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Magnetic properties and circular dichroism of 1D chains built from chiral mononuclear and non-chiral trinuclear Cu(II) complexes with α-aminocarboxylates

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ABSTRACT

Coordination polymers Cu(L-Pro)(ClO_4)(H_2O)$_2$ (**1**) and Cu_3(Gly)$_4$(H_2O)$_2$(NO_3)$_2$ (**2**) were synthesized and characterized structurally. Compound **1** possesses the structure of 1D chain, where Cu(II) ions are linked by carboxyl-group in syn-anti conformation in equatorial–equatorial mode. Compound **2** is polymeric chain, consisting from trinuclear blocks $Cu_3(Gly)_4(H_2O)_2^{2+}$. In each of these units Cu(II) ions are linked by carboxyl-group in the same way as in **1**, while trinuclear units $Cu_3(Gly)_4(H_2O)_2^{2+}$ are linked by NO_3^- ions, acting as the bridges between Cu(II) ions of neighboring trinuclear units. Circular dichroism properties of **1** were studied in solid state and solution. Magnetic measurements revealed that there were ferromagnetic exchange interactions between Cu(II) ions in **1** ($J = +1.22(1)\ \mathrm{cm}^{-1}$ for Hamiltonian $\hat{H} = -2J\sum_i S_iS_{i+1}$) and **2** ($J = +1.17(2)\ \mathrm{cm}^{-1}$ for Hamiltonian $\hat{H} = -2J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3) + \mu_B gH(\hat{S}_1 + \hat{S}_2 + \hat{S}_3)$).

1. Introduction

The interest to coordination polymers is caused by their potential applications for creation of functional materials: ferro- and ferrimagnetics [1–3], materials with non-trivial optical properties [4–6], sorbents [7–9], the catalysts of different reactions [10,11], etc. Simultaneous occurrence of more than one property, for which possible application may be found, in one compound can lead to new effects, which cannot be expected in the case of the compound, possessing only one such property [12–18]. Therefore investigation of compounds possessing at least two such physical properties is important task of coordination chemistry and chemistry of materials. Coordination polymers, containing paramagnetic metal ions, are suitable objects for this purpose because exchange interactions between unpaired spins of metal ions may lead to non-trivial magnetic properties (such as ferromagnetic ordering, or ferromagnetic exchange as necessary condition for ferromagnetic ordering), while one more property (such as rotation of polarized light) may be provided by organic ligands.

Among the variety of methods, which generally conduce to the synthesis of coordination polymers, not all may allow to prepare desired chiral ferromagnetic polymers. Potential applications of coordination compounds for creation of materials may require large quantities of such compound, but synthesis of organic chiral ligands often requires significant efforts, which often makes evident obstacle for large-scale preparation of chiral compounds. Introduction of chiral function into well-known ligands is also a serious problem in the majority of cases. This reason makes attractive the use of natural chiral molecules as ligands for creation of chiral coordination compounds, including polynuclear complexes and coordination polymers [19–24]. α-Aminocarboxylates are suitable candidates for polynuclear assemblies creation, because carboxylic group may act as a bridge between two metal ions, and it also can efficiently transfer exchange interactions between them [25,26].

The aim of this study was to elucidate the role of synthetic conditions in formation of Cu(II) complexes with α-aminocarboxylates of different nuclearity and structure, and to study circular dichroism properties of ferromagnetically-coupled complex of α-aminocarboxylate.

Recently simple synthetic route to 1D chains, built from Cu(II) complexes with α-aminocarboxylates and additional amine, was developed [27], however a lot of factors leading to certain structure of transition metal complex with α-aminocarboxylate (for example, discrete complexes [28–30], hexanuclear complexes [31–35] or polymers [27,36–45]) are still not clear. Such factors may include the nature of counter-anion, additional ligand, solvent, crystal lattice energy, etc., which may have significant influence on the composition and the structure of resulting product.

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In this paper we report synthesis, X-ray structures and magnetic properties of two Cu(II) complexes, $\{Cu(\text{L-Pro})(ClO_4)(H_2O)_2\}_n$ (**1**) and $\{Cu_3(Gly)_4(NO_3)_2(H_2O)_2\}_n$ (**2**), where L-Pro is L-prolinate, and Gly is its non-chiral analogue, glycinate. Both these polymers are characterized by ferromagnetic interactions between metal ions. Circular dichroism of chiral compound – coordination polymer **1** – was studied.

2. Experimental

2.1. Materials and methods

Commercially available reagents and solvents (Aldrich and Merck) were used without further purification. C,H,N-analysis was carried out using Carlo Erba 1106 analyzer. IR-spectra were recorded on Perkin Elmer Spectrum One spectrometer. Electronic spectra were measured from solid samples on Specord M 40 instrument (Carl-Zeiss-Jena) in the range 30,000–12,000 cm^{-1} at 298 K in $BaSO_4$ matrix. Transmission CD spectra were registered on Jasco J-815 CD spectrometer. For CD measurement in solid state the sample was deposited on polycarbonate polymeric film, and blank spectrum of the same film was subtracted from the spectrum of the film with sample. The attempt to prepare a pellet of the compound in KBr resulted in significant color change, which was probably caused by sample reaction with this matrix.

Magnetic measurements were performed using a Quantum Design MPMS SQUID magnetometer operating in the temperature range 2–300 K with a DC magnetic field up to 5 T. The X-band ESR spectra were recorded on BRUKER EMX X-band ESR spectrometer at the temperature 298 K.

