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A solid nickel(II) complex with methionine sulfoxide

Pedro P. Corbi^{a,*}, Petr Melnikov^b, Antonio C. Massabni^a

^aInstitute of Chemistry — UNESP, Department of General and Inorganic Chemistry, Rua Prof. Francisco Degni s/n, CP 355, CEP 14801-970, Araraquara, SP, Brazil

^bCCET, UFMS – Cidade Universitária s/n, CEP 79070-900, Campo Grande, MS, Brazil

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Abstract

Solid Ni($C_5H_{10}NO_3S_2 \cdot 2H_2O$ complex was prepared and characterized. Electronic absorption spectrum shows an octahedral geometry for the complex. Infrared spectroscopy analysis shows that the metal atom is coordinated to the ligand through (COO⁻) and (S=O) groups. Thermal analysis confirmed the composition of the complex and suggests that the water molecules are not coordinated to the metal ion. The complex shows extremely high solubility in water. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Methionine sulfoxide (MetSO, $C_5H_{11}NO_3S$, Fig. 1), a product of vegetal origin, is an amino acid similar to methionine. It is present in garlic [1], onion [2], nuts [3], carrots [4], apples [5,6] and banana plants [7]. Methionine sulfoxide was shown to be associated with Alzheimer disease due to the glutamine synthetase inhibition. This process is performed through the free radical oxidation stress. So, the compound is considered a biological sensor for this transformation [8,9]. This amino acid of easy access and low cost was also shown to possess pronounced anti-inflammatory properties [10]. In this context, the ligand itself and transition metal complexes with MetSO are of interest for obtaining virtual chemical vehicles for safer drugs, pharmaceutical trappers or even antidotes for



Fig. 1. Schematic structure of methionine sulfoxide.

*Corresponding author. *E-mail address:* pedrcorb@iq.unesp.br (P.P. Corbi).

the cases of acute poisonings. Metal(II) ion complexes of the first transition series involving the amino acid D,Lmethionine (Met) have been reported in the literature [11,12]. In these complexes, the central metal ions are coordinated to the ligand through carboxylate and amino groups, in an octahedral arrangement. These complexes are also described as polymeric and insoluble in water compounds, with formula $[M(Met)_2]_n$. However, no data has been reported so far as to the MetSO compounds with trace elements. This work deals with synthesis and characterization of a solid nickel(II) metal complex involving methionine sulfoxide as a ligand, in the form of anion.

2. Experimental

2.1. Materials and methods

D,L-Methionine sulfoxide, cysteine and nickel(II) chloride, NiCl₂· $6H_2O$, were Sigma and Merck products, analytical-grade purities. Elemental analysis for carbon, hydrogen and nitrogen was performed using a CHN-O EA1110 Analyzer (CE Instruments), cysteine being used as a reference substance. Nickel content was determined by using the atomic absorption technique with a Perkin-Elmer A Analyst 300. Infrared spectra were recorded on an FT-IR Spectophotometer Spectrum 2000 (Perkin-Elmer); samples were prepared in the form of KBr pellets. UV-Vis spectrum of the complex, measured in a 3.5×10^{-2} M aqueous solution of the complex, was registered on a Lambda 14 P Spectrophotometer (Perkin-Elmer). Thermal analysis was performed on a Thermoanalyzer TG/DTA simultaneous SDT 2960 TA Instruments, under the following conditions: synthetic air, 100 ml/min, and heating at 10°C/min, from 40 to 1200°C.

2.2. Preparation of the complex

The Ni(II) complex was synthesized by adding 0.002 mol of NiCl₂·6H₂O in alcoholic solution to an alcoholic solution of the potassium salt of MetSO containing 0.004 mol of the ligand (molar proportion metal:ligand equal to 1:2), at room temperature and under stirring. The Ni(II) complex was precipitated as a blue powder, after 18 h of constant stirring, from the resulting blue intense solution at pH 6.0. The compound was filtered, washed with ethanol and maintained in a dessicator together with fresh P_4O_{10} for 2 weeks. The yield of the synthesis was about 76%. Crystals of the complex could not be obtained to perform an X-ray study. Preparations in aqueous medium were also tested but no solid product could be isolated probably due to the high affinity of the complex to water. The potassium salt solution of methionine sulfoxide used in the synthesis, was previously prepared by adding 0.004 mol of potassium hydroxide in alcoholic solution to a fine suspension containing 0.004 mol of MetSO (molar proportion of 1:1) in alcoholic medium. This reaction was carried out under stirring and heating the mixture near its boiling point (ca. 70°C).

3. Results and discussion

3.1. Chemical analysis rendered the following values

Anal. calcd. for Ni($C_5H_{10}NO_3S$)₂·2H₂O (%): C, 28.52; H, 5.76; N 6.65; Ni, 13.94. Found: C, 27.73; H, 5.20; N, 6.17; Ni, 14.55. In spite of a prolonged drying until constant mass, water content in the samples may show variations within the limits 0 < n < 2 for each mol of the complex. Inner location of water molecules within the structural units of the complex may be an explanation, as it was observed for other similar metal complexes [13].

