Structural Data and Vibrational Spectra of the Copper(II) Complex of L-Selenomethionine

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A Cu(II) complex of the amino acid L-selenomethionine of stoichiometry Cu(L-SeMet)$_2$, has been prepared and characterized. Crystallographic data were obtained by means of X-ray powder diffractometry and showed that the compound is isostructural with the related complex of L-methionine, Cu(L-Met)$_2$. The structural analogy is also supported by the analysis of the IR and Raman spectra of the complex, which are briefly discussed in comparison with those of free L-selenomethionine.

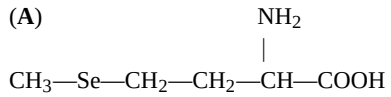
Key words: Bis(L-selenomethioninato)copper(II), Crystallographic Data, IR Spectra, Raman Spectra

Introduction

Copper(II) complexes of amino acids are of great pharmacological interest and importance as several of them present a wide spectrum of effects, including *anti*-inflammatory, anti-ulcer, anti-convulsant and even anti-tumoral activity [1 – 5]. It has also been established that when the pharmacological activity of certain copper complexes is compared with that of the free ligands, the complexes are usually more active than the parent ligands [1 – 3]. Other studies have suggested that copper(II) complexes of amino acids, small peptides, and other low molecular weight ligands may also be useful for copper supplementation [5]. On the other hand, selenomethionine (**A**) has been found to be a very useful form for selenium supplementation [6 – 8]. Therefore, and as a continuation of our own studies on copper complexes of amino acids and peptides [9 – 16], we have now prepared and investigated in detail the complex which copper(II) forms with L-selenomethionine, a compound which appears to be potentially useful as a novel pharmacological form for simultaneous copper and selenium supplementation, and investigated its structural and vibrational-spectroscopic behavior.

Although copper complexes of the related sulfur containing amino acid, L-methionine or DL-methionine, of stoichiometry Cu(Met)$_2$, have been well characterized [12, 17, 18], information concerning similar complexes of selenomethionine is relatively scarce,

(**A**)



as only a brief report on the existence of a species containing DL-selenomethionine, with a 2:1 ligand-to-metal stoichiometry was published some years ago [19].

Experimental Section

Synthesis of the complex

L-selenomethionine was purchased from Sigma and $CuSO_4 \cdot 5H_2O$ and NaOH from Carlo Erba. Bis(L-selenomethioninato)copper(II) was obtained by a similar procedure as that described for the synthesis of the respective methioninato complex [12, 20], as follows: 0.01 mol of the amino acid was dissolved in 10 ml of a 1 N NaOH solution. This solution was slowly mixed, under continuous stirring, with 25 ml of a 0.2 M solution of $CuSO_4$. The complex, which precipitates immediately as a fine microcrystalline powder, was filtered off, washed several times with small portions of distilled water, and finally dried in air. Analytical results for $CuC_{10}H_{20}N_2O_4Se_2$: calcd. C 26.46, H 4.41, N 6.17; found C 26.35, H 4.35, N 6.15. The complex is insoluble in water and in all common organic solvents. Therefore, it was impossible to attain single-crystals for crystallographic studies.

For comparative purposes a sample of the analogous L-methioninato complex, Cu(L-Met)$_2$, was prepared as described earlier [12, 20] and its purity confirmed by chemical analysis and IR spectroscopy [12].

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X-ray diffraction analysis

X-ray powder diagrams were recorded with a Philips PW 1710 diffractometer using Cu-K$_\alpha$ radiation [λ = 1.5425 Å]. A step scanning procedure was used, with a step size of 0.020° (2θ) and a recording time of 1.00 s per step. Reflections were collected in the 2θ-range between 3 and 60°. The experimental density was determined pycnometrically in benzene, at 25 °C. The indexation of the diagrams and determination of the unit cell parameters were performed with a locally modified version of the program PIRUM of Werner [21].

Spectroscopic measurements

The IR spectra were recorded in the range between 4000 and 400 cm^{-1} with a Bruker IFS 66 FTIR instrument, using the KBr pellet technique. The Raman spectra were recorded with the FRA 106 Raman accessory of the same instrument. The 1064 nm line of a Nd : YAG laser was used for excitation.

Results and Discussion

Crystal structure

The chemical analysis of the obtained L-selenomethionine complex suggests the same stoichiometry as that of the corresponding complex of L-methionine, also in agreement with the previous report [19]. The X-ray powder diagrams of Cu(L-Met)$_2$ and Cu(L-SeMet)$_2$ are largely identical, suggesting that both complexes may be isostructural.