2.2. Syntheses

Caution*: although perchlorate-containing polymer (**1**) described here has not proved to be mechanically sensitive, perchlorates are potentially explosive and should be handled with due caution.*

2.2.1. $\{Cu(\text{L-Pro})(H_2O)_2(ClO_4)\}_n$ (**1**)

0.371 g (1 mmol) of $Cu(ClO_4)_2{\cdot}6H_2O$ were dissolved in 10 mL of water, 0.115 g (1 mmol) of L-proline were added. This solution was neutralized by slow addition of 0.1 M aqueous NaOH at vigorous stirring until precipitate formation. The mixture was filtered and solution was left on air. Blue octahedral crystals[1] formed in several weeks. Crude product was crystalized by slow evaporation of the solution in the mixture of 2-propanol and water (1:1 by volume). After several weeks blue needle crystals formed. Yield 75%. *Anal. Calc.* for $C_5H_{16}NO_{10}ClCu$ ($\mathbf{1}{\cdot}2H_2O$): C, 17.2; H, 4.58; N, 4.01. Found: C, 16.8; H, 4.88; N, 4.30%. Electronic spectrum: $\lambda_{max} = 695$ nm. IR (KBr pellet, cm^{-1}): 1625 (ν(NH)), 1595 ($\nu_{as}(COO^-)$), 1455 ($\nu_{sym}(COO^-)$), 1145 (ρ_t(NH)), 1115 ($\nu_3(ClO_4^-)$), 1090 ($\nu_3(ClO_4^-)$), 933 ($\nu_1(ClO_4^-)$), 630 ($\nu_4(ClO_4^-)$).

2.2.2. $\{Cu_3Gly_4(H_2O)_2(NO_3)_2\}_n$ (**2**)

0.296 g (1 mmol) of $Cu(NO_3)_2{\cdot}6H_2O$ were dissolved in 10 mL of water, then 0.075 g (1 mmol) of glycine were added. This solution was neutralized by slow addition of 0.1 M aqueous NaOH at vigorous stirring until precipitate formation. The reaction mixture was filtered and the filtrate was evaporated on the water bath to one third of initial volume, and resulting solution was left in a desiccator with $CaCl_2$. Blue needles formed after 2 weeks, they were filtered and air-dried. Yield 75%. *Anal. Calc.* for $C_8H_{23.5}N_6O_{17.75}Cu_3$ ($\mathbf{2}{\cdot}1.75H_2O$): C, 14.1; H, 3.46; N, 12.4. Found: C, 14.0; H, 3.34; N, 12.2%. Electronic spectrum: $\lambda_{max} = 705$ nm. IR (KBr pellet, cm^{-1}): 1590 ($\nu_{as}(COO^-)$), 1490 (δ(NH)), 1400 ($\nu_{sym}(COO^-)$), 1390 ($\nu_3(NO_3^-)$), 1300 ($\nu_3(NO_3^-)$), 1155 (ρ_t(NH)), 1120 (ρ_N(NH)).

2.3. X-ray structure determiantion

For X-ray structure determination, single crystals of compounds **1** and **2** were mounted on a Nonius four circle diffractometer equipped with a CCD camera and a graphite monochromated Mo Kα radiation source ($\lambda = 0.71073$ Å), from the Centre de Diffractométrie (CDFIX), Université de Rennes 1, France. Data were collected at 293 K. Effective absorption correction was performed (SCALEPACK [46]). Structure of complexes **1** and **2** were solved with direct method using SIR-97 [47] software, and were refined with full matrix least squares method on F^2 using SHELXL-97 program [48]. Hydrogen atoms were assigned an isotropic thermal parameter 1.2 times that of the parent atom (1.5 time for methyl hydrogen) and allowed to ride. Crystallographic data are summarized in Table 1. Complete crystal structure results as CIF files, including bond lengths, bond angles, and atomic coordinates, are deposited in CCDC (deposition Nos. for **1** – 763503, for **2** – 763504).

3. Results and discussion

3.1. Synthesis of **1** and **2** and the influence of composition of reaction mixture on composition of the product

The compounds were prepared by slow evaporation of solutions, containing Cu(II) salt (nitrate or perchlorate) and α-amino-acid both in protonated and deprotonated forms in 2-propanol/water (1:1 by volume) (**1**) or water (**2**). Initial pH of reaction mixture was adjusted by addition of 0.1 M aqueous NaOH to the value, at which precipitation of $Cu(OH)_2$ began. Similar procedure was employed for the synthesis of hexanuclear Cu(II) complexes [31–33], but the result appeared to be sensitive to minor changes of reaction mixture's composition and treatment conditions. Probably hexanuclear complex $NaCu_6(Pro)_8(ClO_4)_4(OH)(H_2O)$ formed as the intermediate in the synthesis of $\mathbf{1}^1$, and then this compound

Table 1
Crystallographic data and structure refinements for complexes **1** and **2**.

	1	2
Empirical formula	$CuC_5H_{14}NO_9Cl$	$Cu_3C_8H_{20}N_6O_{16}$
Formula weight	331.17	646.93
Crystal size (mm)	0.5 × 0.1 × 0.1	0.6 × 0.2 × 0.2
Space group	*P*2(1)	*P*2(1)/*n*
T (°C)	293(2)	293(2)
λ (Å)	0.71073	0.71073
Unit cell dimensions		
a (Å)	7.6053(4)	5.20740(10)
b (Å)	9.7784(3)	7.0343(2)
c (Å)	8.1617(4)	26.7354(10)
α (°)	90.00	90.00
β (°)	106.359(2)	91.877(2)
γ (°)	90.00	90.00
V (Å^3)	582.39(5)	978.80(5)
Z	2	2
μ (mm^{-1})	2.141	3.327
Reflections measured	8932	11349
Reflections unique	6252	2959
θ (°)	0.982–40.33	0.987–30.53
Goodness-of-fit (GOF)	1.041	1.149
(R_{int})	0.1244	0.1201
D_{calc} ($g\ cm^{-3}$)	1.865	2.195
R_1 ($[I > 2\sigma(I)]$)[a]	0.0717	0.0790
wR_2 $[I > 2\sigma(I)]$[b]	0.1851	0.2170

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

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[1] Probably the compound $NaCu_6(Pro)_8(ClO_4)_4(OH){\cdot}H_2O$, as was shown in [31] and confirmed by analytical data.

