PHOTOACOUSTIC AND EPR STUDIES OF TWO COPPER(II) COMPLEXES WITH SPERMINE ANALOGUES

N. Guskos[1,2], V. Likodimos[3], J. Typek[2], M. Maryniak[2], E. Grech[4] and B. Kolodziej[4]

[1]Solid State Section, Department of Physics, University of Athens, Panepistimiopolis, 157 84 Zografou, Athens, Greece
[2]Institute of Physics, Szczecin University of Technology, Al.Piastow 17, 70-310 Szczecin, Poland
[3]Department of Physics, National Technical University, 157 80 Athens, Greece
[4]Department of Inorganic and Analytical Chemistry, Szczecin University of Technology, Al.Piastow 42, 71-065 Szczecin, Poland

Abstract. Two polyamine copper(II) compounds of spermine analogues: $Cu[H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2](ClO_4)_2$ (abbreviated as Spc323) and $Cu[H_2N(CH_2)_3NH(CH_2)_3NH(CH_2)_3NH_2](ClO_4)_2$ (abbreviated as Spc333) have been synthesized and characterized by spectroscopic methods. The electron paramagnetic resonance (EPR) and photoacoustic spectroscopies have been used for studying Cu^{2+} d-d transitions. The EPR spectra of copper(II) ions in both complexes have displayed a different crystal field symmetry: orthorhombic for Spc323 complex, and axial, with the hyperfine interaction, for Spc333 complex. In the visible region of electromagnetic radiation the photoacoustic absorptions from the d-d electron transitions with different energies and linewidths have been observed. Comparison of the obtained results is made with previous measurements on similar spermine compounds.

1. INTRODUCTION

Biogenic amines, among them spermine, play an important role in many biological processes [1-3]. The medicinal properties of both copper and copper compounds (inorganic and organic) are well known. As early as 3000 BC, the Egyptians used copper as an antiseptic to sterilize drinking water [4]. To better understand the role of copper(II) complexes, the investigation of electronic structure of active copper(II) complexes important for the living matter by using spectroscopic methods is needed. Recently, a series of polyamine spermine copper (II) complexes have been studied using spectroscopic and magnetic methods [5-8]. The spectroscopic and magnetic properties essentially depend on substitution of distant groups as well as on the presence of water molecules. Protein structure and dynamics is the key to a wide range of problems in active biological systems where direct application of quantum mechanics to protein systems has been prohibited by the large molecular size of proteins [9]. The spectroscopic methods used to study electronic states and dynamic processes of some metal organic complex components of proteins have provided very important information about active biogenic compounds. Previously, an idea has been put forward that the electron transitions between the ground state and the

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Corresponding author: J. Typek, e-mail: Janusz.Typek@ps.pl

excited states of copper could play the role of a very sensitive "channel selector", especially for the transition metals ions with extended wave functions [10].

The aim of this work is to study two other polyamine copper complexes, namely $Cu[H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2](ClO_4)_2$ and $Cu[H_2N(CH_2)_3NH(CH_2)_3NH(CH_2)_3NH_2](ClO_4)_2$, by using the methods of electron paramagnetic resonance (EPR), photoacoustic (PA) and UV/VIS spectroscopies. The d-d transitions will be studied and the importance of their splitting by the crystal field will be stressed. It will be suggested that the photoacoustic effect could play a very important role in the living matter.

2. EXPERIMENTAL

Two polyamine copper(II) compounds, $Cu[H_2N(CH_2)_3NH(CH_2)_2NH (CH_2)_3NH_2](ClO_4)_2$ (abbreviated as Spc323) and $Cu[H_2N(CH_2)_3NH-(CH_2)_3NH (CH_2)_3NH_2](ClO_4)_2$ (abbreviated as Spc333), have been prepared by slow evaporation of methanol from the appropriate solution of the corresponding polyamine complexes with $Cu(ClO_4)_2 \cdot 6H_2O$, as described previously [11,12]. We have adopted the shorthand nomenclature where linear tetramines are characterized by the number of CH_2 units in each bridge [11]. Fig. 1 presents the schematic structure of Cu(323)$^{2+}$ and Cu(333)$^{2+}$ complexes in Spc323 and Spc333 compounds, respectively. The crystal structure of Spc333 has been determined by X-ray diffraction [11,12]. Spc333 compound crystallizes in the orthor-

