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Synthesis and structural characterization of Cd(II) complexes with 2-acetylpyridine-aminoguanidine – A novel coordination mode

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Abstract: The structures of the first two complexes with bidentate coordination of aminoguanidine Schiff base, *i.e.*, 2-acetylpyridine-aminoguanidine (**L**), are reported. The complex of the formula $[\text{Cd}_2\text{Cl}_6(\text{HL})_2]$ (**1**) was obtained in the reaction of warm aqueous solutions of chloride salts of Cd(II), Zn(II) and the ligand, while the reaction of cadmium bromide and the ligand in the presence of deprotonating agent as well as ammonium thiocyanate resulted in the formation of the complex in which Schiff base has both the role of the ligand and the counterion, *viz.*, $[\text{HL}][\text{Cd}(\text{HL})(\text{NCS})_2\text{XY}]\cdot\text{H}_2\text{O}$ (**2**), where X is Cl^- or Br^- , and Y Br^- or SCN^- . The complexes were characterized by IR spectroscopy, elemental analysis, conductometric measurements and single crystal X-ray diffraction. The unusual bidentate coordination of the Schiff base lead to significant changes in the geometry of this molecule (from almost planar in free form and as a tridentate ligand to twisted as a bidentate ligand). Besides, in complex **1** relatively rare bridging coordination of Cl^- in octahedral Cd(II) is found, while the crystal structure of complex **2** exhibits substitutional disorder, and contains four different anions: $[\text{Cd}(\text{HL})(\text{NCS})_2\text{Br}(\text{SCN})]^-$ (*ca.* 61 %), $[\text{Cd}(\text{HL})(\text{NCS})_2\text{Cl}(\text{SCN})]^-$ (*ca.* 35 %), $[\text{Cd}(\text{HL})(\text{NCS})_2\text{Br}_2]^-$ (*ca.* 3 %) and $[\text{Cd}(\text{HL})(\text{NCS})_2\text{ClBr}]^-$ (*ca.* 1 %).

Keywords: guanylhydrazone; Schiff base; crystal structure; physicochemical properties; metal complexes.

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INTRODUCTION

This study emerged from our ongoing research on metal complexes with Schiff base ligands, as this class of compounds has shown wide spectra of biological activities,¹ catalytic behavior,² magnetism³ and optoelectronic properties,⁴ depending on the choice of the particular metal, and Schiff base ligand. Besides the simple synthetic routes, the importance of these compounds lies in their ability to act as ligands of various denticities, thus the structural versatility and different potential application.^{5,6} Thiocyanate is an interesting ambidentate co-ligand due to its ability to coordinate to the metal ion not only in the monodentate manners at one of its terminal atoms but also as a $\mu_{1,1}$ bridge (through sulfur or nitrogen) and $\mu_{1,3}$ bridge (*via* both).⁷

Researches have shown that Group 12 complexes are important in the field of supramolecular chemistry, crystal growth⁸ and materials science.⁹ However, cadmium is known to be a human carcinogen¹⁰ and environmental pollutant, and some studies show^{11,12} cadmium exposure can lead to genomic instability and inhibition of DNA damage repair. On the other hand, there is also evidence of anticancer activity of cadmium and its complexes with bioactive heterocyclic Schiff bases.^{13–16} Since the mechanisms of these processes remain unknown it is of high importance to broaden the knowledge on structural properties of cadmium(II) complexes with potentially bioactive Schiff bases. Here, the syntheses and structure of two new Cd(II) complexes with 2-acetylpyridine-aminoguanidine (L), of the formulas $[\text{Cd}_2\text{Cl}_6(\text{HL})_2]$ (**1**) and $[\text{HL}][\text{Cd}(\text{HL})(\text{NCS})_2\text{XY}] \cdot \text{H}_2\text{O}$ (**2**) (where X is Cl^- or Br^- and Y Br^- or SCN^-) is described. The free Schiff base is isolated as chloride (Fig. 1) and thiocyanate salt, while the coordinated form is usually neutral.¹⁷ These are the first two complexes in which this Schiff base coordinates in a monoprotonated form and acts as a bidentate ligand.

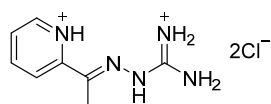


Fig. 1. Structural formula of 2-acetylpyridine-aminoguanidine dihydrogendichloride, $[\text{H}_2\text{L}]\text{Cl}_2$.

