

## Model Compounds for Metal-Protein Interaction: Crystal Structures of Four Silver(II) Complexes with Glycine, Glycylglycine, and Imidazole

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**Summary** The crystal structures of glycinatosilver(I), glycinatosilver(I) hemihydrate, glycylglycinesilver(I) nitrate, and bisimidazolesilver(I) nitrate have been determined.

WE report the crystal structures of glycinatosilver(I) [Ag(Gly), *A*], glycinatosilver(I) hemihydrate [Ag(Gly),  $\frac{1}{2}$ H<sub>2</sub>O, *B*], glycylglycinesilver(I) nitrate [Ag(HGly-Gly)NO<sub>3</sub>, *C*], and bisimidazolesilver(I) nitrate [Ag(ImH)<sub>2</sub>NO<sub>3</sub>, *D*]. Structural formulae are shown in the Figure.

In all four complexes the Ag<sup>I</sup> ions exhibit digonal coordination, which is the preferred geometry for Ag<sup>I</sup> with primarily  $\sigma$ -binding ligands.<sup>1</sup> The closure of five-membered chelate rings, which is characteristic of the amino-acid and peptide complexes of other metals,<sup>2</sup> becomes geometrically impossible with a linear arrangement of metal-ligand bonds. The requirement of two metal-ligand bonds per Ag<sup>I</sup> ion must hence be fulfilled by bonding to functional groups of two *different* ligand molecules, since H<sub>2</sub>O molecules are only weak ligands with respect to Ag<sup>I</sup> ions.

In *A* and *B* the complexes are linked in infinite ligand-metal-ligand chains. In *A* each Ag<sup>I</sup> ion is bound to an O(carboxyl) atom of one glycinate and to the N(amino) atom of another. In *B*, alternate Ag<sup>I</sup> ions are bound to two O(carboxyl) and two N(amino) atoms, respectively. Both these complexes crystallise—often from the same solution—under basic conditions, where not only the carboxyl groups but also the amino-groups of the ligands are available for co-ordination.

The complex *C* is formed at pH *ca.* 6, where the ligand exists mainly as the zwitterion <sup>+</sup>NH<sub>3</sub>CH<sub>2</sub>·CONH·CH<sub>2</sub>·CO<sub>2</sub><sup>-</sup>, and the Ag<sup>I</sup> ions do not displace the protons from the terminal NH<sub>3</sub><sup>+</sup> group. In the crystalline complex each Ag<sup>I</sup> ion is again co-ordinated by the O(carboxyl) atoms of two different ligand molecules, but both oxygen atoms of each carboxyl group are now involved in metal-binding. Two Ag<sup>I</sup> ions link the carboxyl groups of two peptide molecules with the formation of an eight-membered ring. This type of bonding has previously been found in the structure of the ferroelectric complex, glycinesilver(I) nitrate [Ag(HGly)NO<sub>3</sub>].<sup>3</sup>

In *D*, the Ag<sup>I</sup> ion is bound to N(imidazole) atoms of two ligand molecules. The two Ag–N bonds lie 5.7° and 3.2° out of the imidazole planes, respectively, and the dihedral angle between the imidazole groups is 20.2°. The complex is formed at pH *ca.* 4, suggesting that Ag<sup>I</sup> ions compete against protons for imidazole groups more successfully than for amino-groups. Amines are in fact much stronger bases than imidazole towards protons [ $pK_1(\text{CH}_3\text{NH}_2) = 10.7$ ,<sup>4</sup>  $pK_1(\text{imidazole}) = 7.1$ <sup>5</sup>], while imidazole is a slightly stronger base towards Ag<sup>I</sup> ions [ $pK_1(\text{CH}_3\text{NH}_2) = 3.2$ ,<sup>4</sup>  $pK_1(\text{imidazole}) = 3.8$ <sup>5</sup>].