rhombic group Pbca with *a*=0.1576 nm, *b*=0.1532 nm, *c*=0.1452 nm, and *Z*=4. The structure contains tetragonal, distorted CuN_4O_2 units. Of the two unique perchlorate groups in the structure, one is not bound to copper. The second perchlorate group, which bridges symmetry-related copper atoms and accounts entirely for axial coordination, is distorted [11].
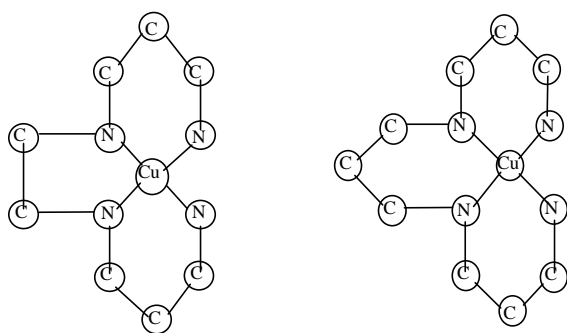
PA spectra were measured by using fine powder samples at room temperature, on the conventional equipment [13] comprising a light source of a 1 kW power xenon arc lamp with a ¼ m ORIEL monochromator of a bandpass width of 5 nm at 500 nm. Signal bandwidth narrowing to reduce the low frequency noise was accomplished by the use of lock-in detection. That is, the light output from the monochromator was mechanically chopped at a frequency of 10 Hz. The acoustic signal was detected by a TREVIE M27, a very sensitive microphone, attached to the PA cell. A dual Stanford Research SR830 lock-in amplifier recorded the amplitude and phase of the microphone signal relative to the input excitation. For an averaging of 20 modulation periods, the signal-to-noise ratio was at least 50 for a particular wavelength of incident light, representing an approximately five-fold improvement over the unmodulated case. All the data were very good reproduced. The raw amplitude and phase of the sample signal were normalized for the PA spectrum of a graphite blackbody reference in order to correct for the modulation frequency dependence of the thermal diffusion length [14].

The EPR measurements were carried out with a conventional X-band (ν=9.5 GHz) Bruker E 500 spectrometer at 100 kHz magnetic field modulation. The samples, each containing around 30 mg of loose powder, were placed into 4 mm diameter quartz tubes. The measurements were performed at room temperature. As usual, the first derivative of the power absorption has been recorded as a function of the applied magnetic field.

The UV/VIS measurements were performed on a Hitachi-2000 double beam spectrometer at room temperature, in water and methanol solution, for 0.1% concentration of the investigated compounds.

3. RESULTS AND DISCUSSION

Electronic absorption spectra for Spc323 and Spc333 have already been published [15]. Studies of visible and ultraviolet absorption spectra have revealed one broad, intense peak in VIS and another, even more intense, peak in the UV part of radiation, at 18300 cm^{-1} and 37500 cm^{-1} for Spc323,

Spc323   Spc333

Fig. 1. Schematic structure of Spc323 (left) and Spc333 (right) copper complexes.

Table 1. UV/VIS and PA peak wavelengths along with the ground state coefficients and bonding parameters calculated from EPR data [4,5].

	λ_0 (nm)	λ_1 (nm)	λ_2 (nm)	λ_3 (nm)	λ_4 (nm)	α	β	k_1	$k_\perp$
Spn323	536(4)	483	567	694		0.997	0.084	0.62	0.96
Spm323	540(3)	486	566	670		0.998	0.066	0.66	0.88
Spc323	541(3)	457(1)	527(5)	644(4)		0.998	0.060	0.65	0.80
Spn333	590(3)	516	610	730		0.999	0.046	0.58	0.93
Spm333	594(3)	570	698	795		0.992	0.125	0.64	0.83
Spc333	597(4)	476(2)	662(6)	785(4)	540(3)	0.997	0.084	0.63	0.95

and 16700 cm^{-1} and 37 300 cm^{-1} for Spc333, respectively. The stability in aqueous solution and the ligand field strength was greater for Spc333 than for Spc323 [15]. Our UV/VIS absorption spectra of Spc323 and Spc333 in water and methanol are consistent with these observations. A very intense absorption band is detected below 350 nm for Spc323 and Spc333, which is consistent with the metal-ligand charge transfer transitions occurring at relatively high energies. At lower energies a much weaker intense absorption band is recorded for both complexes, at 541 nm for Spc323, and at 597 nm for Spc333. The wavelength of the corresponding peak (λ_0) complies with the expected energy range for the Cu^{2+} ions of d-d electron transitions in polyamine copper(II) complexes with fourfold nitrogen coordination in the equatorial plane. The position of maximum absorption is comparable to that for polyamine copper(II) dinitrate complexes (Spn) and sulfate complexes (Spm) (Table1).