3.2. Electronic absorption spectra

As shown in Fig. 2, the spectrum of Ni($C_5H_{10}NO_3S)_2$ · 2H₂O is characterized by the presence of three welldefined bands and a shoulder corresponding to the following spectral bands: $\lambda_{max. I}$ 370 nm (27 016 cm⁻¹); $\lambda_{max. II}$ 619 nm (16 162 cm⁻¹); $\lambda_{max. III}$ 744 nm (13 439 cm⁻¹, shoulder); $\lambda_{max. IV}$ 1000 nm (9998 cm⁻¹). The analysis of these bands show an octahedral geometry for the compound. According to literature [14] the maxima are assigned to the following transitions: $\lambda_{max. IV}^{-3}T_{1g}$ (P) \leftarrow ${}^{3}A_{2g}$, $\lambda_{max. II}^{-3}T_{1g} \leftarrow {}^{3}A_{2g}$ and $\lambda_{max. IV}^{-3}T_{2g} \leftarrow {}^{3}A_{2g}$. The shoulder ($\lambda_{max. III}$) is assigned to the forbidden transition ${}^{1}E_{g} \leftarrow {}^{3}A_{2g}$. These results permitted to calculate the 10 Dq and *B* values as 9998 and 884 cm⁻¹, respectively, being similar to those obtained for the octahedral Ni(II) complex of the amino acid methionine [11] and *S*,*S*'methylenebis(cysteine) [13], structurally related to methionine sulfoxide.



Fig. 2. Electronic absorption spectrum for the Ni(II) complex with methionine sulfoxide.

Table 1										
Infrared al	osorption	frequencies	(cm^{-1}) o	f methionine	sulfoxide.	potassium	methioninate-si	ulfoxide and	l Ni(II)	complex ^a

1 1			
Methionine sulfoxide $C_5H_{11}NO_3S$	Potassium methioninate- sulfoxide $K^+(C_5H_{10}NO_3S)^-$	$Ni(C_3H_{10}NO_3S)_2 \cdot 2H_2O$	Assignments [13,15]
3410 w	_		ν (O–H)
		3665-2912 vs	$\nu_{\rm as.} (\rm NH_2)$ $\nu (\rm NH_2)$
2700–3200 s	3696–2839 vs		$\nu_{\rm as.}$ (CH ₂)
			$\nu_{\rm s.}$ (CH ₂)
1589 vs	1589 vs	1587 s	$\nu_{\rm as.}$ (COO ⁻)
1516 s	_	_	δ_{s_1} (NH ₂)
1452 m	_	_	δ (CH ₂)
1414 s	1419 s	1390 m	$\nu_{\rm s}~({\rm COO}^-)$
1345 m	1357 m	1337 w	$\delta_{\rm s}$ (CH ₃)
1276 m	_	_	δ (C–H)
1187 w	_	_	ν (C–COO ⁻)
1156 w	-	_	ν_{as} (C–C–N)
1027 s	1027 s	1000 m	ν (S=O)
664 w	660 w	654 m	ν (C–S)

^a vs, very strong; s, strong; m, medium; w, weak.

3.3. Infrared absorption spectroscopy

 $Ni(C_5H_{10}NO_3S)_2 \cdot 2H_2O$ infrared vibration frequencies are shown in Table 1, in comparison to those of methionine sulfoxide and its alkaline metal salt, the latter compound being considered as an ionic approximation to evaluate the free ligand frequencies (see infrared spectra in Fig. 3).

According to these comparative data, one of the coordination sites is certainly the bidentate carboxylate group. It is well-known that the difference between the vibrational $\nu_{\rm as.}$ (COO⁻) and $\nu_{\rm s.}$ (COO⁻) frequencies, Δ , in amino acids, generally increases with an increasing of the M-O bond strength and with the coordination form, which can be bidentade or monodentade. The latter coordination entity gives rise to higher Δ values [16–18] while the former leads to Δ values similar to those found in ionic carboxylate compounds, as, for instance, the potassium carboxylate salt. As one can see from Table 1, the vibrational modes related to the v_{as} (COO⁻) and v_{s} (COO⁻) in the potassium methioninate-sulfoxide occur at 1589 and 1419 cm^{-1} , while in the nickel complex they are observed at 1587 and 1390 cm⁻¹. So, for potassium methioninate-sulfoxide, $\Delta = 170 \text{ cm}^{-1}$ and for nickel complex, $\Delta = 197$ cm⁻¹. For the carboxylate group, these relatively small differences indicate a bidentade coodination through metal ion. This inference is strongly confirmed by the results described to the relative first row transition metal complexes with the amino acid methionine $[M(Met)_2]_n$ [11] in which the coordination of the metal atoms to the ligand occur through the bidentade carboxylate and show the same difference between ν_{as}

(COO⁻) and $\nu_{s.}$ (COO⁻) frequencies of that one found for the Ni(II) complex with MetSO.