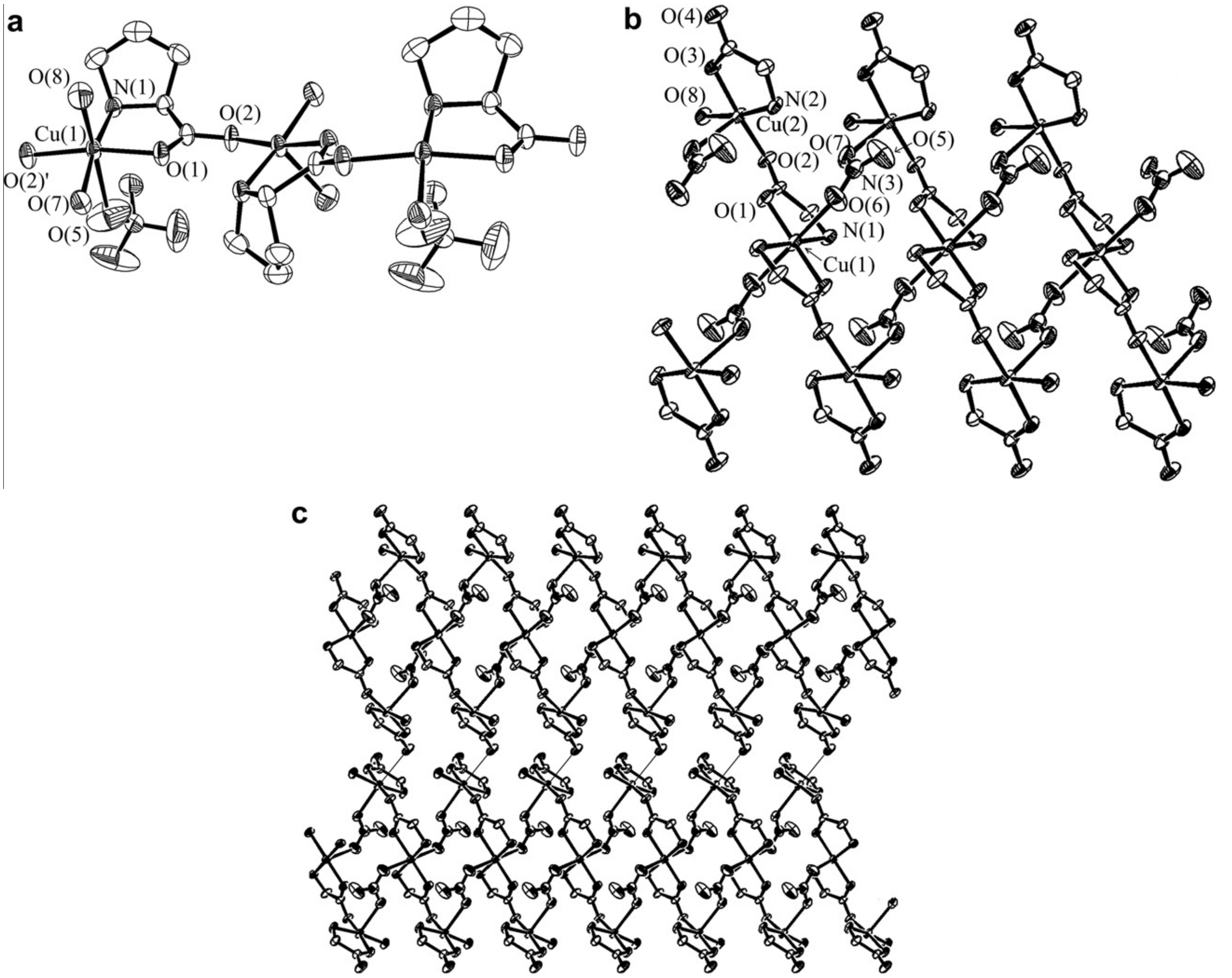

Fig. 1. Fragment of polymeric chain of complex **1** (a), trinuclear units of **2** (b) and packing of such trinuclear units in 2D layer in **2** (c). Symmetry equivalent positions for **1**: '*x*, *y*, *z*', '−*x*, *y* + 1/2, −*z*', for **2**: '*x*, *y*, *z*', '−*x* + 1/2, *y* + 1/2, −*z* + 1/2', '−*x*, −*y*, −*z*', '*x* − 1/2, −*y* − 1/2, *z* − 1/2'

decomposed giving final product at crystallization from 2-propanol/water (1:1 in the beginning of crystallization) mixture by its evaporation on air. It seems that Na^+ plays the role of template in the reaction of $NaCu_6(AA)_8(ClO_4)_4{}^+$ formation,[2] and equilibrium in the reaction mixture should depend on Na^+ concentration in the solution (where AA is the anion of aminoacid). Thus, formation of **1** at crystallization of $NaCu_6(Pro)_8(ClO_4)_4(OH)(H_2O)$ may be explained by lower concentration of Na^+ in solution of this compound compared to Na^+ concentration in reaction mixture at the first stage of the synthesis (after pH adjustment by NaOH).

Reactions of Cu(II) acetate, hydroxide or basic carbonate with various aminoacids in water without pH adjustment and at Cu^{2+}:AA ratio about 1:2 or higher usually produce complexes $Cu(AA)_2(H_2O)_n$ ($n = 0$, 1 or 2) [28,42,49–53] (Table S1, Supporting materials). Increase of Cu^{2+}:AA ratio in reaction mixture to the values above 1:1 (when the quantity of aminoacid is not sufficient to form compound of $Cu(AA)_2$ type) leads to formation of 1D polymer Cu(AA)(X)(L), where L is additional neutral ligand and X is anion like Cl, $NO_3{}^-$, $ClO_4{}^-$ [27,37,38,40,54], similarly to formation of **1**.

