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Cyclic configuration of the aspartate ion in the crystal structure of zinc, cobaltous and nickelous aspartate trihydrate.

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The salts of L-aspartic acid with divalent zinc, cobalt and nickel crystallize as tri-hydrates, and are isomorphous. Unit-cell dimensions are:

	Zinc aspartate.$3H_2O$	Cobaltous aspartate.$3H_2O$	Nickelous aspartate.$3H_2O$
a (Å)	$9{\cdot}38_6$	9·39	9·40
b (Å)	$7{\cdot}92_0$	7·85	7·83
c (Å)	$11{\cdot}53_2$	11·37	11·35
ϱ (g.cm.$^{-3}$)	1·97	1·91	1·91

The common space group is $P2_12_12_1$.

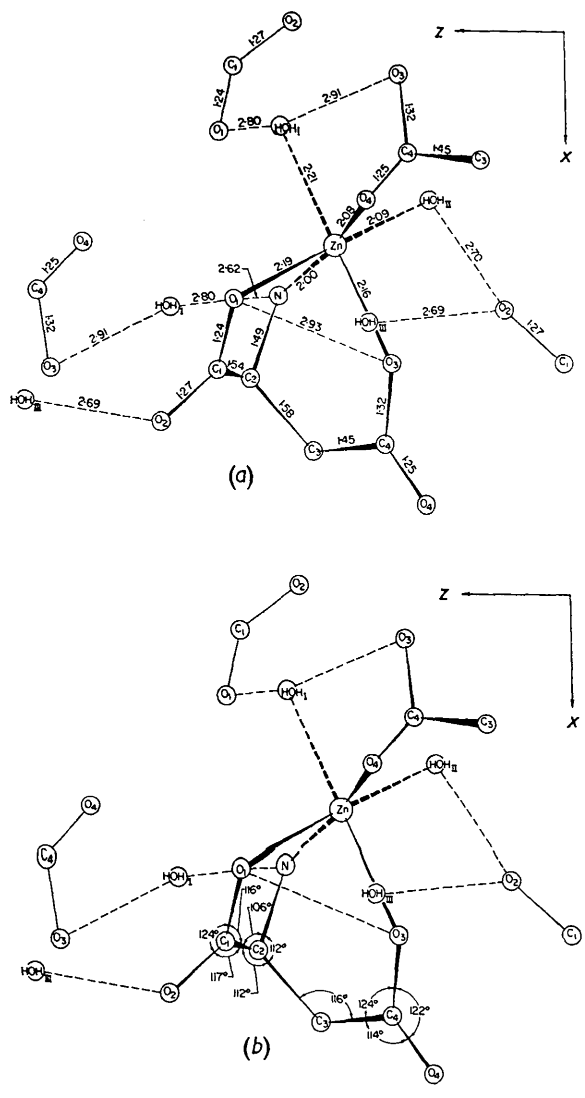

Fig. 1. (*a*) Interatomic distances (Å) and (*b*) bond angles in zinc aspartate trihydrate.

Cu $K\alpha$ radiation was used to obtain $|F_{hkl}|^2-|F_{\bar h\bar k\bar l}|^2$ values, to compute the $P_s(u)$ function of Okaya & Pepinsky (1956) for cobaltous aspartate trihydrate. From this, Taylor's expression (1953) for evaluation of Buerger's minimum image-seeking function (1950, 1951) was computed directly on X-RAC, in three dimensions, according to the technique of Takeuchi, Okaya & Pepinsky (1956). This procedure directly revealed the structure and absolute configuration (Pepinsky, 1956) of the cobaltous salt.

Coordinates from the cobaltous salt have been used to refine the structure of the zinc salt, using least-square methods and individual temperature factors for each atom. Calculations were accomplished on an IBM 704 machine, and a disagreement factor of 12% was achieved for the three-dimensional data.

The structure and absolute configuration of zinc aspartate trihydrate is shown in Fig. 1. The zinc ion is surrounded by a distorted octahedron of O and N atoms. One group chelated to Zn is comprised of O_1, C_1, C_2 and N; and a second is formed of O_3, C_4, C_3, C_2 and N. The atoms O_1, C_1, C_2, C_3, C_4, O_3 and H_I form a seven-membered ring, in which the unexpectedly short distance of 1·45 Å appears between C_3 and C_4. A distance of 1·47 Å between atoms C_3 and C_4 was found by Cochran & Penfold (1952) in L-glutamine.

The above seven-membered ring recalls the cyclic formulation proposed by Steward & Thompson (1952) for asparagine. Although an extended structure was reported in asparagine monohydrate by Saito, Cano-Corona & Pepinsky (1955), that structure refuses to refine and appears to be incorrect. Inconsistencies in the asparagine structure have also been pointed out to us privately by Woolfson (1955). Cyclic configurations have been considered for the asparagine monohydrate structure, but a satisfactory arrangement remains to be found. The molecules in crystalline L-glutamine (Cochran & Penfold, 1952) and DL-glutamic acid hydrochloride (Dawson, 1953) have extended configurations.

