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# Synthesis and properties of $Zn^{II}$ and $Cd^{II}$ complexes with chiral N-derivatives of aminoacetic acid based on natural monoterpenes (+)-3-carene and (–)-α-pinene. Crystal structure of coordination polymer $[Zn(HL)Cl \cdot 2H_2O]_n$*

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Chiral sodium salts of N-derivatives of aminoacetic acid based on (+)-3-carene (HLNa) and (–)-α-pinene (HLNa) were synthesized. Complexes Zn(HL)Cl (**1**), $Cd(HL)Cl \cdot 0.5H_2O$ (**3**), $Zn(HL')Cl \cdot 0.5H_2O$ (**4**), and $Cd(HL')Cl \cdot 0.5H_2O$ (**5**) were obtained. The single crystals of the coordination polymer $[Zn(HL)Cl \cdot 2H_2O]_n$ (**2**) were grown. According to the X-ray diffraction analysis, the crystal structure of **2** consists of 1D chains built of Zn(HL)Cl and water molecules. The coordination polyhedron $ClN_2O_2$ is a distorted square pyramid. The $HL^-$ ligand performs the chelating tetradentate-bridging function, and the $COO^-$ group binds two adjacent Zn atoms. The IR spectroscopy data for compounds **1** and **3**—**5** indicate the coordination of the $COO^-$, NOH, and NH functional groups. The excitation and photoluminescence (PLM) spectra of the solid samples of compounds HLNa, HL´Na, **1**, and **3**—**5** were recorded at room temperature. The compounds exhibit blue PLM. The intensity of PLM of the $Cd^{II}$ complexes is higher than that of the $Zn^{II}$ complexes, which is a characteristic feature of PLM of the studied compounds.

**Key words:** synthesis, $Zn^{II}$ and $Cd^{II}$ complexes, coordination polymer, structure, aminoacetic acid, terpenes, photoluminescence.

Saturated and unsaturated carboxylic acids (including natural) and their derivatives are widely used in chemical industry, chemical analysis, and pharmacology (vitamins F and $B_{15}$, aspirin).[1—3] Heterofunctional derivatives of carboxylic acids, first of all amino acids, play an irreplaceable role in biochemistry.[4,5] Some of amino acids are produced in large amounts and widely used in medicine, agriculture, and food industry (glycine, lysine, methionine, and glutamic acid).[2] The interaction of carboxylic and amino acids with metal ions is a subject of many studies.[1,6—9] In the chemistry of natural substances, considerable attention is given presently to chiral terpenoids isolated from plant raw materials.[4] A series of monoterpenoids is used in medicine (terpin hydrate, camphor). Compounds bearing the carboxyl group, especially, triterpenoid derivatives (for example, ursolic and glycyrrhizic acids), in the series of terpenoids are intensively studied. These acids exhibit valuable medicinal properties, in particular, antiphlogistic.[4] Therefore, it seems interesting to purposefully synthesize chiral "hybrid" organic substances, whose molecules include the fragments of both terpenoid and amino acid. The preparation of these reagents opens the way for the synthesis of complexes of metal ions and investigation of their properties. The metal complexes with the ligands of the considered type can exhibit photoluminescence properties and biological activity. Search for chiral and luminescent complexes is promising for the use as biosensors, including those for the determination of $Zn^{II}$ and $Cd^{II}$.

The purpose of this work is the synthesis and determination of the characteristics of the chiral derivatives of (+)-3-carene and (–)-α-pinene, *viz.*, *N*-[(1*S*,3*S*,6*R*)-4-hydroxyimino-3,7,7-trimethylbicyclo[4.1.0]hept-3-yl]-aminoacetic acid sodium salt (HLNa) and *N*-[(1*R*,2*R*,5*R*)-

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* Dedicated to Academician of the Russian Academy of Sciences R. Z. Sagdeev on the occasion of his 70th birthday.

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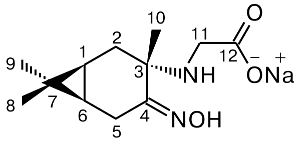
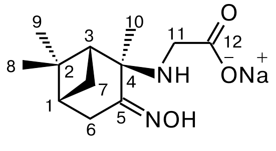
3-hydroxyimino-2,6,6-trimethylbicyclo[3.1.1]hept-3-yl]-aminoacetic acid sodium salt (HL´Na), and the synthesis of Zn$^{II}$ and Cd$^{II}$ complexes **1**—**5** with these reagents and the study of the structures and photoluminescence properties of the synthesized compounds.



HLNa



HL´Na

The chiral sodium salts of N-derivatives of aminoacetic acid based on (+)-3-carene (HLNa) and (–)-α-pinene (HL´Na) were synthesized using esters HLEt and HL´Et. The anhydrous complex Zn(HL)Cl (**1**) was synthesized in EtOH. Single crystals of hydrate Zn(HL)Cl • 2H$_2$O (**2**) are formed, most likely, due to the presence of water in EtOH. Hydrate Zn(HL´)Cl • 0.5H$_2$O (**4**) was obtained in an aqueous-ethanol medium, because HL´Na is poorly soluble in EtOH. A small excess of ZnCl$_2$ was required for the syntheses of compounds **1** and **4** (the molar ratio ZnCl$_2$ : HLNa or HL´Na was 1.5 : 1). Compounds Cd(HL)Cl • 0.5H$_2$O (**3**) and Cd(HL´)Cl • 0.5H$_2$O (**5**) were synthesized in an aqueous-ethanol medium at the stoichiometric ratio of the starting reactants. Complexes **1** and **3**—**5** are soluble in polar solvents (EtOH, Pr$^i$OH, acetone) and are poorly soluble in nonpolar solvents. According to the NMR spectroscopy data, complexes **1** and **3**—**5** dissociate on dissolving in polar solvents. Therefore, we failed to measure the optical rotation angles [α] for the synthesized compounds.

The results of thermal analysis along with the elemental analysis data were used for the estimation of the water content in complexes **1** and **3**—**5**. The thermal analysis curves for complexes **1** and **4** are shown in Fig. 1. No change in the mass is observed up to 215 °C in the TG curve of complex **1**. Complex **4** loses water of crystallization on storage in air already at ~20 °C. The TG curve of this complex in the temperature range 30—220 °C shows a smooth mass loss of 2.1%, which is somewhat smaller than the calculated water content (2.6%). The thermal destruction of complex **1** and dehydrated complex **4** occurs at the temperature higher than 220 °C, and the decomposition of the both complexes in the temperature range from 220 to 280 °C is accompanied by *exo*-effects. According to literature data, Zn$^{II}$ glycinate dihydrate is more thermally stable than compounds **1** and **4**. The dehydration of Zn$^{II}$ glycinate at a heating rate of 5 °C min$^{-1}$ under nitrogen occurs at 280—360 °C.**10** Anhydrous Zn$^{II}$ glycinate starts to decompose at 382 °C. Evidently, the presence of the terpene fragment in the composition of the N-derivatives of aminoacetic acids HLNa and HL´Na decreases the thermal stability of the Zn$^{II}$ complexes with these amino acids.

