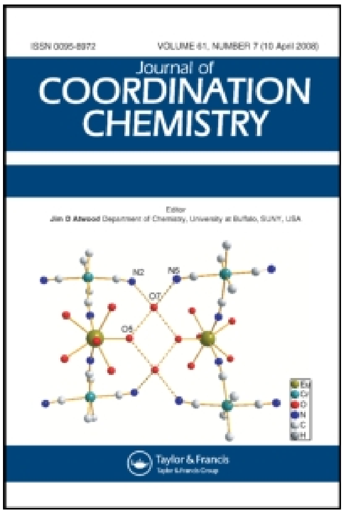

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Synthesis and spectroscopic characterization of new metal(II) complexes with methionine sulfoxide

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SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF NEW METAL(II) COMPLEXES WITH METHIONINE SULFOXIDE

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Methionine sulfoxide complexes of iron(II) and copper(II) were synthesized and characterized by chemical and spectroscopic techniques. Elemental and atomic absorption analyses fit the compositions $K_2[Fe(metSO)_2]SO_4 \cdot H_2O$ and $[Cu(metSO)_2] \cdot H_2O$. Electronic absorption spectra of the complexes are typical of octahedral geometries. Infrared spectroscopy suggests coordination of the ligand to the metal through the carboxylate and sulfoxide groups. An EPR spectrum of the Cu(II) complex indicates tetragonal distortion of its octahedral symmetry. ^{57}Fe Mössbauer parameters are also consistent with octahedral stereochemistry for the iron(II) complex. The complexes are very soluble in water.

Keywords: Amino acids; Methionine sulfoxide; Iron(II); Copper(II)

INTRODUCTION

Amino acids and esters of amino acids can act as coordinating agents through their amino (NH_2) and carboxylate (COO^-) groups [1]. For sulfur-containing amino acids, the sulfur atoms confer a more versatile coordination activity toward metal ions. Amino acids as coordinating or even chelating agents are of interest for obtaining safer drugs and antidotes for metal poisoning [2]. One well-known example of application to metal intoxication is related to the use of the sulfur-containing amino acid D-penicillamine (D-3 mercaptovaline) against Pb(II) poisoning. Indeed, treatment of Wilson's disease, in which Cu(II) is not accepted in the body even in normal quantities, is based on the treatment with D-penicillamine [2]. In the case of iron(II) intoxication, treatment is based on the use of deferoxamine as the chelating agent [2]. Both iron(II)

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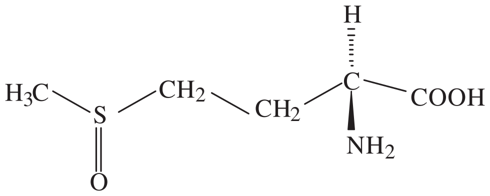

FIGURE 1 Structural formula of methionine sulfoxide.

and copper(II) are essential elements for human health, acting as cofactors in enzymatic reactions [3,4]. Iron(II) is present in hemoglobin [4].

The development of new drugs that could act as chelating agents, controlling metal concentration in the body, is of great interest and amino acids such as penicillamine are an important class of compounds in which these studies could be centered.

Methionine sulfoxide ($C_5H_{11}NO_3S$, metSO, Figure 1) is a sulfur-containing amino acid of vegetal origin present in garlic and onion [5,6]. This amino acid also shows high solubility and stability in water, permitting its use as a chelating agent for metal ions. Ni(II) and Co(II) complexes with metSO have previously been obtained in our laboratories [7,8]. The present work is dedicated to the synthesis and characterization of new iron(II) and copper(II) complexes with metSO.

EXPERIMENTAL

Reagents and Equipment

DL-methionine sulfoxide, copper(II) chloride ($CuCl_2 \cdot 2H_2O$), and iron(II) sulfate ($FeSO_4 \cdot 7H_2O$) were, respectively, Fluka, Sigma and Merck products, of analytical grade. Elemental analyses for carbon, hydrogen, nitrogen and sulfur were performed using a CHNS-O EA1110 instrument, CE Instruments. Copper and iron content was determined by atomic absorption using Perkin Elmer AAnalyst 300 equipment. Infrared spectra were measured using an FT-IR spectrophotometer Spectrum 2000, Perkin-Elmer. Samples were prepared as KBr pellets. The UV-vis/near-IR spectrum of the Cu(II) complex in aqueous solution was recorded on a Cary 500 spectrophotometer while the Fe(II) spectrum was recorded on a Perkin-Elmer Lambda 14 P spectrophotometer. The EPR spectrum of the Cu(II) complex was measured at 9.45 GHz using a Brucker ESP 300E instrument at 77 K. Mössbauer spectroscopy of the Fe(II) complex was performed in a constant-acceleration spectrometer using a ^{57}Co(Rh) source. Both source and absorber were kept at room temperature. A metallic iron foil was used for velocity calibration and as an isomer shift reference.