In some cases it may be supposed that pH adjustment is important, as it is evidenced from the comparison of our results (formation of **2**) and the results of Davies et al. (formation of polymer $Cu(Gly)(NO_3)(H_2O)$) [40]. Clearly, the presence of nitrate is critically important for formation of **2**, at least because it acts as a bridge between trinuclear blocks (vide infra). Reaction of copper(II) perchlorate with glycine in similar conditions, but at the presence of Na^+, lead to hexanuclear compound $Na[NaCu_6(Gly)_8(H_2O)_2](ClO_4)_6{\cdot}2H_2O$ [31]. Interaction of the same reagents (copper(II) perchlorate and glycine) without addition of Na^+ resulted in formation of 1D chain $Cu(Gly)(H_2O)(ClO_4)$ [27].

3.2. X-Ray structures

3.2.1. Compound *1*

Crystal structure of compound **1** consists of discrete infinite 1D chains. Each chain is formed by Cu(L-Pro)$(H_2O)(ClO_4)$ building blocks, connected by bridging carboxylate group of L-prolinate in *syn-anti* conformation with equatorial–equatorial coordination mode (Fig. 1a). Positive charge of each Cu^{2+} ion is compensated by one prolinate and one perchlorate. In each Cu(L-Pro)$^+$ unit, L-prolinate forms chelate ring with Cu(II) ion through N atom of amino-group and one O-atom of carboxy-group. Thus, Cu(II) ions are located in distorted octahedral donor sets NO_5, formed by one oxygen and one nitrogen donor atoms of chelating L-prolinate, one oxygen atom of carboxy-group of neighboring Cu(L-Pro)$^+$ unit, two coordinated water molecules and oxygen atom of perchlorate anion. Cu–N bond is 1.984(3) Å, three $Cu–O_{equatorial}$ bonds lie in

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[2] It was mentioned that other cations, such as Ca^{2+} or Ag^+, also may lead to formation of hexanuclear copper(II) complexes with α-aminocarboxylates [33].

range from 1.943(3) to 1.968(3) Å, while Cu–O bonds with O atoms in axial positions are much longer (2.326(4) Å to O atom of H_2O and 2.811(8) Å to O atom of ClO_4^-, Table 2).

The distances between the closest Cu^{2+} ions within the chain are 5.2297(6) Å, whereas the distances between the closest Cu^{2+} ions from neighboring chains are about 7.6053(8) Å.

The complexes with bridging carboxylic group are known for the majority of transition metals [25,26,38,55–57]. Six 1D copper(II) polymers with the structure similar to the structure of **1** were reported recently [27,37]. Five of them contain amine ligand, coordinated to copper(II), and have formula Cu(AA)(L)(ClO_4) (AA = L-alanine, L = imidazole or pyrazole; AA = L-phenylalanine, L = imidazole; AA = Gly, L = pyrazole; AA = L-prolinate, X = pyrazole) [27]. Only one polymer of composition Cu(AA)(H_2O)(ClO_4) was reported, for the case AA = Gly [27,37]. Since there are similar structures differing by additional ligand (amine or water), such as Cu(Gly)(pz)(ClO_4) and Cu(Gly)(H_2O)(ClO_4), Cu(L-Pro)(pz)(ClO_4) and reported by us Cu(L-Pro)$(H_2O)_2$(ClO_4), it is clear that "blocking" of some coordination position in coordination sphere of Cu(II) by amine has no influence on formation of the polymer or mononuclear compound. This conclusion is supported by comparison of the above compounds with three 1D chains, containing Cl^- or NO_3^- as counter-anions: Cu(Pro)(H_2O)Cl, Cu(Pro)(CH_3OH)Cl [38] and Cu(Gly)(H_2O)(NO_3) [40], which have compositions similar to **1**, but different structures. In these three cases carboxy-groups of aminoacids adopt apical–equatorial coordination mode and bridging O-atom is located not in the plane of chelate ring, whereas in **1** and Cu(AA)(H_2O)(ClO_4) [27] carboxy-groups have equatorial–equatorial coordination mode and oxygen atom of neighboring fragment is coordinated to copper(II) in the plane of Cu(AA) chelate ring.

3.2.2. Compound **2**

Crystal structure of compound **2** consists of infinite chains, formed by centrosymmetric trinuclear fragments $Cu_3(Gly)_4(H_2O)_2(NO_3)_2$ (Fig. 1b). In each fragment Cu(II) ions are linked by bridging carboxylate group of glycinate in *syn-anti* conformation with equatorial–equatorial coordination mode. In turn, these trinuclear blocks are connected by nitrate anions (two NO_3^- bridges, also in *syn-anti* conformation, between each two neighboring $Cu_3(Gly)_4(H_2O)_2^{2+}$ units), coordinated to two Cu(II) ions by two different oxygen atoms (Fig. 1c).

Table 2
Selected bond lengths and angles for **1** and **2**.

Compound **1**			
Bond	Length (Å)	Bond	Length (Å)
Cu(1)–N(1)	1.984(3)	Cu(1)–O(7)	1.968(3)
Cu(1)–O(1)	1.943(3)	Cu(1)–O(8)	2.326(4)
Cu(1)–O(2)	1.965(3)	Cu(1)–O(5)	2.811(8)
Angle	Value (°)	Angle	Value (°)
O(1)–Cu(1)–O(2)	170.98(15)	O(7)–Cu(1)–N(1)	169.39(15)
O(1)–Cu(1)–O(7)	89.20(14)	O(1)–Cu(1)–O(8)	91.08(15)
O(2)–Cu(1)–O(7)	85.08(14)	O(2)–Cu(1)–O(8)	95.51(15)
O(1)–Cu(1)–N(1)	85.36(12)	O(7)–Cu(1)–O(8)	86.53(16)
O(2)–Cu(1)–N(1)	99.15(13)	N(1)–Cu(1)–O(8)	102.65(15)
Compound **2**			
Bond	Length (Å)	Bond	Length (Å)
Cu(1)–N(1)	1.994(6)	Cu(2)–O(3)	1.938(5)
Cu(1)–O(1)	1.965(6)	Cu(2)–O(8)	1.972(5)
Cu(1)–O(6)	2.478(9)	Cu(2)–N(2)	1.976(6)
Cu(2)–O(2)	1.940(5)	Cu(2)–O(7)	2.472(8)
Angle	Value (°)	Angle	Value (°)
O(1)–Cu(1)–O(1)’	180.0(5)	O(3)–Cu(2)–O(2)	172.7(3)
O(1)–Cu(1)–N(1)	84.1(2)	O(3)–Cu(2)–O(8)	86.7(2)
O(1)–Cu(1)–N(1)	95.9(2)	O(2)–Cu(2)–O(8)	90.6(2)
O(1)–Cu(1)–N(1)	95.9(2)	O(3)–Cu(2)–N(2)	85.7(2)
O(1)–Cu(1)–N(1)	84.1(2)	O(2)–Cu(2)–N(2)	96.3(2)
N(1)–Cu(1)–N(1)	180.0(4)	O(8)–Cu(2)–N(2)	170.8(3)

