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Vibrational spectra, electronic excited states and magnetic properties of the copper(II) ions in alkylaminoacetylurea complexes

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Copper(II) complexes with alkylaminoacetylurea ligands were synthesized and studied by means of IR, Raman, electron absorption and luminescence spectroscopies, as well as by ESR and magnetic methods. The spectroscopic and magnetic studies were performed in the 4–300 K and 1.9–300 K temperature ranges, respectively. The Cu^{2+} ions in these complexes are four coordinated having distorted square-planar surroundings. The dependence of the spectroscopic parameters on the alkyl radical of the ligand is discussed. At low temperatures, very weak ferromagnetic interactions are observed for the C_3 and C_5 alkyls, and an antiferromagnetic one is observed for the remaining complexes, with C_4 and C_6–C_{18} alkyls.

Key words: *copper(II) complexes; alkylaminoacetylureas; IR; Raman; UV absorption spectra; luminescence; ESR; magnetic properties*

1. Introduction

Copper ions play a vital role in a number of biological processes. They are recognised to be plant nutrients and serve as catalysts [1] in plant enzyme systems and as urease inhibitors [2]. Cu^{2+} complexes with macrocyclic polyamines act as mimics of metalloenzyme active sites [3–8], redox-active species for electrocatalytic processes [9–14] or photoredox molecular devices for converting the light energy into other forms [15–19]. Complexes of transition metal ions with urea were the subjects of several works [20–23]. A considerable interest of these studies has been focused on their interaction with drugs administered for therapeutic purposes.

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Our present work concerns the structure, spectroscopic and magnetic properties of copper(II) compounds with alkylaminoacetylureas. These ligands have been synthesised for the first time [24, 25] and their complexes have not been studied in detail. Our preliminary studies showed that these urea derivatives effectively extract Cu^{2+} ions from diluted acid solutions formed in the flotation process of very poor copper deposits [26].

2. Experimental

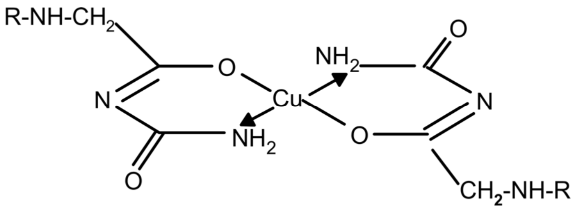
Synthesis of alkylaminoacetylurea copper(II) complexes. Syntheses of the copper(II) complexes with alkylaminoacetylureas have been described in our previous paper [26], where the chemical and magnetic properties were reported for a few derivatives. Their chemical compositions, colours, formulae, molecular masses and melting points are presented in Table 1.

Table 1. Complex compounds of alkylaminoacetyl ureas (Scheme 1) with copper(II)

No.	Alkyl radical (R) Molecular formula Molecular mass	Colour	Melting point [°C]	Composition	
				Calculated [%]	Found [%]
1	2	3	4	5	6
1	C_3H_7 $C_{12}H_{24}N_6O_4Cu$ 379.91	violet	193	C 37.94 H 6.37 N 22.12	C 38.08 H 6.33 N 22.03
2	C_4H_9 $C_{14}H_{28}N_6O_4Cu$ 407.95	rose	192	C 41.22 H 6.92 N 20.60	C 41.18 H 6.93 N 20.61
3	C_5H_{11} $C_{16}H_{32}N_6O_4Cu$ 436.01	violet	187	C 44.07 H 7.40 N 19.28	C 43.98 H 7.40 N 19.17
4	C_6H_{13} $C_{18}H_{36}N_6O_4Cu$ 464.07	violet-red	165	C 46.58 H 7.82 N 18.11	C 46.80 H 7.57 N 17.91
5	C_7H_{15} $C_{20}H_{40}N_6O_4Cu$ 492.12	violet-rose	163D	C 48.55 H 8.19 N 17.08	C 48.55 H 8.54 N 16.90
6	C_8H_{17} $C_{22}H_{44}N_6O_4Cu$ 520.18	violet-blue	155	C 50.79 H 8.53 N 16.16	C 50.72 H 8.98 N 15.99
7	C_9H_{19} $C_{24}H_{48}N_6O_4Cu$ 548.23	dark rose	152	C 52.28 H 8.83 N 15.33	C 52.75 H 9.12 N 15.21
8	$C_{10}H_{21}$ $C_{26}H_{52}N_6O_4Cu$ 576.28	blue	152	C 54.18 H 9.10 N 14.58	C 53.94 H 9.52 N 14.16

Table 1 continued

1	2	3	4	5	6
9	$C_{12}H_{25}$ $C_{30}H_{60}N_6O_4Cu$ 632.39	dark rose	150	C 56.98 H 9.56 N 13.29	C 56.66 H 9.91 N 13.26
10	$C_{14}H_{29}$ $C_{34}H_{68}N_6O_4Cu$ 688.59	rose	146	C 59.31 H 9.96 N 12.21	C 59.30 H 10.27 N 12.10
11	$C_{16}H_{33}$ $C_{38}H_{76}N_6O_4Cu$ 744.61	rose	143	C 61.29 H 10.29 N 11.29	C 61.60 H 10.27 N 11.40
12	$C_{18}H_{37}$ $C_{42}H_{84}N_6O_4Cu$ 800.72	light rose	137	C 63.00 H 10.57 N 10.50	C 63.30 H 10.75 N 10.80



Scheme 1. Alkylaminoureas under investigation (see Table 1)

Spectroscopic studies. Electronic absorption spectra of the copper complexes and free ligands (non-coordinated alkylaminoureas) were recorded at room temperature in ethyl alcohol solutions and Nujol mulls with JASCO V-570 UV/VIS and Varian Cary 5E UV/VIS/NIR spectrophotometers with a resolution of 0.5 nm. The mulls for all samples were prepared using the same ratio (2:1) of the complex to Nujol.