EXPERIMENTAL

Reagents

All commercially obtained reagent-grade chemicals were used without further purification except for the ligand 2-acetylpyridine-aminoguanidine dihydrogendichloride, $[\text{H}_2\text{L}]\text{Cl}_2$, which was synthesized according to the previously described procedure.¹⁷

*Preparation of the complex $[\text{Cd}_2\text{Cl}_6(\text{HL})_2]$ (**1**)*

The mixture of 0.5 mmol (0.09 g) CdCl_2 , 0.5 mmol (0.07 g) ZnCl_2 , and 0.5 mmol (0.125 g) $[\text{H}_2\text{L}]\text{Cl}_2$ was mildly heated in 6 mL H_2O until dissolution. The resulting yellow solution was left at the room temperature and after 3 weeks orange prismatic single crystals were filtered and washed with EtOH. Yield: 0.14 g (70 %). Anal. Calcd. for $\text{C}_{16}\text{H}_{24}\text{N}_{10}\text{Cl}_6\text{Cd}_2$: C, 24.20; H, 3.05; N, 17.65. Found: C, 24.62; H, 3.18; N, 18.02 %. Conductivity, $\Lambda = 130 \text{ S cm}^2$

mol⁻¹ (in DMF). M.p. > 250 °C. Selected IR bands (wavenumber, cm⁻¹): 3337 (s), 3206 (s), 3084 (s), 1688 (vs), 1610 (s), 1580 (s), 1529 (s), 1450 (m), 1298 (m), 1225 (m), 1163 (m), 1093 (m), 935 (w), 782 (m), 622 (m), 591 (m), 558 (m), 519 (m).

Preparation of the complex [HL][Cd(HL)(NCS)₂XY]·H₂O (2)

The mixture of the ligand (0.5 mmol; 0.125 g) and LiOAc (1 mmol; 0.1 g) was dissolved in 5 mL of warm H₂O. To this solution the CdBr₂ (0.5 mmol; 0.09 g) and NH₄NCS (1 mmol; 0.08 g) were added and slightly heated for about 5 min. The yellow solution was left at the room temperature and after 8 days the orange precipitate was filtered, washed with H₂O and EtOH. Upon recrystallization from MeOH rod-like single crystals of the complex were obtained. Yield: 0.14 g (42 %). Anal. Calcd. for C₁₉H₂₆N₁₃OS₃BrClCd: C, 29.39; H, 3.37; N, 23.46; S, 12.39. Found: C, 29.87; H, 3.50; N, 22.95; S, 12.78 %. Conductivity, $\Lambda = 142 \text{ S cm}^2 \text{ mol}^{-1}$ (in DMF). M.p. = 175 °C. Selected IR bands (wavenumber, cm⁻¹): 3420 (s), 3345 (s), 3157 (s), 2112 (vs), 2077 (vs), 2058 (vs), 1676 (vs), 1629 (vs), 1586 v(s), 1477 (m), 1434 (m), 1162 (m), 1149 (m), 1100 (w), 1003 (w), 786 (m), 561 (w).

Analytical methods

Elemental analyses (C, H, N and S) of air-dried compounds were carried out by standard micro-methods. Molar conductivity measurements of freshly prepared solutions ($c = 1 \text{ mmol L}^{-1}$) were performed on a Jenway 4010 conductivity meter. IR spectra were recorded on a Nicolet Nexus 670 FTIR (Thermo Scientific) spectrophotometer, in the range of 400–4000 cm⁻¹ by the KBr pellet technique. Melting points were measured on a Nagema melting point microscope Rapido.

Single crystal X-ray diffraction

Diffraction experiments for **1** and **2** were performed on Bruker APEX-II CCD and Oxford Diffraction Gemini S diffractometers at 140 and 295 K, respectively. Reflection integration and data reduction were performed with the corresponding software Bruker SAINT¹⁸ and CrysAlisPro.¹⁹ Crystal structures were solved with the SHELXT²⁰ and refined with the SHELXL.²¹ In the case of [HL][Cd(HL)(NCS)₂XY]·H₂O (**2**) the coordination site X was refined as being substitutionally disordered between bromine and chlorine ligands, with the corresponding occupancies of 0.640(2) and 0.360(2), respectively; the coordination site Y was refined as being substitutionally disordered between SCN⁻ and Br⁻ ligands with the corresponding occupancies of 0.943(2) and 0.057(2), respectively. Hydrogen atoms bonded to carbon atoms were introduced in idealized positions and treated with a riding model. Hydrogen atoms bonded to nitrogen were found in residual electron density maps and refined with distance restraints ($d(\text{N-H}) = 0.88(2) \text{ \AA}$ for **1** and $0.86(2) \text{ \AA}$ for **2**) or introduced in idealized positions and treated with a riding model. Their displacement parameters are derived from their parent atoms ($U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$). Hydrogen atoms of water molecule were refined freely. Crystallographic and refinement details are listed in Table I.