Central Cu(II) ion in trinuclear unit $Cu_3(Gly)_4(H_2O)_2(NO_3)_2$ is located in distorted octahedral donor set, where the plane is formed by two chelate cycles involving O and N donor atoms of glycinate (Cu–N bonds are 1.994(6) Å, $Cu–O_{equat.}$ bonds are 1.965(6) Å), and axial positions are occupied by two oxygen atoms of nitrate ions ($Cu–O_{axial}$ bonds are 2.478(9) Å).

Terminal Cu(II) ions in $Cu_3(Gly)_4(H_2O)_2(NO_3)_2$ adopt square-pyramidal environments, containing in N and O donors or glycinate, coordinated water molecule and oxygen atom from carboxylate group in equatorial plane (Cu–N bonds are 1.976(6) Å, $Cu–O_{equatorial}$ bonds lie in range between 1.938(5) and 1.972(5) Å), and oxygen from nitrate-ion on the long axis ($Cu–O_{axial}$ bond is 2.472(8) Å). In addition, there are long Cu···O contacts (2.897(8) Å) between terminal Cu(II) ions of one $Cu_3(Gly)_4(H_2O)_2(NO_3)_2$ unit and oxygen atom of carboxy-group of glycinate from another $Cu_3(Gly)_4(H_2O)_2(NO_3)_2$ unit (from neighboring chain $Cu_3(Gly)_4(NO_3)_2(H_2O)_2$, this distance is very close to the sum of van der Waals radii of Cu^{2+} and oxygen atom).

The difference between Cu–D bonds (where D is donor atom) with equatorial and axial donor atoms in **2** evidences for a significant Jahn–Teller distortion of coordination polyhedra of these Cu(II) ions, which is important for magnetic data fitting, *vide infra*.

The distances between central and terminal Cu(II) ions in $Cu_3(Gly)_4(H_2O)_2(NO_3)_2$ are 5.061(1) Å, while the distance between two terminal Cu(II) ions is 10.123(1) Å. The separations between Cu(II) ions through bridging nitrate are 5.565(1) Å. The closest intermolecular Cu···Cu separation is 5.581(1) Å.

Isolated trinuclear units, similar to trinuclear "building blocks" in **2**, were found in complex $Cu_3(L)_3Cl_2(H_2O)$] (H_2L = 2-(diethylamino)-N-(2-[(diethylamino)acetyl]amino}ethyl)acetamide) [58].

On the basis of the comparison of crystal structures of Cu(II) complexes with α-aminocarboxylates it may be assumed that formation of chelate ring (Cu–N–C–C–O) favors to *syn-anti* conformation of bridging carboxylate, since in the complexes without such chelate cycle carboxyl group often acts as *syn–syn* bridge [54,59,60]. However, carboxyl-group of aminocarboxylate also can act as bridge in *anti–anti* conformation [43,54,61].

Usually donor atoms of α-aminocarboxylate in complexes $Cu(AA)_2(H_2O)_n$ occupy equatorial positions in coordination spheres of Cu(II) ion, and in such case formation of coordination polymer is possible only due to formation of "long bond" between Cu(II) and donor atom in axial position. In such case despite of possible formal assignment of compound $Cu(AA)_2(H_2O)_n$ to coordination polymer, any interactions between unpaired electrons of neighboring Cu(II) ions are expected to be negligible small, first of all due to location of magnetic orbital in equatorial plane and zero density of unpaired electron in direction of $Cu–O_{axial}$ bond.

In the case of compounds Cu(AA)(X)(L), polymerization of "building blocks" via Cu–O bonds can occur in such was that oxygen atom can occupy equatorial positions in coordination spheres of Cu(II) ions (though apical–equatorial coordination mode was also found, *vide supra*). However, general conclusion may be that the ratio Cu^{2+}:AA $\geqslant$ 1 should favor to formation of exchange-coupled coordination polymers of Cu(II) with α-aminocarboxylates (opposite is not true: this Cu^{2+}:AA ratio does not ensure that exchange interactions between Cu(II) ions would occur in resulting compound).