Fig. 2 presents the EPR spectra for the two polyamine complexes Spc323 and Spc333 at room temperature. In both cases, very intense and anisotropic EPR spectra of Cu^{2+} ions in low symmetry of the crystal field are recorded. For Spc333 the crystal field splitting is stronger and the EPR spectrum is more resolved. An additional EPR line is observed for Spc333, arising from the hyperfine interaction of copper(II) ion (Fig. 2b). The MONOQ [16] simulation program for spin S=1/2 was used to reliably determine the principal g values allowing for a g tensor of rhombic symmetry with the anisotropic linewidths w_i (i=x,y,z) and the presence of the strain producing inhomogeneous broadening. The obtained values of spin Hamiltonian parameters, linewidths (w_i) and strains (c_{ji}- j=1,2,3 and i=x,y,z) for the two samples are presented in Table 2. The hyperfine structure of copper(II) isotopes is found to be suppressed for the Spc323 complex, as is often observed for concentrated copper(II) com-

Table 2. The EPR parameters for copper(II) complexes derived from the simulated EPR powder spectra [4,5].

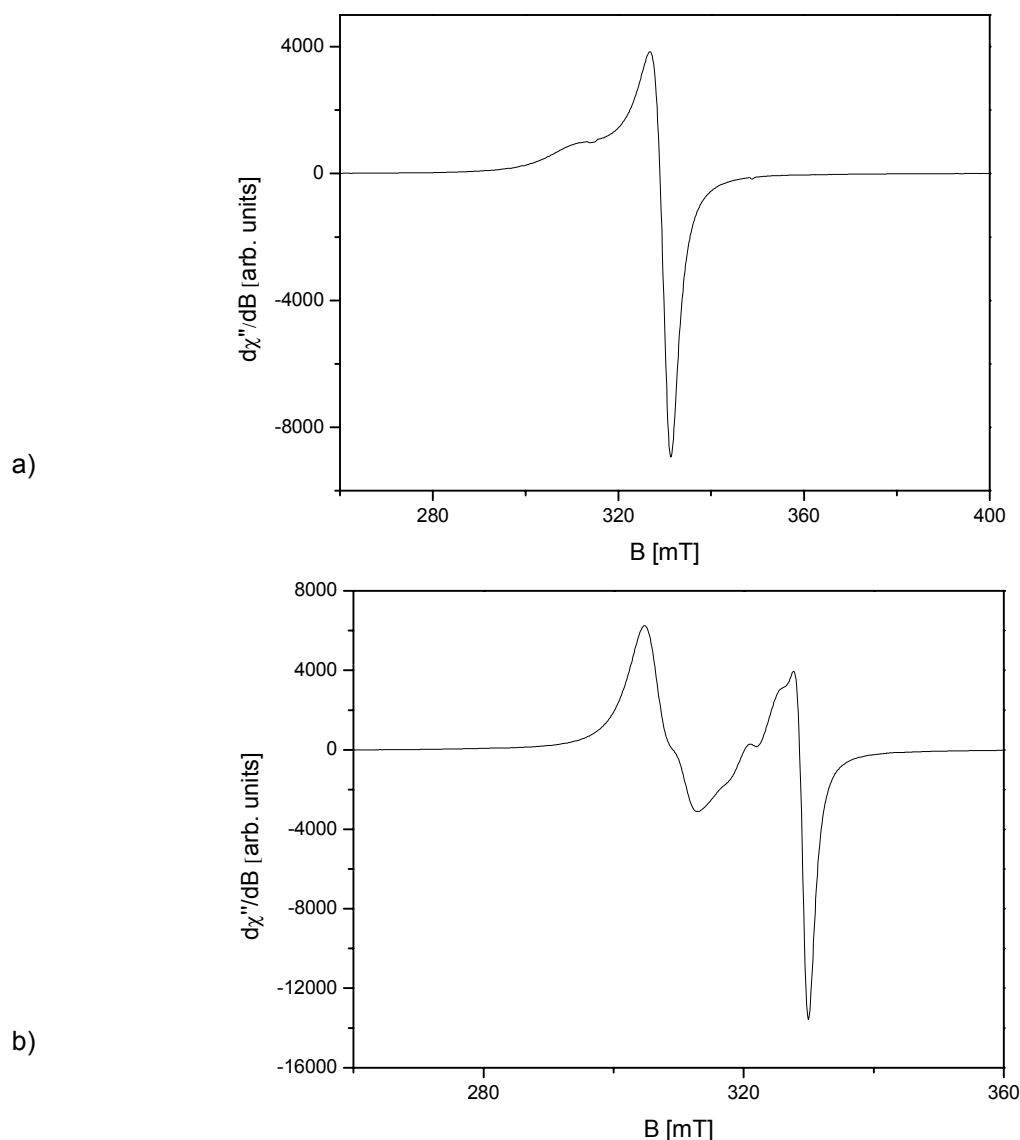|	g_x	g_y	g_z	w_x (MHz)	w_y (MHz)	w_z (MHz)	c_{1x}	c_{2y}	c_{3z}
Spn323	2.0620	2.0580	2.1770	115	187	400			
Spm323	2.0572	2.0777	2.1920	37	67	130			
Spc323	2.0445	2.0599	2.1832	46	71	353			
Spn333	2.0737	2.0854	2.1650	115	48	165			0.0015
Spm333	2.0480	2.0950	2.2150	34	33	84	0.004	0.0006	0.0012
Spc333	2.0586	2.0586	2.1932						