The sulfoxide (S=O) group represents another possibility for the Ni(II) ion coordination to the ligand. In order to confirm or not the contribution of this site, electronic structure of sulfoxides may be of value as represented by



Fig. 3. Infrared absorption spectra for methionine sulfoxide, potassium methioninate-sulfoxide and nickel(II) complex.



Fig. 4. Schematic structures of the hybrids of sulfoxide group.

the resonance hybrids in Fig. 4 [19]. If the coordination occurs through oxygen, giving rise to a partially ionized bond, the frequency characteristic of ν (S=O) in the structure (II) would be shifted toward lower values. If, on the contrary, the coordination occurs via sulfur, the (S⁺–O⁻) frequency in the structure (I) should be shifted to higher values. Indeed, as shown in Table 1, the ν (S=O) frequency of the free ligand and its closely related potassium salt is observed at 1027 cm⁻¹, while in the nickel complex this band is shifted to 1000 cm⁻¹. So, we can conclude that the coordination of the metal ion to the (S=O) group of the ligand occurs basically through oxygen atom.

Possibility of coordination through the amino group is discarded by analysing the infrared spectra (Fig. 3), in comparison to other well-known complexes involving the amino acid methionine [11,12]. For the Mn(II), Co(II), Cu(II) and Ni(II) complexes with methionine, of general formula $[M(Met)_2]_n$, the coordination of the metal ion by the amino group was attested by the lowering of the absorption range of the $\nu_{as.}$ (NH₂) and $\nu_{s.}$ (NH₂) group (broad band) in the complexes in relation to the potassium

Table 2 Thermogravimetric data for Ni(C₅H₁₀NO₃S)₂·2H₂O

Temperature (°C)	Mass change (%)			
40-180	Δm_1	4.69		
180–940	Δm_2	78.62		
950	Residual mass	16.69		

salt of the ligand. In the case of the Ni(II) complex with methionine sulfoxide, there is no shifting of the frequencies of the amino group in comparison to the potassium salt of the ligand, which suggest that there is no metal ion coordination through NH_2 group.

3.4. Thermal analysis

3.4.1. Thermogravimetric analysis (TG)

Thermogravimetric analysis has been useful for confirmation of the complex compositions as well as for the identification of the final product. Actually, the number of water molecules of the complex occurs to be in the range 0-2 per mol of the complex. These water molecules are lost at the beginning of the heating, at temperatures not exceeding to 200°C (see Fig. 5a and Table 2). According to this thermogravimetric behavior, we inferred that water molecules do not participate in metal coordination. The ligand oxidation in the Ni(II) complex starts simultaneously with the end of water molecules lost. Residue com-



Fig. 5. TG (a) and DTA (b) curves for $Ni(C_5H_{10}NO_3S)_2 \cdot 2H_2O$.



Fig. 6. Structural scheme proposed for the coordination through metal ion in the complex.

position after Ni(C₅H₁₀NO₃S)₂·2H₂O decomposition was identified by X-ray diffractometry as NiO [20]. No sulfide or oxosulfite phases have been detected as could be expected. Thermogravimetric data are listed in Table 2, where Δm_1 represents water loss, and Δm_2 is inferred to the ligand elimination.

3.4.2. Differential thermal analysis (DTA)

Differential thermal analysis has been useful to determine the nature of the event occurring during the constant heating of the compound from 40 to 1200°C. The DTA analysis shows two well-defined exothermic peaks with their maxima at 257 and 517°C (Fig. 5b). These peaks can be inferred to the ligand oxidation in the Ni($C_5H_{10}NO_3S$)₂·2H₂O complex in two stages, leading to the NiO as the final product at 950°C.

3.5. Solubility

The Ni(II) complex with methionine sulfoxide shows extremely high solubility in water, differing from the Mn(II), Co(II), Cu(II) and Ni(II) complexes with methionine $[M(Met)_2]_n$, which are insoluble.

Based on the chemical and spectroscopic results, the following structural scheme (Fig. 6) is proposed to the coordination of the metal ion to the ligand in the complex. This proposed structure can give isomers, but their occurrence was not confirmed.

4. Final conclusions

The composition of the Ni(II) complex with methionine sulfoxide corresponds to the molar proportion 1:2 (metal: ligand), with absorbed water molecules varying from 0 < n < 2 per mol of complex in each synthesis. The central Ni(II) ion is coordinated to the ligand via carboxylate (COO⁻) and sulfoxide (S=O) groups, in an octahedral arrangement. Thermal decomposition leads to NiO as the unique final product.

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