Therefore, we have attempted to index the powder diagram of Cu(L-SeMet)$_2$ starting with the known unit cell parameters of Cu(L-Met)$_2$ [18]. This indexing procedure shows a rapid convergence, allowing to index the entire diffractogram without problems, giving a consistent set of values for the unit cell parameters, and confirming the initially suspected structural relation between Cu(L-SeMet)$_2$ and Cu(L-Met)$_2$. Besides, the indexing of all the reflections satisfy the extinction rules for space group $P2_1$, [22] determined for Cu(L-Met)$_2$ by single-crystal X-ray diffractometry [18].

The completely indexed powder diagram of Cu(L-SeMet)$_2$ is shown in Table 1 and the derived unit cell parameters and structural data are presented in Table 2. A comparison of these data with those of Cu(L-Met)$_2$ ($a = 9.487$, $b = 5.061$, $c = 15.563$ Å and $\beta = 92.46°$) [18] shows only a slight increment of all the unit cell parameters and of the unit cell volume in the present case, as expected from the replacement of sulfur by the greater selenium atom.

Table 1. X-ray powder diagram of Cu(L-SeMet)$_2$.

(h, k, l)	$d_{observ.}$	$d_{calc.}$	I/I_o	(h, k, l)	$d_{observ.}$	$d_{calc.}$	I/I_o
0 0 1	15.67	15.61	100	1 0 1	8.02	7.94	12
0 0 3	5.220	5.201	47	2 0 0	4.777	4.764	2
−2 0 1	4.620	4.630	3	2 0 1	4.489	4.487	7
−1 1 1	4.346	4.361	4	1 1 1	4.305	4.300	3
2 0 2	3.971	3.968	9	0 0 4	3.886	3.901	3
−1 0 4	3.683	3.684	2	−2 0 3	3.617	3.617	2
2 1 0	3.500	3.487	3	−1 1 3	3.455	3.452	7
2 0 3	3.411	3.418	4	−1 0 5	3.198	3.017	5
−3 0 2	3.005	3.002	1	−2 1 3	2.958	2.953	2
3 0 2	2.878	2.885	3	3 1 0	2.698	2.698	1
0 1 5	2.665	2.664	2	−1 1 5	2.618	2.600	2
−3 1 2	2.590	2.589	2	−3 0 4	2.539	2.534	3
0 2 2	2.431	2.431	2	4 0 0	2.382	2.382	1
3 1 3	2.354	2.350	2	−3 0 5	2.291	2.292	1
−3 1 4	2.271	2.271	3	1 2 3	2.219	2.219	2
0 2 4	2.139	2.139	1	−4 0 4	2.084	2.086	1
2 1 6	2.045	2.044	1	3 1 5	1.996	1.995	1
3 2 1	1.966	1.967	1				

Table 2. Crystallographic data of Cu(L-SeMet)$_2$.

Empirical formula	$CuC_{10}H_{20}N_2O_4Se_2$
Formula weight	453.46
Crystal system	monoclinic
Space group	$P2_1$ ($C_2{}^2$, No. 4)
a [Å]	9.54(1)
b [Å]	5.11(1)
c [Å]	15.63(2)
β [°]	93.25(8)
Z	2
Volume [Å^3]	760.73
$D_{exper.}$ [g·cm^{-3}]	1.95
D_{calc} [g·cm^{-3}]	1.98

If the two compounds are isostructural, then coordination of the metal center must be a distorted octahedron, identical to that described for the Cu(L-Met)$_2$ complex [18]. This octahedron is formed by *trans* coordination of the two amino acid anions generating an equatorial CuN_2O_2 ligand set. Additional interaction with two carboxylate oxygen atoms from neighboring selenomethionine molecules gives rise to the apical bonds and links the Cu(II) species into a carboxylate bridged sheet structure.

Infrared and Raman spectra

The assignment of the IR and Raman spectra of the complex was performed on the basis of its structural characteristics, by comparison with the spectra of the free ligand and of the related Cu(L-Met)$_2$ complex [12], using some standard references [23–26]

Table 3. Assignment of the vibrational spectra of L-selenomethionine and of the Cu(L-SeMet)$_2$ complex (Band positions in cm^{-1}).