Fig. 2. EPR spectra of Spc323 (a) and Spc333 (b) at room temperature.

pounds where the exchange narrowing is effective, and thus it was not taken into account. In both cases, the anisotropy of *g* parameters is present along the three principal axes, although significant differences exist among the two compounds. The EPR spectrum of copper(II) ions could be described very well by the following well known relations [17]: $g_z=2-8\lambda_{so}k_1^2\alpha^2/E_{xy}$, $g_x=2-2\lambda_{so}k_2^2(\alpha-\sqrt{3}\,\beta)^2/E_{yz}$, $g_y = 2-2\lambda_{so}k_3^2\,(\lambda+\sqrt{3}\,\beta)^2/E_{xz}$, where $\lambda_{so}=828$ cm^{-1} is the spin-orbit coupling constant for the free copper(II) ion, E_{ij} (i,j=x,y,z) are the relative energies of the d_{ij} levels with respect to the ground one, and k_i (i=1,2,3) are the combined orbital and spin-orbit reduction parameters yielding information on the bonding interaction. The main problem is to obtain the values of energies E_{ij}. Unfortunately, it is impossible to know them from UV/VIS measurements because the d-d electron transitions overlap, giving only a very broad line. For the sample Spc333, an additional EPR spectrum of exchange-coupled copper(II) ions has appeared (Fig. 2b), centered at g_1=2.163 and g_2=2.184. EPR spectroscopy is a powerful technique for the structural and functional investigation of metalloproteins, whence the dimers could produce absorptions in the visible region (near λ_4 – Table 2) of electromagnetic radiation at the O_2^{2-}→d charge transfer band [18].
