High Co-ordination Numbers in the Crystal Structures of Calcium Hydrazinecarboxylates

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Summary Hydrazinecarboxylic acid forms, with calcium, chelates with co-ordination numbers seven and eight, and with very short Ca · · · Ca distances between adjacent chelates.

HYDRAZINECARBOXYLIC ACID $NH_2{\cdot}NH{\cdot}CO_2H$, can form octahedral chelates with the bivalent cations Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+}.[1] We have determined the structures of the compounds [(I) and (II)] formed by this ligand with calcium.

$Ca(NH_2{\cdot}NH{\cdot}CO_2)_2$ $Ca(NH_2{\cdot}NH{\cdot}CO_2)_2,H_2O$
(I) (II)

These structures are of interest in connection with studies on amino-acids because of the close similarity of the complexes of hydrazinecarboxylic acid to those of glycine and its derivatives.[2,3]

Crystal data (obtained from Weissenberg photographs, Cu-K_α radiation) Compound (I): $Ca(NH_2{\cdot}NH{\cdot}CO_2)_2$, M = 190·2, unit cell: a = 9·59(1), b = 9·43(1), c = 9·29(1) Å, β = 127·83(30)°, U = 663·2 Å^3, Z = 4, D_m = 1·90, D_c = 1·90 g cm^{-3}, space group $P2_1/c$ (C_{2h}^5, No. 14) from systematic absences. Intensities of 1058 independent reflections have been measured photometrically on integrated Weissenberg photographs, by rotation around [100] and [010].

Compound (II): $Ca(NH_2{\cdot}NH{\cdot}CO_2)_2,H_2O$, M = 208·2, unit cell: a = 7·67(1), b = 7·86(1), c = 6·37(1) Å, α = 84·02(45), β = 72·88(55), γ = 78·65(30)°, U = 359·3 Å^3, Z = 2, D_m = 1·92, D_c = 1·92 g cm^{-3}, space group $P\bar{1}$ (C_i^1, No. 2). Intensities of 1113 independent reflections have been measured photometrically on integrated Weissenberg photographs, by rotation around [010]. The structures have been solved by Patterson and Fourier methods and refined with anisotropic thermal parameters, by differential syntheses [R = 7·7% for (I) and R = 10·7% for (II)]. Further refinement is now in progress in order to locate the hydrogen atoms.

In the anhydrous compound (I) the co-ordination number

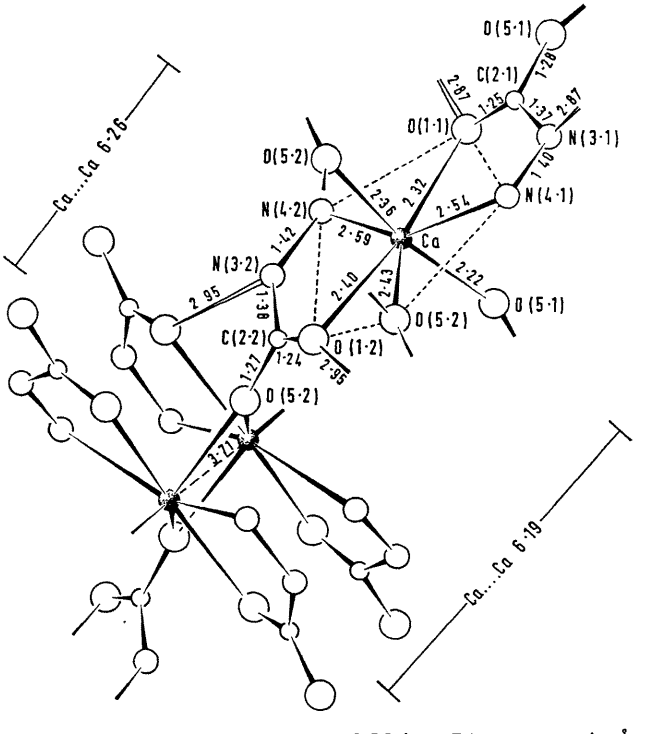

FIGURE 1. *Chelates in* $Ca(NH_2{\cdot}NH{\cdot}CO_2)_2$. *Distances are in* Å. *Unfilled lines indicate hydrogen bonds. Numbering of the atoms follows the scheme* N(4·*n*)–N(3·*n*)–C(2·*n*)–O(5·*n*), with n *indicating* O(1·*n*) *the first or the second independent ligand molecule.*

around calcium is 7 (Figure 1), with an average Ca–O distance of 2·35 Å. The co-ordinated atoms form a distorted pentagonal bipyramid. The calcium atoms are coupled *via* bridging ligands to form dimers with the distance Ca · · · Ca 3·71 Å; the distances between calcium atoms belonging to different dimers are 6·19, 6·26 Å. The dimers are joined to one another by hydrogen bonds (2·87, 2·95 Å) and by bridging ligands, thus giving rise to a three-dimensional network throughout the crystal. The situation in this compound is very similar to that found in $CaCl_2$·glycylglycylglycine,$3H_2O$ [2] where the calcium cations are surrounded by seven oxygen atoms forming a distorted pentagonal bipyramid, the average Ca–O distance being 2·39 Å and the distance Ca · · · Ca between calcium ions of adjacent polyhedra 4·0 Å. This similarity is worth noting because in compound (I) some of the donor atoms are N.

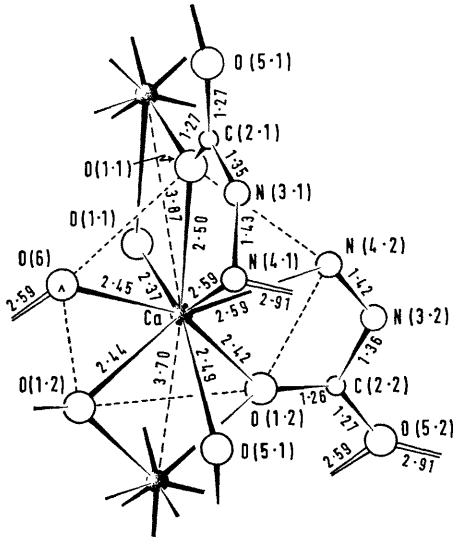

FIGURE 2. *Chelates in* $Ca(NH_2{\cdot}NH{\cdot}CO_2)_2,H_2O$. *Distances are in* Å. *Symbols are the same as in Figure* 1. *A hydrogen bond* (2·72 Å) *from* O(6) *points towards the reader.*

In the hydrated compound (II) the co-ordination number is 8 (Figure 2) with an average Ca–O distance of 2·44 Å. The co-ordinated atoms appear to form a pentagonal bipyramid with a centred face. The groups around calcium are bound in chains parallel to [001] *via* bifurcated atoms, bridging ligands, and hydrogen bonds (2·59, 2·72 Å). The interaction distances along the chain are Ca · · · Ca 3·70 Å and 3·87 Å alternately. The connections between chains are hydrogen bonds of length 2·91 Å.

The distances in the ligand are in agreement with those previously found in other chelates.

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