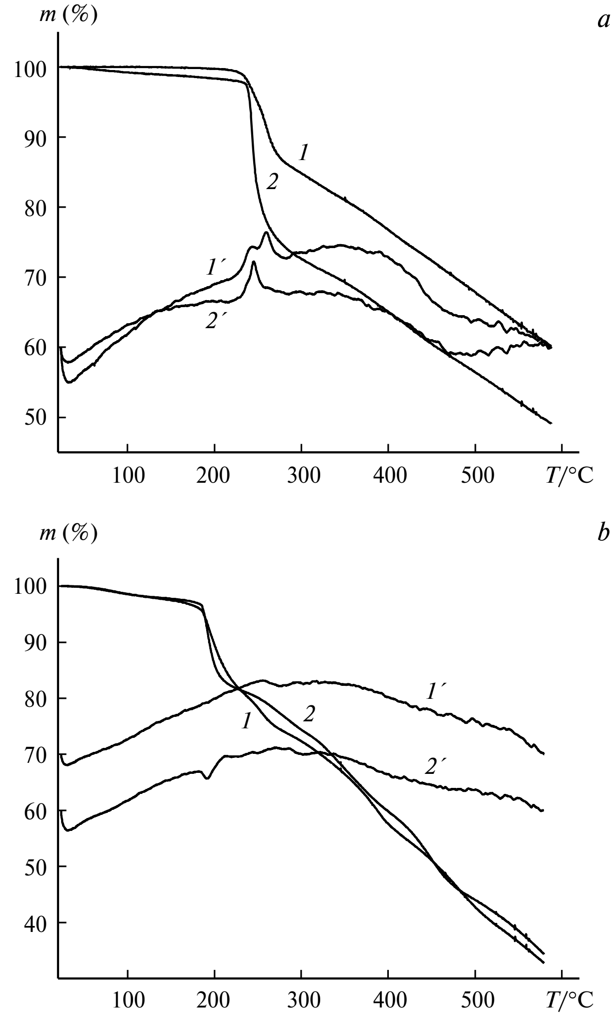


**Fig. 1.** Thermal analysis curves for complexes **1** (*1*, *1´*), **4** (*2*, *2´*) (*a*) and **3** (*1*, *1´*), **5** (*2*, *2´*) (*b*) obtained by thermogravimetry (*1*, *2*) and differential thermal analysis (*1´*, *2´*).

As a whole, the thermal decomposition of complexes **3** and **5** in an inert atmosphere proceeds similarly. The first step of decomposition of complex **3** (see Fig. 1, *b*) is observed in the range 40—150 °C. The mass loss at this step is 2.5%, which corresponds to the complete removal of water of crystallization (the calculated amount of water in complex **3** is 2.3%). The mass loss at the first step of thermolysis of complex **5** is also 2.5%, which agrees well with the calculated amount of water in the compound. The further decomposition occurs at a temperature higher than 180 °C, and the second step of decomposition of the Cd$^{II}$ complexes is accompanied by *endo*-effects, unlike similar Zn$^{II}$ complexes.

The crystal structure of compound **2** consists of 1D chains of the coordination polymer formed of the Zn(HL)Cl molecules (the fragment of the chain is shown in Fig. 2) and molecules of water of crystallization. The coordination polyhedron ClN$_2$O$_2$ of the Zn atom is a dis-

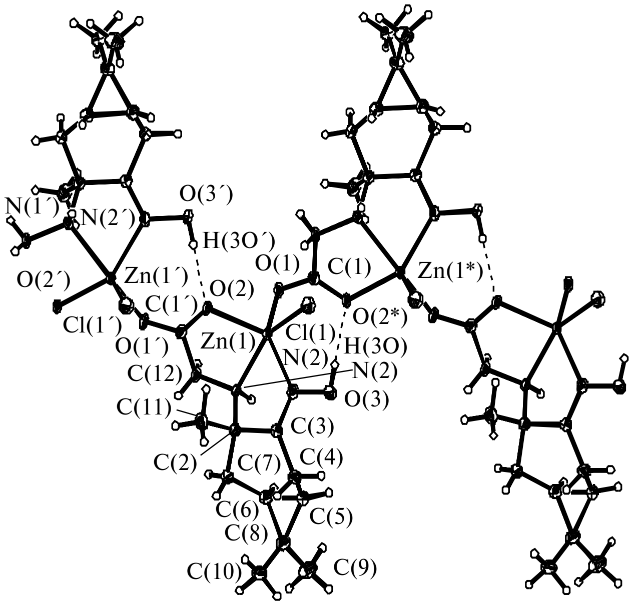


**Fig. 2.** Structure of the independent fragment of the chain coordination polymer $[Zn(HL)Cl]_n$ (thermal ellipsoids are shown at the 50% probability level).

torted square pyramid, whose base includes the O(1) and O(2) atoms of the COO$^-$ bidentate-bridging groups (the Zn—O spacings are 2.061(1) and 2.097(1) Å, respectively) and two N atoms (Zn—N, 2.098(2) and 2.138(2) Å). The distance from the Zn atom to the N(2) atom of the oxime group is noticeably shorter (by 0.04 Å) than that to the N atom of the NH group. The axial vertex of the pyramid is occupied by the Cl atom at the Zn—Cl spacing, being 2.246(1) Å, and the Zn atom is shifted from the base plane to the vertex by 0.65 Å. The HL$^-$ ligand performs the chelating bridging function. A comparison of the obtained parameters for coordination polymer **2** with the literature data[11] for complex $[ZnClHL^H]_n$ shows that both the Zn—O and Zn—N bond lengths and the Zn—Cl axial bond lengths are comparable for these complexes.

Two five-membered chelate cycles $ZnN_2C_2$ (the N(1)—Zn(1)—N(2) angle is 76.83°) and $ZnNOC_2$ (N(1)—Zn(1)—O(2) 79.70°) undergo ring closure upon the coordination of HL$^-$. The both cycles have the envelope conformation with shifts of the C(2) atom by 0.548(3) Å and the N(1) atom by 0.387(3) Å from the plane of four atoms with statistical mean deviations of the atoms in the cycles of 0.051(1) and 0.09(1) Å, respectively. The six-membered carbocycle has the conformation of a distorted bath: the C(4) and C(7) atoms deviate from the plane of four other atoms by 0.699(3) and 0.530(3) Å. The dimethylcyclopropane fragment adjoins the six-membered carbocycle C(2)C(3)C(4)C(5)C(6)C(7) by the common edge C(5)—C(6) and forms the dihedral angle with the C(2)C(3)C(4)C(5)C(6) plane equal to 140.7°. The deprotonated carboxyl group of the HL$^-$ ligand is oriented in such a way that the strong intramolecular hydrogen bond O(2*)...H—O(3) appears between this group and the oxime group (O(2*)...O(3) 2.735(2) Å, angle O(2)—H(30)—O(3) 175.7°), due to which the Zn(1)O(1)C(1)O(2*)O(3)N(2) cycle is formed (see Fig. 2). The cycle has the envelope conformation with the shift of the O(1)C(1)O(2*)O(3)N(2) and the average deviation of atoms of this fragment by 0.082(5) Å.