The photoluminescence spectra were recorded with the 366 nm excitation (the Hg line) and the emission lifetimes with the 337 nm excitation (2 ns nitrogen laser). A spectrometer consisting of a SPM-s Carl Zeiss Jena monochromator, a cooled GaAs R 943-03 Hamamatsu photomultiplier, a gated photon counter of the SR400 Stanford research system, a box integrator of the Stanford research system and the PC were used. The emission spectra obtained in this arrangement were compared to those obtained at 260 nm excitation from the Xenon lamp and recorded with the SSF1 spectrometer (produced by LOMO, Sankt Petersburg).

Room temperature Fourier transform IR spectra (FTIR) were recorded in the 4000 –30 cm^{-1} range using the BIORAD 575 spectrophotometer with a 2 cm^{-1} resolution. Room temperature FT Raman spectra (FTRS) were recorded in the 4000–80 cm^{-1} range using a BRUKER 110/S spectrometer with the Nd:YAG excitation and 2 cm^{-1} resolution. The Gaussian deconvolution of the spectra was made using the Origin 7.0 computer program.

Magnetic studies. The ESR spectra were recorded at X-band with an ESP 300 Bruker spectrometer equipped with a ER 035M Bruker NMR gaussmeter and a HP

5350B Hewlett-Packard microwave frequency counter. The measurements were made at room temperature. The ESR measurements at 5 K were performed with a conventional X-band reflection spectrometer equipped with an Oxford Instruments ESR-900 helium flow cryostat. The magnetic studies of the polycrystalline samples were performed for 12 compounds using a quantum design SQUID magnetometer (MPMS-5 type) at the magnetic field of 0.5 T in the temperature range 1.9–300 K. The magnetization in function of magnetic field was measured in the range 0–5 T. The corrections consist in subtracting the sample holder signal and that for diamagnetism of the constituent atoms, calculated using Pascal's constants [27]. The value 60×10^{-6} $\mathrm{cm^3\cdot mol^{-1}}$ was used for the temperature-independent paramagnetism of copper(II) ions. The effective magnetic moment was calculated from the equation $\mu_{\mathrm{eff}}=2.83(\chi_{\mathrm{m}}T)^{1/2}$ [μ_{B}].

3. Results

3.1. FT-IR and Raman spectra

The FT-IR and FT-Raman spectra of the representative complex under study, namely $\mathrm{Cu(C_{14}H_{28}N_6O_4)}$, are shown in Fig. 1. They are compared to the spectra of a free ligand recorded in the same conditions. Noticeable changes in the IR and Raman spectra are observed in the regions of vibrations of C=O and NH_2 groups. Upon coordination, these bands shift towards longer wavelengths, indicating formation of new bonds with copper ions. The most characteristic changes are observed for the following bands: $\nu(\mathrm{NH_2})$ Raman doublet at 3392 + 3315 $\mathrm{cm^{-1}}$ → 3170 $\mathrm{cm^{-1}}$ and the IR band at 3317 $\mathrm{cm^{-1}}$ → 3164 $\mathrm{cm^{-1}}$; $\nu(\mathrm{C{=}O})$ Raman band at 1697 $\mathrm{cm^{-1}}$ → 1642 + 1612 $\mathrm{cm^{-1}}$, the doublet at 1721 + 1683 $\mathrm{cm^{-1}}$ → 1637 $\mathrm{cm^{-1}}$ and the 1598 $\mathrm{cm^{-1}}$ band → 1567 $\mathrm{cm^{-1}}$; $\rho(\mathrm{NH})$ IR band at 1416 $\mathrm{cm^{-1}}$ → 1353 + 1347 $\mathrm{cm^{-1}}$. In the 800–1200 $\mathrm{cm^{-1}}$ region, several bands of dicarbonylimide –CO–NH–CO– groups are observed [28].

The most informative changes occur in the 60–500 $\mathrm{cm^{-1}}$ region, in which the stretching and bending vibrations of the coordination polyhedron are expected. Let us assume, in the first step, that the structure of the $\mathrm{CuO_2N_2}$ unit is described by the D_{2h} symmetry, i.e. the Cu–O and Cu–N bonds form two bond pairs of the same length, and the Cu ion lies on the plane formed by the oxygen and nitrogen atoms with the inversion centre in this plane. Such a structure can be derived from the electron absorption studies of the complex in the alcoholic solution (see below). The vibrational normal modes of this unit are described by the representation $2A_{1g} + B_{1g} + 2B_{1u} + 2B_{2u} + 2B_{3u}$ in which the stretching vibrations $\nu(\mathrm{CuN_2})$ and $\nu(\mathrm{CuO_2})$ correspond to the $A_{1g} + B_{3u}$ and A_{1g} + B_{2u} representations, respectively. Three types of bending vibrations, $\delta(\mathrm{NCuN})$, $\delta(\mathrm{OCuO})$ and $\delta(\mathrm{NCuO})$, correspond to the remaining representations ($B_{1g} + 2B_{1u} + B_{2u} + B_{3u}$). Because g and u modes are Raman and IR active, respectively, two bands of the stretching vibrations are expected in both spectra. For the bending modes one Raman band and four IR bands should be observed for the considered