RESULTS AND DISCUSSION

Syntheses and characterization

The previous research concerning coordination behavior of Zn(II) and Cd(II) and the titled Schiff base, showed that there are a lot of similarities, but also there are some fine differences, *i.e.*, Cd(II) being prone to form dimeric complexes with bridging coordination of ions.²² Hence, in the attempt to examine the competitive coordination of these two cations to the ligand, in the reaction of metal

chlorides and the chloride ligand salt in the aqueous solution, complex **1** was obtained in the form of yellow prismatic single crystals.

TABLE I. Crystal data, data collection and refinement details

Chemical formula	C ₁₆ H ₂₄ N ₁₀ Cl ₆ Cd ₂ (1)	C ₁₉ H ₂₆ N ₁₃ OS ₃ BrClCd (2)
Temperature, K	140(2)	295(2)
Formula weight, g mol ⁻¹	793.95	776.47
Crystal system	triclinic	triclinic
Space group	<i>P</i> 1	<i>P</i> 1
<i>a</i> / Å	8.4921(6)	7.9033(3)
<i>b</i> / Å	8.7865(7)	11.4014(4)
<i>c</i> / Å	10.6536(8)	16.5784(7)
α / °	76.4318(13)	97.450(3)
β / °	70.7718(12)	90.557(3)
γ / °	64.4782(12)	99.580(3)
<i>V</i> / Å ³	673.32(9)	1459.84(10)
Crystal size, mm ³	0.50×0.25×0.20	0.56×0.37×0.29
Reflections collected / unique	27790 / 6537	19089 / 6799
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	6367	5829
<i>R</i> _{int}	0.021	0.022
<i>R</i> [<i>I</i> > 2σ(<i>I</i>)]	0.015	0.030
<i>R</i> (all data)	0.016	0.039
Goodness-of-fit	1.179	1.010
Δρ _{max} , Δρ _{min} , e Å ⁻³	0.562, -0.656	0.561, -0.541

Complex **2** was formed in the reaction of warm aqueous solutions of CdBr₂ and [H₂L]Cl₂, in mole ratio 1:1, in the presence of double excess of LiOAc and NH₄NCS. The white rod-like single crystals suitable for single crystal X-ray diffraction (SC-XRD) were obtained upon the recrystallization from MeOH.

It is interesting to mention that a similar reaction with CdCl₂, and in the absence of deprotonating agent, yielded in the hydrolysis of the imine group of the Schiff base thus the formation of Cd(II) complex with 2-acetylpyridine with thiocyanates as bridging ligands. This complex was previously synthesized in the reaction of Cd(NO₃)₂, 2-acetylpyridine and ammonium thiocyanate in methanolic solution thus structurally characterized.²³

Having in mind the pronounced alkaline nature of the aminoguanidine residue it is not surprising that its Schiff bases in the complexes can have a role of both the ligand and the counter-ion.²² The survey of Cambridge Structural Database (CSD)²⁴ revealed 49 complex compounds containing Schiff bases of aminoguanidine. Namely, the majority of these contain the Schiff base coordinated in the tridentate manner (33 structures), while there are only 4 structures with the Schiff base of AG having the role of a tetradentate^{25–28} and only 1 structure in which monodentate²⁹ coordination was found. In 11 structures the guanylhyazone has the role of counter-ion. However, these are the first two examples in

which the bidentate mode of coordination of Schiff base of aminoguanidine is found. Details of CSD search are given in Supplementary material to this paper (Tables S-I–S-IV).

Both complexes are well soluble in DMF, while poorly soluble in H₂O and alcohols. Molar conductivity of DMF solution complex **1** has value characteristic for the 2:1 type of electrolytes, which suggests the substitution of anionic ligands by solvent molecules. Complex **1** is stable at higher temperatures (m.p. >250 °C), while complex **2** appears to decompose at higher temperatures (135 °C) and the residue finally melts at 175 °C.

Comparative analysis of the IR spectrum of the free ligand and the spectra of the complexes showed a lot more similarities than differences, thus very few things about the coordination of the Schiff base could be concluded with certainty. The reasons for this were revealed by X-ray analysis (*vide infra*). Namely, the ligand coordinates as NN bidentate, *via* pyridine and azomethine nitrogen atoms, while the aminoguanidine residue stays protonated thus non-coordinated. So, in the spectra of both the complexes $\nu(\text{CN})$ bands originating from the imino group of aminoguanidine residue appear at nearly the same wavenumbers (1622 cm⁻¹ for complex **1** and 1629 cm⁻¹ for complex **2**) as in the spectrum of the ligand (1624 cm⁻¹).¹⁷ Also, in the structure of complex **2** one cation of the Schiff base is coordinated, while the other has a role of a counterion. This makes the identification of the corresponding bands' shifts, upon coordination, difficult. Additionally, in the spectrum of complex **2** three very strong bands, present in the range 2060 to 2110 cm⁻¹, are attributed to coordinated NCS⁻ – two coordinated through N atom (2060 and 2077 cm⁻¹) and the third coordinated through S atom (2110 cm⁻¹).

