Materials Science-Poland, Vol. 23, No. 4, 2005

The linewidths and pintegrated intensities of the d–d transitions in photoacoustic spectra of polyamine copper(II) complexes

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Photoacoustic spectra of the d–d transitions for three different series of copper(II) complexes of spermidines Spn (Spn323, Spn333, Spn343), Spm (Spm323, Spm333, Spm343) and Spc (Spc323, Spc333) have been investigated. Replacements of distant atoms, the presence or absence of water molecule in the structure, the kind of ligands surrounding the metal(II) ions have a strong influence on the crystal field splitting and the intensities of the non-radiative transitions. Non-radiative processes are involved in important mechanisms of the dynamic interactions between the electrons and the lattice. Studies of the intensities of the non-radiative transitions provide a very important data for the thermodynamic states of these systems. Photoacoustic absorption band of the d–d transitions could be decomposed into three lines (due to the crystal field splitting) with different intensities, positions and linewidths. The integrated intensities may yield information about the number of non-radiative processes, while the linewidths about the mechanisms of the relaxation processes.

Key words: *photoacoustic spectroscopy; copper complexes*

1. Introduction

Crystal field splittings of the d–d transitions for three different series of copper(II) complex of spermidines: Spn (Spn323, Spn333, Spn343), Spm (Spm323, Spm333, Spm343) and Spc (Spc323, Spc333) have been investigated by using photoacoustic (PA) and electron paramagnetic resonance (EPR) methods [1–3]. The following fac-

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tors: (i) replacement of distant atoms, (ii) the presence of additional water molecules, and (iii) different kinds of ligands, strongly influence the crystal field splittings and the lineshape of the PA spectra of the d–d transitions. The complexes of spermidines are very important in the bio-active systems due to their role in the processes of information transfer between the DNA and proteins [4–6]. It has been proposed that the transition metal complexes of spermidine act as a channel selector in bio-active systems, e.g. by switching between the ground and excited d-orbital states after irradiation by proper electromagnetic wave [7].

Non-radiative processes might be very important for this kind of mechanism. Thus the study of the intensities of the non-radiative processes could provide important data for determination of the thermodynamic state of systems including the DNA and proteins involved in the bio-active activities with. The d–d absorption band observed in photoacoustic spectroscopy (PAS) could be decomposed into three lines (due to the crystal field splitting) with different intensities, positions and linewidths. The integrated line intensities yield information about the amount of non-radiative processes while the linewidths about the relaxation processes. The PA spectra of hematite, spermidine and organometallic rare earth complexes exhibit an intense absorption (near 586 nm – yellow colour) in the same region of electromagnetic spectrum. It has been suggested that this radiation plays an important role in the living systems [8]. It is especially important because the most intense Sun radiation occurs in this very region. The study of the d–d and n–π^* transitions in spermidines may be very useful for a proper understanding of the static and dynamical processes occurring in the living matter [9–11].

In this report, we present and discuss the variations of the intensities and the linewidths in PA spectra of the d–d transitions for three different series of spermidine copper(II) complexes.

2. Experimental

Three series of copper(II) complexes of spermidines (designated as Spm, Spn and Spc) have been prepared according to the procedure described elsewhere [1–3].

The PA spectra of polycrystalline powder samples have been obtained by using a modified PAS method initially proposed by Papadopoulos and Mair [12]. A 1 kW Xenon arc lamp and a 1/4 m ORIEL monochromator were used as light sources, with bandpass widths of 5 nm (at 500 nm). The light, with intensity modulated by a chopper at frequency of 10 Hz was directed into a photoacoustic cell equipped with TREVI EM27 microphone. A dual SR830 lock-in amplifier measured the amplitude and phase of the PA signal detected on the microphone. Data acquisition ensured that each final value was an average of 20 runs at the same wavelength of the incident light. A carbon black was used as a standard to re-calibrate the final spectrum. The PA spectra of all the complexes were recorded at room temperature in the range of 300–700 nm.