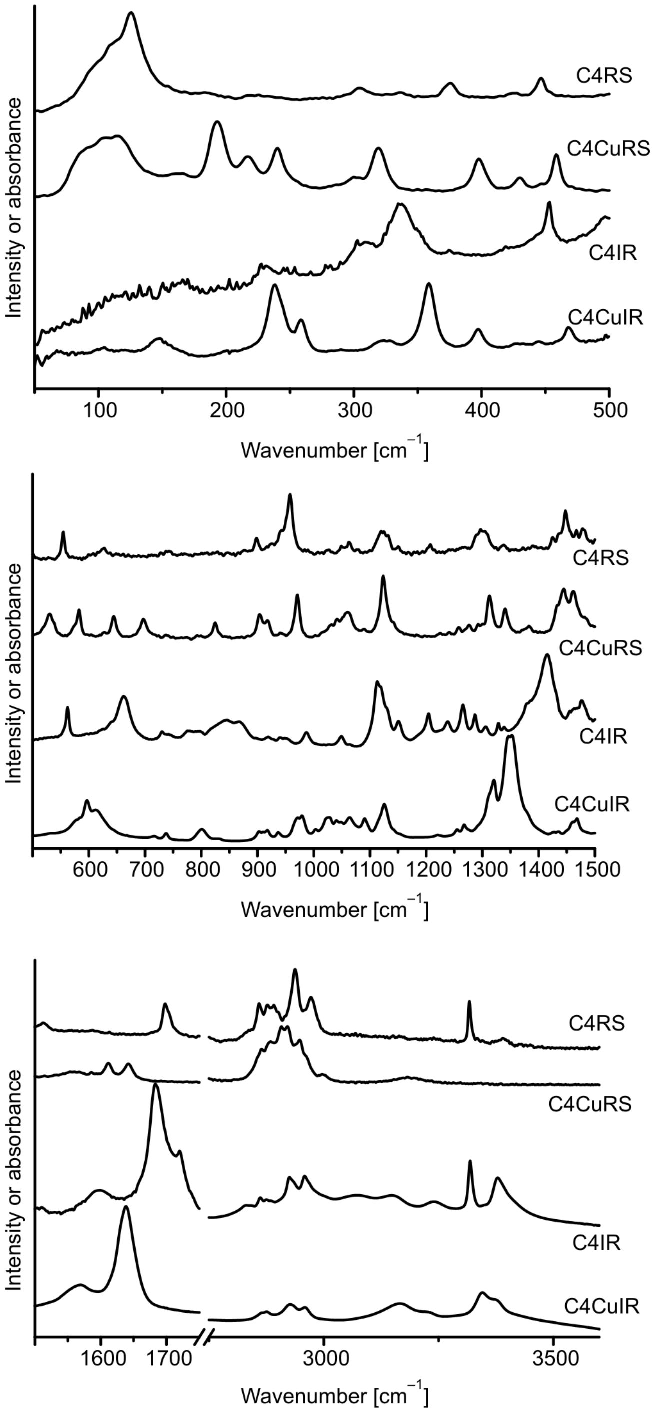


Fig. 1. FT-IR (IR) and FT-Raman (RS) spectra of the $Cu(C_{14}H_6N_4)$ complex (No. 2 in Table 1; C_4H_9 group)compared to the free ligand spectra

polyhedron of the D_{2h} symmetry. When the copper atom is situated above the N_2O_2 plane, the C_{2v} symmetry should be adopted for the discussion of the vibrational dynamics of the orthorhombic pyramidal polyhedron. The vibrations of this system are described by the representation $4A_1 + A_2 + 2B_1 + 2B_2$. These nine modes can be characterized as four stretching $\nu(CuN_2)$ $(A_1 + B_1)$ and $\nu(CuO_2)$ $(A_1 + B_2)$ modes, as well as five bending δ(NCuN), δ(OCuO) and δ(NCuO) $(2A_1 + A_2 + B_1 + B_2)$ modes. For the C_{2v} symmetry, all modes are active in the Raman spectra, whereas the A_1, B_1 and B_2 modes are active also in the IR spectra. Therefore, four bands are expected in both spectra in the stretching mode regions whereas five Raman bands and four IR bands should be observed in the bending modes region. A further lowering of the symmetry to C_2, C_s or C_1 makes all nine bands active in the IR and Raman spectra. These considerations provide insight into a real structure of the CuN_2O_2 coordination polyhedron in the complexes studied here.

Upon comparing the FTIR and Raman spectra of the free ligand and its Cu-complex in the range 60–500 cm^{-1} (Fig. 1), it is clearly seen that several new bands appear in this region. Two Raman lines at 430 (medium) and 398 cm^{-1} (strong) and the IR counterparts at 425 (weak) and 397 cm^{-1} (medium) correspond to two $\nu(CuN_2)$ modes. Two other bands in the IR spectrum at 358 (strong), 330 cm^{-1} (weak) and 320 cm^{-1} (strong) should be assigned to $\nu(CuO_2)$ stretching modes. Bending vibrations of the considered unit can be easily assigned to the Raman lines at 249, 217, 195 and 164 cm^{-1} and IR bands at 259, 245 (shoulder), 238, 220 (shoulder) and 148 cm^{-1}. The wavenumbers of these modes are in good agreement with those reported in the literature for the copper(II) complexes with nitrogen and oxygen donor ligands ([29–32] and references therein). It should be noted that nine IR bands and eight Raman lines are observed in this region that could be assigned to the vibrations of the CuN_2O_2 unit. This result means that the coordination polyhedron of the studied complexes is a distorted orthorhombic pyramid and its symmetry could be described by the C_2, C_s or even C_1 point group.