The structure of compound **2** in the projection onto the plane (100) is shown in Fig. 3. The $[Zn(HL)Cl]_n$ chains are extended along the *b* axis. The spacing between the

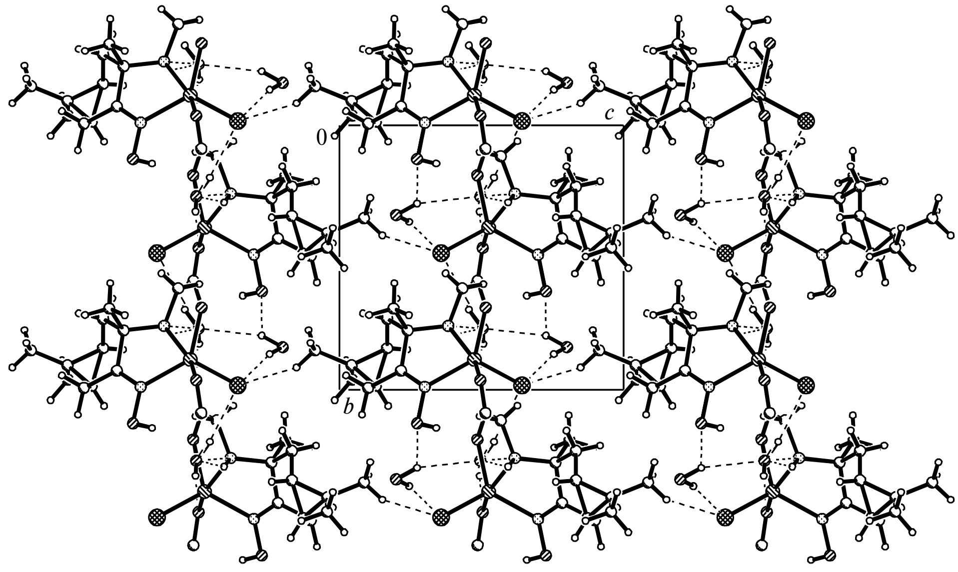


**Fig. 3.** Packing of the 1D chains $[Zn(HL)Cl]_n$ and molecules of water of crystallization in structure **2** in projection onto the plane (100).

nearest Zn atoms in the chain is 5.359(1) Å. The packing fragment of the chains and water molecules occupying cavities between the chains in crystals **2** is presented in Fig. 4. These translationally identical zigzag chains (the Zn(1´)—Zn(1)—Zn(1*) angle is 128.9°) are joined with molecules of water of crystallization by hydrogen bonds: O(2W)...O(1) 2.817(2) Å, O(2W)...N(1) 2.906(3) Å, O(1W)...O(3) 3.086(3) Å, and O(1W)...Cl(1) 3.336(3) Å.

The IR spectra of HLNa and HL´Na exhibit bands $\nu_{as}(COO^-)$, $\nu_s(COO^-)$, and ν(N—O) and the group of bands at 3520—3041 cm$^{-1}$ corresponding to ν(NH) and ν(OH) (Table 1). The positions of the $\nu_{as}$ and $\nu_s$ bands of the COO$^-$ group differ slightly from the position of the bands in the IR spectrum of $H_2NCH_2COO^-$ (see Ref. 12). The change in the position of these bands in the IR spectrum of complex **1** compared to that of HLNa corresponds to the X-ray diffraction data on the character of coordination of the HL$^-$ ligand in the $[Zn(HL)Cl]_n$ chains from the composition of compound **2** (coordination of the COO$^-$ group and the N atoms of the NH and NOH groups). The bands at 1570 cm$^{-1}$ ($\nu_{as}(COO^-)$) and 1392 cm$^{-1}$ ($\nu_s(COO^-)$) are shifted to the low-frequency range compared to the position of these bands in the spectrum of HLNa. Similar shifts were observed for the Zn$^{II}$—glycine complex.[12] The coordination of the N atom of the oxime group is indicated by the change in the position of the ν(N—O) band in the spectrum of complex **1**. The position of the absorption bands in the IR spectrum of compound **3** (see Table 1) indicates that the coordination mode of ligand HL$^-$ is similar to that found for complex **1** in the composition of hydrate **2**. The IR spectra of complexes **4** and **5** also exhibit changes in the position of the $\nu_{as}(COO^-)$, $\nu_s(COO^-)$, and ν(N—O) bands compared to the position of these bands in the spectrum of the starting reactant HL´Na (see Table 1), which indicates the coordination of the COO$^-$ and NOH functional groups. The shift of the frequencies in the ranges of ν(NH) and ν(OH) in the spectra of complexes **1** and **3—5** compared to the