3.3. Circular dichroism

CD spectra of the complex **1** were measured in the wavelengths range 200 – 700 nm. The spectrum of solid sample (Fig. 2a)

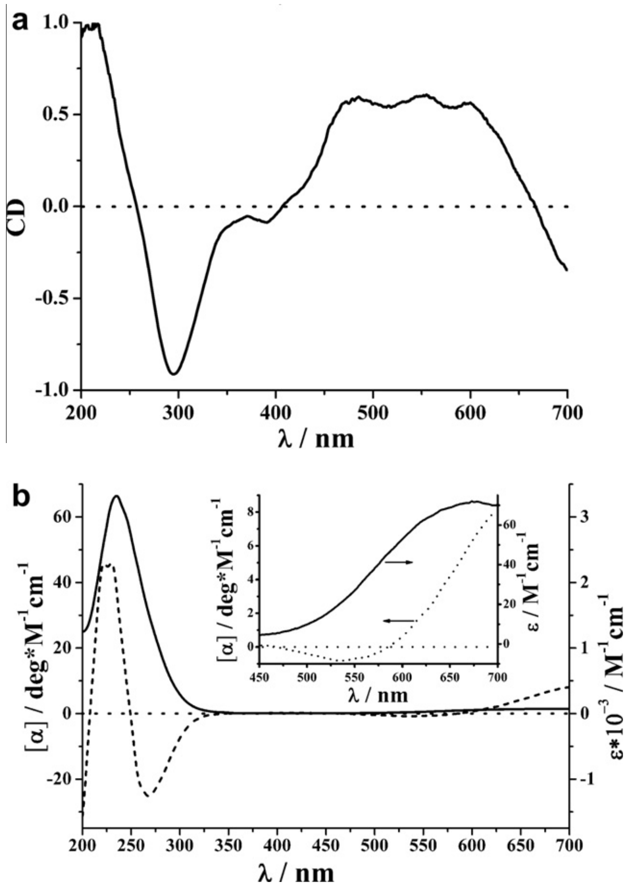

Fig. 2. (a) CD spectra in solid state and (b) CD (- - -) and absorption (—) spectra in water solution of **1**.

revealed six bands at 215, 295, 390, 485, 555 and 600 nm. The band at 215 nm with positive rotation may be assigned to associated with $\pi_n \rightarrow \pi^*$ transition of carboxy group of L-prolinate and this band is observed in the spectrum of pure L-proline at 210 nm [62]. Two bands in the spectrum of **1** at 295 and 390 nm with negative rotation may be assigned to $\sigma(N) \rightarrow b_1$ and $e_g \rightarrow \pi^*(O)$ charge transfer transitions, respectively [63]. Three bands in the range 450–650 nm with positive rotation are probably caused by Cu-centered d–d transitions [64], and their position is consistent with adsorption maximum of **1** in solid state ($\lambda_{max} = 695$ nm, see Section 2).

CD spectrum of **1** in solution (Fig. 2b) contains only two bands, which may correspond to charge transfer, at 225 and 265 nm. The band of prolinate is shifted to the long-wave region compared to its position in CD spectrum of solid sample. Vice versa, CD band arising due to ligand–metal charge transfer $\sigma(N) \rightarrow b_1$, is shifted to short-wave region. The positions of bands, associated with d–d transitions, also change in solution spectrum with respect to the positions of these bands in solid sample. Though absolute rotation of solid sample cannot be estimated, we can compare relative intensities of the bands, associated with d–d transitions, with the intensities of ligand-based band at 215 nm. In solution relative rotation of the bands, associated with d–d transitions, is much lower than in solid state. Clearly, polymeric structure of **1** is destroyed at dissolving, and from the differences between solid-state and solution spectra it may be concluded that Cu(II) donor set is changed. Such changes may involve coordination of extra H_2O molecules to Cu(II) or partial dissociation of $Cu(Pro)^+$ cations into Cu^{2+} and Pro^-, which should result in decrease of CD band intensity.

The positions of CD bands in solution spectrum of **1** also differ from the positions of CD bands in solution spectrum of $Cu(Pro)_2$, but the signs of rotation of these bands are the same [65].

3.4. Magnetic properties and ESR

The ESR spectra on **1** and **2**, at room temperature exhibit only one, relatively broad band. The g values for complexes **1** and **2** are 2.121(5) and 2.135(5), respectively.

The magnetization of polycrystalline samples of the complexes **1** and **2** was measured in the temperature range 2–300 K. For these complexes $\chi_M T$ (where χ_M is magnetic susceptibility per formula unit, and T is temperature in K) decreases with increase of temperature, which indicate that exchange interactions between copper(II) ions are of ferromagnetic nature.

For complex **1**, on cooling $\chi_M T$ product increases from 0.45 cm^3 K mol^{-1} at 300 K to 1.01 cm^3 K mol^{-1} at 2 K (Fig. 3a). The value of $\chi_M T$ at 300 K for **1** is consistent with expected room-temperature $\chi_M T$ for Cu(II) compounds with $g = 2.121$ (0.459 cm^3 K mol^{-1}).

The magnetic data were fitting by the model for one-dimensional Cu(II) chain with isotropic nearest-neighbor Heisenberg exchange interactions [66]. Magnetic susceptibility was calculated by the equation:

$$\chi_M = \frac{Ng^2\mu_B^2}{4kT}\left(\frac{A}{B}\right)^{2/3} \text{ where}$$

$$A = 1.0 + 5.797991y + 16.902653y^2 + 29.376885y^3 + 29.832959y^4 + 14.036918y^5$$

$$B = 1.0 + 2.7979916y + 7.0086780y^2 + 8.6538644y^3 + 4.5743114y^4$$

and $y = J/kT$, the spin Hamiltonian being defined as

$$\hat{H} = -2J\sum_i \hat{S}_i\hat{S}_{i+1}$$

where J is the magnetic coupling parameter and g is the Zeeman factor of spins of Cu(II) ions, which is considered to be isotropic ($g_x = g_y = g_z$). The best fit of $\chi_M T$ versus T (Fig. 3a) corresponded to $J = +1.22(1)$ cm^{-1}, $g = 2.148(2)$ and tip $= 3 \times 10^{-6}$, with $R^2 = 3.9 \times 10^{-5}$ (hereinafter $R^2 = \Sigma(\chi T_{calc.} - \chi T_{obs.})^2/\Sigma(\chi T_{obs.})^2$). g factor is consistent with g, extracted from room-temperature ESR spectrum (2.121(5)).

For complex **2**, on cooling, $\chi_M T$ product increases from 1.25 cm^3 K mol^{-1} at 300 K (expected value of $\chi_M T$ is 1.282 cm^3 K mol^{-1} for trinuclear Cu(II) complex with $g = 2.135$) to 1.79 cm^3 K mol^{-1} at 2 K (Fig. 3b).