3.2. Near infrared, visible and ultraviolet absorption spectra

The electronic spectra of the complexes studied in the solid state and in the ethyl alcohol solution are shown in Figs. 2 and 3. Figure 3 also shows deconvolution of the spectra into Gaussian components. As a representative example, a $C_{38}H_{76}N_6O_4Cu$ sample, with the $C_{19}H_{39}N_3O_2$ ligand and the R = $C_{16}H_{33}$ alkyl radical, was chosen. The reference spectrum of a free (non-coordinated) ligand is also shown for the comparison. The spectra generally consist of seven components. In order to make the discussion easier, the observed bands were labelled as $N = \nu_1$–ν_7 (in the order of increasing energy). These data are collected in Table 2. Three types of electronic transitions, appearing in different energy regions, are expected for the copper(II) complexes studied. These are d–d transitions, ligand-to-metal charge transfer (LMCT) and charge transfer inside the electronic shell of the ligand (CT). The electronic spectrum of the free ligand (Fig. 3) reveals the CT transitions of the alkylaminoacetylureas in the UV region, i.e., above 30 000 cm^{-1}. Their energies are significantly higher than those observed for the two other types of transitions. The spectra of the free and coordinated ligands show three strong bands at ca. 45 000–49 000 cm^{-1}, 40 000 cm^{-1} and 30 000 cm^{-1}. These bands correspond to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ CT transitions inside the electron shell of the ligand. The appearance of few components for the CT transitions results from the presence of several chromophores in this molecule: two carbonyl and three amino groups.

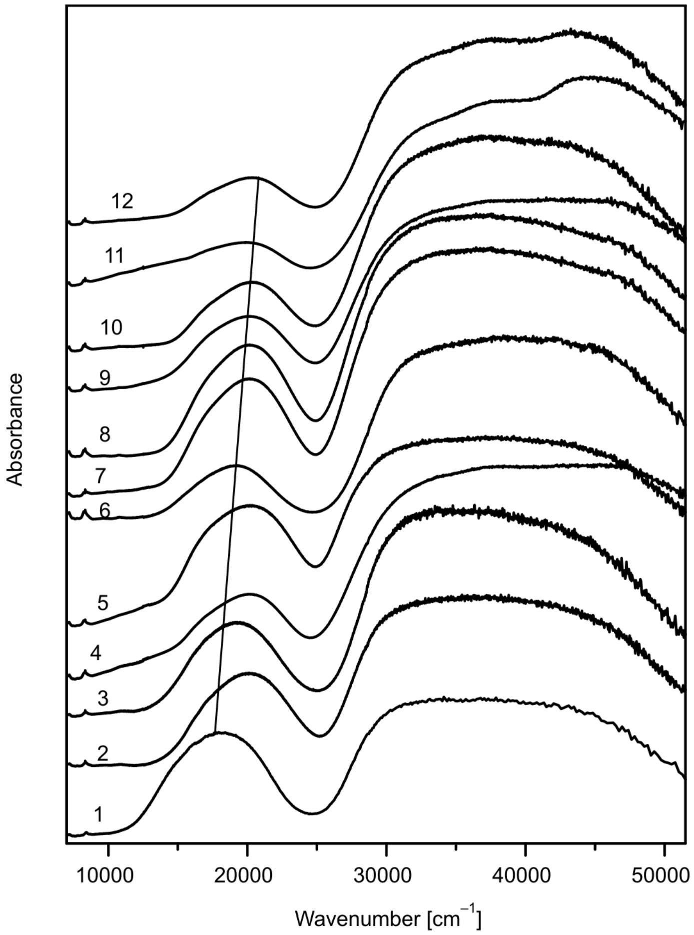


Fig. 2. Room temperature electronic absorption spectra of copper(II) complexes with alkylaminoacetylureas; in the solid state the sample specification as in Table 1. The experimental error of the determination of the positions of band maxima does not exceed 10 cm^{-1}

