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### The Spectrochemical Properties of bis-( $\alpha$ -Methioninephosphonato)Copper(II) in Aqueous Solution

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THE SPECTROCHEMICAL PROPERTIES  
OF BIS-( $\alpha$ -METHIONINEPHOSPHONATO)COPPER(II)  
IN AQUEOUS SOLUTION

**Key Words:** angular overlap model, electronic spectra, copper(II) complexes, phosphomethionine, species in solution, low symmetry,

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**ABSTRACT**

The combined results of spectrophotometric measurements and e.s.r. spectra, as well as those obtained from potentiometric titration studies, are used to determine the structure of the individual complex species formed between copper(II) ion and 1-amino-3-methylthiopropane-phosphonic acid ( $\alpha$ -MetP) in aqueous solution. The e.s.r. parameters are typical for  $\text{CuN}_2\text{O}_2$  coordination geometries. The d-d absorption spectrum of  $[\text{Cu}(\alpha\text{-MetP})_2]^{2-}$  chromophore in aqueous solution has been treated by the Angular Overlap Model in  $\text{C}_{2h}$  symmetry. Low-symmetry splittings of the broad asymmetric absorption band in the measured spectrum were found by Gaussian analysis. The effect of the  $\sigma$ - and  $\pi$ -bonding of bidentate ligand upon the central ion d-orbital energies is described in a ligand-field framework.

## INTRODUCTION

The main aim of this work is interpretation of the properties of novel chelate copper(II) complex on the basis of calculated ligand field parameters (AOM). The present studies are essentially limited to a discussion of  $[\text{CuL}_2]$  species with unsymmetrical bidentate ligand (i.e.  $\text{L}_1\text{L}_2$ , where  $\text{L}_1$  and  $\text{L}_2$  are O-donor and N-donor ligators) for which the central ion moiety has  $\text{C}_{2h}$  symmetry. For above mentioned reasons was confirmed existing individual complex species in aqueous solution by using combined methods i.e., e.s.r. spectra and potentiometric titration. In compliance in these solution studies and x-ray data for the solid state of similar complexes (probability of geometry) the solution spectrum have been treated in the  $\text{C}_{2h}$  symmetry.

## EXPERIMENTAL

Phosphomethionine (1-amino-3-alkylthiopropanephosphonic acid; molecular formula:  $\text{C}_4\text{H}_{12}\text{NO}_3\text{PS}$ ) was prepared by the method of Tam *et al.*<sup>1</sup>. The results of the elementary analysis agreed with the expected composition. Additional the purity was confirmed potentiometrically.

Solution of the complex species was prepared by dissolving a weight amount of the ligand in an aqueous solution of  $\text{CuCl}_2$ . The titrations were carried out at 25°C at 0.2M ionic strength (KCl). For the determination of the stability constants of the studied complexes, the Cu(II) concentration in all samples was  $4 \times 10^{-3}\text{M}$  and the concentration ratio of metal-ligand was 1:4. All the pH-metric titrations were carried out with carbonate-free KOH solution, which was added from a ABU-80 microburette (Radiometer), the initial sample volume being 5.0 cm<sup>3</sup>. The titrations performed under argon in water-thermostated beaker using a Radelkis OP-208/1 pH meter equipped with a micro combined glass/calomel electrode calibrated by the method of Malina *et al.*<sup>2</sup>. Resulting titration data were used to calculate hydrogen ion concentrations from the potential readings.

The e.s.r. spectra measurements were performed on a Bruker ESP 300E spectrometer at the X-band frequency (9.45 GHz) at 120K in ethylene glycol-water (1:1 v/v) solutions. The ligand concentration was  $1.6 \times 10^{-2}$  M and the concentration ratio of metal-ligand was 1:4.

The visible absorption spectra have been obtained at room temperature on a Beckman DU-68 spectrophotometer. The spectra were recorded digitally (with 0.5 nm steps) in the 900-350 nm range in a 5.0 cm quartz cuvette. The concentration was the same as used in the potentiometric titrations. The pH of the final solution was adjusted with HCl and KOH.

