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The Interaction of Copper(II) with S-methylcysteine. Crystal and Molecular Structure of Bis(S-methyl-L-cysteinato)copper(II)

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Abstract

Crystals of a copper(II) complex of S-methylcysteine, bis(S-methyl-L-cysteinato)copper(II), have been grown from a solution on the surface of a solid copper(II) hydroxysalt. They are monoclinic, space group $P2_1$, with $a = 13.265(8)$, $b = 5.036(3)$, $c = 9.571(6)$ Å, $\beta = 97.55°$ and $Z = 2$. The crystal structure was determined from diffractometer data and refined by the full-matrix least-squares technique to a final $R = 0.045$ and $R_w = 0.052$ for 921 observed reflections. The structure consists of Cu(S-methyl-L-cysteine)$_2$ units with an approximately square planar *trans* coordination of copper(II) by two O(carboxylate) and two N(amino) atoms. These units are linked by two weak additional Cu–O(carboxylate) bonds to form a two-dimensional polymer. There is no interaction of copper(II) with the ether sulfur of the ligand; overall features of the structure are very similar to that of the analogous cadmium complex. In accordance with the interpretation of infrared data, weak intermolecular hydrogen bonds of the type N–H···O with N···O distances ranging from 2.94 Å to 3.10 Å are observed.

Introduction

Metal ion–sulfur interactions (or their absence) are of increasing interest in bioinorganic chemistry [1]. In view of their coordination properties, bioligands containing sulfur may be separated in different classes. Ligands with one or more thiol groups R–SH as, for example, cysteine, penicillamine and glutathione; ligands with thioether groups R–S–R (S-methyl-cysteine (SMC), methionine (Met), biotin) or ligands with disulfide linkages R–S–S–R (cystine, lipoic acid). While only a few well-characterized metal thiol complexes involving neutral R–SH molecules are known [1], investigations into R–S$^-$ metal thiolate complexes have a long history [2], especially in view of the therapeutic activity of the ligands involved for the treatment of metal poisoning and, in view of the biochemical importance of sulfur-containing amino acids as, for example, cysteine bound to metal ions at the active site of iron–sulfur proteins, molybdenum-containing enzymes or metallothionein [3]. In contrast to R–S$^-$, the ether sulfur is an extremely weak base, and it is only its softness that provides the basis for interaction of thioethers with metal ions. Thus, it is expected that thioethers coordinate best to soft metal ions and, only marginally, to borderline metal ions such as Cu^{2+} [4].

Several spectroscopic investigations have dealt with the interaction of S-methyl-cysteine with copper(II). McCormick *et al.* [5] have observed that appreciable broadening of the methyl proton NMR signals in solutions containing 0.2 M SMC and 10^{-4} M metal ions occurs for Cu^{2+} but not for Mn^{2+}. This fact was interpreted in terms of a complex formation of Cu^{2+} involving the sulfur atom of SMC. Chelation of Cu^{2+} at the glycinate site of SMC and a weak interaction of the thioether group in an apical position, under conditions of excess ligand in solution, was suggested by Espersen and Martin [6] from an interpretation of detailed NMR data.

On the other hand, crystallographic data of SMC complexes of Cd^{2+} and Zn^{2+}, which also have to be considered as borderline metal ions, show that the thioether group is not coordinated to the metal [7].

This paper reports on the preparation, crystal growth and crystal structure of bis(S-methyl-L-cysteinato)copper(II), Cu(L-SMC)$_2$.

Experimental

Preparation and Analytical Data

Bis(S-methyl-L-cysteinato)copper(II) could be prepared by different methods. Pure, but only microcrystalline samples, were precipitated from aqueous solution by the dropwise addition of a 0.5 M SMC/0.07 M sodium–acetate solution (pH = 6.1) to a 0.25 M copper(II) chloride solution. Very small agglomerates of blue needle-shaped crystals were able to be

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grown, either by slow cooling of aqueous solutions (0.1 mmol copper(II) acetate, 0.05 mmol sodium-acetate and 0.2 mmol SMC in 20 ml water) or by gel-growth from a tetramethoxysilane gel. Well-formed crystals suitable for an X-ray structure determination were obtained by extremely slow evaporation at 310 K of a 10^{-3} M aqueous SMC solution containing a solid hydroxysalt of copper(II), $Cu_2(OH)_2CO_3$.