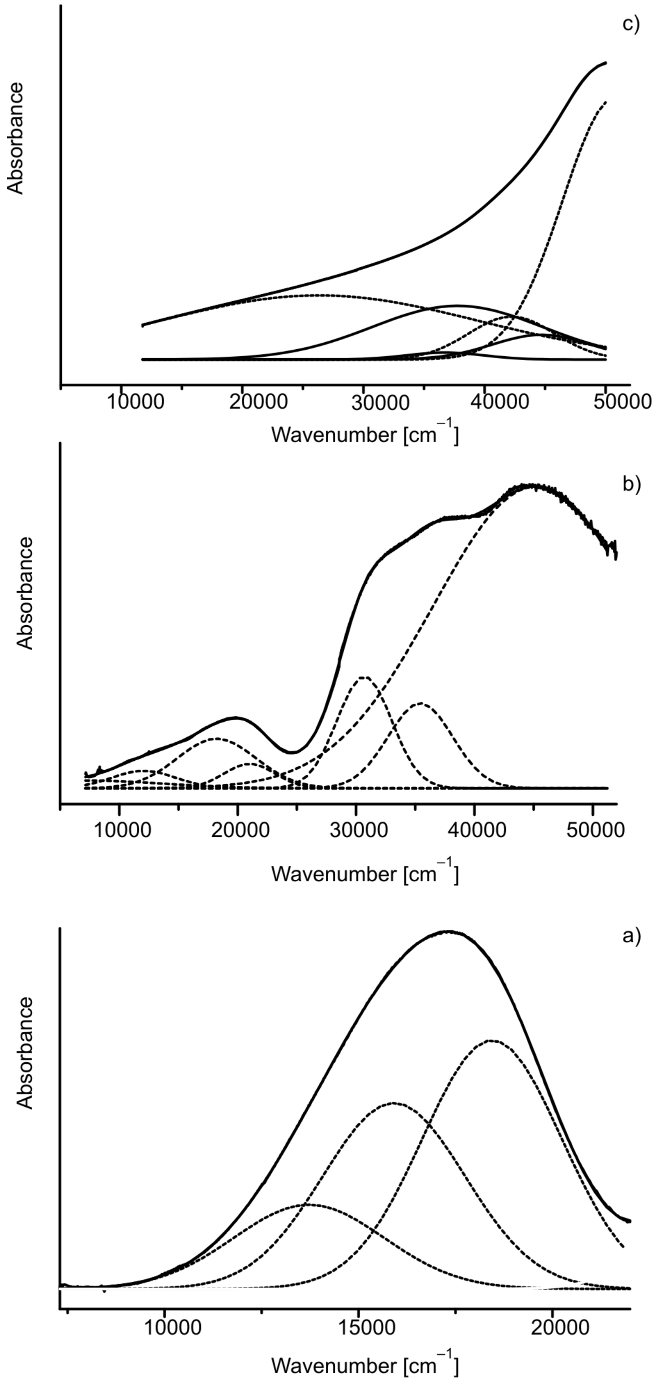


Fig. 3. The Gaussian deconvolution of the representative absorption spectrum of $C_{38}H_{76}N_6O_4Cu$ complex int the solid state (a) and ethanol (b) and its comparison with the spectrum of a free $C_{19}H_{39}N_3O_2$ ligand (c)

The LMCT transitions in the complexes studied appear at about 29 000 and 22 000 cm^{-1}. The spectra of the free ligands do not show any band in this region. For the complex compounds these transitions appear as medium intensity bands. The alkylaminoacetylureas have low lying empty orbitals of the non-bonded electrons as well as empty π-antibonding orbitals connected with double bonds of the ligand. Therefore, the components of these transitions, observed at about 29 000 and 22 000 cm^{-1}, can be denoted as N→Cu and O→Cu LMCT because the complexation of the ligand to the copper ion occurs through oxygen and nitrogen atoms.

Table 2. Positions of maxima of the absorption bands for twelve complexes studied (data obtained from their Gaussian deconvolutions)[cm^{-1}]

R	d–d transitions			N→Cu ligand to metal CT	O→Cu ligand to metal CT	$n\to\pi^*$ CT of the ligand	$\pi\to\pi^*$ CT of the ligand
C_3H_7	7680		15780	19980	29290	32710	43200
C_4H_9	8290		17840	21420	29790	34010	44550
C_5H_{11}		10350	17210	20770	29900	33620	42180
C_6H_{13}		12520	18300	21560	30120	35710	45870
C_7H_{15}		12220	17560	21410	28600	32570	43190
C_8H_{17}	7700	11340	17980	21060	30350	34040	43660
C_9H_{19}	7670	12020	18090	21830	29330	33980	45500
$C_{10}H_{21}$	8710		18120	21630	29460	34150	45180
$C_{12}H_{25}$	8130	12860	18010	21670	29710	34220	45770
$C_{14}H_{29}$	8630	12380	18290	21620	29810	33790	43130
$C_{16}H_{33}$	7290	12070	18220	21000	30690	35430	45200
$C_{18}H_{37}$	8570	12750	17410	21140	30040	33850	43790

The d-d transitions of the complexes studied are observed in the NIR region from 8000 to 18 000 cm^{-1}. The intensities of these bands are a few orders of magnitude lower than those of the CT transitions. Two clear bands appear in this region at about 17 500 and 12 000 cm^{-1}. The third component of this contour can be obtained from the Gaussian deconvolution. This procedure locates the third component at about 8000 cm^{-1}. Among the electronic transitions characteristic of the Cu^{2+} ion, the band at about 17 500 cm^{-1} is the most informative since it has relatively high intensity and is clearly visible as a shoulder on the slope of the LMCT contour.

In the discussion of the observed electron spectra, the C_{2v} symmetry derived from the vibrational studies should be taken into account in the first approximation. The order of the 3d electronic states for related systems have been established by means of polarized crystal spectra and theoretical calculations based on the angular overlap model (AOM) [33–37]. The order of the 3d orbitals, as derived by these authors, for the C_{2v} symmetry was $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{yz} > d_{xz}$. The selection rules of magnetic dipole transitions predict that the $d_{xy} \to d_{x^2-y^2}$, $d_{yz} \to d_{x^2-y^2}$, and $d_{xz} \to d_{x^2-y^2}$ transitions are allowed, while the

$d_{z^2} \to d_{x^2-y^2}$ transition is forbidden. Therefore, in the spectra recorded by us, three bands are apparently in agreement with the experiment. The bands at 17 500, 12 000 and 8 000 cm–1 can be assigned to the $d_{xz} \to d_{x^2-y^2}$, $d_{yz} \to d_{x^2-y^2}$ and $d_{xy} \to d_{x^2-y^2}$ transitions, respectively. This result indicates that symmetry of the coordination polyhedron for the studied complexes in the solid state is not higher than C_{2v}, i.e. the coordination polyhedron is a distorted CuN_2O_2 pyramid. The energy ranges of the electron transitions obtained in the present work fit well with the data presented in the literature [37–39].

The spectra of the complexes in ethyl alcohol solutions exhibit a splitting of the 17 500 cm^{-1} band into a doublet at 15 910 and 18 440 cm^{-1}. This result indicates that three components are observed in the 10 000–20 000 cm^{-1} range at 13 720, 15 910 and 18 440 cm^{-1}. The extinctions of these bands are as follows: 45.9, 80.6 and 81.2 [$dcm^3 \cdot mol^{-1} \cdot cm^{-1}$], respectively. Low intensities of these bands suggest that the *trans*-CuN_2O_2 unit may have a symmetry being a slight modification of a centrosymmetric group.

3.3. Luminescence spectra

Luminescence spectra of the complexes studied at room temperature (RT) are presented in Fig. 4. The comparison of the RT spectra with those recorded at 15 K (LT) for the representative samples is shown in Fig. 5.