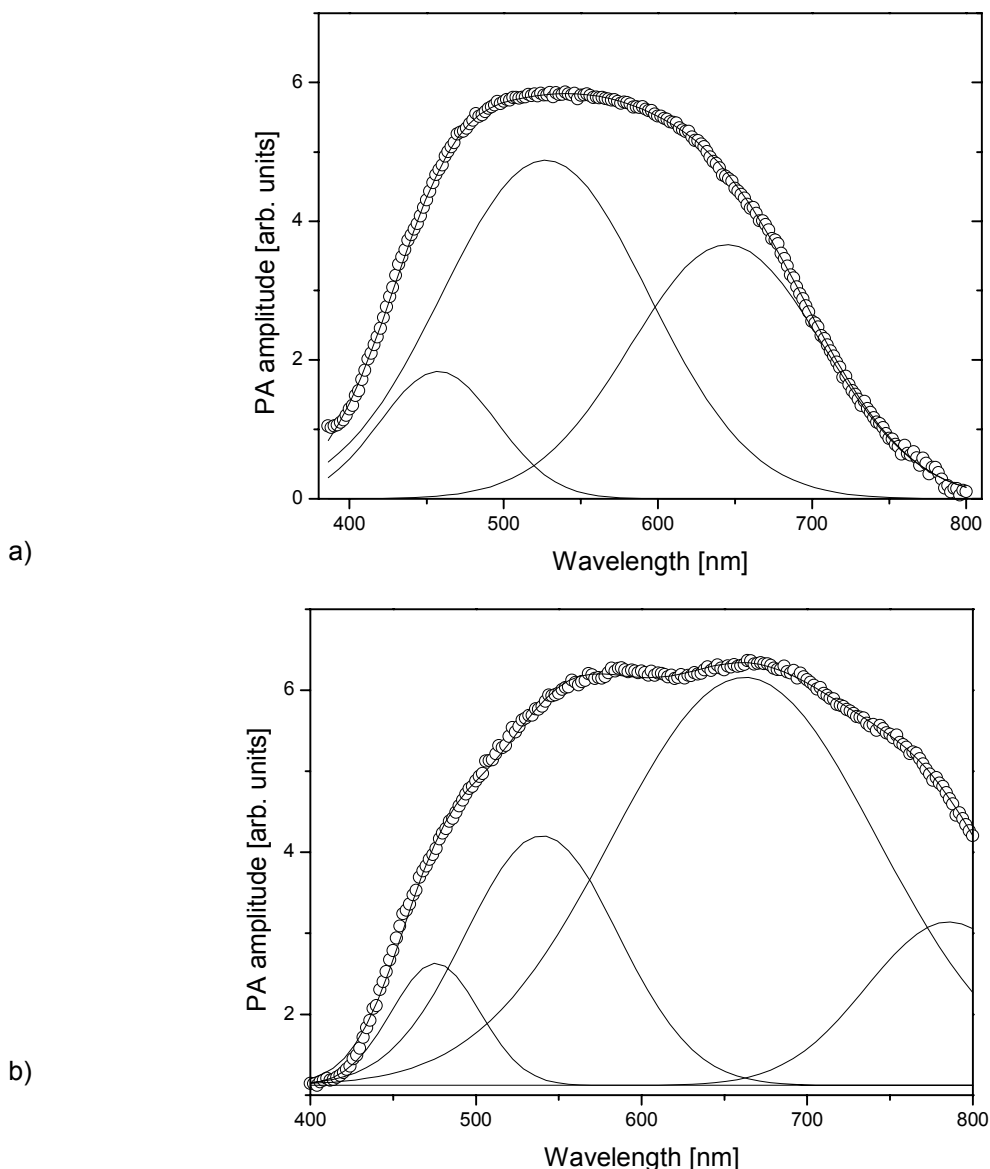
Fig. 3. PA spectra of Spc323 (a) and Spc333 (b) at room temperature.

Fig. 3 presents the photoacoustic spectra (PAS) for the two investigated Spc323 and Spc333 powder state compounds. The PAS are formed by an intense and broad inhomogenous absorption band in the visible range, with a weakly resolved fine structure. The positions and widths of these PA bands are close to that observed by UV/VIS spectroscopy in solution, with the unresolved electron d-d transitions coming from the crystal field interaction. Strong differences in the PAS are recorded between both investigated complexes (Fig. 3). The introduced ClO_4 groups have stronger influence with respect to the photoacoustic reaction and electronic structure in the presently studied Spc323 and Spc333 compounds than the sulphate and dinitrate groups in previously investigated Spn and Spm samples. As mentioned above, the EPR spectrum changes strongly upon replacing structure elements in the Spc complexes. The great differences between PAS of Spc323 and Spc333 complexes arise from the splitting of d levels by changing the crystal field interaction after replacing molecules within the complex. Using MCD spectroscopy, almost similar values of the d-d transitions for blue copper(II) complexes (λ_1=489 nm, λ_2=550 nm and λ_3=621 nm) have been obtained [19].

