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Conformational Analysis of Double Carboxylic Bridges in Bis(DL-α-alanine)manganese(II) Dibromide Dihydrate and the Related Compounds

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Our systematic studies of stereochemistry of the Mn(II) α-amino acid complexes were carried out to determine relative changes in Mn(II) coordination by the amino acid molecules in the crystalline states. In these complexes the amino acid molecules occur as zwitterions and Mn^{2+} ions interact with the O atoms of carboxyl groups.

Crystallographic studies showed a typical property of these complexes which is their polymeric nature. Of the eleven complexes investigated only two are monomers [1, 2] and the other nine are polymers. The polymeric nature is also a specific property of the Mn(II) complexes with carboxylic acids. In this group of compounds the Mn^{2+} ions are linked by single carbonyl bridges (SCB) [3–10] whereas in the complexes with amino acids the Mn^{2+} ions are linked via single [11–14] and double carboxyl bridges (DCB).

In the monomeric complexes the O atoms of glycine and proline molecules located closer to the N atoms, O(*cis*N), form the syn bond type with the Mn(II) atoms. Deviations of the Mn(II) atoms from the $C^{\alpha}COO$ planes are 1.27 Å (max.). A common property of the polymeric Mn(II) complexes with α-amino acids is the formation of syn, anti bonds by the bridging carboxyl groups.

In the SCB Mn(II) α-amino acid complexes, the syn bonds are formed by the O(*cis*N) atoms. Deviations of the Mn(II) atoms from the $C^{\alpha}COO$ planes do not exceed 0.52 Å and Mn–Mn distances range from 5.36 to 5.52 Å.

The title compound is one of four DCB Mn(II) α-amino acid complexes. The crystals of $[Mn(DL\text{-}\alpha\text{-}ala)_2(H_2O)_2]Br_2\cdot 2H_2O$ are monoclinic, space group $P2_1/c$, $a = 4.790(2)$, $b = 19.596(5)$, $c = 9.289(3)$ Å, $\beta = 102.26(2)^{\circ}$, $Z = 2$, $D_{calc} = 1.81$, $D_{obs} = 1.80$ g cm^{-3}, MW = 464.9, $\mu(CuK\alpha) = 120.0$ cm^{-1}, R = 0.065 for 1238 reflections. The structure was solved by the heavy-atom method and refined on the basis of a three-dimensional diffractometer set of data using the Syntex XTL structure determination system [15], to yield the parameters given in Table I. The investigated compound is the DCB polymer parallel to the x axis (Mn–Mn = 4.79 Å). The Mn(II) atoms have an octahedral coordination. The mean Mn–O(ala) bond length is 2.171 ± 0.006 Å and is shorter than the Mn–O(W1) which is 2.201 Å. The valency angles in this octahedral vary from 88.6 to 93.9°. The O(1) *i.e.* O(*cis*N) atom forms the anti bond with the Mn^{2+} ion. Deviation of this ion from the $C_1^{\alpha}COO$ plane is 1.34 Å, but the deviation of the second one is 0.06 Å.

A branched lattice of hydrogen bonds ($H_2O\ldots H_2O$, $H_2O\ldots Br$ and $NH_3\ldots Br$) links the adjacent polymer chains $[Mn(DL\text{-}\alpha\text{-}ala)_2(H_2O)_2]_n^{2n+}$ and only one hydrogen bond, N–H. . .O(2) = 2.85 Å is created between the nearest alanine molecules (Fig. 1b).