The RT emission spectra consist of two transitions: a broad and strong band at ca. 14 000 cm^{-1} and another one, of weak intensity, observed at ca. 17 000 cm^{-1} as a shoulder on the slope of the former band. Its behaviour upon the temperature decrease depends on the R radical mass. For the C_{10} sample, the emission has a nearly constant position. For the C_{14} sample the maximum of the emission shifts from 14 000 cm^{-1} at RT to 15 800 cm^{-1} at LT. The largest shift is observed for the C_6 sample ranging from 10 000 to 18 000 cm^{-1}. The emissions at 17 000 and 14 000 cm^{-1} can be described, as before, by $d_{x^2-y^2} \to d_{xz}$ and $d_{xy} \to d_{xz}$, respectively. The large width of these bands suggests that more than one site could appear in the complexes studied. This problem will be discussed in the later part of this paper. The decay curves obtained for the complexes studied from the time resolved experiment are non-exponential, giving two life times of a few ns order. This suggests a different symmetry of some Cu^{2+} ions in these materials.

The electronic transitions observed in the absorption and emission spectra can be compared with the complexes studied. The dependence of their energies on the R-radical mass (i.e. the length of the R radical chain) is shown in Fig. 2 (the straight line between the band maxima for the samples 1 and 12). Energy increases according to a general trend, although the course is irregular. For the lighter ligands some differences in the transition energies are observed, and stabilization occurs for the ligands above C_{10}. This result shows that the mass and length of the radical chain in the ligand influence, to some extent, the energy of the electronic levels and the properties of the complexes studied.

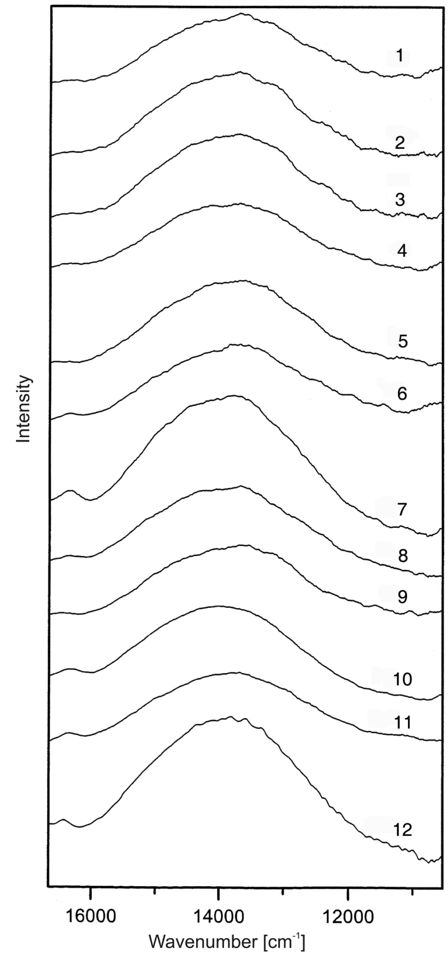


Fig. 4. Room temperature emission spectra of Cu^{2+} complexes studied (λ_{exc} = 488 nm); the sample specification as in Table 1. The experimental error of the determination of the positions of band maxima does not exceed 10 cm^{-1}

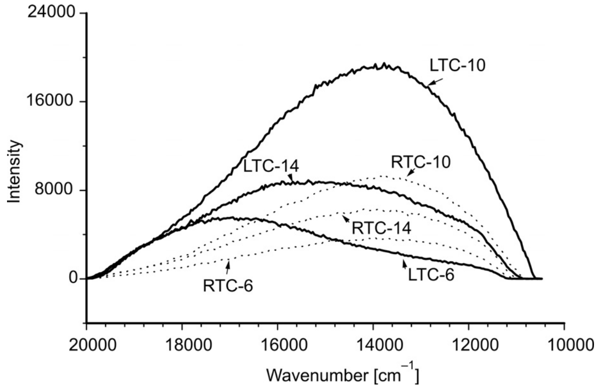


Fig. 5. Comparison of the room (RT) and liquid helium (LT) temperature emission spectra for representative samples: R = C_6H_{13}, R = $C_{10}H_{21}$ and R = $C_{14}H_{29}$ and cross-section of the energetic levels

3.4. ESR spectra and magnetic properties

The magnetic susceptibility data obtained for twelve copper(II) complexes with alkylaminoacetylurea ligands in the temperature range 1.9–300 K are collected in Table 3. It has been shown [26] that magnetic moments and susceptibilities of the compounds studied change with the length of the alkyl chain. In the present paper, syntheses of two other complexes belonging to this group with R = C_3H_7 and C_4H_9 are reported and properties of these materials are compared with the properties of the previously studied compounds.

Table 3. Magnetic data of the Cu^{2+} complexes studied

No.	R	μ_{eff}(300 K) [B.M.]	μ_{eff}(80 K) [B.M.]	μ_{eff}(1.9 K) [B.M.]	Weiss constant θ [K]^a	Curie constant C [$cm^3 \cdot K \cdot mol^{-1}$]^a
1	C_3H_7	1.80	1.78	1.81	0.13 ^{b}	0.410 ^{b}
2	C_4H_9	1.76	1.74	1.03	–2.21	0.391
3	C_5H_{11}	1.83	1.79	1.90	0.42 ^{b}	0.433 ^{b}
4	C_6H_{13}	1.75	1.73	0.98	–2.34	0.386
5	C_7H_{15}	1.71	1.69	1.01	–2.43	0.379
6	C_8H_{17}	1.74	1.74	1.01	–1.50	0.388
7	C_9H_{19}	1.87	1.80	1.69	–3.00	0.431
8	$C_{10}H_{21}$	1.73	1.74	1.05	–0.93	0.398
9	$C_{12}H_{25}$	1.81	1.72	1.06	–5.00	0.420
10	$C_{14}H_{29}$	1.70	1.68	1.02	–2.20	0.369
11	$C_{16}H_{33}$	1.85	1.73	1.05	–3.10	0.405
12	$C_{18}H_{37}$	1.99	1.81	1.10	–9.35	0.449

[a] In the temperature range 6–300 K.
[b] In the temperature range 6–40 K.