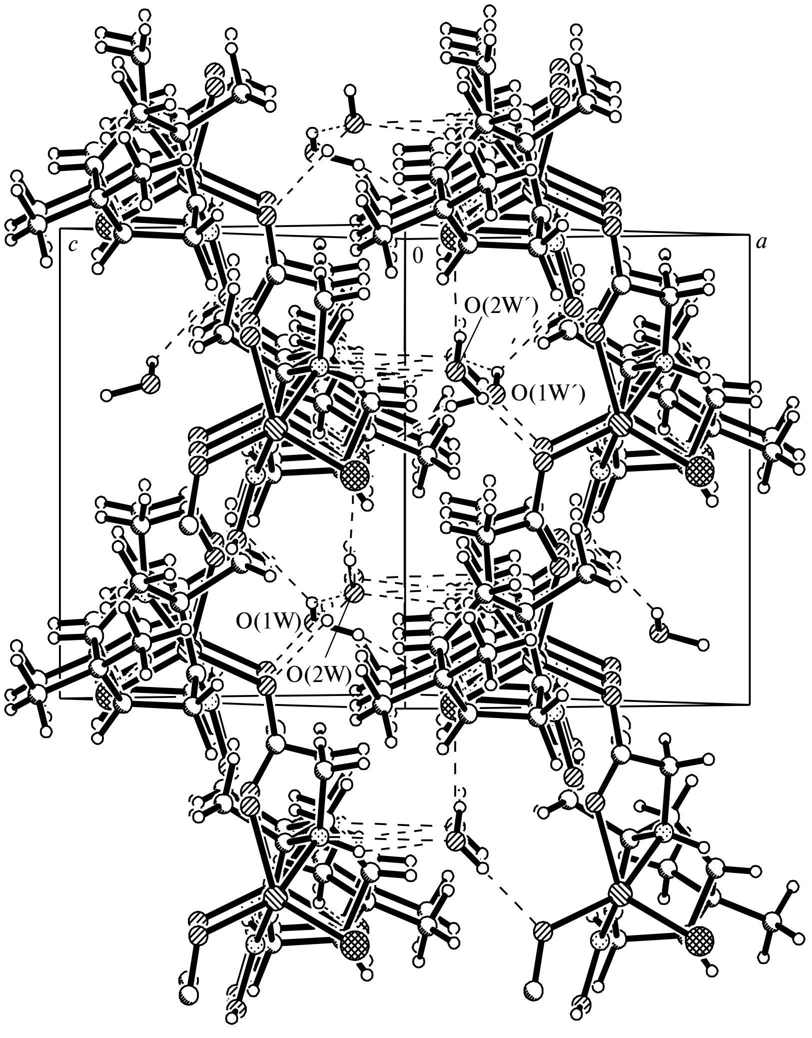


**Fig. 4.** Crystal packing of the polymer chains $[Zn(HL)Cl]_n$ and molecules of water of crystallization in the direction of the *b* axis.

**Table 1.** Selected vibrational modes (cm$^{-1}$) in the IR spectra of compounds HLNa, HL´Na, **1**, and **3**—**5**

| Compound | $\nu$(N—O) | $\nu_{as}$(COO$^-$) | $\nu_s$(COO$^-$) | $\nu$(N—H), $\nu$(O—H) |
|---|---|---|---|---|
| HLNa | 945 | 1599 | 1411 | 3073, 3210, 3295 |
| **1** | 960 | 1569 | 1392 | 3181, 3179, 3303 |
| **3** | 940 | 1588 | 1383 | 3100, 3255, 3400 |
| HL´Na | 972 | 1584 | 1389 | 3041, 3173, 3400, 3480 |
| **4** | 968 | 1575 | 1394 | 3020, 3090, 3220, 3295 |
| **5** | 940 | 1581 | 1388 | 3090, 3253, 3400 |

position of these bands in the spectra of the starting compounds HLNa and HL´Na is consistent with the coordination of the NH group. It is most likely that the (HL´)$^-$ anion similarly to HL$^-$ is a chelating tetradentate-bridging ligand.

Reagent HLNa is excited by UV radiation in the region 250—400 nm with an intense narrow maximum ($\lambda_{max}$ = 375 nm). Complexes **1** and **3** are UV-excited in the same region but with a broader band ($\lambda_{max}$ ~350 nm). Based on these data, $\lambda_{exc}$ = 350 nm was used (Fig. 5) when recording the photoluminescence (PLM) spectra. The photoluminescence of HLNa is observed at 370—520 nm with $\lambda_{max}$ = 419 nm. The half-width of the band ($H_{1/2}$) is ~126 nm. Complexes **1** and **3** luminesce at 320—520 nm with $\lambda_{max}$ = 378 ($H_{1/2} \approx$ 150 nm) and 412 nm ($H_{1/2} \approx$ 170 nm), respectively. Thus, a noticeable hypsochromic shift of $\lambda_{max}$ of PLM of compound **1** is observed relative to $\lambda_{max}$ of HLNa, which possibly indicates a significant influence of the Zn$^{2+}$ ions on the PLM process of complex **1**. The PLM intensity of reagent HLNa estimated by $\lambda_{max}$ of PLM is 1.3 times higher than the PLM intensity of complex **3** and 1.5 times higher than that of complex **1**. The decrease in the PLM intensity of the complexes compared to that in the case of HLNa is related, most likely, to the interaction of the ligands *via* the ligand-to-ligand charge transfer (LLCT) mechanism.[13,14]

Reagent HL´Na and complexes **4** and **5** are UV-excited at 250—400 nm. The spectra contain two maxima: intense maxima at $\lambda_{max}$ = 350 (**4**) and 340 nm (**5**) and a weakly pronounced maximum at $\lambda_{max}$ = 265 nm (Fig. 6). Based on these data, $\lambda_{exc}$ = 350 nm was also used when recording the PLM spectra. The photoluminescence of HL´Na is observed at 350—570 nm with $\lambda_{max}$ = 421 nm ($H_{1/2} \approx$ 115 nm). These characteristics are similar to those obtained for HLNa. Complexes **4** and **5** luminesce at 300—570 nm with $\lambda_{max}$ = 418 ($H_{1/2} \approx$ 138 nm) and 423 nm ($H_{1/2} \approx$ 119 nm), respectively, *i.e.*, the luminescence region of these complexes becomes broader compared to that of HL´Na. The PLM intensity of complex **5** is twofold higher than that for compound **4** and 1.2-fold lower than that for HL´Na. The insignificant shift of $\lambda_{max}$ of PLM of complexes **4** and **5** relative to $\lambda_{max}$ of PLM of HL´Na can indicate the weak influence of the Zn$^{2+}$ and Cd$^{2+}$ ions on the PLM processes in these compounds.

Thus, a characteristic feature of the PLM of the studied compounds **1** and **3**—**5** is that the PLM intensity of the Cd$^{II}$ complexes is higher than that of the Zn$^{II}$ complexes. A similar behavior is typical of the coordination polymers [CdL″(H$_2$O)$_3$H$_2$O]$_n$ and [ZnL″]$_n$ (L″ = bis(benzoamido)-diacetate), which in the solid state at ~20 °C exhibit a strong PLM in the blue spectral range, and the PLM intensity of the Cd$^{II}$ complex is ~2.3 times higher than that in the case of the Zn$^{II}$ complex.[14] It has been shown to date that the presence of even an insignificant number of water molecules in the Cd$^{II}$ complexes does not impede luminescence.[15,16]

The new group of the Zn$^{II}$ and Cd$^{II}$ complexes with the chiral N-derivatives of aminoacetic acid based on

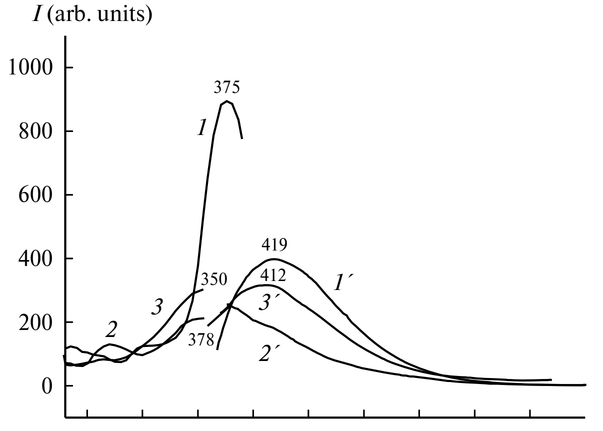


**Fig. 5.** Luminescence excitation (*1*—*3*) and photoluminescence spectra (*1´*—*3´*) of compounds HLNa (*1*, *1´*), **1** (*2*, *2´*), and **3** (*3*, *3´*).