Crystal structure analysis

Molecular structures of complexes **1** and **2** are presented in Fig. 2, while selected structural data are summarized in Table II. Both complexes are characterized by unusual, bidentate coordination mode of 2-acetylpyridine-aminoguanidine ligand and, to our knowledge, represent the first cases of metal complexes where this Schiff base coordinates as a bidentate ligand. Up to now several complexes of Cu(II), Zn(II), as well as Cd(II) with the same organic ligand, have been reported.^{17,22,30} In these compounds the ligand is present in its neutral form and exhibits tridentate coordination by pyridine N5, azomethine N3 and imino N1 nitrogen of aminoguanidine. The specific feature of **1** and **2** is that the organic ligand is protonated at aminoguanidine nitrogen N1. The resulting monocation coordinates to the Cd(II) in a bidentate fashion by pyridine N5 and azomethine N3 donors, forming a single chelate ring (Fig. 2).

Complex **1** consists of the neutral binuclear units, where two Cd(II) centers are bridged by a pair of chloride ions to form a Cd₂Cl₂ square-like metallocycle (Fig.

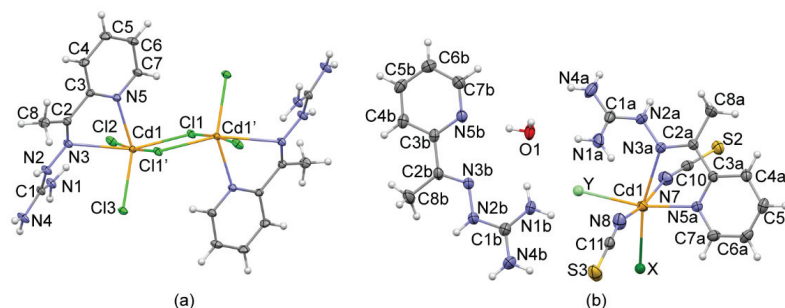


Fig. 2. Molecular structure of: a) $[\text{Cd}_2\text{Cl}_6(\text{HL})_2]$ (**1**) and b) $[\text{HL}][\text{Cd}(\text{HL})(\text{NCS})_2\text{XY}] \cdot \text{H}_2\text{O}$, $\text{X} = \text{Cl}^-$ or Br^- and $\text{Y} = \text{Br}^-$ or SCN^- (**2**) with the atom labelling scheme. Displacement ellipsoids are drawn at the 30 % probability level.

TABLE II. Selected bond lengths and bond angles (comprehensive list is given in Tables S-V and S-VI of the Supplementary material)

Bond	1	2	
		A	B
Bond length, Å			
Cd1–N3	2.7483(8)	2.605(2)	–
Cd1–N5	2.2992(8)	2.348(2)	–
C1–N1	1.3212(13)	1.297(4)	1.303(3)
C1–N2	1.3512(12)	1.337(3)	1.335(3)
C1–N4	1.3253(12)	1.325(3)	1.326(3)
C2–N3	1.2939(12)	1.282(3)	1.277(3)
N2–N3	1.3796(11)	1.377(3)	1.378(3)
Bond angle, °			
N3–Cd1–N5	64.33(3)	65.86(6)	–
N2–N3–C2	115.94(8)	116.8(2)	116.8(2)
N3–N2–C1	118.98(8)	118.4(2)	117.9(2)
N1–C1–N2	121.19(8)	121.0(2)	120.3(2)
N1–C1–N4	121.41 (9)	121.7(3)	121.6(3)
N3–C2–C3	115.76(8)	115.5(2)	115.0(2)
C2–C3–N5	117.62(7)	117.3(2)	117.1(2)

2a). Each Cd(II) is placed in a distorted octahedral environment which, apart from two bridging Cl, also includes two terminal Cl ligands as well as the pyridine and azomethine N donors of the cationic Schiff base. The binuclear complex has a crystallographic inversion center in the middle of the Cd_2Cl_2 bridge. The $\text{Cd} \cdots \text{Cd}$ atom separation is 3.901(3) Å. Though the CSD²⁴ search reveals the relatively frequent occurrence of the Cd_2Cl_2 square-like fragment (223 CSD hits), it mainly belongs to the polymeric structures, while only in 34 cases it belongs to the discrete binuclear complexes. A similar bridge between the octahedrally coordinated Cd(II) centers is rare. It is found in two neutral Cd(II) complexes where the monodentate organic ligands bind next to the Cl (CSD Refcodes:

LOYZAC,³¹ FOKMEZ³²) and also in two anionic species where the water molecules bind next to the Cl ligands (QELLAX²² and WIPTAQ³³). The structures show wide variation in bridging Cd–Cl bond lengths, with values ranging from 2.36 to 2.76 Å, and bridging Cd–Cl–Cd' angles, with values ranging from 91.8 to 105.6 Å.