The results of susceptibility measurements for the new complexes with R = C_3H_7 and C_4H_9 are presented in Fig. 6 in the form $\chi_m T = f(T)$, where χ_m is the corrected molar magnetic susceptibility per Cu^{2+} and T is the absolute temperature. The observation of weak magnetic interactions at very low temperatures for the studied complexes suggests that copper(II) ions are not isolated in the crystal lattice. For the R = C_3H_7 complex a weak ferromagnetic interaction is observed, as evidenced through a very small increase of $\chi_m T$ and magnetic moments below 25 K, as well as a positive value of the Weiss constant (Fig. 6, Table 3). Similar results were previously observed for the complex with R = C_5H_{11} [26]. The behaviour of the complex with R = C_4H_9 is also similar to the behaviour of other compounds studied (see Table 1), i.e. below 25 K decrease of the $\chi_m T$ values is observed, and the magnetic moment decreases from 1.76 B.M. at RT to 1.03 B.M. at 1.9 K (B.M. – Bohr magneton). This behaviour suggests the existence of weak antiferromagnetic interactions between Cu^{2+} ions. The plot of χ_m versus T shows a maximum at ca. 2 K (Fig. 7). This result confirms the presence of weak antiferromagnetic interactions. The calculated Weiss constant is negative and its value is –2.21 K (Table 3).

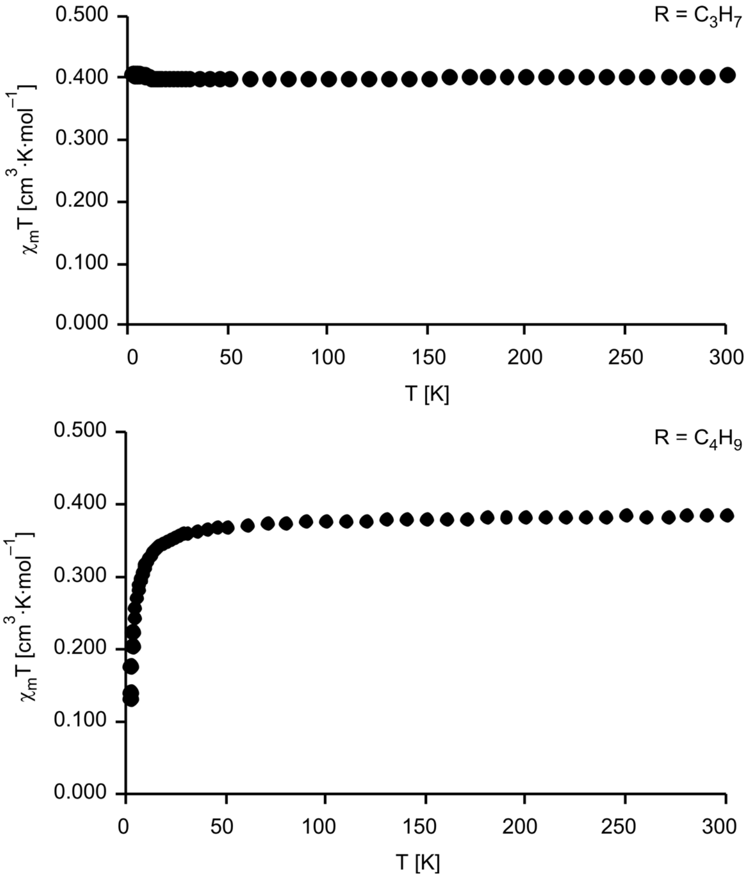


Fig. 6. Temperature dependences of the $\chi_m T$ product for the complexes with alkyls R = C_3H_7 and R = C_4H_9

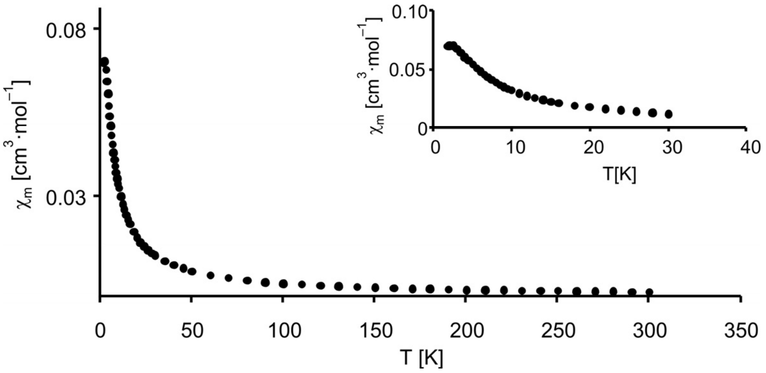


Fig. 7. Temperature dependences of the magnetic susceptibility for the sample R = C_4H_9

Figure 8 shows representative ESR spectra for three samples (R = C_3H_7, C_4H_9 and C_5H_{11}).

