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PREPARATION AND STRUCTURE OF Ag(I) COMPLEX WITH CYCLO(L-METHIONYL-L-METHIONYL)

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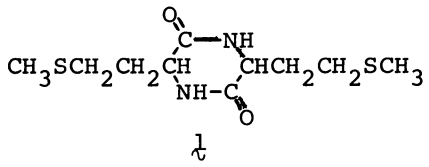
The structure of a Ag(I) complex with cyclo(L-methionyl-L-methionyl) was examined by means of ^{1}H NMR spectra and X-ray structure analysis. The spectra suggest that the sulfur atoms of the ligand coordinate to Ag(I) ion. In crystaline state, each Ag atom is coordinated linearly to two sulfur atoms to give a helical polymer along *b*-axis.

It is well known in many metalloproteins and metalloenzymes that the functional groups in the side chains of the peptides, such as imidazole and thioether, coordinate to metal ions as ligating groups.

Authors have used cyclo(L-histidyl-L-histidyl)[1] and cyclo(L-methionyl-L-methionyl) (1)[2] as protein model compounds in order to examine metal-protein interactions at histidine and methionine residues.



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This paper reports the preparation and structure of Ag(I) complex with 1.

The mixture of 1(0.50mmol) and Ag(I) perchlorate(0.53mmol) was completely dissolved in hot water(50ml) with stirring, and the solution was cooled to a room temp. After a few days, a precipitate was filtered off and recrystallized from water. Yield; 78%. mp 223∿227°dec. Found: C, 25.58; H, 3.84; N, 5.99%. Calcd for Ag-$(C_{10}H_{18}N_2O_2S_2)ClO_4$: C, 25.57; H, 3.86; N, 5.96%.

Table 1 shows the chemical shifts of the methyl group of 1 and 2[Ag(I) complex ion with 1] in D_2O at 50 and 65°C. 1 and 2 give a sharp singlet peak at δ=2.11 and 2.38 ppm at 50°C, respectively. The downfield shift (Δδ=0.27) of the peak of the methyl group of 2 from 1 suggest that the sulfur atom of 1 coordinates to Ag(I) ion, because the chemical shift(2.1∿3.0 ppm, m) of β-methylene of 1 was almost identical with that of 2. The signals of methine of 1 and 2 were not observed because of the overlapping of the signal of D_2O. Table 1 also indicated that the mixture of 1 and 2 gives a peak(s) of methyl group at δ=2.30. These results suggest the existence of coordination equilibrium between free and coordinated ligands.

Table 1. The chemical shifts(ppm) of CH_3 groups of 1 and 2(DSS*, D_2O)

T/°C	1	1(8.9mmol/l)+2(7.0mmol/l)	2
50	2.11	2.30	2.38
65	2.12	2.29	2.37

*Sodium 3-(trimethylsilyl)-propansulfonato

A transparent crystal(0.23×0.20×0.13mm), grown from aqueous solution, was carefully sealed in a Lindemann capillary to avoid decomposition.

Crystal data: $Ag(C_{10}H_{18}N_2O_2S_2)ClO_4 \cdot 2H_2O$, MW=505.7, orthorhombic, space group $P2_12_12_1$, a=29.380(7), b=10.429(2), and c=6.026(2)Å, V=1846.4(7)Å^3, Dc=1.82g·cm^{-3}, Do=1.78g·cm^{-3}, Z=4, μ(Mo Kα)=14.7cm^{-1}.

The structure was solved by MULTAN.[3] Full-matrix least-squares refinement[4] with anisotropic temperature factors for Ag, S, and Cl atoms and isotropic ones for remaining atoms converged to a conventional R value of 0.082. Atomic positional and thermal parameters are listed in Table 2.

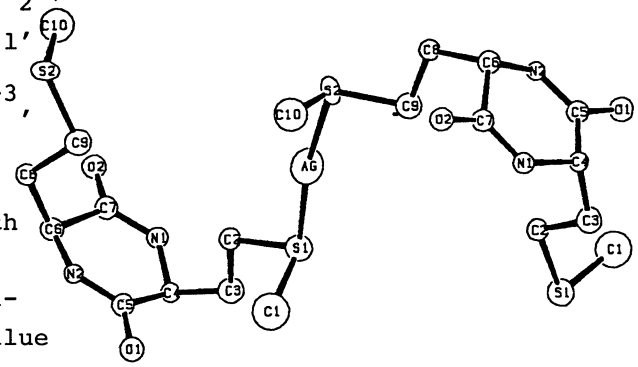

Fig.1. A perspective view of the complex.