Magnetic data fitting taking into account all possible interactions for **2** is difficult because of complexity of this system (infinite polymer made from trinuclear blocks, or even 2D polymer, if all possible interactions are taken into account, *vide supra*). To estimate numerical value of exchange coupling parameter, simple model was used, which takes into account three interacting Cu(II) ions with $S = 1/2$ for each, which are linked by carboxy-groups of aminoacids.

Taking into account significant Jahn-Teller distortion of coordination environment of all Cu(II) ions (X-ray structures discussion, *vide supra*), it may be concluded that magnetic orbital ($d(x^2-y^2)$) is located in CuO_2N_2 plane in the case of Cu(1) atom, where O- and N-atoms are oxygen atoms from carboxy- and nitrogen atoms of amino-groups from glycinate, and such orbital in the case of Cu(2) ion is located in CuO_3N plane, where O- and N-atoms are oxygen atoms of carboxy- and nitrogen atoms of amino-groups

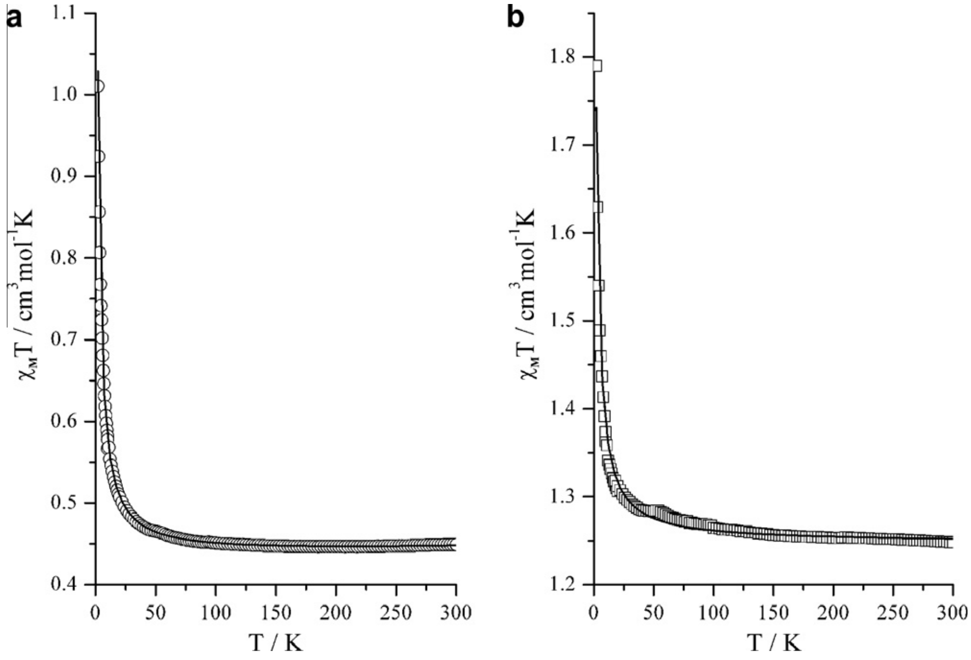

Fig. 3. The curves $\chi_M T$ vs. T for complexes **1** (a) and **2** (b). Solid lines correspond to the best fits with parameters from text.

of glycine and of water molecule. Thus, it is possible to neglect by exchange interactions between Cu(II) ions through nitrate anion because d-orbital of Cu(II) directed towards bridging nitrate (d(z^2)) does not contain unpaired electrons [67]. Also, exchange interactions between Cu(II) ions from different chains through long inter-trimer Cu···O contact or hydrogen bonds are expected to be negligible compared to intramolecular Cu···Cu interactions.

In this approximation, it is also reasonable to neglect the coupling between terminal Cu(II) ions from trinuclear unit in **2**, since the distance between terminal Cu(II) ions in such trinuclear unit is two times higher (10.123(1) Å) than the closest distance between neighboring Cu(II) ions (5.061(1) Å). Thus, magnetic data for complex **2** may be described in the frames of simple model for trinuclear complex:

$$\hat{H} = -2J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3) + \mu_B gH(\hat{S}_1 + \hat{S}_2 + \hat{S}_3)$$

where $\hat{S}_1$, $\hat{S}_2$ and $\hat{S}_3$ are spin operators of the three copper(II) ions ($S_1 = S_2 = S_3 = 1/2$), g is the Zeeman factor of spins of Cu(II) ions, which is considered to be isotropic ($g_x = g_y = g_z$) and identical for the three ions for simplicity. The best fit of $\chi_M T$ versus T (Fig. 3b) using the expression [68]

$$\chi_M T = \frac{N\mu_B^2 g^2}{4k}\,\frac{1 + \exp(\frac{2J}{kT}) + 10\exp(\frac{3J}{kT})}{1 + \exp(\frac{2J}{kT}) + 2\exp(\frac{3J}{kT})}$$

corresponded to $J = +1.17(2)$ cm^{-1} and $g = 2.106(1)$ with $R^2 = 2.6 \times 10^{-5}$. g factor is consistent with g, extracted from room-temperature ESR spectrum, which was equal to 2.135(5).

The spin levels of trinuclear unit can be represented by $|S_T, S^*, S_2, M_{ST}\rangle$, where $\hat{S}^* = \hat{S}_1 + \hat{S}_3$ and $\hat{S}_T = \hat{S}^* + \hat{S}_2$. With such labeling the energy of levels can be expressed as: $E(|S_T, S^*, S_2, M_{S_T}\rangle) = -J(S_T(S_T{+}1) - S^*(S^* + 1) - S_2(S_2 + 1)) + g\mu_B HM_{S_T}$. In zero magnetic field the trinuclear unit has three spin levels, energies of which are equal to $-J$, 0 and $2J$ with degeneracy 4, 2 and 2, respectively.