3. Results and discussion

The absorption of three series of investigated copper(II) complexes of spermidine (Spm, Spn and Spc) have been investigated by using PAS in the visible region. It has been suggested that the observed broad band arises from the d–d transitions between the energy levels split by the crystal field [1–3]. For illustration, the PA spectrum of Spc323 organic complex simulated by three lines, is given in Fig. 1. The PA spectra can be described very well by the superposition of three lines resulting from the crystal field splitting. In Figures 2 and 3, such composite three-line spectra are presented for the Spn 323 and Spm 323 examples, respectively. A very good agreement has been obtained between this assumption and the results of analysis of the EPR spectra of copper(II) ions in orthorhombic crystal field for all eight investigated copper(II) complexes. The obtained wavelengths λ_i (i = 1, 2, 3) for the three electronic transitions (between the ground state d(x^2–y^2) and excited states (d(xy), d(zx), d(yz)) are listed in Table 1. It is very important to know the dependence of the linewidths (related the relaxation processes) and the line intensities (related to the strength of the non -radiative transitions) in these systems since exactly these processes may play important role in the living matter. The crystal field splittings, the linewidths, and the intensities strongly depend on the kind of complex and the replacement of distant groups in the molecules under investigations.

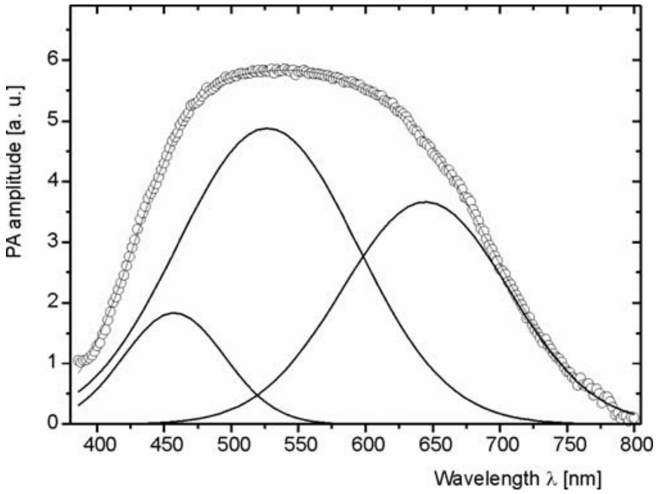

Fig. 1. PA spectrum of the copper(II) complex of spermidine Spc323 and its decomposition into three component lines

The PA spectra were recorded by using detection of the heat generated through the non-radiative relaxation, released by the sample absorbing the modulated incident light. The PA intensity (I) is given by the relation [13]:

$$I = \kappa \alpha_{\text{abs}} \gamma \tag{1}$$

where α_{abs} is the absorbance of the sample, γ is the probability for the non-radiative transitions between the excited and ground states, and κ is a coefficient determined by the thermal properties of the sample and the spectrometer. It is assumed that the coefficients κ and α_{abs} are the same for all samples. The main intensity contribution arises from the coefficient γ related to the non-radiative transitions. Replacement of distant water molecules or Cl atoms influences strongly not only the crystal field splitting of the d–d electronic levels but also the linewidths and intensities of the non-radiative transitions (Table 1).

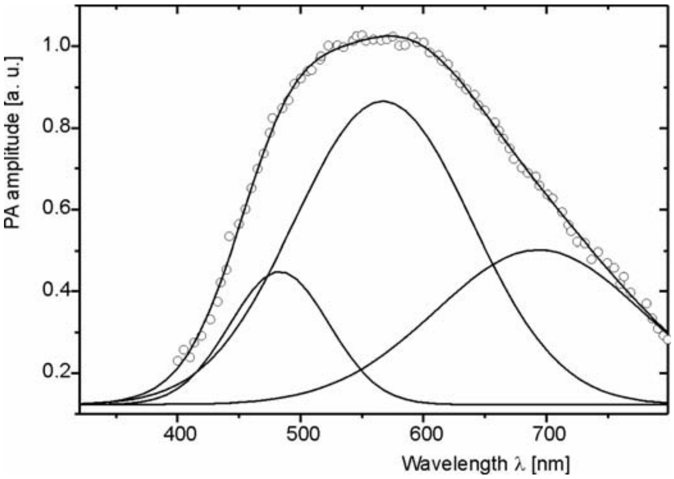

Fig. 2. PA spectrum of the copper(II) complex of spermidine Spn323 and its decomposition into three component lines