Synthesis of the Complexes

The iron(II) complex was synthesized by reaction under N_2 of an aqueous solution of iron(II) sulfate containing 2.0×10^{-3} mol of the metal ion with 4.0×10^{-3} mol of an aqueous solution of the potassium salt of metSO, resulting in a blue-greenish solution. The solid complex was obtained by evaporation of water under vacuum, washed with absolute ethanol and separated using a Schlenk funnel. The complex was dried under vacuum and stored in Schlenk flasks under N_2. This compound is easily oxidized by air with rapid color changes from green to dark brown.

The copper(II) complex was synthesized by adding an alcoholic solution containing 1.6×10^{-3} mol of copper(II) chloride to an alcoholic solution of the potassium salt of metSO containing 3.6×10^{-3} mol of the ligand with stirring at room temperature. The copper(II) complex precipitated as a blue solid. The complex was filtered, washed with ethanol and dried over P_4O_{10}; yield 85–90%. No suitable crystals of the complex were obtained for an X-ray structure determination.

RESULTS AND DISCUSSION

Analytical Results

Anal. Calcd. for $K_2[Fe(metSO)_2]SO_4 \cdot H_2O$(%): C, 20.8; H, 3.85; N, 4.86; S, 16.7; Fe, 9.69. Found: C, 20.4; H, 4.11; N, 4.77; S, 17.0; Fe, 9.10.

Anal. Calcd. for $[Cu(metSO)_2] \cdot H_2O$ (%): C, 29.3; H, 5.40; N, 6.80; S, 15.6; Cu, 15.5. Found: C, 29.3; H, 4.98; N, 6.69; S, 16.2; Cu, 15.4.

Electronic Absorption Spectra

The electronic absorption spectrum for the iron(II) complex shows a broad band with a maximum at $15.4 \times 10^3\,cm^{-1}$ and a shoulder at $11.9 \times 10^3\,cm^{-1}$, typical of a high-spin electronic d^6 configuration [9] and suggesting an octahedral geometry for the complex. Only one well-defined transition $^5E_g \leftarrow {}^5T_{2g}$ would be expected; however, owing to the Jahn–Teller effect, the ^5E_g term is split to $^5A_1$ and $^5B_1$, which give the band and a shoulder in the spectrum.

The spectrum of the Cu(II) complex exhibits a broad band in the visible region with a maximum at $16.1 \times 10^3\,cm^{-1}$ ($\xi = 55.0\,cm^{-1}\,M^{-1}$) and a weak band in the near-infrared region with a maximum at $8.7 \times 10^3\,cm^{-1}$. These bands are characteristic of an elongated tetragonal–octahedral copper(II) complex. According to the literature [9], the band at $16.1 \times 10^3\,cm^{-1}$ can be assigned to a $d_{x^2-y^2} \leftarrow d_{xz},d_{yz}$ transition, while the band at $8.7 \times 10^3\,cm^{-1}$ can be assigned to a $d_{x^2-y^2} \leftarrow d_z^2$ transition. Similar results have been described for $[Cu(H_2O)_4(HCO_2)_2]$ and $[Cu(NH_3)_4(SCN)_2]$ [9,10].

Infrared Absorption Spectroscopy

For amino acids the difference between the vibrational frequencies ν_{asym} (COO$^-$) and ν_{sym} (COO$^-$), Δ, generally increases when the M–O bond strength increases, depending on the carboxylate coordination, which can be monodentate or bidentate [11]. Monodentate coordination gives rise to higher Δ values, while bidentate leads to Δ values closer to those found for ionic carboxylate compounds, as, for instance, in potassium amino acid salts. The vibrational frequencies related to ν_{asym} (COO$^-$) and ν_{sym} (COO$^-$) in potassium methioninato-sulfoxide occur at 1587 and $1407\,cm^{-1}$. For the iron(II) complex, the ν_{asym} (COO$^-$) and ν_{sym} (COO$^-$) frequencies are observed at 1622 and $1408\,cm^{-1}$ and for the copper(II) complex, at 1618 and $1393\,cm^{-1}$. So, in this case, for potassium methioninato-sulfoxide $\Delta = 180\,cm^{-1}$ and for iron(II) and copper(II) complexes with methionine sulfoxide, the Δ values are equal to 214 and 225 cm^{-1}, respectively. For the carboxylate group these relatively small differences suggest bidentate coordination to the two metal ions. This is reinforced by results previously described for first row transition metal complexes with methionine [12] of the type $[M(met)_2]_n$ and based on the data related to the Ni(II) complex with metSO[7], in which coordination of the ligand to the metal occurs through a bidentate carboxylate.