Conformational analysis of the DCB systems in Mn(II) complexes with glycine [16], sarcosine (two isomorphic complexes with Cl^- and Br^- ions) [17], DL-α-alanine and β-alanine [14] indicated that: (a) eight-membered rings of the DCB systems have centrosymmetric conformation, (b) distances between the bridging Mn(II) atoms are above 5.0 Å, (c) the O(*cis*N) atoms of α-amino acids form syn or anti bonds with the Mn(II) atoms, (d) deviations of the Mn(II) atoms from the $C^{\alpha}COO$ planes in the anti positions to the carboxyl groups are large (1.34–1.61 Å), in the syn

TABLE I. The positional ($\times 10^4$) and Thermal ($\times 10$) Atom Parameters with e.s.d.s in Parentheses.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	0	0	0	17(1)	16(1)	22(1)	1(1)	6(1)	4(1)
Br	6654(3)	2562(1)	5098(1)	43(1)	28(1)	30(0)	9(0)	5(0)	8(0)
O(1)	3320(14)	678(3)	–405(7)	20(3)	20(3)	26(3)	–2(2)	10(2)	5(2)
O(2)	7036(14)	659(3)	–1476(8)	18(3)	26(3)	31(3)	7(2)	10(2)	7(3)
O(W1)	–223(17)	613(4)	1957(9)	45(4)	33(4)	30(4)	0(3)	9(3)	–4(3)
O(W1)	4851(20)	1374(5)	2259(10)	61(6)	54(5)	43(5)	–15(4)	12(4)	–10(4)
N	730(18)	1698(4)	–2149(9)	23(4)	20(4)	32(4)	7(3)	8(3)	6(3)
C(1)	4561(21)	840(5)	–1418(10)	25(4)	11(4)	19(4)	0(3)	4(3)	2(3)
C(2)	3042(22)	1293(6)	2684(11)	18(4)	31(5)	19(4)	6(4)	1(4)	7(4)
C(3)	1696(28)	872(6)	–4037(13)	52(7)	38(6)	21(5)	9(5)	–5(5)	–11(4)

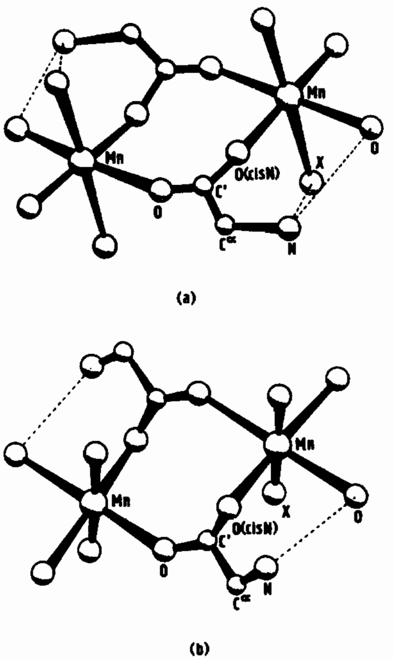

Fig. 1. Schematic representation of the DCB groups in the Mn(II) α-amino acid complexes: (a) Type A, (b) Type B.

position of complexes in which the inner coordination sphere contains *trans*-water molecules, deviations do not exceed 0.53 Å, but if there are Cl atoms instead of water molecules these deviations have values of 0.92 Å [16]; (e) the Mn(II) atoms and NH_3^+ or NH_2^+ groups lie on the opposite side of the $C^\alpha COO$ planes in the α-amino acid complexes. The last property (e) frequency also occurs in other Mn(II) α-amino acid complexes.

DCB groups of five compounds described above may be divided into three types:

Type A: DCB with the large deviations of both Mn(II) atoms from the $C^\alpha COO$ plane in one direction only and as in the glycine complex with the maximal Mn–Mn distance (5.0 Å). If the O(*cis*N) atoms form the anti bonds with the Mn(II) atoms such a situation favours the existence of two hydrogen bonds inside the polymer (Fig. 1a). In sarcosine complexes O(*cis*N) atoms form the syn bonds and these hydrogen bonds do not occur.

Type B: DCB with a large deviation of only one Mn(II) atom from the $C^\alpha COO$ plane in the anti position to the carboxyl group and with the second one near or in the $C^\alpha COO$ plane. In this case the Mn–Mn distance is shorter and only one hydrogen bond inside the polymer is possible (Fig. 1b).

Type C of analyzed DCB groups with two Mn(II) atoms on the opposite side of $C^\alpha COO$ planes was found in β-alanine complex only.

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