Anal. Calc. for $CuC_8H_{16}N_2O_4S_2$: C, 28.95; H, 4.85; N, 8.44. Found: C, 28.72; H, 4.68; N, 8.49%. Thermoanalytical measurements on a Mettler TA-2000C system indicated that there is no water of crystallization present. The complex starts to decompose at 460 K yielding Cu_2O and CuO as final products when heated to 1270 K with a heating rate of 10 °C/min in a flowing nitrogen atmosphere.

X-ray Structural Analysis

Preliminary precession and Weissenberg photographs established monoclinic symmetry and systematic absences consistent with the space group $P2_1$. The centrosymmetric space group $P2_1/m$, also consistent with the systematic extinctions found, could be rejected because the complex contains an optically active ligand. Data collection was performed on a Picker FACS-I diffractometer; unit cell dimensions and crystal orientation were determined by least-squares refinement of 20 automatically centered reflections in the range $0.29 \leqslant (\sin\theta)/\lambda \leqslant 0.33$ Å^{-1}. Early in data collection, the crystal moved and the above parameters were redetermined. Crystal data and details of data collection are given in Table I. Six standard reflections, chosen to lie in different regions of reciprocal space, were monitored periodically and showed no significant variation of their intensities. The intensities were reduced to F_o by applying corrections for Lorentz and polarization effects as well as for absorption. The calculations were performed with a modified version of the Northwestern University Crystallographic Computing Library [8] on a IBM 3033 at the University of Zurich.

The structure was solved using MULTAN 78. Despite the very small volume of the data crystal, most hydrogen atoms could be unambiguously located from difference Fourier maps including methyl hydrogen atoms. They were included as a fixed contribution to F_c at their calculated idealized geometry (H–C–H = 109.5°, C–H = 0.95 Å; N–H = 0.95). The other atoms were refined anisotropically upon F^2 using all data including $F_o^2 < 0$ (1176 unique data). At convergence of the full -matrix least-squares refinement the values for R and R_w on F^2 were 0.083 and 0.108. For the portion of data having $F_o^2 > 3\sigma(F_o^2)$, the values for R and R_w on F were 0.045 and 0.052. An analysis of the weighting scheme ($w = 1/\sigma^2(F_o^2)$, where $\sigma^2(I) = \sigma^2_{\text{counting}} + (0.03\ I)^2$, I being the intensity corrected only for background scattering and attenuator factors) revealed only little dependency of the minimized function upon the magnitude of F_o or $(\sin\theta)/\lambda$. The final difference Fourier was essentially featureless with the highest peaks ($\leqslant 0.77$ e$^-$/Å^3 compared with 0.70–0.40 e$^-$/Å^3 for hydrogen atoms) concentrated around the copper centre. The enantiomorph selected by MULTAN 78 was, by happenstance, the correct one by comparison with the structure of $Cd(SMC)_2$.

TABLE I. Crystal Data and Data Collection Parameters for $Cu(L\text{-}SMC)_2$

Formula	$Cu(C_4H_8NO_2S)_2$
Formula weight	331.90
Extinction	$0k0, k = 2n + 1$
Space group	$P2_1$
a	13.265(8) Å
b	5.036(3) Å
c	9.571(6) Å
β	97.55(2)°
V	632.2 Å^3
Z	2
ρ_{calc}	1.743 g/cm^3
Temperature	295 K
Data crystal	bright blue needle, 0.47 x 0.06 x 0.02 mm
Radiation	Mo Kα, graphite monochromated
Linear absorption coefficient, μ	20.5 cm^{-1}
Transmission factors	0.865–0.952
Scan speed	2.0°/min in 2θ
Background counts	10s at each end with rescan option[a]
Scan range	1.0° below Kα_1 to 0.90° above Kα_2
$(\sin\theta)/\lambda$ limits	$0.047 < (\sin\theta)/\lambda < 0.596$ Å^{-1}
Data collected	$\pm h, \pm k, l$
Unique data with $F_o^2 > 3\sigma(F_o^2)$	921

[a] Ref. 26.

Infrared Spectral Measurements

IR spectra of SMC and of $Cu(L\text{-}SMC)_2$ dispersed in KBR pellets in the range from 600 cm^{-1} to 4000 cm^{-1} were recorded on a Perkin-Elmer Model 297 spectrophotometer.