As mentioned above, unlike the previously reported complexes where 2-acetylpyridine-aminoguanidine ligand exhibits tridentate coordination,^{17,22,30} the protonated ligand in complex **1** binds to the metal ion by two donor atoms. The different coordination mode significantly changes the geometry of the ligand, from almost flat in the previous complexes with tridentate ligand such as [CdCl₂L],²² to markedly twisted geometry in the novel complexes. Thus in complex **1**, the five-membered chelate ring exhibits considerable twisting on Cd1–N3 bond resulting in maximal torsion angle Cd–N3–C2–C3 of 35.5(1)°. In complex [CdCl₂L],²² the maximal torsion angle within the same chelate is Cd–N5–C3–N2 with –10.6°. The most pronounced difference in geometry of the two ligand forms is related to the orientation of their guanidine moiety. Since not coordinated, the guanidine residue in **1** points away from the metal ion (Fig. 2a). The dihedral angle between the mean planes of guanidine moiety and the chelate ring is 48.85(5) in **1**, while only 5.32° in [CdCl₂L]. The dihedral angle between the chelate and pyridine rings is more comparable, with the values of 10.52(6) and 7.05° in **1** and [CdCl₂L],²² respectively. The position of the guanidine moiety in **1** is stabilized by the intramolecular N1–H1b···Cl2 hydrogen bond, and also by the intermolecular hydrogen bonds which engage all N–H donors and terminal Cl ligands as acceptors (Table III). The N–H···Cl interactions arrange the complex molecules into 2D structures parallel to the crystallographic *ac* plane (Fig. 3).

In the complex compound of the formula [HL][Cd(HL)(NCS)₂XY]·H₂O (**2**) the protonated 2-acetylpyridine-aminoguanidine is present as a free cation as well as a coordinated ligand. The coordination environment of Cd(II) in the complex anion is distorted octahedral, with two axial sites occupied by NCS[–], two equatorial sites occupied by bidentate coordinated organic ligand, and the remaining two equatorial sites (X and Y) occupied by Cl[–]/Br[–] and Br[–]/SCN[–], respectively. This means that the crystal structure contains four different anions: [Cd(HL)(NCS)₂Br(SCN)][–] (*ca.* 61 %), [Cd(HL)(NCS)₂Cl(SCN)][–] (*ca.* 35 %), [Cd(HL)(NCS)₂Br₂][–] (*ca.* 3 %) and [Cd(HL)(NCS)₂ClBr][–] (*ca.* 1 %).

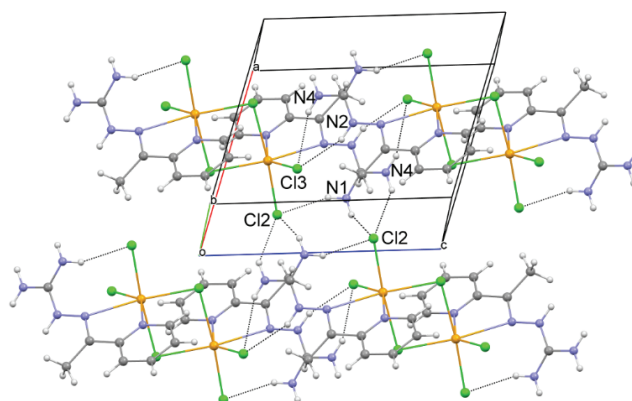
Comparison between organic cations in free and coordinated form reveals little changes in bond lengths and valence angles (Table II). The coordination in **2**, leads to twisting of organic ligand, similar to that found in complex **1**. Thus, the dihedral angle between the pyridine and guanidine moiety is 7.5(2)° in uncoordinated HL⁺, while 51.6(1) and 42.18(5)° in complexes **2** and **1**, respectively. Also similar to **1**, the maximal torsion angle within the five-membered chelate ring is Cd–N3–C2–C3 with –38.4(2)°. In comparison to previously rep-

orted complex $[\text{CdCl}_2\text{L}]^{22}$ with the neutral tridentate ligand, the complexes **1** and **2** show longer Cd–N coordination bonds, which is expected considering their different coordination geometry (square pyramidal vs. octahedral). The changes can be also observed for C1–N2 and N2–N3 bonds which in the cationic form of ligand get shorter and longer for 0.03 Å on average. The main difference is related to the angle C2–N3–Cd which in novel compounds reduces by almost 15° in comparison to the corresponding angle in $[\text{CdCl}_2\text{L}]^{22}$