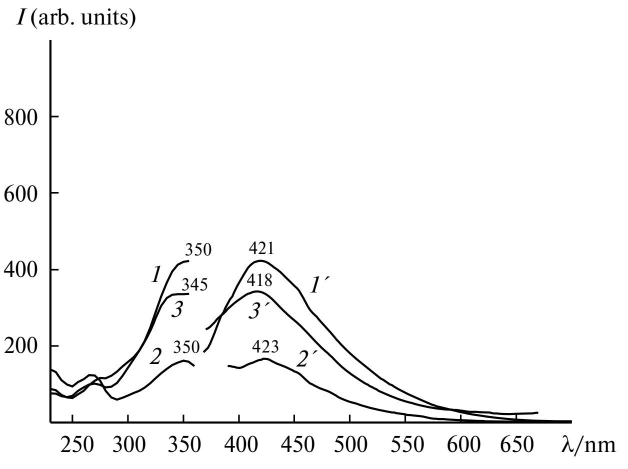


**Fig. 6.** Luminescence excitation (*1*—*3*) and photoluminescence spectra (*1´*—*3´*) of compounds HL´Na (*1*, *1´*), **4** (*2*, *2´*), and **5** (*3*, *3´*).

(+)-3-carene and (–)-α-pinene was synthesized as a result of the study performed. It is shown by the X-ray diffraction data that compound **2** is a coordination polymer. At ~20 °C solid samples of the studied compounds possess the blue PLM. Evidently, the synthesis and study of the properties of complexes of other metals with similar chiral ligands are promising.

## Experimental

The corresponding ethyl esters, which were obtained from nitrosochlorides of (+)-3-carene and (–)-α-pinene and ethyl glycinate using the procedure similar to that described for the synthesis of simplest α-aminooximes, were used for the synthesis of HLNa and HL´Na.[17] For the synthesis of the complexes, $ZnCl_2$ and $CdCl_2 \cdot 2.5H_2O$ (analytical grade), EtOH (rectificate), and acetone (analytical grade) were used. Microanalyses were carried out on Hewlett—Packard 185 and Carlo Erba 1106 analyzers. The thermal properties of the compounds in a helium atmosphere were studied with a TG 209 F1 Iris® thermobalance (NETZSCH) using a weighed sample of ~10 mg, an Al crucible, and a heating rate of 10 °C $min^{-1}$. IR spectra were recorded at 4000—400 $cm^{-1}$ on a Scimitar FTS 2000 FT-IR spectrometer. For KBr pellets the optical rotation was measured on a PolAAr 3005 polarimeter. NMR spectra were recorded on a Bruker DRX-500 instrument ($^1H$, 500.13 MHz; $^{13}C$, 125.75 MHz) for solutions with the concentration 5—10 mg $mL^{-1}$ at 30 °C. Signals of the solvent (DMSO-$d_6$) were used as internal standards: $\delta_H$ 2.50, $\delta_C$ 39.50. The signals were assigned using the $^{13}C$ NMR spectra detected in the *J*-modulation mode (noise proton decoupling, an opposite phase for the signals from the atoms with the even number of attached protons with tuning to the constant *J* = 135 Hz). The mass spectra of the sodium salts were obtained on a micrOTOF-Q high-resolution time-of-flight mass spectrometer. The PLM excitation and luminescence spectra were recorded on a Cary Eclipse spectrophotometer (Varian) at ~20 °C at the same experimental parameters. The excitation spectra were obtained at *V* = 600 V (slit 5 nm). The PLM spectra were detected at *V* = 600 V (slit 5 nm, $\lambda_{exc}$ = 350 nm).

**Ethyl *N*-[(1*S*,3*S*,6*R*)-4-hydroxyimino-3,7,7-trimethylbicyclo[4.1.0]hept-3-yl]aminoacetate (HLEt).** Sodium carbonate (2.12 g, 20 mmol) was added at ~20 °C to a solution of ethyl glycinate hydrochloride (2.79 g, 20 mmol) in ethanol (100 mL), and the mixture was kept for 30 min with vigorous stirring. After this, carene nitrosochloride (4.03 g, 20 mmol) was added to the reaction mixture, and the latter was stirred at ~20 °C until the complete dissolution of nitrosochloride (23 h) and then for 30 min on heating in a water bath (30 °C), after which the mixture was evaporated *in vacuo*. Ethyl acetate (25 mL) and 1 *M* HCl (25 mL) was added to the residue, and the obtained mixture was shaken. The aqueous extract was separated, and the organic phase was extracted with 1 *M* HCl (3×25 mL). A concentrated aqueous solution of $NH_3$ was added to the combined aqueous extract to pH = 10—11, and the reaction products were extracted with ethyl acetate (3×50 mL). The combined organic extract was dried with anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The residue was chromatographed on a column with silica gel (0.040—0.200 mm) in petroleum ether—ethyl acetate, and the product was obtained in a yield of 3.22 g (71%) as a yellowish powder with $[\alpha]_{589}^{26}$ +207 (*c* 1.177, MeOH). High-resolution mass spectrum (HR MS), found: *m/z* 268.1789 $[M]^+$. $C_{14}H_{24}N_2O_3$. Calculated: M = 268.1781. MS, *m/z* ($I_{rel}$ (%)): 268 (12), 251 (32), 210 (12), 195 (22), 187 (9), 186 (100), 177 (8), 170 (36), 167 (12), 166 (23), 165 (117), 150 (10), 148 (9), 136 (6), 128 (12), 113 (28), 106 (14), 97 (20), 95 (13), 94 (11), 91 (11), 85 (12), 82 (13), 79 (13), 77 (10), 70 (14), 67 (11), 56 (13), 42 (15), 41 (20). $^1H$ NMR ($CDCl_3$—$CCl_4$ (1 : 1, vol.), δ: 9.90 (br.s, 1 H, (=NOH)); 4.16—4.00 (m, 2 H, C(13)$H_2$); 3.25 (d, 1 H, H(11), *J* = 17.2 Hz); 3.10 (d, 1 H, H(11), *J* = 17.2 Hz); 2.73 (d, 1 H, H(5 pro-*S*), *J* = 19.4 Hz); 2.39 (br.s, 1 H, (NH)); 2.19 (dd, 1 H, H(5 pro-*R*), *J* = 19.4 Hz, *J* = 8.9 Hz); 2.09 (dd, 1 H, H(2 pro-*S*), *J* = 14.7 Hz, *J* = 9.4 Hz); 1.27 (dd, 1 H, H(2 pro-*R*), *J* = 14.7 Hz, *J* = 5.5 Hz); 1.89 (m, 3 H, H(14)); 1.02 (s, 3 H, H(9)); 0.98 (s, 3 H, H(10)); 0.91 (ddd, 1 H, H(6), *J* = 9.5 Hz, *J* = 8.9 Hz, *J* = 1.8 Hz); 0.78 (ddd, 1 H, H(1), *J* = 9.5 Hz, *J* = 9.5 Hz, *J* = 5.4 Hz); 0.745 (s, 3 H, H(8)). $^{13}C$ NMR ($CDCl_3$—$CCl_4$ (1 : 1 vol.), δ: 172.50 (C(12)); 161.70 (C(4)); 60.81 (C(13)); 54.81 (C(3)); 44.50 (C(11)); 34.30 (C(2)); 27.73 (C(9)); 18.29 (C(6)); 16.24 (C(1)); 19.40 (C(7)); 17.05 (C(5)); 14.32 (C(8)); 21.70 (C(10)); 14.00 (C(14)).