Results and Discussion

Final positional and thermal parameters are given in Table II. Supplementary material including hydrogen atom parameters, anisotropic thermal parameters and F_o/F_c Tables are available on request by one of the authors (E.D.).

The structure consists of $Cu(SMC)_2$ units with an approximately square planar (the maximum deviation of an atom from the best plane through CuN_2O_2 is 0.037(7) Å) *trans* coordination of the

TABLE II. Final Positional Parameters for Cu(L-SMC)$_2$ [a]

Atom	x	y	z	B(Å^2)
Cu	0.49395(9)	0.67414	0.24963(11)	2.05(4)
S(1)	0.14482(19)	0.35518(79)	0.08266(28)	3.41(11)
S(2)	0.83059(19)	1.10823(76)	0.44365(27)	3.37(11)
O(11)	0.4597(4)	0.8814(16)	0.0796(6)	1.90(20)
O(12)	0.3676(5)	0.8759(17)	−0.1319(6)	2.33(24)
O(21)	0.5295(5)	0.4687(15)	0.4219(6)	2.21(25)
O(22)	0.6348(5)	0.4776(16)	0.6223(6)	2.84(25)
C(11)	0.3912(7)	0.7868(21)	−0.0142(10)	1.23(27)
C(12)	0.3352(7)	0.5405(21)	0.0302(9)	1.95(32)
C(13)	0.2301(7)	0.6298(25)	0.0610(10)	3.26(36)
C(14)	0.1108(9)	0.2653(30)	−0.0978(13)	5.02(61)
C(21)	0.6084(7)	0.5553(21)	0.5002(9)	2.01(36)
C(22)	0.6728(7)	0.7525(20)	0.4294(9)	2.43(32)
C(23)	0.7440(7)	0.9175(22)	0.5342(10)	2.69(34)
C(24)	0.9063(9)	1.2493(31)	0.5915(12)	5.38(53)
N(1)	0.3935(5)	0.4115(19)	0.1569(7)	2.02(29)
N(2)	0.6010(5)	0.9240(16)	0.3362(7)	2.11(28)

[a] Estimated standard deviations in the least significant figures are given in parentheses in this and all subsequent tables. The isotropic temperature factors are from the last cycle of isotropic refinement made before the absorption correction.

central copper atom by two O(carboxylate) and two N(amino) atoms (Fig. 1). These units are linked by two weak additional Cu–O(carboxylate) bonds to form a two-dimensional polymer. The overall features of the structure are, therefore, very similar to those found for Cd(L-SMC)$_2$ by de Meester and Hodgson [7], but the metal coordination geometry as well as the conformation of one thioether group are quite different. In Cu(L-SMC)$_2$ the copper(II) atoms show the usual 4 + 2 Jahn–Teller distorted coordination with two equatorial Cu–O bonds of 1.936 and 1.951 Å, two equatorial Cu–N bonds of 2.001 and 1.995 Å and two very long axial Cu–O separations of 2.703 and 2.728 Å, whereas in Cd(L-SMC)$_2$ all Cd–O and Cd–N distances lie in the range from 2.26 to 2.47 Å. The metrical details of the metal coordination in Cu(L-SMC)$_2$ show close agreement with those reported for Cu(L-Met)$_2$ [9] and for Cu(D,L-Met)$_2$ [10]. Figure 2 gives an ORTEP presentation of the structure of Cu(L-SMC)$_2$. Interatomic bond distances, bond angles and hydrogen bonding interactions are presented in Tables III, IV and V.

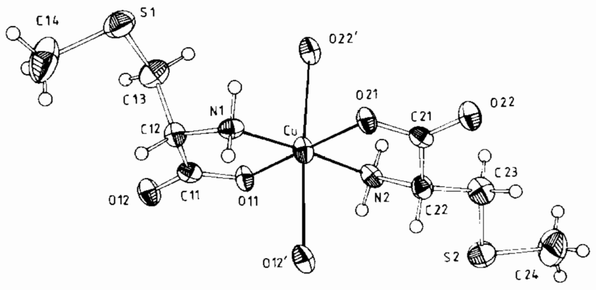

Fig. 1. Molecular structure of Cu(L-SMC)$_2$ showing the atom numbering scheme.