The geometry of the complex ion is illustrated together with the numbering scheme in Fig. 1. Each Ag atom is coordinated almost linearly to two sulfur atoms. This is the first example of linear coordination of the sulfur atoms of thioether groups to Ag atoms. The distances of Ag-S1 and Ag-S2 are 2.393(7) and 2.402(7)Å, respectively, which correspond to the sum of the covalent radii(2.43Å) of Ag and S. The bond angle, S1-Ag-S2, is 171.1(3)°, deviating by 8.9° from 180°. As shown in Fig. 2, ligands are located around the 2_1 screw axis parallel to the b-axis to produce an interesting helical polymer where Ag atoms play roles as joints to bind them. There are four ClO_4^- around each Ag atom with two Ag---O contacts of 3.00(3) and 3.03(3)Å given in Fig. 2 as dotted lines. Other Ag---O distances are longer than 3.41Å. The bending of S1-Ag-S2 bond angle may be partly ascribed to these two weak interactions of Ag---O.

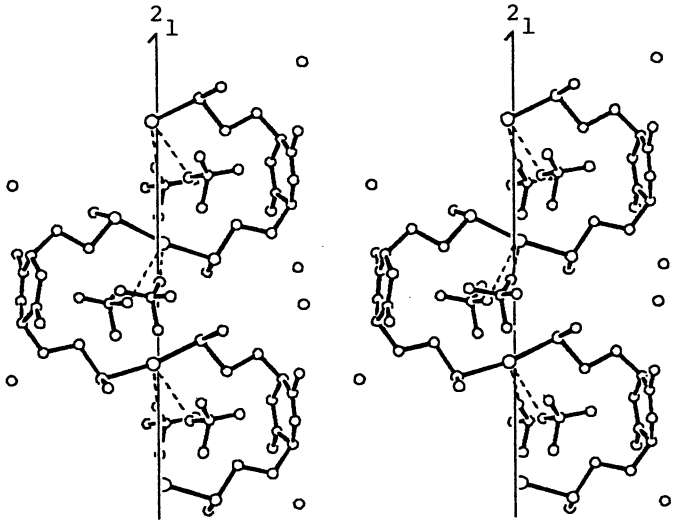

Fig. 2. Stereo drawing of a helical inorganic polymer along 2_1 screw axis.

Table 2. Fractional coordinates and temperature factors. Standard deviations of the least significant figures are given in parentheses.

ATOM	X	Y	Z	U(EQ) OR U
AG	0.4909(1)	0.1408(2)	0.2678(9)	0.095(1)
S1	0.5645(2)	0.2390(6)	0.257(2)	0.052(3)
S2	0.5875(2)	-0.4245(6)	0.224(2)	0.044(3)
C1	0.576(1)	0.274(3)	0.568(7)	0.09(1)
C2	0.6065(7)	0.113(2)	0.226(5)	0.030(6)
C3	0.6543(8)	0.186(2)	0.192(5)	0.042(8)
C4	0.6938(7)	0.089(2)	0.197(4)	0.024(6)
C5	0.6933(8)	0.022(2)	0.414(5)	0.032(7)
C6	0.7027(7)	-0.197(2)	0.272(6)	0.033(6)
C7	0.6968(8)	-0.133(2)	0.032(5)	0.032(7)
C8	0.6714(7)	-0.314(2)	0.290(5)	0.028(7)
C9	0.6189(7)	-0.273(2)	0.257(7)	0.043(7)
C10	0.596(1)	-0.463(3)	-0.061(7)	0.07(1)
N1	0.6913(6)	-0.006(2)	0.015(4)	0.028(6)
N2	0.6942(6)	-0.104(2)	0.441(3)	0.022(5)
O1	0.6915(5)	0.095(2)	0.585(3)	0.038(5)
O2	0.7011(5)	-0.206(2)	-0.128(3)	0.036(5)
CL	0.9568(2)	0.1001(6)	0.250(2)	0.062(2)
O3	0.9101(6)	0.074(2)	0.232(5)	0.087(7)
O4	0.9556(8)	0.235(2)	0.251(6)	0.124(9)
O5	0.9780(9)	0.085(2)	0.035(5)	0.12(1)
O6	0.9805(9)	0.026(2)	0.380(5)	0.12(1)
OW1	0.251(1)	0.061(3)	0.699(8)	0.21(2)
OW2	0.196(2)	0.127(4)	0.381(8)	0.25(2)

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References 1) Y.Kojima, Chem.Lett., 1981,61. 2) 1 was prepared from t-butyloxycarbonyl-L-methionyl-L-methionine methyl ester according to a usual method. 3) G.Germain,P.Main, and M.M.Woolfson, Acta Crystallogr., Sect.A.1971,27,368. 4) W.R.Busing, K.O.Martin, and H.A.Levy, ORFLS, Oak ridge National Laboratory Report ORNL-TM-305(1962).

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