#### METHOD OF CALCULATIONS

All the band maxima reported in this work are derived from Gaussian analysis of the "poor" experimental spectral contour. Absorption spectrum was fitted with Gaussian components using CFP computer program<sup>3</sup> (and refs. herein). The AOM calculations were performed with the modified version<sup>3,4</sup> of LFP program. For these calculations the matrix elements of the excited states given by Kurzak<sup>5</sup> for the orthorhombic d<sup>9</sup> systems (C<sub>2h</sub> symmetry) were adopted. Coordinate system and numbering of the ligators used for AOM calculations are the same as in the previous paper<sup>5</sup>. In order to apply them to interpretation presented in this work i.e., four-coordinate trans-[M(N,O)<sub>2</sub>] complex (which does allow isotropy of oxygen ligators) the simplification has been made as follows. The e<sub>λ</sub>(3) and e<sub>δ</sub> parameters were zeroed and e<sub>π⊥</sub>(2)=e<sub>π||</sub>(2)=e<sub>π</sub>(2) was assumed. Finally, four parameters were fitted (e<sub>σ</sub>(O), e<sub>σ</sub>(N), e<sub>π</sub>(O), and α bite angle) for studied complex. LFP program takes into account all the combination of coordination numbers (number of ligators) and different bonding properties of ligators allowed for orthorhombic geometry. Formation constants were calculated using the SUPERQUAD program<sup>6</sup>. All the calculations were carried out on an IBM PC microcomputer.

## RESULTS AND DISCUSSION

The potentiometry titration results are collected in Table 1. At lower pH (< 7) copper(II) ion forms CuHL, CuL, and CuL<sub>2</sub> species, while at higher pH (within the range 7.0 - 8.5) the last species exists only. The parameters  $g_{\parallel} = 2.271$  and  $A_{\parallel} = 156$  G were obtained in the e.s.r. spectra of  $[\text{Cu}(\alpha\text{-P-Met})_2]^{2-}$ , i.e. CuL<sub>2</sub>. These values are typical for CuN<sub>2</sub>O<sub>4</sub> coordination geometries. Figure 1 shows the spectrophotometric changes as a function of pH. Absorption spectra in the d-d region at pH < 3 exhibit a transition around 820 nm characteristic for the copper(II) aqueous ion. An increase in pH above 3 leads to the appearance of a new d-d band and its maximum shifts towards visible region as the pH increase, which indicates greater complexation. At pH 5.3 and  $\lambda_{\text{max}}$  of 680 nm occurs band corresponding *ca.* to the maximum concentration (68%) of the [CuL] complex. The maximum at 650 nm increases in intensity up to pH 7.5 without any changes in energy ( $\epsilon_{\text{max}}^{\text{obs.}} = 53 \text{ M}^{-1} \text{ cm}^{-1}$  at pH 7.7) and does not change up to pH 9.5, which corresponds to the predominant concentration of the [CuL<sub>2</sub>] complex in this pH range. The further slightly increasing in pH above 9.5 is consistent with the formation of the new [CuL<sub>2</sub>H<sub>1</sub>] complex species (Table 1). The CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>CH(NH<sub>2</sub>)PO(OH)<sub>2</sub> - ( $\alpha$ -MetP) coordinates to copper(II) in a similar way to the simple bidentate alanine analogue (CH<sub>3</sub>CH(NH<sub>2</sub>)-PO(OH)<sub>2</sub>;  $\alpha$ -AlaP), which coordinates in a similar way to the aminocarboxylic acids<sup>7</sup>. Spectral parameters of the corresponding complexes of  $\alpha$ -MetP and  $\alpha$ -Ala and  $\alpha$ -AlaP are as follows: for pH = 8;  $\lambda_{\text{max}}$  - 650 (53), 615 (56) and 645 (50) nm, respectively. In addition to the pH-metric and spectrophotometric studies, e.s.r measurements were also performed on the copper(II) -  $\alpha$ -MetP system. The e.s.r parameters (given above) for  $[\text{Cu}(\alpha\text{-MetP})_2]^{2-}$  complex and parameters  $g_{\parallel} = 2.264$  and  $A_{\parallel} = 168$  G for  $[\text{Cu}(\alpha\text{-AlaP})_2]$  also seem to indicate that two nitrogens are bound to copper(II).