TABLE III. Bond Distances (Å) for Cu(L-SMC)$_2$

Atoms	Distance
CuN$_2$O$_4$ octahedron	
Cu–O(11)	1.936(6)
Cu–N(1)	2.001(8)
Cu–O(12′)	2.728(7)
Cu–O(21)	1.951(6)
Cu–N(2)	1.995(8)
Cu–O(22′)	2.703(7)
SMC, molecule I	
O(11)–C(11)	1.282(10)
O(12)–C(11)	1.215(10)
C(11)–C(12)	1.535(13)
C(12)–C(13)	1.531(12)
C(12)–N(1)	1.498(11)
C(13)–S(1)	1.816(11)
C(14)–S(1)	1.785(13)
SMC, molecule II	
O(21)–C(21)	1.282(10)
O(22)–C(21)	1.238(10)
C(21)–C(22)	1.525(12)
C(22)–C(23)	1.530(13)
C(22)–N(2)	1.492(11)
C(23)–S(2)	1.804(10)
C(24)–S(2)	1.773(12)

There is no interaction of the metal atom with the ether sulfur atom in Cu(L-SMC)$_2$. Although an energetically favorable five-membered ring could result from bidentate N/S chelation, the analogous

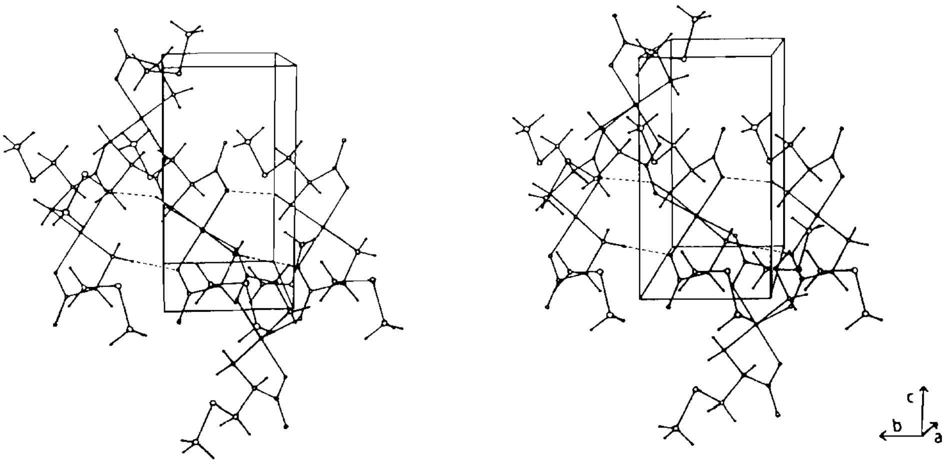

Fig. 2. ORTEP presentation of the structure of Cu(L-SMC)$_2$ demonstrating the polymeric nature of the complex. The two strongest intermolecular hydrogen bonds are indicated by dotted lines.

TABLE IV. Bond Angles (°) for Cu(L-SMC)$_2$

Atoms	Angle
CuN$_2$O$_4$ octahedron	
O(11)–Cu–O(21)	179.3(4)
O(11)–Cu–N(1)	85.1(3)
O(11)–Cu–N(2)	94.9(3)
O(11)–Cu–O(12′)	92.6(2)
O(11)–Cu–O(22′)	89.1(2)
O(21)–Cu–N(1)	95.6(3)
O(21)–Cu–N(2)	84.5(3)
O(21)–Cu–O(12′)	87.5(2)
N(1)–Cu–N(2)	176.3(3)
O(21)–Cu–O(22′)	90.8(2)
N(1)–Cu–O(12′)	84.1(2)
N(1)–Cu–O(22′)	98.7(3)
N(2)–Cu–O(12′)	92.2(3)
N(2)–Cu–O(22′)	85.0(2)
O(12′)–Cu–O(22′)	176.8(2)
Cu–O(11)–C(11)	117.1(7)
Cu–N(1)–C(12)	108.4(6)
Cu–O(21)–C(21)	113.7(6)
Cu–N(2)–C(22)	104.3(6)
SMC, molecule I	
O(11)–C(11)–O(12)	125.8(10)
O(11)–C(11)–C(12)	115.5(8)
O(12)–C(11)–C(12)	118.7(9)
C(11)–C(12)–N(1)	110.9(7)
C(11)–C(12)–C(13)	107.6(8)
N(1)–C(12)–C(13)	111.0(7)
C(12)–C(13)–S(1)	113.3(8)
C(13)–S(1)–C(14)	99.5(5)
SMC, molecule II	
O(21)–C(21)–O(22)	123.5(9)
O(21)–C(21)–C(22)	115.0(7)
O(22)–C(21)–C(22)	121.3(8)
C(21)–C(22)–N(2)	107.0(7)
C(21)–C(22)–C(23)	113.3(7)
N(2)–C(22)–C(23)	111.6(8)
C(22)–C(23)–S(2)	110.6(6)
C(23)–S(2)–C(24)	99.2(5)