None of the Ag<sup>I</sup> ions has purely digonal co-ordination. The smallest donor–Ag–donor bond angle (160°) occurs in *C*, where it is probably caused by repulsion between the two Ag<sup>I</sup> ions of the dimer. If the co-ordination were linear, the Ag–Ag distance (2.92 Å) would become smaller than in metallic silver. In addition to geometrical deviations from linearity, several of the Ag<sup>I</sup> ions have additional contacts with oxygen atoms which are close enough to be considered bound weakly. In *A* the Ag<sup>I</sup> ion interacts with an O (carboxyl) at 2.87 Å. In *B* an O(water) of an adjacent chain lies 2.79 Å from the amino-binding Ag<sup>I</sup> ion. In *C* there are contacts of 2.61 Å and 2.64 Å between each Ag<sup>I</sup> ion and an O(carboxyl) and an O(peptide) in adjacent complexes, respectively. In this structure, as in Ag(HGly)NO<sub>3</sub>,<sup>3</sup> the mean Ag–O(carboxyl) bond-length is significantly greater (2.19 Å) than in *A* and *B* (2.12 Å). The other mean bond-lengths in structures *A*, *B*, and *D* are Ag–N(amino) = 2.15 Å and Ag–N(imidazole) = 2.12 Å.

All the hydrogen atoms of the nitrogen atoms of the amino-, peptide, and imidazole groups in these complexes are used in hydrogen-bonding. In *A* and *B* the hydrogen bonds are from amino- to carboxyl groups, in *C* from amino- and peptide groups to O(nitrate) atoms, and in *D* from the 'pyrrole' N(imidazole) to O(nitrate) atoms.

*Crystal data:* Crystals of *A* and *B* grew from the same solution. They were prepared by a published method.<sup>6</sup> Crystals of *C* grew on evaporation of a solution 0.5 M with respect to silver(I) nitrate, glycylglycine, and potassium nitrate. (In the absence of potassium nitrate the crystals were too soft to be manipulated.) Crystals of *D* grew from a solution of silver(I) nitrate (0.5 M) and imidazole (1.2 M). The pH of the solution was lowered to about 4 by the addition of nitric acid to dissolve the initial precipitate of imidazolato-silver(I).<sup>7</sup>

Ag(Gly): Triclinic,  $a = 5.24(1)$ ,  $b = 5.71(1)$ ,  $c = 6.90(1)$  Å,  $\alpha = 84.21(1)^\circ$ ,  $\beta = 71.33(1)^\circ$ ,  $\gamma = 84.44(1)^\circ$ ,  $\mu(\text{Cu-}K\alpha) = 425 \text{ cm}^{-1}$ ,  $D_x = 3.11$ ,  $D_m = 3.06 \text{ g.cm}^{-3}$ , space group  $P\bar{1}$ .

Ag(Gly)·½H<sub>2</sub>O:† Monoclinic,  $a = 8.90(1)$ ,  $b = 6.43(1)$ ,  $c = 15.35(2)$  Å,  $\beta = 97.83(1)^\circ$ ,  $\mu = 385 \text{ cm}^{-1}$ ,  $D_x = 2.91$ ,  $D_m = 2.94 \text{ g.cm}^{-3}$ , space group  $P2_1/n$ .

Ag(HGly-Gly)NO<sub>3</sub>: Monoclinic,  $a = 5.04(1)$ ,  $b = 28.02$

† The unit-cell dimensions correspond to those reported by A. I. Kitaigorodskii and V. M. Kozin for Ag(Gly) [*J. Exp. Theor. Phys. (U.S.S.R.)*, 1939, **9**, 1127]. The structure found by these authors was known to be erroneous (*Structure Reports*, 1940–1941, **8**, 281).

‡ An independent structure analysis of this has been made at the University of Umeå, Sweden (C. J. Antti and B. K. S. Lundberg, personal communication).

<sup>1</sup> F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, second edn., 1966, p. 1040.