The crystal of bis(L-methioninato)copper(II), Cu(L-Met)<sub>2</sub> consists of isolated sheets of Cu(II) ions with rhombic N<sub>2</sub>O<sub>4</sub> ligand sets formed by trans co-

TABLE 1

Deprotonation constant ( $pK$ ) and copper(II) complex stability constants ( $\log\beta$ ) of 1-amino-3-methylthiopropaneephosphonic acid at 25°C and  $I=0.2M$ . Standard deviations are given in parentheses; the ion charges are omitted.

System	Species	$\log\beta$	pH range (main species)
$H^+ - \alpha\text{-MetP}$	$[HL]$	9.47(1)	
	$[H_2L]$	14.93(1)	
$Cu - \alpha\text{-MetP}$	$[Cu(HL)]$	12.16(8)	3.5 - 5.5
	$[CuL]$	8.21(1)	3.5 - 6.6
	$[CuL_2]$	14.89(3)	4.5 - 11.0
	$[CuLH_{-1}]$	4.10(1)	(7.5 - 8.5 100%) > 9.0

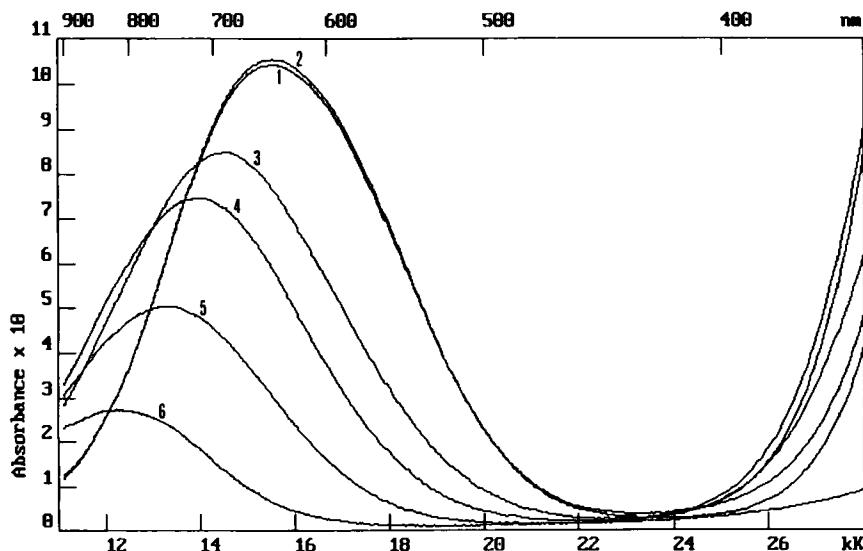


FIG. 1. Changes of the d-d absorption bands in the 1:4 copper(II) - ( $\alpha$ -MetP) system as a function of pH for the measurement conditions:  $c_M = 4.0 \times 10^{-3} M$ ;  $c_L = 1.6 \times 10^{-2} M$ ;  $l = 5.0 \text{ cm}$ ; pH values: 1 - 12.0, 2 - 7.7, 3 - 5.3, 4 - 4.8, 5 - 4.2, and 6 - 2.8. (computer print).

ordination of two L-methionine molecules<sup>8</sup>. Visible absorption spectra and e.s.r of frozen solution suggest that the structure is similar to that of analogous complexes in aqueous solution<sup>7,8</sup>. At high pH, the aminophosphonic acids coordinate in a similar way to the aminocarboxylic acids, forming chelate species ML and ML<sub>2</sub>, in which the ligands are bounded to the metal ions *via* the amino and the PO<sub>3</sub><sup>2-</sup> groups<sup>7</sup>. Thus, in this work the spectrum of [Cu(α-MetP)<sub>2</sub>]<sup>2-</sup> (whose x-ray structure is not yet known) has been assigned to C<sub>2h</sub> symmetry to predict the transition energies and AOM parameters. Figure 2 shows the experimental spectrum ( $\epsilon_i = f(v_i)$ ) of [Cu(α-MetP)<sub>2</sub>]<sup>2-</sup> complex along with Gaussian components. Table 2 shows the results of the Gaussian analysis, parameters of the components band, their oscillator strength values and relative root mean squares error (RMS%) for the studied complex.