TABLE III. Geometrical parameters for intermolecular interactions

D–H⋯A	$d(\text{D–H}) / \text{Å}$	$d(\text{H}⋯\text{A}) / \text{Å}$	$\angle(\text{D–H}⋯\text{A}) / ^\circ$	Symmetry codes
1				
N1–H1a⋯Cl2	0.87(1)	2.56(1)	150(1)	$-x+2, -y+1, -z+1$
N1–H1b⋯Cl2	0.88(1)	2.36(1)	155(1)	
N2–H2⋯Cl3	0.88	2.56	151	$-x+1, -y+1, -z+1$
N4–H4a⋯Cl3	0.85(1)	2.51(1)	157(1)	$-x+1, -y+1, -z+1$
N4–H4b⋯Cl2	0.88(1)	2.54(1)	144(1)	$-x+2, -y+1, -z+1$
C5–H5⋯Cl1	0.95	2.68	161	$1+x, -1+y, z$
C6–H6⋯Cl2	0.95	2.79	156	$1-x, -y, -z$
2^a				
N1a–H11a⋯O1	0.86	1.97	170	
N1a–H12a⋯N8	0.86	2.51	146	
N1b–H11b⋯S3	0.86	2.90	148	
N1b–H12b⋯O1	0.86	2.13	164	
N4a–H41a⋯S2	0.86	2.84	123	$-x+1, -y+1, -z+2$
N4b–H21⋯S3	0.86	2.59	161	
O1–H1a⋯N5b	0.83	1.96	175	
C4a–H4a⋯S2	0.93	2.88	162	$-x+1, -y, -z+2$
C6a–H6a⋯S3	0.93	2.93	145	$-x+1, -y, -z+1$
C7b–H7b⋯S2	0.93	2.97	120	$-x+1, -y+1, -z+2$

^aOnly parameters involving the ordered part of the complex are listed (see also Table S-VII of the Supplementary material)

Fig. 3. Hydrogen bonding in **1**.

The crystal structure of **2** is stabilized by a complex hydrogen-bonding network involving N–H donors from both charged species, the acceptors form monodentate ligands as well as the molecule of crystal water (Fig. 4). Table III lists the hydrogen bonding contacts involving only ordered part of the structure.

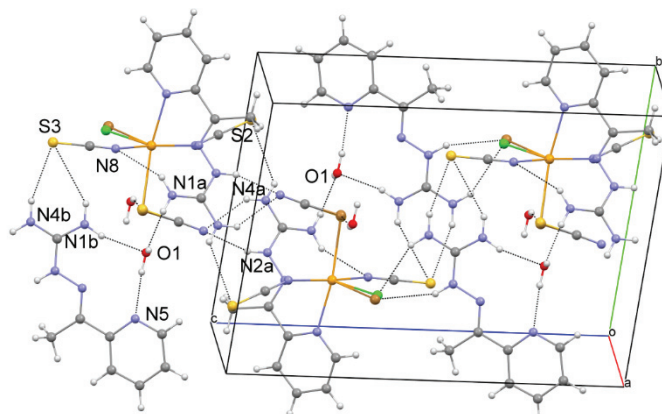


Fig. 4. Hydrogen bonding in **2**. Only two major anion components are shown: $[\text{Cd}(\text{HL})(\text{NCS})_2\text{Br}(\text{SCN})]^-$ (ca. 61 %) and $[\text{Cd}(\text{HL})(\text{NCS})_2\text{Cl}(\text{SCN})]^-$ (ca. 35 %).

To gain more insight in crystal packing features of both complexes, Hirshfeld surface analysis was performed. Hirshfeld surface of complex **1** decorated with d_{norm} has several prominent red patches (Fig. 5b), which correspond to short $\text{Cl}\cdots\text{H}$ contacts, details of which are listed in Table III. In the fingerprint plot (Fig. 5c), these are displayed as two symmetric prongs with peaks at $d_e = 1.5 \text{ \AA}$ and $d_i = 0.8 \text{ \AA}$, and at $d_e = 0.8 \text{ \AA}$ and $d_i = 1.5 \text{ \AA}$.