<sup>2</sup> H. C. Freeman, *Adv. Protein Chem.*, 1967, **22**, 257.

<sup>3</sup> J. K. M. Rao, *Indian J. Pure Appl. Phys.*, 1968, **6**, 51; R. S. Krishnan, J. K. M. Rao, and M. A. Viswamitra, *J. Phys. Soc. Jap. Suppl.*, 1969, **28**, 298.

<sup>4</sup> L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes", *Chem. Soc. Special Publ. No. 17*, 1964, p. 358.

<sup>5</sup> Ref. 4, p. 387.

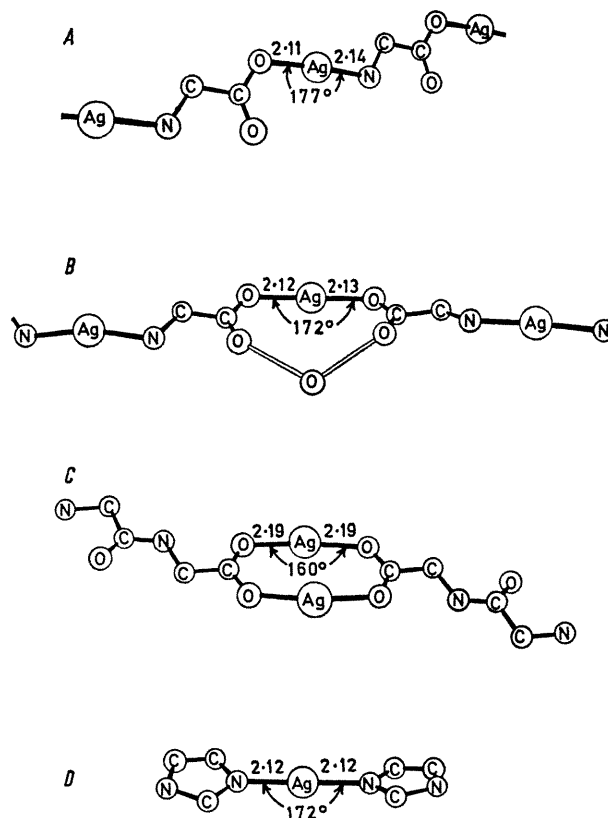
<sup>6</sup> K. Kraut and F. Hartman, *Annalen*, 1865, **133**, 101.

<sup>7</sup> J. E. Bauman and J. C. Wang, *Inorg. Chem.*, 1969, **3**, 368.

<sup>8</sup> H. C. Freeman, J. M. Guss, C. E. Nockolds, R. Page, and A. Webster, *Acta Cryst.*, 1970, *A*, **26**, 149.

(3),  $c = 5.78(1)$  Å,  $\beta = 93.83(1)^\circ$ ,  $\mu = 206 \text{ cm}^{-1}$ ,  $D_x = 2.47$ ,  $D_m = 2.43 \text{ g.cm}^{-3}$ , space group  $P2_1/c$ .

Ag(ImH)<sub>2</sub>NO<sub>3</sub>:‡ Orthorhombic,  $a = 10.94(1)$ ,  $b = 18.10$  (2),  $c = 5.10(1)$  Å,  $\mu = 166 \text{ cm}^{-1}$ ,  $D_x = 2.03$ ,  $D_m = 2.05 \text{ g.cm}^{-3}$ , space group  $P2_12_12_1$ .



FIGURE

All X-ray data were recorded on a computer-controlled equi-inclination diffractometer,<sup>8</sup> using Ni-filtered Cu-*K*<sub>α</sub> radiation. The numbers of independent reflections (followed by the numbers which were unobservably weak) and the residuals *R* at the present stage of full-matrix least-squares refinement, are: *A*, 700 (28), 0.041; *B*, 1468 (246), 0.049; *C*, 1445 (131), 0.041; *D*, 1708 (128), 0.033.

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