The values of the angular overlap parameters and corresponding transition energies are collected in Table 3. The best fit with the experimental data was obtained for these results. We have made assignment of the d-d bands of the studied complex and concluded that the energy order of the d-orbitals is as follow: d<sub>xy</sub> << d<sub>z<sup>2</sup></sub> < d<sub>yz</sub> = d<sub>x<sup>2</sup>-y<sup>2</sup></sub> < d<sub>xz</sub>. The strongest rhombic splitting (bite angle effect) is observed for d<sub>xy</sub><sup>2</sup> (A<sub>g</sub>(3)), d<sub>z<sup>2</sup></sub> (<sup>2</sup>A<sub>g</sub>(3)), and d<sub>x<sup>2</sup>-y<sup>2</sup></sub> (<sup>2</sup>A<sub>g</sub>(3)) orbitals. The bonding parameters of studied complex in aqueous solution suggest that the σ-antibonding effect of the amino nitrogens are considerably less than this of oxygen ligators .

## CONCLUSIONS

We found that the σ-bonding effect of the O-ligator (from phosphonate group) with π isotropic bonding, is considerably greater than the N-ligator (amine group). The described bonding abilities are similar as in the case of the bis(amino hydroxamate)copper(II) complexes<sup>5</sup> (with unsymmetrical bidentate N1N2 ligands, where N1=amino nitrogen and N2=hydroxamic nitrogen).

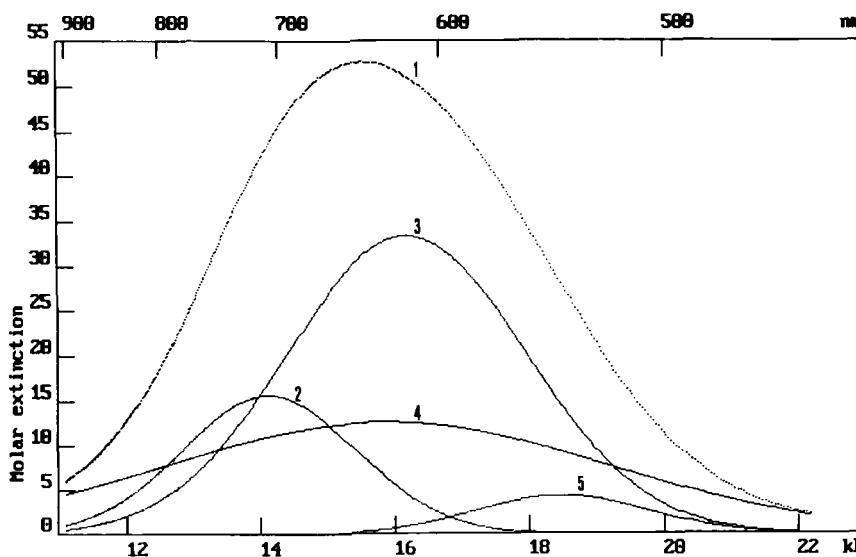


FIG. 2. Absorption electronic spectrum and Gaussian line-shapes of  $[\text{Cu}(\alpha\text{-MetP})_2]^{2-}$  complex in aqueous solution (RMS% = 0.15). 1 - experimental contour, 2-5 component bands;  $c_M = 4.0 \times 10^{-3}$  M,  $c_L = 1.6 \times 10^{-2}$  M,  $l = 5.0$  cm, and pH = 7.7, (computer print).

TABLE 2

Parameters of the component bands resulting from Gaussian analysis of the electronic spectrum of  $[\text{Cu}(\alpha\text{-MetP})_2]^{2-}$ , symmetry  $C_{2h}$ .