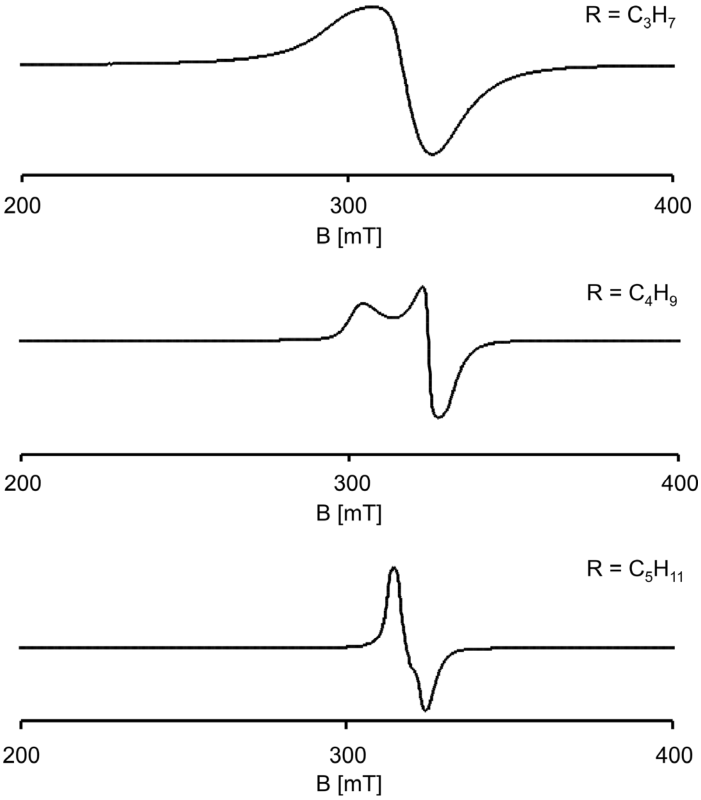


Fig. 8. ESR spectra of selected polycrystalline complexes:
R = C_3H_7, R = C_4H_9, R = C_5H_{11}, at 5 K

The ESR spectra were measured for polycrystalline samples at 300 and 5 K. Spectroscopic splitting parameters are the same for all measured complexes, $g_{av} = 2.10$. However, clear differences between the compounds with R = C_3H_7, R = C_5H_{11} and the remaining analogues are observed in the ESR spectra (Fig. 8). Since weak magnetic interactions were observed only at the lowest temperatures, we have analyzed the ESR spectra measured at 5K in order to obtain some information about these interactions. The spectrum of the complex with R = C_3H_7 exhibits only one symmetrical line at about 3000 G, whereas the spectrum of the R = C_4H_9 complex (which is representative of the remaining complexes) exhibits signal with two components. These components are characteristic of monomeric Cu^{2+} ions when the unpaired electron occupies the d_{x2-y2} orbital and $g_{\|} = 2.18 > g_{\perp} = 2.05$. The different type of spectrum was observed for the complex with R = C_5H_{11}, with $g_{\perp} = 2.11$ and $g_{\|} = 2.05$. The reverse ($g_{\|} < g_{\perp}$) ESR spectra are obtained in complexes with a single electron in a d_z^2 orbital [40]. For the complex with R = C_5H_{11} weak ferromagnetic interaction was observed. The distance between the Cu^{2+} centres in the crystal lattice must be long and, therefore, the observed magnetic interactions are very weak.

For all complexes the magnetization in function of the magnetic field strength was measured and the results obtained at 1.9 K are presented in Fig. 9.

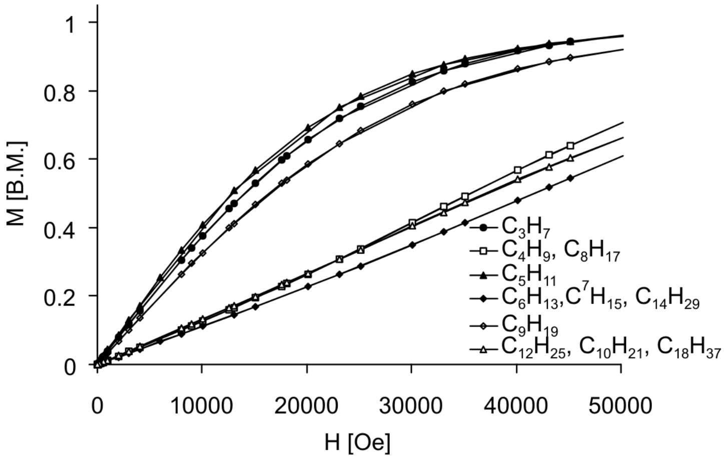


Fig. 9. Magnetic field dependence of the magnetisation for the copper(II) complexes studied at 1.9 K

For isolated magnetic ions, when H is small enough, the molar magnetization is linear and the Curie Law is valid. When H becomes large, M tends to the saturation value M_S [41]. The molar magnetization is $M = Ng\beta SB_S(y)$, where $B_S(y)$ is the Brillouin function [41]. When H becomes very large, $B_S(y)$ tends to unity and M tends to the saturation value $M_S = Ng\beta S$. If the saturated magnetization is expressed in $N\beta$ units, its value for $S = 1/2$ and $g = 2.0$ tends to 1. Figure 9 shows that for the two measured complexes, with R = C_3H_7 and C_5H_{11}, magnetization tends to the saturation value at high magnetic fields. It confirms the ferromagnetic character of magnetic interaction observed in the two complexes. For the remaining compounds, up to H = 50 000 G, the magnetization is linear.

4. Conclusion

The absorption and emission spectra as well as magnetic and ESR data obtained for the new copper(II) complexes with alkylaminoacetylurea ligands suggest that the physicochemical properties of these compounds change with the length of the alkyl chain. The coordination polyhedron of the Cu^{2+} ions in these complexes is four coordinated and pyramidal with small distortion from the square-planar. The very weak ferromagnetic interactions are observed for the C_3 and C_5 alkyls and the antiferromagnetic ones for the remaining complexes with C_4 and C_6–C_{18} alkyls. These studies will be continued using other physicochemical and X-ray methods when on single crystals of these compounds.

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