis either.

3. CRYSTALLOGRAPHY: DATA COLLECTION AND REFINEMENT

Diffraction measurements on light yellow [Cd(C₁₂H₁₀N₄)(C₁₅H₉O₂)₂(CH₃OH)]·0.5H₂O·CH₃OH (**I**) were carried out at 100 K on an Agilent SuperNova diffractometer [8] equipped with Mo-*K*α

radiation up to $2\theta_{\max}$ of 55° . A sphere of reflections was measured; the 89,570 reflections averaged to 17,891, with 14,199 satisfying the $I > 2\sigma(I)$ cutoff. A numerical absorption correction based on the Gaussian integration of a multi-faceted crystal [9] was applied. In the initial stages of refinement with *SHELXL-2013* [10], the residual index did not fall below 0.047 and the difference Fourier map had two peaks (2.98 and $4.46 e\text{\AA}^{-3}$) larger than $1 e\text{\AA}^{-3}$. The weighting scheme [$\omega^{-1} = \sigma^2 + (0.0520P)^2 + 25.1399P$] had an unusually large second parameter. These peaks could not be treated by assuming a disordered water molecule.

The *SQUEEZE* program in the most recent version of crystallographic checking program, *PLATON* [11], was used to read the *.cif and *.fcf that were generated by *SHELXL-2013*. The run generated several files, with *_sq.ins and *_sq.hkl being used for further refinement. (Information on the solvent-accessible volume and the estimated number of electrons in the voids is given as a *_sq.sqf.) The *_sq.sqf file showed that there are four 39\AA^3 voids (in general positions), with each void holding an approximately 7-electron species. (The program assumes a triclinic primitive cell in the calculation of the voids for all crystal structures). The 7-electron species was assumed to be a water molecule on the basis of the volume of the void since a water molecule has an approximately 40\AA^3 volume. Subsequent refinements proceeded to a final residual of 0.039; the final difference map was featureless; furthermore, the weighting scheme [$\omega^{-1} = \sigma^2 + (0.0353P)^2 + 12.1175P$] was much improved. Some minor disorder in the $-\text{C}=\text{N}-\text{N}=\text{CH}-$ segment of the bridging ligand was treated by the use of distance restraints. Figure 1 depicts a portion of the chain motif. (CCDC deposition No. 1001480)

A sphere of reflections was also collected on $[\text{Cd}(\text{C}_{12}\text{H}_{10}\text{N}_4)_{1.5}(\text{C}_{15}\text{H}_9\text{O}_2)_2]\text{CH}_3\text{OH}$ (**II**). The 45,445 reflections averaged to 10,043, with 8,862 satisfying the $I > 2\sigma(I)$ cutoff. A numerical correction for absorption was applied. In the initial stages of refinement, the residual index did not fall below 0.067 and the difference Fourier map had five peaks that were not near any atom, with the largest being $4.80 e\text{\AA}^{-3}$ [$\omega^{-1} = \sigma^2 + (0.1191P)^2 + 21.6051P$]. The *_sq.sqf file showed that there are two 294\AA^3 voids (on Wyckoff $2d$ special positions), with a 37-electron species in each void. The 37-electron unit is assumed to consist of two methanol molecules. Subsequent refinements on proceeded to a final residual of 0.036; the final difference map was featureless and the weighting scheme [$\omega^{-1} = \sigma^2 + (0.0423P)^2 + 3.9095P$] was similarly much im-

proved. Figure 2 depicts a portion of the layer motif; the layer motif is represented as an *OLEX* [12] plot in Figure 3 (CCDC deposition No. 1001481).