TABLE V. Hydrogen Bonding Interactions in Cu(L-SMC)$_2$; Distances (Å) and Angles (°)

Atoms	
O(11) . . . N(1)	2.935(12)
H1(N1) . . . O(11)	2.01
N(1)–H1(N1) . . . O(11)	162
O(12) . . . N(2)	3.065(11)
H1(N2) . . . O(12)	2.24
N(2)–H1(N2) . . . O(12)	144
O(21) . . . N(2)	3.050(11)
H2(N2) . . . O(21)	2.17
N(2)–H2(N2) . . . O(21)	151
O(22) . . . N(1)[a]	3.097(11)
H2(N1) . . . O(22)[a]	2.43
N(1)–H2(N1) . . . O(22)[a]	127

[a] Hydrogen bond of dubious reality; included for reasons of symmetry.

N/O chelation with an oxygen atom of the carboxylate group, obviously, is preferred. Reviewing all crystallographic data available on metal complexes of four α-amino acids containing a thioether group (SMC, SEC, Met and Et, see Table VI), this fact is not at all surprising. A factor which often has been overlooked in previous investigations is the influence of the pH and, hence, of the degree of protonation of the ligand on the type of coordination realized. With the exception of the two Co(III) complexes Co(en)$_2$-(SMC$^-$)(NCS)$_2$ [11] and Co(L-SMC$^-$)$_2$ClO$_4$·H$_2$O [12] there is no metal–sulfur interaction with

TABLE VI. Coordination Properties of Amino Acids Containing a Thioether Group as Established by X-ray Structure Analysis: S-methyl-cysteine (SMC), S-ethyl-cysteine (SEC), Methionine (Met) and Ethionine (Et)

Coordination	Complex	Reference	Structure type
(A) Bidentate N/O, five-membered chelate ring	Cu(L-SMC$^-$)$_2$	This work	two-dimensional polymer
	Zn(L-SMC$^-$)$_2$	7	one-dimensional polymer
	Cd(L-SMC$^-$)$_2$	7	two-dimensional polymer
	Hg(L-SMC$^-$)$_2$	17	polymeric chains
	Cu(L-Met$^-$)$_2$	9	isolated sheets
	Cu(D,L-Met$^-$)$_2$	10	isolated sheets
	Zn(L-Met$^-$)$_2$	14	isolated sheets
	Cd(L-Met$^-$)$_2$	18	isolated sheets
	CH_3Hg(D,L-Met$^-$)	19	hydrogen-bonded sheets
(B) Bidentate N/S, five-membered chelate ring	Co(en)$_2$(SMC$^-$)(NCS)$_2$	11	monomeric
	Pd(L-SMC$^\circ$)Cl_2·H_2O	23	three-dimensional polymer
	Pt(L-SEC$^\circ$)Cl_2	24	monomeric
(C) Bidentate N/S, six-membered chelate ring	Pd(D,L-Met$^\circ$)Cl_2	20	monomeric, H-bonded to dimers
	Pd(D,L-Et$^\circ$)Cl_2	21	monomeric, H-bonded to dimers
	Pt(L-Met$^\circ$)Cl_2	22	monomeric, H-bonded to dimers
	Pt(D,L-Met$^\circ$)Cl_2	22	monomeric, H-bonded to dimers
(D) Bidentate O/S, bridging two metal atoms	Hg(D,L-Met$^\circ$)$_2$(ClO_4)$_2$·2H_2O	25	polymeric
	Hg(D,L-Et$^\circ$)$_2$(ClO_4)$_2$	17	polymeric
(E) Terdentate N/O/S	Co(L-SMC$^-$)$_2$$ClO_4$·$H_2O$	12	[Co(SMC)$_2$]$^+$ cations