L-Selenomethionine Infrared	L-Selenomethionine Raman	Complex Infrared	Assignment
		3294 s	ν_{as} (NH_2)
		3238 vs	ν_s (NH_2)
3165 m			ν_{as} (NH_3^+)
	2994 m	2997 w	ν_{as} (CH_3)
2922 vs	2910 vs	2924 s	ν_{as} (CH_2)
		2902 sh	ν_s (CH_3)
	2857 w	2863 vw	ν_s (CH_2)
2831 w	2821 w	2818 vw	
1616 vs, br	1615 vw		δ (NH_3^+)
1583 vs, br			ν_{as} (COO^-)
		1616 vs	ν (C=O)
1508 vs, br			δ (NH_3^+) + ν_{as} (CN)
		1570 m	ν_{as} (CN) + δ(NH_2)
1444 m		1448w/1425w	δ(CH_2) + δ(CH_3)
1406 vs, br	1421 s		ν_s (COO^-)
		1403 s	ν (C-O)
1360sh/1346s	1360w/1345m	1331 s	δ (CH) + δ (CH_2)
1315 s	1315 w/1300 m	1316 vw	δ (CH_2)
1275m/1263m	1277 w	1254 m/1242w	δ (CH_2)
1219 vs	1120 m		δ (CH_2)
1174 m	1177 w	1181 w	ν (CC)
1150 s	1155 vw		ρ (NH_3^+)
		1136 vs	ρ (NH_2)
1113 s	1120 w		
1065 m	1065 w	1041 m	ν_s (CN)
1022w/968s	1020vw/970m	971 w	δ (CH_2)
923 sh	920 vw	926 w	ρ (CH_3)
903 m/862s	900 vw/864m	900 vw/867 w	ν (CC)
793 m	790 vw	814 s	ρ (CH_2)
760 m	764 vw	762 w	δ (COO)
727s/698s			
678w	679 w	675m/662s	
638s/594w	625m/600vs		
577 m	577 s	575 s	ν (CH_3-Se)
538 vs	542 s		
		456 w	ν (Cu-N)
420 vs	420 w	430 m	

vs: very strong; s: strong; m: medium: w: weak; vw: very weak; sh: shoulder; br: broad.

and also data reported in a recent spectroscopic study of L-methionine-L-methioninium perchlorate monohydrate [27].

The assignment is shown in Table 3. Since it was very difficult to attain good quality Raman spectra of the complex, these data were not included in the Table but some of the obtained Raman data are considered in the following discussion, in which the proposed assignment is briefly commented:

• Not all of the typical CH_3 and CH_2 stretching vibrations could be identified in the spectra. For the "free" amino acid, a strong and very broad IR band makes the exact identification of these modes difficult. In the Raman spectrum of the complex, the ν_s (CH_2) vibration appears as a relatively strong line at 2919 cm^{-1}.

• The presence of characteristic ν(NH_3^+) and δ(NH_3^+) bands and the position of the two carboxylate stretchings, of the free ligand clearly show its existence in the form of a *zwitterion*.

• After complexation, the two NH_2 stretching vibrations together with some typical deformational motions of this group are observed. The position of these bands clearly confirms the participation of this group in bonding. Also, the ν_s(CN) mode is clearly displaced to a lower frequency after complex formation.

• The displacement observed for the carboxylate vibrations confirms the involvement of this group in copper coordination. In the "free" amino acid in its zwitterionic crystalline form two vibrations for the COO^- moiety are expected (ν_s (COO^-) and ν_{as} (COO^-)). After coordination, a lowering of one of these bands is expected, due to the generation of the Cu-O bond and an increase of the other one, because a C-O double bond is partially reconstructed. Both effects can be observed in Table 3. This behavior is somewhat different from that observed for Cu(Met)$_2$ [12] and some other Cu(II) complexes of amino acids [9–11] in which the latter band also suffers a small energy diminution after coordination. This behavior probably implies relatively weak apical bonds in the present case. From the two carboxylate vibrations, only that related to the ν(CO) vibration could be observed in the Raman spectrum of the complex, as a weak line located at 1403 cm^{-1}, *i. e.*, at the same wavenumber as in the IR spectrum.

• The ν_{as} (CN) vibration is partially overlapped by the strong δ(NH_3^+) band in the IR spectrum of the "free" ligand, and is seen at 1570 cm^{-1} in the IR spectrum of the complex, probably coupled with an NH_2 deformational mode. This band could be identified in the Raman spectra neither of the amino acid nor of the complex.

• The (CH_3-Se) stretching vibration is expected to appear at about 590 cm^{-1} [28]. For the "free" ligand it is seen at 577 cm^{-1} in both the IR and Raman spectra, whereas for the complex it is found at 575 cm^{-1} in the IR and at 571 cm^{-1} in the Raman spectrum.

• Regarding the ligand-to-metal-vibrations, only the stretching vibration of the Cu-N bonds could tentatively be assigned in the IR spectrum, as a weak band at 456 cm^{-1}. The Raman counterpart was found at

460 cm^{-1}. As it is known from the spectroscopic behavior of other Cu(II) complexes of amino acids, the stretchings related to the Cu-O bonds are located at frequencies below 400 cm^{-1} [9 – 12]. Therefore, we have tentatively assigned to this mode a weak Raman signal found at 383 cm^{-1}. In the Raman spectra of the $Cu(Met)_2$ complex these bands have been found at 477 (Cu-N) and 354 cm^{-1} (Cu-O), respectively [12].

This brief analysis shows the existence of important spectral similarities between $Cu(L\text{-}SeMet)_2$ and $Cu(L\text{-}Met)_2$, supporting the idea of a close structural relationship between both complexes.

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