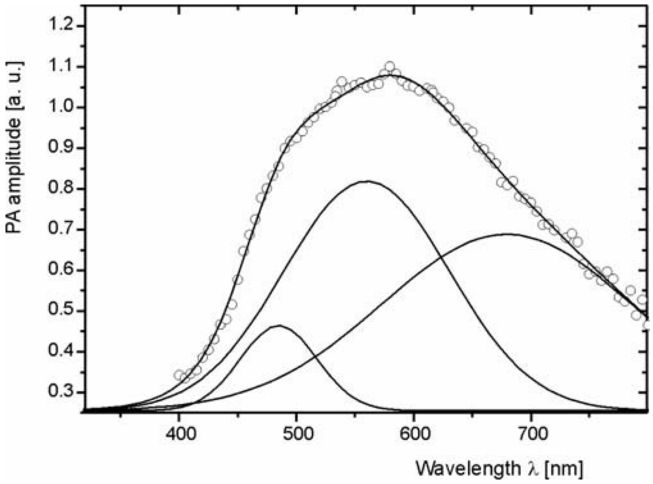

Fig. 3. PA spectrum of the copper(II) complex of spermidine Spm323 and its decomposition into three component lines

Table 1. The values of the photoacoustic spectral parameters (λ_i – position, $\Delta\lambda_i$ – linewidth, I_i – intensity) for the d–d electron transitions in polyamine copper(II) complexes [1–3]

Complex	Transition 1			Transition 2			Transition 3		
	λ	$\Delta\lambda$	I	λ	$\Delta\lambda$	I	λ	$\Delta\lambda$	I
Spn323	483(2)	80(3)	3(1)	568(9)	143(9)	14(9)	694(9)	167(50)	8(5)
Spn333	517(9)	99(3)	6(2)	612(9)	155(9)	11(5)	730(9)	203(50)	12(4)
Spn343	483(2)	58(6)	1(1)	565(9)	144(9)	11(5)	681(9)	113(10)	3(5)
Spm323	485(2)	66(5)	2(1)	560(9)	141(9)	10(3)	679(9)	212(30)	12(6)
Spm333	577(9)	126(3)	13(3)	703(6)	120(9)	14(5)	798(5)	72(6)	5(2)
Spm343	498(2)	73(3)	3(1)	577(9)	144(9)	9(4)	687(9)	221(30)	13(6)
Spc323	457(1)	79(3)	2(1)	526(6)	130(9)	8(5)	642(4)	120(15)	6(3)
Spc333	476(2)	53(3)	1(1)	540(2)	92(9)	4(2)	662(6)	160(30)	10(5)
Average	497	79	4	585	134	10	695	158	9

The line positions λ_i vary by over 100 nm for the eight investigated spermidine copper(II) complexes. The average values of the wavelengths ($\lambda_{av} = \Sigma_i\lambda_i/8$) for the corresponding d–d transitions split by the crystal field are the following: λ_{1av} = 497 nm, λ_{2av} = 585 nm, and λ_{3av} = 695 nm. The second transition has the same energy as that recorded by the PAS in hematite [14] and organometallic neodymium(III) complex (the f–f transitions) [7]. It was suggested that exactly this region of radiation could be very important for the living matter [8].

The linewidths $\Delta\lambda_i$ (the difference of wavelengths between the centre of the line and at the point of half height) depend strongly on the kind of spermidine complexes and the following average linewidths ($\Delta\lambda_{av} = \Sigma_i\Delta\lambda_i/8$) were obtained: $\Delta\lambda_{1av}$ = 79 nm, $\Delta\lambda_{2av}$ = 134 nm, $\Delta\lambda_{3av}$ = 158 nm for the three d–d transitions split by the crystal field. The relation $\Delta\lambda_{1av} < \Delta\lambda_{2av} < \Delta\lambda_{3av}$ indicates that in near infrared the relaxation processes are more intense.

Concerning the integrated intensities I_i defined as the area under the line, more significant differences are observed. The following average ($I_{av} = \Sigma_i I_i/8$) values of the corresponding d–d transitions: I_{1av} = 4, I_{2av} = 10, I_{3av} = 9, were calculated. The relation $I_{1av} < I_{2av} \approx \mathrm{I}_{3av}$ differs from that for the linewidths, namely the last two intensities are of comparable strength and much stronger than the rather weak first line. Hence the non-radiative processes are more intense for the region of radiation with longer wavelengths.