deprotonated, anionic ligands. However, in all complexes involving a protonated, neutral ligand, a metal–sulfur bond has been found. If deprotonated carboxylate groups are available, the bidentate N/O chelation of the metal atom seems to be highly preferred to a metal–sulfur bonding in complexes with ether sulfur containing α-amino acids. From the data given in Table VI it is evident, in addition, that the soft ether sulfur coordinates only with soft or, marginally, with borderline metal atoms. Again, with the exception of the two Co(III) complexes mentioned earlier, all complexes exhibiting metal interaction with sulfur involve the soft metal ions Pd(II), Pt(II) or Hg(II). The fact that in two Co(III) complexes a metal–sulfur bonding of deprotonated SMC$^-$ has been established may be in consequence of the inert character of Co(III) complexes. The coordination type, therefore, appears to depend on other factors, some of which are kinetically determined [4]. In addition, Co(III)–S complexes in solution are susceptible to rearrangements from N/S to N/O coordination induced by base and/or Co(II) [11].

The geometry of the SMC ligands shows no unusual features and there are no significant differences between the interatomic bond distances of the two crystallographically independent SMC molecules. Some of the corresponding bond angles of the two molecules, however, differ substantially, as shown by the data presented in Table IV. The terminal C–S bonds of the thioether groups are about 0.03 Å shorter than the corresponding values of the non-terminal bonds (1.785 Å compared to 1.816 Å in molecule **I**, 1.773 Å compared to 1.804 Å in molecule **II**). Although, in view of the σs involved, this bond length difference of 0.03 Å is at the limit of significance. It is interesting to note that a similar difference is also found in most of the other crystallographically characterized metal complexes with non-coordinating thioether groups (e.g. 1.75 Å/1.81 Å and 1.79 Å/1.82 Å in Cd(L-SMC)$_2$ [7], 1.785 Å/1.806 Å in Cu(D,L-Met)$_2$ [10] and 1.800 Å/1.823 Å in glycyl-L-methioninato–copper(II) [13]. The C–S–C thioether bonding angles in Cu(L-SMC)$_2$ are 99.5° in molecule **I** and 99.2° in molecule **II**. Corresponding literature data are 100° and 102° in Cd(L-SMC)$_2$ [7], 99.5° and 99.4° in Zn(L-SMC)$_2$ [7], 102.1° in Cu(D,L-Met)$_2$ [10], 101.8° and 101.9° in Zn(L-Met)$_2$ [14] and 100.6° in glycyl-L-methioninato–copper(II) [13].

The data given in Table V summarizes the weak intermolecular hydrogen bonding interactions of the type N(amino)–H···O(carboxylate) found in Cu(L-SMC)$_2$. Corresponding N···O distances range from 2.94 to 3.10 Å. IR spectra were recorded to check these findings. The overall features of the spectra are very similar to those reported for Cu(L-Met)$_2$ [9] and for Zn(L-SMC)$_2$ [15]. Cu(L-SMC)$_2$ exhibits two sharp and intense NH_2 stretching modes at ~3300 and ~3230 cm^{-1}, a weak but sharp band at ~2920

cm^{-1} which can be ascribed to C–H stretching modes and an intense carboxylate asymmetric stretching vibration at ~ 1620 cm^{-1}, with a sharp shoulder at ~ 1570 cm^{-1} which has been attributed to a NH_2 deformation mode in the $Cu(L\text{-}Met)_2$ complex. Lautié *et al.* [16] have given a graphic representation for the correlation between hydrogen bonded N•••O distances ranging from 3.25 to 2.60 Å and the corresponding experimental N–H stretching frequencies ranging from 3450 to 2200 cm^{-1}. In good agreement with this data, the 3230 cm^{-1} band in $Cu(L\text{-}SMC)_2$ can be assigned to the N(1)–H1(N1)•••O hydrogen bond with a N•••O distance of 2.94 Å, whereas the 3300 cm^{-1} frequency corresponds to the weaker N–H•••O bonds with N•••O distances of 3.05–3.10 Å.

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