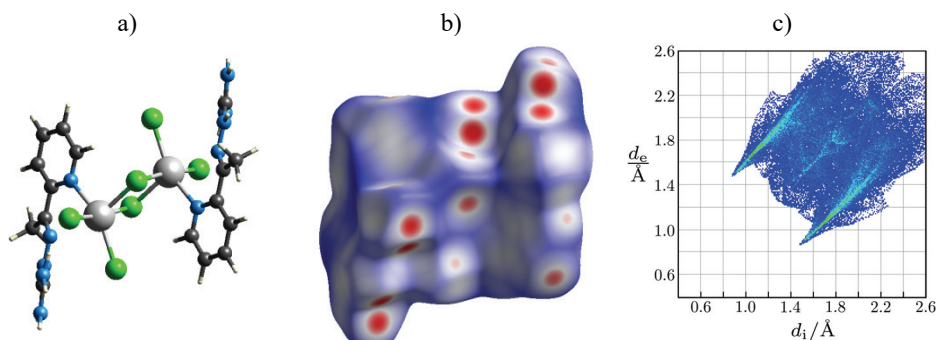


Fig. 5. Molecular structure (a), Hirshfeld surface (b) and corresponding fingerprint plot (c) of $[\text{Cd}_2\text{Cl}_6(\text{HL})_2]$ (**1**).

The investigation of complex **2** by means of Hirshfeld surface analysis is complicated because of the ionic nature of the compound and presence of four

different anions in the crystal structure. It is worth emphasizing peculiarities of anionic Hirshfeld surfaces to gain insights why this four-component mixture is stable. These are calculated for idealized structures containing only one type of anion (Fig. 6). Two main anions that comprise 61 and 35 % of the mixture ($[\text{Cd}(\text{HL})(\text{NCS})_2\text{Br}(\text{SCN})]^-$ and $[\text{Cd}(\text{HL})(\text{NCS})_2\text{Cl}(\text{SCN})]^-$, respectively) show negligible overall difference in the molecular shape defined by their Hirshfeld surfaces. Both structures involve N \cdots H hydrogen bond involving S-coordinated SCN^- , which is represented in their fingerprint plots by two symmetric prongs with peaks at $d_e = 1.1$ and $d_i = 0.8$ Å (N6 \cdots H2A(i)–N2A(i) hydrogen bond), and at $d_e = 0.8$ and $d_i = 1.1$ Å (N2A–H2A \cdots N6(i) hydrogen bond); symmetry code (i) $-x+1, -y+1, -z+2$.

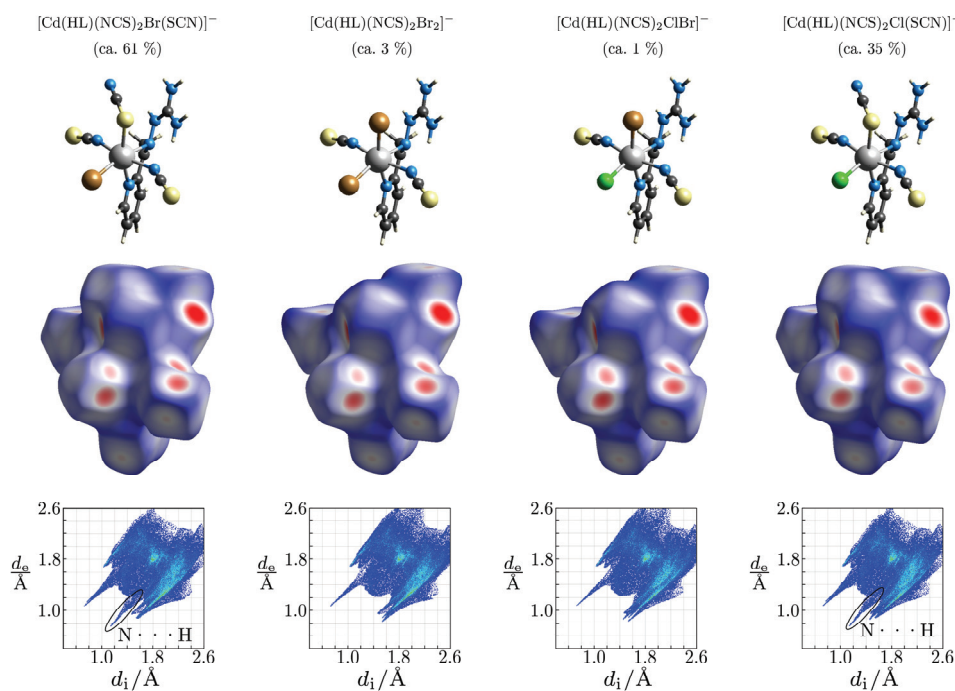


Fig. 6. Molecular structures (top), Hirshfeld surfaces (middle), and corresponding fingerprint plots (bottom) of the four structural components present in substitutionally disordered $[\text{HL}][\text{Cd}(\text{HL})(\text{NCS})_2\text{XY}]\cdot\text{H}_2\text{O}$.