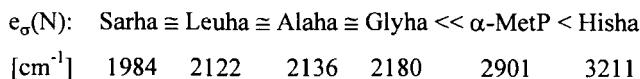
No	$\epsilon$ [dm <sup>3</sup> mole <sup>-1</sup> cm <sup>-1</sup> ]	$\nu_0$ [ cm <sup>-1</sup> ]	$\delta_{1/2}$ [ cm <sup>-1</sup> ]	f
1	15.568	14134.5	3068.8	$2.20 \cdot 10^{-4}$
2	12.595	15858.6	7824.2	$4.53 \cdot 10^{-4}$
3	33.313	16184.3	4175.4	$6.39 \cdot 10^{-4}$
4	4.285	18478.9	3020.6	$5.97 \cdot 10^{-5}$
RMS%	0.151			

TABLE 3

Assignments, transition energies, and AOM parameters of  $[\text{Cu}(\alpha\text{-MetP})_2]^{2-}$  complex (in  $\text{cm}^{-1}$ );  $^2\text{A}_\text{g}(1)/\text{d}_{xy}$  ground term,  $\epsilon_\pi(\text{N})=0$ .

Assignment	Resolved	Calculated
$^2\text{A}_\text{g}(3)/\text{d}_{z^2}$	14135	14135
$^2\text{B}_\text{g}(1)/\text{d}_{yz}$	15859	15860
$^2\text{A}_\text{g}(2)/\text{d}_{x^2-y^2}$	16184	16182
$^2\text{B}_\text{g}(2)/\text{d}_{xz}$	18479	18679
$\epsilon_\sigma(\text{N})$		2901(1)
$\epsilon_\sigma(\text{O})$		8349(1)
$\epsilon_\pi(\text{O})$		1310(1)
$\alpha$		84.7(0)
r.m.s.		1.0

Influence of the first ligator in copper(II) chelates on coordinated properties (bonding abilities) of amino nitrogen (N) is as follow. The bonding parameters of  $[\text{Cu}(\alpha\text{-MetP})_2]^{2-}$  (i.e.  $\text{Cu}(\text{N},\text{O})_2$ -chromofore, and O-phosphonate oxygen) system suggests that the  $\sigma$ -bonding effect of the amino nitrogen is considerably stronger than this of bis(aminohydroxamato)copper(II) complexes (i.e.  $\text{Cu}(\text{N},\text{N}')_2$  - chromofore, and  $\text{N}'$ - hydroxamate nitrogen). The series for  $\sigma$ -bonding was found and runs as follows<sup>9</sup>:



The overall stability constant of  $[\text{Cu}(\alpha\text{-MetP})_2]^{2-}$  complex is considerably less than these in the bis(aminohydroxamato)copper(II) complexes. The difference is probably due to the difference in basicities of O and N' and in  $\sigma$ -bonding abilities ones.

The bonding parameters of the second ligator (phosphonate oxygen) suggest that  $\sigma$ -bonding effect this one is considerably less than  $\text{N}^+$  (hydroxamate nitrogen):

$e_\sigma(\text{O}/\text{N}^+)$ :	$\alpha\text{-MetP} < \text{Hisha} \approx \text{Glyha} \approx \text{Sarha} \approx \text{Leuha} \approx \text{Alaha}$
[cm <sup>-1</sup> ]	8349      9497      9589      9593      9679      9728

The series of  $\pi$ -bonding runs as follows, ( the  $\pi$  abilities O and  $\text{N}^+$  are comparable neglecting except Hisha):

$e_\pi(\text{O}/\text{N}^+)$ :	$\text{Sarha} \approx \text{Glyha} \approx \text{Alaha} < \alpha\text{-MetP} \approx \text{Leuha} \ll \text{Hisha}$
[cm <sup>-1</sup> ]	931      993      1102      1310      1335      1945

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<sup>9</sup> Abbreviations:  $\alpha$ -Ala -  $\alpha$ -alanine, Alaha - L- $\alpha$ -alaninehydroxamic acid,  $\alpha$ -AlaP -  $\alpha$ -alanine-phosphonic acid, Glyha - glycinehydroxamic acid, Hisha - L-histidinehydroxamic acid, Leuha - L- $\alpha$ -leucinehydroxamic acid, L-Met - methionine,  $\alpha$ -MetP - methioninephosphonic acid, Sarha - sarcosinehydroxamic acid.

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