***N*-[(1*S*,3*S*,6*R*)-4-Hydroxyimino-3,7,7-trimethylbicyclo[4.1.0]-hept-3-yl]aminoacetic acid sodium salt (HLNa).** Water (2 mL) and HLEt (1.77 g, 6.60 mmol) were added to a solution of sodium metal (0.159 g, 6.90 mmol) in methanol (10 mL). The reaction mixture was stirred at ~20 °C (20—23 °C) until the starting ester disappeared (20—30 h, TLC monitoring on the Silufol plates in a benzene—ethanol (9 : 1, vol.) eluent system). The solvent was evaporated on a rotary evaporator, the reaction product was liberated from water by distillation with benzene (for this purpose, the residue after evaporation was mixed with anhydrous benzene (5 mL)), and the resulting mixture was evaporated to dryness. Evaporation with benzene was repeated four times more and obtained HLNa (1.73 g, 6.60 mmol, 100% yield) as a white powder with $[\alpha]_{589}^{23}$ +150 (*c* 0.61, $H_2O$). HR MS (ESI, negative ions), found: *m/z* 239.139 $[M - Na^+]^-$. $[C_{12}H_{19}N_2O_3]^-$. Calculated: M = 239.140. HR MS (ESI, positive ions), found: *m/z* 263.133 $[M + H^+]$. $[C_{12}H_{20}N_2O_3Na]^+$. Calculated: M = 263.137. $^1H$ NMR ($D_2O$), δ: 3.08 (d, 1 H, H(11), *J* = 16.5 Hz); 2.84 (d, 1 H, H(5 pro-*S*), *J* = 19.2 Hz); 2.79 (d, 1 H, H(11), *J* = 16.5 Hz); 2.26 (dd, 1 H, H(5 pro-*R*), *J* = 19.2 Hz, *J* = 8.9 Hz); 2.11 (dd, 1 H, H(2 pro-*S*), *J* = 15.2 Hz, *J* = 9.5 Hz); 1.43 (dd, 1 H, H(2 pro-*R*), *J* = 15.5 Hz, *J* = 5.5 Hz); 1.07 (s, 3 H, H(9)); 1.03 (s, 3 H, H(10)); 1.05—1.00 (m, 1 H, H(6)); 0.89 (ddd, 1 H, H(1), *J* = 9.5 Hz, *J* = 9.5 Hz, *J* = 5.4 Hz); 0.78 (s, 3 H, H(8)). $^{13}C$ NMR ($CDCl_3$—DMSO-$d_6$ (1 : 3 vol.)), δ: 175.59 (C(12)), 159.34 (C(4)), 53.81 (C(3)), 46.96 (C(11)), 34.68 (C(2)), 27.96 (C(9)), 22.66 (C(6)), 19.23 (C(1)), 18.03 (C(7)), 17.30 (C(5)), 16.29 (C(10)), 14.38 (C(8)).

**Ethyl *N*-[(1*R*,2*R*,5*R*)-3-hydroxyimino-2,6,6-trimethylbicyclo[3.1.1]hept-2-yl]aminoacetate (HL´Et).** Sodium carbonate (2.12 g, 20 mmol) was added at ~20 °C to a solution of ethyl glycinate hydrochloride (5.58 g, 40 mmol) in methanol (50 mL), and the mixture was kept for 10 min with vigorous stirring. Then pinene nitrosochloride (4.03 g, 20 mmol) was added to the reaction mixture, and the obtained mixture was stirred at ~20 °C for 48 h with interruptions for 16 h. After the end of the reaction, the reaction mixture was treated as described above for the synthesis of HLEt. After chromatographic purification of the crude product, the product was obtained in a yield of 3.802 g (84%) as a white powder with $[\alpha]_{589}^{23}$ –70.2 (*c* 0.732, EtOH).

HR MS, found: *m/z* 268.1788 $[M]^+$. $C_{14}H_{24}N_2O_3$. Calculated: M = 268.1781. MS, *m/z* ($I_{rel}$ (%)): 268 (1), 253 (23), 252 (12), 251 (64), 239 (16), 237 (45), 210 (11), 195 (19), 177 (10), 167 (81), 166 (100), 156 (89), 150 (22), 150 (17), 148 (15), 142 (66), 128 (11), 123 (17), 110 (52), 108 (14), 106 (30), 94 (15), 91 (16), 82 (52), 79 (20), 77 (16), 69 (19), 55 (22), 53 (20), 41 (42). $^1H$ NMR ($CDCl_3$—$CCl_4$ (1 : 1 vol.)), δ: 9.42 (br.s, 1 H, (=NOH)); 4.18—4.06 (m, 2 H, $C(13)H_2$); 3.54 (d, 1 H, H(11), *J* = 17.5 Hz); 3.27 (d, 1 H, H(11), *J* = 17.5 Hz); 2.79 (ddd, 1 H, H(6 pro-*S*), *J* = 18.48 Hz, *J* = 2.0 Hz, *J* = 2.0 Hz); 2.43 (dd, 1 H, H(6 pro-*R*), *J* = 18.48 Hz, *J* = 1.5 Hz); 2.27 (m, 1 H, H(7 pro-*R*), *J* = 10.8 Hz); 2.09 (br.s, 1 H, NH); 1.57 (d, 1 H, H(7 pro-*S*), *J* = 10.8 Hz); 1.30 (s, 3 H, H(10)); 1.27 (s, 3 H, H(9)); 1.22 (t, 3 H, H(14), *J* = 7.2 Hz); 1.942 (m, 1 H, H(1)); 1.927 (m, 1 H, H(3)); 0.875 (s, 3 H, H(8)). $^{13}C$ NMR ($CDCl_3$—$CCl_4$ (1 : 1 vol.)), δ: 173.13 (C(12)), 159.95 (C(5)), 60.54 (C(4)), 59.33 (C(13)), 51.66 (C(3)), 44.09 (C(11)), 39.36 (C(2)), 38.09 (C(1)), 29.73 (C(6)), 28.18 (C(7)), 27.64 (C(9)), 24.07 (C(10)), 22.66 (C(8)), 14.20 (C(14)).