The sulfoxide (**SO**) group represents another possibility for coordination to Fe(II) and Cu(II). If coordination occurs through oxygen, giving rise to a partially ionized bond, the characteristic frequency of ν (**SO**) would be shifted to lower values. If coordination occurs *via* sulfur, the ν (**SO**) frequency should be shifted to higher values [11]. The ν (**SO**) stretching frequency of the free ligand and its closely related potassium salt are observed at 1027 and 1019 cm^{-1}, respectively, while for iron(II) and copper(II) complexes these bands are shifted to 1003 and 1034 cm^{-1}, respectively, indicating that the (**SO**) group is coordinated to Fe(II) through the oxygen atom, while for Cu(II) coordination occurs through the sulfur. For the Cu(II)–metSO complex, coordination through sulfur is in accord with the theory of hard and soft acids and bases in which Cu(II) is classified as an intermediate hard/soft acid, being able to coordinate to hard (oxygen atom) and soft (sulfur atom) bases [13], and with the previously reported Cu(II) complex with penicillamine in which one of the sites of ligand coordination to the metal is the sulfur atom [2].

Coordination through the amino group is discounted by analyzing the infrared spectra in comparison to other well-known complexes involving methionine. For Mn(II), Co(II), Cu(II) and Ni(II) complexes with methionine, of general formula $[M(met)_2]_n$, coordination of the amino group of the ligand to the metal ion was confirmed by the lowering of the absorption range of ν_{asym} (NH_2) and ν_{sym} (NH_2) of the amino group (broad band) for the complexes in comparison to the potassium salt of the ligand [11,12]. For the Fe(II) and Cu(II) complexes with metSO, there is no shift of the frequencies of the amino group in comparison to the potassium salt of the ligand, suggesting no coordination through the NH_2 group. A previously reported [7] infrared spectrum of the Ni(II) complex with metSO, in which NH_2 is a non-coordinating group, shows close similarities with the infrared absorption data of Fe(II) and Cu(II) complexes with metSO described here.

The presence of the sulfate group (SO_4^{2-}) in the composition of the iron(II) complex is confirmed by two well-defined stretching bands at 1120 and 620 cm^{-1}, typical of the ionic sulfate group [11].

Cu EPR spectroscopy

The EPR spectrum of the Cu(II) complex, measured in the solid state, shows that g_1 and g_2 values are equal to 2.05 and 2.21, respectively. Comparing these g values with those described in the literature for Cu(II) complexes, it is possible to conclude that the Cu(II) complex with metSO exhibits tetragonal distortion of its octahedral symmetry. Similar results were also observed for $[Cu(H_2O)_4(HCO_2)_2]$ in a tetragonal arrangement with g_1 and g_2 values equal to 2.06 and 2.35, respectively [10]. The small difference observed between the experimental g values for $[Cu(metSO)_2] \cdot H_2O$ and $[Cu(H_2O)_4(HCO_2)_2]$ may arise from different ligands around Cu(II) causing different degrees of distortion of the octahedral symmetry. The EPR spectrum is shown in Figure 2.

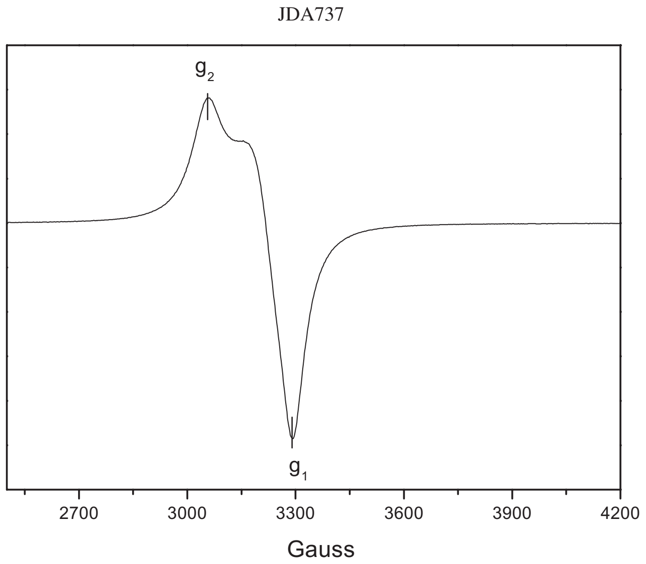

FIGURE 2 EPR spectrum of $[Cu(metSO)_2]\cdot H_2O$.