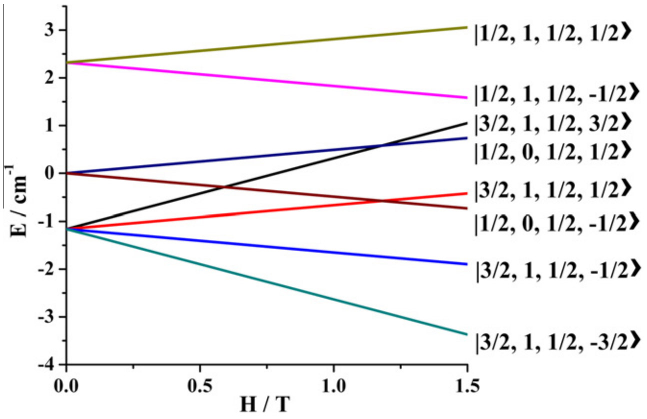

Fig. 4. The energy of spin levels in magnetic field for **2**.

Table 3
Magnetic properties of selected Cu(II) complexes with bridging carboxylate group in *syn-anti* conformation with equatorial–equatorial coordination mode. All J values are recalculated for Hamiltonian $\hat{H} = -2J\hat{S}_1\hat{S}_2$.

Compound[a]	J (cm^{-1})	g	Ref.
1	+1.22(1)	2.148(2)	This work
2	+1.17(2)	2.106(1)	This work
$NaCu_6(Pro)_8(ClO_4)_5(CH_3OH)(H_2O)$	+0.56	2.17	[33]
$NaCu_6(Hpro)_8(ClO_4)_5 \cdot 4H_2O$	+1.39	2.11	[33]
$NaCu_6(Thr)_8(H_2O)_2(ClO_4)_5 \cdot 5H_2O$	+0.43	2.01	[32]
$NaCu_6(Gly)_8(ClO_4)_3(H_2O)(ClO_4)_2$	+1.79	2.16	[35]
$Cu(Ala)(im)(H_2O)(ClO_4)$	+2.25	2.20	[27]
$Cu(Ala)(pz)(ClO_4)$	+1.79	2.17	[27]
$Cu(Phe)(im)(H_2O)(ClO_4)$	+2.50	2.22	[27]
$Cu(Gly)(H_2O)(ClO_4)$	+1.46	2.21	[27]
$Cu(Gly)(pz)(ClO_4)$	+2.73	2.19	[27]
$Cu(Pro)(pz)(ClO_4)$	+2.59	2.18	[27]
$Cu_4(L1)_4(H_2O)_4 \cdot 3.5NO_3 \cdot 0.5N_3$	+3.44	2.12	[57]
$Cu_4(O_2CCH_2CO_2)_4(L2)] \cdot 7H_2O$	+6.75	2.14	[63]
$[[Cu_2(pic)_3(H_2O)]ClO_4]_n$	+1.74; +0.19	2.034	[69]
$[[Cu_2(pic)_3(H_2O)]BF_4]_n$	+0.99; +0.25	2.044	[69]
$[Cu_2(pic)_3(H_2O)_2(NO_3)]_n$	+1.19	2.05	[69]

[a] HproH = 4-hydroxy-L-proline; ProH = proline; ThrH = threonine; GlyH = glycine; AlaH = alanine; PheH = phenylalanine; im = imidazole; pz = pyrazole; L1 = Schiff base from pyridine 2-carboxaldehyde and anthranilic acid; L2 = hexamethylenetetramine; Hpic = 2-picolinic acid.

These levels are split in magnetic field by Zeeman interaction (Fig. 4). Since *J* value for trinuclear unit is positive, this unit has ground state with $S_T = 3/2$.

Carboxylate group in *syn-anti* conformation with equatorial–equatorial coordination mode usually transfers ferromagnetic interactions. *J* values of some Cu(II) complexes with bridging carboxylate group in *syn-anti* conformation with equatorial–equatorial coordination mode are presented in Table 3. Typically *J* values are less than 3 cm^{-1} (hereinafter for comparison *J* values are recalculated for Hamiltonian $\hat{H} = -2J\hat{S}_1\hat{S}_2$). *J*-values for compounds **1** and **2** are consistent with the values, found for similar systems (Table 3). At the same time there are few examples when carboxylate in *syn-anti* configuration transfers antiferromagnetic exchange interactions. In all these cases carboxy-group has equatorial-axial coordination mode [36,69,70]. Unlike this, bridging carboxy group in *syn–syn* configuration may transfer strong antiferromagnetic interactions, for example, for $[\mathrm{Cu(CH_3COO)_2(H_2O)}]_2$ *J* is $-143\ \mathrm{cm}^{-1}$ [71].

4. Conclusions

Two new 1D coordination polymers were isolated and characterized – one was built from $\mathrm{Cu(L\text{-}Pro)}^+$ units, and the second was made from trinuclear $\mathrm{Cu_3}$ blocks $\mathrm{Cu_3(Gly)_4(H_2O)_2(NO_3)_2}$. It was shown that $\mathrm{Cu(L\text{-}Pro)(ClO_4)(H_2O)_2}$ rotated polarized light. Relative rotation of polarized light for the bands associated with d–d transitions (compared to rotation in UV region, associated with carboxy-group of L-prolinate), was higher in solid state than in solution, which along with changes of the positions of bands in CD spectra at dissolving of $\mathrm{Cu(L\text{-}Pro)(ClO_4)(H_2O)_2}$ may evidence for changes of Cu(II) donor set. In both compounds $\mathrm{Cu(L\text{-}Pro)(ClO_4)(H_2O)_2}$ and $\mathrm{Cu_3(Gly)_4(H_2O)_2(NO_3)_2}$ Cu(II) ions were linked through carboxy-groups in *syn-anti* configuration, donor atoms of which occupied equatorial positions in coordination spheres of Cu(II) ions, which propagated ferromagnetic exchange interactions. The magnitude of *J* was comparable with *J* values in similar carboxylato-bridges systems.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.06.052.

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