For a satisfactory line shape analysis of PAS for the two Spc323 and Spc333 complexes,

Gaussian-type functions have been employed for the component lines. It was shown that the broad PAS can be accurately fitted with three individual absorption lines (Fig. 3). The corresponding values derived by applying the same procedure for PAS of the three polyamine dinitrate complexes [6] are also included. The values of wavelengths λ_i (i=1,2,3) found in fitting and also the value of λ_0 determined from the solution spectra are presented for both complexes in Table 1. It has to be noted that the latter values shows some essential differences in comparison to those for Spm or Spn complexes. The value of λ_1 is almost the same but the values λ_2 and λ_3 are significantly lower for the complex Spn323 than for Spn323 or Spm323 complexes, while all three values λ_i are greater for complex Spc333 than for Spn or Spm complexes. Comparison between the other two sets of PAS transitions for the dinitrate and sulfate copper polyamine copper(II) complexes shows that, although a similar trend in crystal field strength for the same polyamine ligand conformation can be deduced, distinct differences, practically unresolved in the solution absorption spectra, occur in the electronic structure of the copper site in accord with the variation of the metal coordination and the local structure in the crystalline complexes.

The PAS are obtained by detecting the heat generated through the non-radiative relaxation, released by the sample absorbing the modulated incident light. The PAS intensity P is given by the relation [20]:

$$P = k\,A_{abs}\,\gamma,$$

where A_{abs} is the absorbency of the sample, γ is the probability for non-radiative transitions after excitation and k is a coefficient that is determined by the thermal properties of the sample and the spectrometer. It is supposed that k and A_{abs} coefficients are the same for both samples. The main contribution is arising from γ connected with the non-radiative transitions. The complex Spc333 has two times greater integrated line intensity as compared to Spc323. Substitution of different molecules at sites of ClO_4 groups influences strongly not only the crystal field splitting of the d-d electron transitions but, possibly, also the intensities of lines responsible for non-radiative processes.

It has been proposed that polyamine copper(II) complexes could play a leading role in transferring information in DNA as a "channel selector" [10]. The wavefunction of copper(II) is extended in the molecule and the electronic state of this molecule could be a little different if copper is in an excited state. The living matter is very sensitive and this kind of physical process could form a very precise mechanism for the processing of information in DNA.

Copper complexes are amongst the most important biological compounds and copper ion is known as an essential trace element for many biological functions [21]. The daily intake for humans is ~1.5-3 mg of Cu [22]. Photoactive metal complexes can act as spectroscopic report probes for relaying information about DNA conformation [22]. The spectroscopic properties of the copper(II) complexes are often quite sensitive to the local environment, capable of providing unique information about binding interactions. The peak of emission spectra of $Cu(bcp)_2^+$ and $Cu(dmpp)_2^+$ have appeared [23] at $1/\lambda'$~14800 cm^{-1} and using relation $(1/\lambda_{2av}-1/\lambda')=1/\lambda_{non}$, where $1/\lambda_{2av}$=16500 cm^{-1} (average of λ_2 from Table 2), it is obtained that $1/\lambda_{non}$=1700 cm^{-1}. Using the data of PAS ($1/\lambda_a$~15000 cm^{-1}) and emission spectra ($1/\lambda_e$~13300 cm^{-1}) of cyanobacterium Synechococcus (containing biliproteins) and bacterium Prostheecochloris aestuarii in polymer film [24,25], it is obtained that $1/\lambda_a-1/\lambda_e$~1700 cm^{-1}. This value is in very good agreement with the value of $1/\lambda_{non}$ obtained above.

For the living matter three entities: a photon (involved in a very fast information transmission), a phonon (involved with thermal processes),and an electron (involved in excitation processes) are of paramount importance. From macrocosmos to microcosmos the humans obtain information by means of photons. We believe that for better understanding of processes in the living matter the study of biogenic active compounds by using spectroscopy methods is of value. Especially, investigations involving photoacoustic spectroscopy might be very informative. In this spirit, in the present work, the metal ion electronic structure of normal copper proteins is unveiled as playing a critical role in information transfer.

To summarize, PA spectra provide insight in thermal deactivation through non-radiative processes and we think that photoacoustic processes are important for the living matter. The EPR and PAS measurements for Spc323 and Spc333 complexes have provided interesting spectra, with unusual crystal field splitting and absorption intensity characteristics. Thus, the electronic structure has been well described with respect to copper(II) ions, showing that in the visible region the structure of the PAS for polyamine copper(II) complexes arise

from the d-d electron transitions. The intensities of the non-radiative transitions strongly depend on substitution of the distant molecular groups.

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