4. RESULTS AND DISCUSSION

Cadmium bis(anthracene-9-carboxylate) forms two different adducts with the Schiff base, 4-[(*E*)-[(*E*)-2-pyridin-4-methylidene]hydrazin-1-ylidene]methylpyridine, in the same synthesis. The formula unit of (**I**), features two metal atoms; each is *O,O'*-chelated by the carboxylate anion and is also coordinated by a methanol molecule. The Schiff base links adjacent metal atoms to form a linear chain. The geometry of the metal atoms is a *trans*-pentagonal bipyramid in which the nitrogen atoms occupy axial sites (Fig. 1).

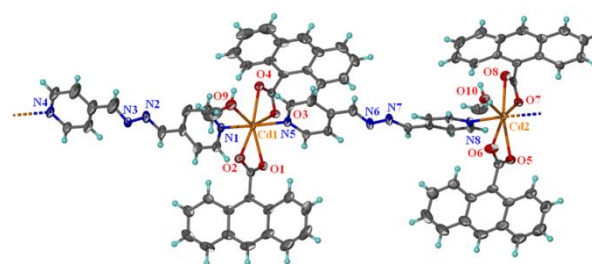


Fig. 1. 70% probability *ORTEP* plot of a portion of (**I**) without lattice solvent molecules

Water molecules (predicted by *SQUEEZE*) and lattice methanol molecules connect adjacent chains to generate a hydrogen-bonded 3D network structure. In (**II**), the metal atom is similarly *O,O'*-chelated by the carboxylate ion; however, the metal atom is coordinated to two different Schiff-base ligands so that the *N*-heterocycles link adjacent metal atoms to generate a layer (Fig. 2); the honeycomb network has the common honeycomb topology (Fig. 3).

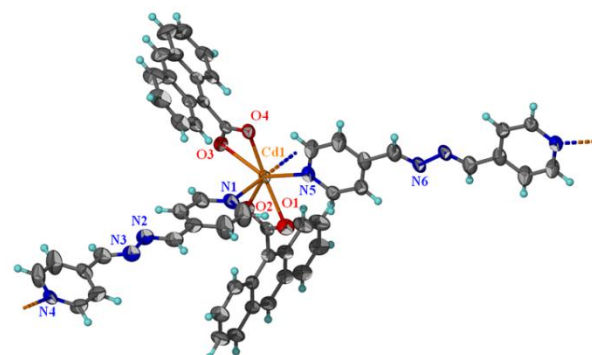


Fig. 2. 70% probability *ORTEP* plot of a portion of (**II**) without lattice solvent molecules

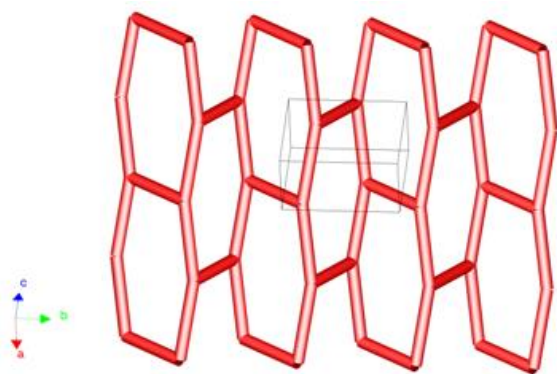


Fig. 3. OLEX representation of the layer structure of (II)

The methanol solvent molecules (predicted by *SQUEEZE*) are presumed to occupy the space between adjacent layers, and these connect the layers to generate a hydrogen-bonded 3D network. The two adduct are expected to exhibit light-emitting properties since some cadmium dicarboxylates are known to exhibit such behavior [6, 7, 13].

In (II), the voids are each presumed to hold two methanol molecules; however, instead of regarding these lattice occupants as being severely-disordered solvent molecules, the electron density in the voids is better thought of in terms of channels of inter-connected electron density. The main voids as well as the smaller ones (before the application of *SQUEEZE*) are shown as a single unit-cell isosurface plot [14] (Fig. 4); the plot, which is essentially an $F_{\text{obs}} - F_{\text{calc}}$ plot, shows that the regions of electron density are not localized but are instead spread over the unit cell. A somewhat simpler depiction of the electron density map can be made with *ShelXle* [15]. The coordination polymer (II) adopts an undulating layer motif, and adjacent honeycomb-like layers are stacked over each other (Fig. 5).