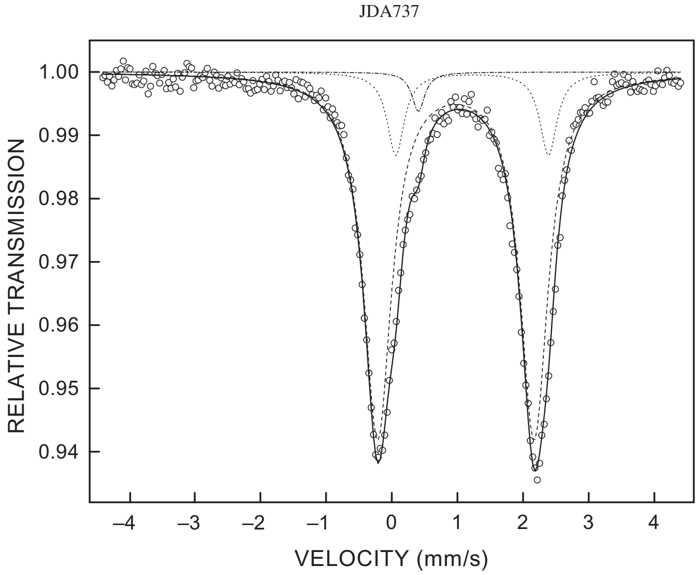

FIGURE 3 Mössbauer spectrum of $K_2[Fe(metSO)_2]\ SO_4\cdot H_2O$.

^{57}Fe Mössbauer Spectroscopy

The Mössbauer spectrum for $K_2[Fe(metSO)_2]SO_4\cdot H_2O$ is shown in Figure 3. This spectrum was least-square fit with a superposition of two doublets and one singlet, all with Lorentzian lineshape. The fitted parameters are given in Table I.

According to the collected data presented in Table I, the percentage of iron(II) in the sample is 98%. The isomer shift of $1.09\pm0.01\,\mathrm{mms^{-1}}$ (85.9%) corresponds to the expected value for octahedral iron(II) complexes, as previously described for an

TABLE I Mössbauer parameters obtained for $K_2[Fe(metSO)_2]\ SO_4 \cdot H_2O$

Oxidation state	$\delta (mm\,s^{-1})$	$\Delta (mm s^{-1})$	$\Gamma (mm s^{-1})$	*Relative area %*
$Fe^{2+(a)}$	1.09(1)	2.38(1)	0.52(1)	86(1)
$Fe^{2+(b)}$	1.34(2)	2.33(2)	0.31(1)	12(1)
Fe^{3+}	0.52(2)	–	0.24(1)	2.0(5)

δ: isomer shift relative to Fe metal, Δ: quadrupole splitting, Γ: linewidth.

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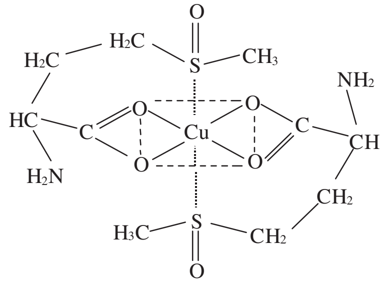

FIGURE 4 Structural formula proposed for the Cu(II)-metSO complex

iron(II) cysteine complex [14,15], which exhibits distorted octahedral symmetry with an isomer shift of $1.05\,mm\,s^{-1}$ and a quadrupolar splitting of $3.14\,mm\,s^{-1}$. In the present case, iron(II) exists in two chemical environments. $Fe^{2+(a)}$ with an isomer shift of $1.09\,mm\,s^{-1}$ is predominant in the sample (85.9%). The presence of iron(III) (2%) is well characterized by the isomer shift of $0.52 \pm 0.01\,mm\,s^{-1}$. The presence of iron(III) in the complex is due to the rapid oxidation of the sample when exposed to the air.

CONCLUSIONS

Composition of the Fe(II) and Cu(II) complexes with metSO are 1 : 2 (metal:ligand) with coordination *via* bidentate carboxylate (COO^-) and sulfoxide (**SO**) groups, in an octahedral arrangement. For the iron(II) complex, the sulfoxide group is coordinated to the metal ion through the oxygen atom while for the Cu(II) complex coordination occurs through the sulfur atom. The EPR spectrum indicates a tetragonally distorted octahedral symmetry for the Cu(II)-metSO complex. The Mössbauer spectrum shows 98% of iron(II) in the Fe(II)-metSO complex in an octahedral arrangement.

Based on these results, the proposed structure for iron(II) complex with metSO would be analogous to that previously described for the Ni(II) complex with metSO[7]. For the Cu(II) complex, the proposed structure is shown in Figure 4.

Acknowledgments

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