***N*-[(1*R*,2*R*,5*R*)-3-Hydroxyimino-2,6,6-trimethylbicyclo-[3.1.1]hept-2-yl]aminoacetic acid sodium salt (HL´Na).** The hydrolysis of compound HL´Et was carried out similarly to the procedure described above for hydrolysis HLEt → HLNa, except that the water was removed from the hydrolysis product by distillation with isopropyl alcohol instead of benzene. Product HL´Na was obtained as a white powder with $[\alpha]_{589}^{23}$ −57 (*c* 0.74, $H_2O$) in a yield of 2.07 g (7.89 mmol, 99.9% yield) from ester HL´Et (2.12 g, 7.90 mmol). HR MS (ESI, negative ions), found: *m/z* 239.139 $[M - Na^+]^-$. $[C_{12}H_{19}N_2O_3]^-$. Calculated: M = 239.140. HR MS (ESI, positive ions), found: *m/z* 263.134 $[M + H^+]$. $[C_{12}H_{20}N_2O_3Na]^+$. Calculated: M = 263.137. $^1H$ NMR ($D_2O$—DMSO-$d_6$ (3 : 1, vol.)), δ: 3.15 (d, 1 H, H(11), *J* = 16.4 Hz); 2.83 (d, 1 H, H(11), *J* = 16.4 Hz); 2.66 (d, 1 H, H(6 pro-*S*), *J* = 18.8 Hz); 2.33 (d, 1 H, H(6 pro-*R*), *J* = 18.8 Hz); 2.19 (m, 1 H, H(7 pro-*R*), *J* = 10.8 Hz); 1.83 (m, 2 H, H(1), H(3)); 1.26 (d, 1 H, H(7 pro-*S*), *J* = 10.9 Hz); 1.15 (s, 6 H, H(9), H(10)); 0.72 (s, 3 H, H(8)). $^{13}C$ NMR ($D_2O$—DMSO-$d_6$ (3 : 1, vol.)), δ: 180.10 (C(12)), 164.05 (C(5)), 60.62 (C(4)), 52.51 (C(3)), 46.84 (C(11)), 40.36 (C(2)), 38.98 (C(1), 31.32 (C(6)), 28.88 (C(7)), 28.42 (C(10)), 24.63 (C(9)), 23.47 (C(8)).

**Chloro(*N*-[(1*S*,3*S*,6*R*)-4-hydroxyimino-3,7,7-trimethylbicyclo[4.1.0]hept-3-yl]aminoacetato)zinc(II), Zn(HL)Cl (1).** A solution of $ZnCl_2$ (0.048 g, 0.35 mmol) in EtOH (3 mL) was added to a solution of HLNa (0.058 g, 0.23 mmol) in EtOH (3 mL). The obtained solution was filtered through the paper filter and kept in a closed beaker for 24 h at ~20 °C. The solution with fine crystals that formed were stirred, and then the solvent was distilled to a minimum volume (~2 mL). The white precipitate was filtered off with suction, washed with cooled $Pr^iOH$, and dried in a vacuum desiccator. The yield was 0.030 g (38%). Found (%): C, 42.8; H, 5.8; N, 8.1. $C_{12}H_{19}ClN_2O_3Zn$. Calculated (%): C, 42.4; H, 5.6; N, 8.2.

**Growth of single crystals of catena-chloro{μ-(*N*-[(1*S*,3*S*,6*R*)-4-hydroxyimino-3,7,7-trimethylbicyclo[4.1.0]hept-3-yl]aminoacetato)}zinc(II) dihydrate, $[Zn(HL)Cl \cdot 2H_2O]_n$ (2).** Single crystals suitable for X-ray diffraction analysis were grown by the slow evaporation of a solution of complex **1** in an ethanol—acetone (1 : 1, vol.) mixture. The single crystals were taken from the solution and immediately covered with Nujol, because they decompose in air.

**Chloro(*N*-[(1*S*,3*S*,6*R*)-4-hydroxyimino-3,7,7-trimethylbicyclo[4.1.0]hept-3-yl]aminoacetato)cadmium(II) hemihydrate, $Cd(HL)Cl \cdot 0.5H_2O$ (3).** A solution of $CdCl_2 \cdot 2.5H_2O$ (0.057 g, 0.25 mmol) in an EtOH—$H_2O$ (1 : 1, vol.) mixture (2 mL) was added to a solution of HLNa (0.065 g, 0.25 mmol) in the 6 mL of the same mixture. The beaker with the solution and precipitate that formed was kept for 1.5 h at ~20 °C. The mixture was stirred, and the solvent was distilled off to ~0.5 of the initial volume. The white precipitate was filtered with suction, washed with cooled water, and dried in a vacuum desiccator. The yield was 0.025 g (25%). Found (%): C, 36.1; H, 5.3; N, 6.9. $C_{12}H_{20}CdClN_2O_{3.5}$. Calculated (%): C, 36.4; H, 5.1; N 7.1.

**Chloro(*N*-[(1*R*,2*R*,5*R*)-3-hydroxyimino-2,6,6-trimethylbicyclo[3.1.1]hept-2-yl]aminoacetato)zinc(II) hemihydrate, $Zn(HL´)Cl \cdot 0.5H_2O$ (4).** A solution of $ZnCl_2$ (0.048 g, 0.35 mmol) in EtOH (3 mL) was added to a solution of HL´Na (0.058 g, 0.23 mmol) in EtOH (3 mL) and $H_2O$ (2 mL). Then the mixture was treated similarly to the synthesis of compound **1**. The yield of the white product was 0.050 g (60%). Found (%): C, 41.8; H, 5.7; N, 8.0. $C_{12}H_{20}ClN_2O_{3.5}Zn$. Calculated (%): C, 41.3; H, 5.8; N, 8.0.

**Chloro(*N*-[(1*R*,2*R*,5*R*)-3-hydroxyimino-2,6,6-trimethylbicyclo[3.1.1]hept-2-yl]aminoacetato)cadmium(II) hemihydrate, $Cd(HL´)Cl \cdot 0.5H_2O$ (5).** A solution of $CdCl_2 \cdot 2.5H_2O$ (0.057 g, 0.25 mmol) in an EtOH—$H_2O$ (1 : 1, vol.) mixture (2 mL) was added to a solution of HL´Na (0.065 g, 0.25 mmol) in 6 mL of