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On the structure of some manganites.

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A preliminary report on the crystal structure of the manganites ($A^{2+}Mn_2^{3+}O_4^{2-}$) of some bivalent metals (A) such as Cd, Mg, Co, Fe, Cu and Ni, prepared in this Laboratory, is given below.

The manganites were prepared by heating for several hours 1:1 mixtures of manganese sesquioxide with the bivalent metal oxides at temperatures between 700 and 900° C. The products were quenched in air to room temperature and examined by X-ray powder diffraction using a 14 cm. Debye–Scherrer camera and Mo $K\alpha$ radiation ($\lambda = 0{\cdot}709$ Å). The lines in the diffraction patterns were indexed on the basis of crystal data set out in Table 1.

The crystals were found to possess either a tetragonally deformed spinel structure isomorphous with $Mn[Mn_2]O_4$ and $Zn[Mn_2]O_4$ (Mason, 1947; Romeijn, 1953), or a spinel structure isomorphous with $Mg[Al_2]O_4$ (Bragg, 1915*a*, *b*). There are eight molecules in the unit cell, where the 32 oxygen ions form a cubic close-packed arrangement with 8 of the 64 tetrahedral and 16 of the 32 octahedral sites occupied by the cations.

The intensities of the reflexions were estimated visually and compared with those calculated for the three models: normal, $A[Mn_2]O_4$; random $A_{\frac{1}{3}}Mn_{\frac{2}{3}}[A_{\frac{2}{3}}Mn_{\frac{4}{3}}]O_4$; and inverse $Mn[AMn]O_4$. The cations in the octahedral sites are conventionally indicated by enclosing them in square brackets. The distribution of cations is sensitive to the intensities of 220, 400 and 422 reflexions (Bertaut, 1950) and is determined from a correlation of these intensities and also from overall agreement index $R = \Sigma|\sqrt{I_o}-\sqrt{I_c}| \div \Sigma|\sqrt{I_o}|$, the latter varying between 10 and 25% in different cases.

Owing to the relatively low scattering power, the oxygen-ion parameter, u, could not be determined accurately from the X-ray data. For the manganites of Cu, Ni and Cd, u is within 1% of 0·389, 0·381 and 0·400, respectively. In other cases also, the steric factors (size of cations and tetrahedral hole) suggest (Table 2) a similar increase from the value 0·375 corresponding to the ideal close-packing of oxygen ions.

The distortion of the lattice and the distribution of the cations are explained on the basis of their bond-forming properties and relative affinities for a particular site. The distortion of cubic symmetry is brought about by coplanar square-bond-forming cations such as Mn^{3+} in the octahedral site (Goodenough & Loeb, 1955). A group of four equivalent dsp^2 covalent coordinate bonds are formed in a plane defined by the a and b axes and two ionic bonds parallel to the c axis. Since the covalent bonds are the stronger, the a and b axes are shorter than c, i.e. c/a is greater than unity.

The cationic arrangement is influenced in the first place by the strong tendency of the Mn^{3+} ions to form dsp^2 bonds (Table 2). They are therefore accommodated preferentially in octahedral sites where the geometrical factors favour the formation of square coplanar bonds.

In the manganites of Cd, Mn and Zn, the normal arrangement is stabilized by the strong tendency of these ions to form sp^3 bonds (regular or distorted) in the tetrahedral sites. The Mg^{2+} ion, which is unlikely to form covalent bonds, is stabilized in the tetrahedral holes through the formation of electrovalent bonds. The random structure in the case of cobalt manganite indicates that Co^{2+} shows more or less equal affinity for both types of

Table 1. *Crystallographic data*

Compound	Symmetry*	a (Å)	c (Å)	c/a	Cation arrangement†
$Cd[Mn_2]O_4$	T	8·22	9·87	1·20	Normal
$Mn[Mn_2]O_4$‡	T	8·15	9·44	1·16	Normal
$Mg[Mn_2]O_4$	T	8·07	9·28	1·15	Normal
$Zn[Mn_2]O_4$‡	T	8·10	9·25	1·14	Normal
$Co_xMn_{1-x}[Co_{1-x}Mn_{1+x}]O_4$	T	8·04	9·04	1·12	Random
$Fe_xMn_{1-x}[Fe_{1-x}Mn_{1+x}]O_4$	T	8·31	8·85	1·05	Random
$Cu[Mn_2]O_4$	C	8·33	8·33	1·00	Normal
$Mn[NiMn]O_4$	C	8·37	8·37	1·00	Inverse

* T: tetragonal; C: cubic.

† Nomenclature according to Barth & Posnjak (1932).

‡ Mason (1947); Romeijn (1953).