Complex functional materials are formed by biogenic systems where the spermidine complexes in protein play a very important role in the information transfer to DNA. Dynamical processes like relaxation or non-radiative processes are of importance for the phenomena occurring in the living matter. We believe that a vital role in the forming processes of the living matter is played by species created by the “glass” phenomenon upon irradiation in the yellow spectral range. Such systems (e.g., membranes) allow an easy transfer of radiation while being insulating to the heat transfer.

4. Conclusions

The PA spectroscopy enabled studies of splittings of the d–d energy levels by the crystal field. All spectral parameters of the PA lines (positions, linewidths and intensities) strongly depend on the kind of spermidine. The average values of the linewidths and intensities show the same tendency to increase with increasing wavelengths ($\Delta\lambda_{1av}<\Delta\lambda_{2av}<\Delta\lambda_{3av}$ and $I_{1av}<I_{2av}\approx I_{3av}$) for the d–d levels split by the crystal field. The relaxation and non-radiative processes are more effective upon irradiation with light of higher wavelengths. As it might be expected, these phenomena are more intensive in the infrared regions but the photoacoustic reaction in the yellow region could be responsible for many important processes studied in biophysics.

References

[1] GUSKOS N., PAPADOPOULOS G.P., LIKODIMOS V., MAIR G.L.R, MAJSZCZYK J., TYPEK J., WABIA M., GRECH E., DZIEMBOWSKA T., PERKOWSKA A., J. Phys. D, 33 (2000), 1.

[2] GUSKOS N., PAPADOPOULOS G.P., LIKODIMOS V., MAJSZCZYK J., TYPEK J., WABIA M., GRECH E., DZIEMBOWSKA T., PERKOWSKA A., AIDINIS K, J. Appl. Phys., 90 (2001), 1436.

[3] GUSKOS N., TYPEK J., ANAGNOSTAKIS E.A., PASCHALIDIS D.G., submitted for publication to Rev. Adv. Mat. Sci. (Russia).

[4] TABOR C.W., TABOR H., Annu. Rev. Biochem., 53 (1984), 749.

[5] VERMA A., BOUTWELL R.K., [in:] *Inhibition of Oilyamine Metabolism, Biological Significance and Basis for New Therapies*, P. P. McCann, A. E. Pegg, and A. Sjoredsma (Eds.), Academic, Orlando, 1987, p. 113.

[6] LOMZIK L., [in:] *Handbook of Metal-Ligand Interactions in Biological Fluids*, Vol. I, G. Berton (Ed.), Dekker, New York, 1995, p. 686.

[7] GUSKOS N., PAPADOPOULOS G.P., MAJSZCZYK J., TYPEK J., WABIA M., LIKODIMOS V., PASCHALIDIS D.G., TOSSIDIS I.A., AIDINIS K., Acta Phys. Pol. A, 103 (2003), 301.

[8] GUSKOS N., MAJSZCZYK J., TYPEK J., WABIA M., ANAGNOSTAKIS E.A., Mol. Phys. Rep., 39 (2004), 66.

[9] GUSKOS N., GLENIS S., LIKODIMOS V., TYPEK J., FUKS H., WABIA M., SZYMCZAK R., LIN C.L., PERKOWSKA A., J. Appl. Phys., 93 (2003), 9834.

[10] GUSKOS N., MAJSZCZYK J., TYPEK J., GRECH E., KOLODZIEJ B., submitted for publication to Mat. Res. Bull.

[11] GUSKOS N., LIKODIMOS V., TYPEK J., FUKS H., GLENIS S., WABIA M., LIN C.L., GRECH E., DZIEMBOWSKA T., PERKOWSKA A., NATO Science series: Math. Phys. Chem., 76 (2002), 519.

[12] PAPADOPOULOS G.P., MAIR G.L.M., J. Phys. D: Appl. Phys., 25 (1992), 722.

[13] ADAMS M.J., HIGHFIELD J.G., KIRKBRIGHT G.F., Anal. Chem., 52 (1980), 1260.

[14] GUSKOS N., PAPADOPOULOS G.J., LIKODIMOS V., PATAPIS S., YARMIS D., PRZEPIERA A., PRZEPIERA K., MAJSZCZYK J., TYPEK J., WABIA M., AIDINIS K., DRAZEK Z., Mat. Res. Bull., 37 (2002), 1051.

Received 17 October 2004
Revised 11 February 2005