**Table 2.** Crystallographic characteristics and experimental refinement details for the structure of coordination polymer **2**

| Parameter | Value |
|---|---|
| Empirical formula | $C_{12}H_{23}ClN_2O_5Zn$ |
| *M* | 376.14 |
| Crystal system | Monoclinic |
| Space group | $P2_1$ |
| *a*/Å | 8.0810(5) |
| *b*/Å | 9.6711(5) |
| *c*/Å | 10.9080(7) |
| β/deg | 107.775(2) |
| $V/Å^3$ | 811.79(8) |
| *Z* | 2 |
| $d_{calc}/g\ cm^{-3}$ | 1.539 |
| $\mu/mm^{-1}$ | 1.698 |
| Crystal sizes/mm | 0.19×0.13×0.07 |
| Scan range, θ/deg | 2.65—28.31 |
| Number of measured reflections | 8931 |
| Number of independent reflections | 3346 |
| *R*(int) | 0.0242 |
| Number of reflections with $I > 2\sigma(I)$ | 3102 |
| Number of refined parameters | 279 |
| Goodness-of-fit for $F^2$ | 0.719 |
| *R* Factor, $I > 2\sigma(I)$ | |
| $R_1$ | 0.0187 |
| $wR_2$ | 0.0446 |
| *R* Factor (for all $I_{hkl}$) | |
| $R_1$ | 0.0205 |
| $wR_2$ | 0.0449 |
| Residual electron density $/e \cdot Å^3$, $\rho_{max}/\rho_{min}$ | 0.477/−0.230 |

**Table 3.** Selected interatomic spacings and bond angles in the structure of coordination polymer **2**

| Parameter | Value |
|---|---|
| Bond | *d*/Å |
| Zn(1)—O(1) | 2.061(1) |
| Zn(1)—O(2) | 2.097(1) |
| Zn(1)—N(2) | 2.098(2) |
| Zn(1)—N(1) | 2.138(2) |
| Zn(1)—Cl(1) | 2.2459(6) |
| O(1)—C(1) | 1.261(2) |
| O(2)—C(1´) | 1.260(2) |
| O(3)—N(2) | 1.400(2) |
| O(3)—H(3O) | 0.83(2) |
| N(1)—C(12) | 1.473(2) |
| N(1)—C(2) | 1.499(2) |
| N(1)—H(1N) | 0.9100 |
| N(2)—C(3) | 1.273(2) |
| C(1)—O(2´) | 1.260(2) |
| C(1)—C(12´) | 1.517(3) |
| C(2)—C(3) | 1.520(3) |
| C(2)—C(11) | 1.536(3) |
| C(2)—C(7) | 1.549(3) |
| C(3)—C(4) | 1.503(3) |
| C(4)—C(5) | 1.532(3) |
| C(5)—C(8) | 1.516(3) |
| C(5)—C(6) | 1.522(3) |
| C(6)—C(7) | 1.518(3) |
| C(6)—C(8) | 1.518(3) |
| C(8)—C(10) | 1.501(3) |
| C(8)—C(9) | 1.517(3) |
| C(12)—C(1´) | 1.517(3) |
| N(1)—H(1N) | 0.91 |
| Angle | ω/deg |
| O(1)—Zn(1)—O(2) | 87.99(5) |
| O(1)—Zn(1)—N(2) | 94.36(6) |
| O(2)—Zn(1)—N(2) | 131.82(6) |
| O(1)—Zn(1)—N(1) | 152.95(6) |
| O(2)—Zn(1)—N(1) | 79.70(5) |
| N(2)—Zn(1)—N(1) | 76.83(6) |
| O(1)—Zn(1)—Cl(1) | 101.72(4) |
| O(2)—Zn(1)—Cl(1) | 113.86(4) |
| N(2)—Zn(1)—Cl(1) | 112.67(5) |
| N(1)—Zn(1)—Cl(1) | 105.28(5) |
| C(1)—O(1)—Zn(1) | 126.1(1) |
| C(1´)—O(2)—Zn(1) | 115.8(1) |
| C(12)—N(1)—C(2) | 116.1(2) |
| C(12)—N(1)—Zn(1) | 109.1(1) |
| C(2)—N(1)—Zn(1) | 108.9(1) |
| C(3)—N(2)—O(3) | 115.3(2) |
| C(7)—C(6)—C(8) | 121.4(2) |
| C(7)—C(6)—C(5) | 114.7(2) |
| C(6)—C(7)—C(2) | 113.0(2) |
| C(10)—C(8)—C(5) | 121.8(2) |
| C(10)—C(8)—C(9) | 112.8(2) |
| C(5)—C(8)—C(9) | 115.0(2) |
| H(11W)—O(1W)—H(12W) | 94(2) |
| C(3)—N(2)—Zn(1) | 117.8(1) |
| O(3)—N(2)—Zn(1) | 126.3(1) |
| O(2´)—C(1)—O(1) | 124.3(2) |
| O(2´)—C(1)—C(12´) | 119.2(2) |
| O(1)—C(1)—C(12´) | 116.5(2) |
| N(1)—C(2)—C(3) | 106.3(2) |
| N(1)—C(2)—C(11) | 109.9(2) |
| C(3)—C(2)—C(11) | 108.2(2) |
| N(1)—C(2)—C(7) | 112.4(2) |
| C(3)—C(2)—C(7) | 109.8(2) |
| C(11)—C(2)—C(7) | 110.1(2) |
| N(2)—C(3)—C(4) | 126.4(2) |
| N(2)—C(3)—C(2) | 116.1(2) |
| C(4)—C(3)—C(2) | 117.4(2) |
| C(3)—C(4)—C(5) | 104.5(2) |
| C(8)—C(5)—C(6) | 59.9(1) |
| C(8)—C(5)—C(4) | 123.4(2) |
| C(6)—C(5)—C(4) | 114.1(2) |
| C(10)—C(8)—C(6) | 121.6(2) |
| C(5)—C(8)—C(6) | 60.2(1) |
| C(9)—C(8)—C(6) | 115.8(2) |
| N(1)—C(12)—C(1´) | 111.6(2) |
| H(21W)—O(2W)—(22W) | 105(3) |

the same mixture. The mixture was treated similarly to the synthesis of compound **3**. The white precipitate was dried in a vacuum desiccator. The yield of the white product was 0.035 g (36%). Found (%): C, 36.0; H, 5.3; N, 6.8. $C_{12}H_{20}CdClN_2O_{3.5}$. Calculated (%): C, 36.4; H, 5.1; N, 7.1.

**X-ray diffraction study of compound 2.** Unit cell parameters and reflection intensities were measured at low temperature (150 K) on a Bruker X8 Apex CCD automated diffractometer equipped with a two-coordinate detector using a standard procedure (Mo-Kα radiation, $\lambda$ = 0.71073 Å, graphite monochromator). The crystallographic characteristics and details of diffraction experiment and refinement of the structure of compound **2** are given in Table 2. The structure was solved by a direct method and refined by full-matrix least squares for $F^2$ in the anisotropic approximation (for non-hydrogen atoms) by the SHELXL-97 program package.[18] The positions of the H atoms of the water molecules were localized from the difference electron density synthesis and included in the refinement in the isotropic approximation along with the non-hydrogen atoms. The final values of selected interatomic spacings and bond angles are listed in Table 3. The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CCDC 814614) and are available from the authors.

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