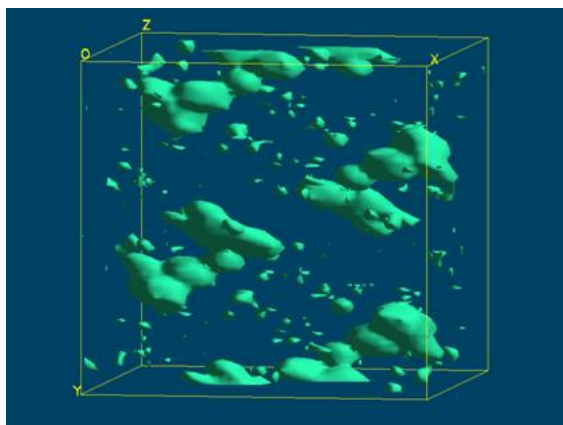


Fig. 4. Isosurface showing electron density of (II) (before *SQUEEZE*)



Fig. 5. Stacking of undulating honeycombs of (II)

The analysis of voids (that are presumably filled by the solvent molecules) is best performed with *CrystalExplorer* [16]; in addition to the analysis of voids [17], the program can also be used to investigate Hirshfeld surfaces [18]. In (II), the methanol solvent molecules insert themselves between the layers, which adopt a wave-like conformation. According to the depiction by *CrystalExplorer*, the solvent molecules are better regarded as molecules that are organized into channels (Fig. 6).

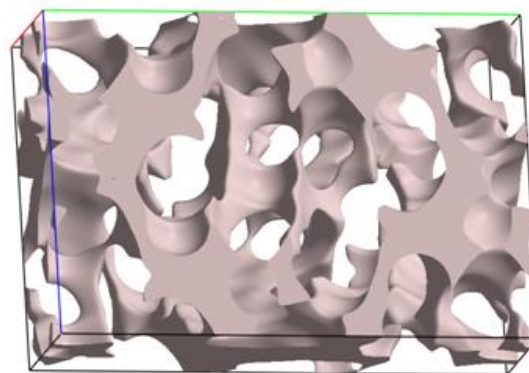


Fig. 6. Voids of (II) depicted as channels

The presence of rigid ligands in coordination polymers gives rise to rigid chain, layer and 3D motifs, and if the ligands themselves are large, then the resulting structures can accommodate larger solvent molecules. The coordination polymer, $[\text{Zn}_2(\text{C}_{12}\text{H}_{12}\text{N}_2)(\text{C}_8\text{H}_4\text{O}_4)_2]_\infty$ ($\text{C}_{12}\text{H}_{12}\text{N}_2$ is 2,2',4,4'-bipyridine) is reported to crystallize with solvent molecules as $[\text{Zn}_2(\text{C}_{12}\text{H}_{12}\text{N}_2)(\text{C}_8\text{H}_4\text{O}_4)_2\text{DMF}\cdot 2\text{H}_2\text{O}]_\infty$; the nature and number of solvent molecules were assumed from a *SQUEEZE* run on the room-temperature measurements [19]. A low-temperature study established the formulation as $[\text{Zn}_2(\text{C}_{12}\text{H}_{12}\text{N}_2)(\text{C}_8\text{H}_4\text{O}_4)_2\text{DMF}]_\infty$; i.e., the 3D network has no water as is only a DMF solvate. The independent DMF molecules were located and refined [3], which underscores the importance of accurate measurements because *SQUEEZE* estimates as the complex scattering factors, which are

then used in the structure-factor calculations. *SQUEEZE* was used in an extreme case of a cadmium carboxylate having a huge carboxylate group: the uncoordinated anion could not be located in the difference Fourier map; the formulation was supported by other chemical analyses [20].

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