In two minor components, in which coordinated SCN^- is substituted by Br^- , these hydrogen bonds are absent. Therefore, in the corresponding fingerprint plots, only a single spike is present, with peak at $d_e = 1.1$ Å and $d_i = 0.8$ Å, that correspond to N1–H11a \cdots O1 hydrogen bond, and the prongs corresponding to H \cdots N hydrogen bonds are missing.

Crystal packing coefficient for idealized structures containing only one type of anion are within expected range, as CSD average packing coefficient for crystal structures of metal-organic molecules is 0.67(5). This explains that all four anions satisfy very well the principle of closest packing and maximal interaction, thus ensuring stability of the crystal structure (weighted average of the packing coefficient is 0.672). However, there is a noticeable trend between anions' amount ratio in the mixture and packing coefficients for its idealized structures, as well as to some extent, also of the volumes of the anions based on their Hirshfeld surfaces calculated for idealized structures (see Supplementary material, Table S-VIII).

CONCLUSION

In the reaction of warm aqueous solutions of the chloride salts of Cd(II), Zn(II), and the ligand, orange prismatic single-crystals of the complex $[\text{Cd}_2\text{Cl}_6(\text{HL})_2]$ (**1**) were formed, while the reaction of cadmium bromide, chloride ligand salt, lithium acetate and ammonium thiocyanate yielded in the formation of an unusual complex of the formula $[\text{HL}][\text{Cd}(\text{HL})(\text{NCS})_2\text{XY}] \cdot \text{H}_2\text{O}$ (**2**) where L = 2-acetylpyridine-aminoguanidine, X = Cl^- or Br^- , Y = Br^- or SCN^- . These are the first two complexes in which the bidentate mode of aminoguanidine Schiff base is proven. The coordination is realized through pyridine and azomethine nitrogen, while the protonated aminoguanidine residue does not take part in coordination. The complexes are physicochemically and structurally characterized and compared to the previously synthesized ones. This gave great insight into the structural differences that are caused by the protonation of the aminoguanidine residue and could lead to different properties of these compounds in further research which will include the investigation of photoluminescence and antioxidant properties.

SUPPLEMENTARY MATERIAL

CCDC 2129140 and 2129141 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (<https://www.ccdc.cam.ac.uk/structures/>). The characterization data and pertinent crystallographic and refinement details are available electronically at the pages of journal website: <https://www.shd-pub.org.rs/index.php/JSCS/article/view/11928>, or from the corresponding author on request.

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ИЗВОД
СИНТЕЗА И КАРАКТЕРИЗАЦИЈА КОМПЛЕКСА Cd(II) СА 2-АЦЕТИЛПИРИДИН-
-АМИНОГВАНИДИНОМ – НОВИ НАЧИН КООРДИНАЦИЈЕ

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У овом раду описане су структуре прва два комплекса са бидентатном координацијом Шифове базе аминогванидина и 2-ацетилпиридина. Комплекс формуле $[Cd_2Cl_6(HL)_2]$ добијен је у реакцији топлих водених раствора хлоридних соли Cd(II), Zn(II) и лиганда, док је реакцијом кадмијум-бромида и лиганда у присуству агенса за депротонацију, као и амонијум-тиоцијаната добијен комплекс у којем поменута Шифова база има улогу бидентатног лиганда, али и улогу контра-јона. Координациона формула комплекса је $[HL][Cd(HL)(NCS)_2XY] \cdot nH_2O$, где је L = 2-ацетилпиридин-аминогванидин, а X Cl⁻ или Br⁻ и Y Br⁻ или SCN⁻. Оба комплекса су окарактерисана ИЦ спектрима, елементалном анализом и кондуктометријским мерењима, а структура им је одређена дифракцијом рендгенских зрака на монокристалу. Необичан бидентатни начин координације Шифове базе доводи до значајних одступања у геометрији овог молекула (од готово планарне геометрије у слободној и тридентатно координованој форми до увијене у бидентатно координованом облику). Осим тога, у комплексу **1** нађен је релативно редак мостовни начин координације Cl⁻, док је у кристалној структури комплекса **2** присутна супституциона неуређеност, те ова структура садржи четири различита јона, и то: $[Cd(HL)(NCS)_2Br(SCN)]^-$ (око 61 %), $[Cd(HL)(NCS)_2Cl(SCN)]^-$ (око 35 %), $[Cd(HL)(NCS)_2Br_2]^-$ (око 3 %) и $[Cd(HL)(NCS)_2ClBr]^-$ (око 1 %).

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