

especially in two papers quoted by the authors (Norrby & Franzen, 1970; Moret, Huber & Comès, 1976). The reason why Wiegiers & Jellinek (1970) and Norrby & Franzen (1970) did not observe the superstructure may be attributed to slight differences in the crystal-growth conditions.

The occurrence of the superstructure was also confirmed in the course of a study of the composition-dependent two-dimensional (2D) titanium ordering in $Ti_{1+x}S_2$ (Moret *et al.*, 1976; Moret, 1977; Legendre & Huber, 1980). In fact, as x reaches $\frac{1}{3}$, both partial 2D order and stacking correlations lock in the formation of long-range order (Moret, Tronc, Huber & Comès, 1978).

It may be useful to note that the crystals we studied exhibit the coexistence of six types of orientation domains. This corresponds to a symmetry transformation from the substructure to the superstructure, namely $P6_3mc$ (order 12) $\rightarrow Cc$ (order 2), and is consistent with Bartram's results. In this respect it would be interesting to look for the presence of such domains, in crushed samples, by the authors' technique.

The paper reports the observation of another superstructure named $(4H)_3-6C$. We also found this structure in some crystals. Its space group is Cc and its titanium stacking sequence can be represented as ...*ABCDEF*A..., according to the authors' notations, instead of ...*ABCD*A... for $(4H)_2-4C$ (see Fig. 7 of their paper).

Finally, we point out that these two superstructures, and especially $(4H)_3-6C$, have been carefully refined, despite difficulties due to the unavoidable domain coexistence (Tronc & Moret, 1979, 1980). The refinement has shown that the completely filled Ti layers are corrugated as a consequence of interlayer correlations. Since these distortions most likely result from Ti-Ti pair interactions they should exhibit a weak dependence on both titanium concentration and titanium state of order in the defective layers. Consequently, they should occur over a broad composition range and are probably related to the structural complexity of the Ti-S system.

Since these comments were submitted other papers from the same group have come to hand. The authors agree with

us on the stacking sequence of $(4H)_3-6C$ (Bando, Saeki, Onoda, Kawada & Nakahira, 1979). They acknowledge Bartram's work but stress it contained an error (Onoda, Saeki & Kawada, 1979). It is true that Bartram erroneously assigned $C2/c$ as the space group of $(4H)_2-4C$, instead of Cc . However, since the atomic positions were thoroughly and correctly determined, there is no doubt about the originality and value of Bartram's findings.

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Acta Cryst. (1980). B36, 2855-2856

A comment on structural relationships among tris(ethylenediamine) complexes $M(en)_3X_m$. By CLARA BRINK SHOEMAKER and DAVID P. SHOEMAKER, *Department of Chemistry, Oregon State University, Corvallis, OR 97331, USA*

(Received 30 April 1980; accepted 8 July 1980)

Abstract

Spinat, Brouty & Whuler [*Acta Cryst.* (1980), B36, 544-551] have demonstrated certain structural relationships among crystalline tris(ethylenediamine) complexes by considering the types of packing of the large complex ions. It is pointed out that one of the types of packing discussed by them, called 'pentagonal', corresponds to the packing of the metal atoms in the well known cubic Friauf-Laves phases exemplified by $MgCu_2$ (*Strukturbericht* designation C15).

Spinat, Brouty & Whuler (1980) have demonstrated structural relationships among crystalline $M(en)_3X_3 \cdot xH_2O$ complexes [$M = Co^{III}, Cr^{III}, Rh^{III}$ and $X = Cl^-, Br^-, (SCN)^-$] possessing several different crystallographic symmetries by approximating the complex ion $[M(en)_3]^{3+}$ to a sphere of radius approximately 4 Å and considering the types of packings of these spheres. Those authors observe five types of packings: cubic close packing (c.c.p.), hexagonal close packing (h.c.p.), distorted hexagonal close packing, body-centered cubic, and 'a more complex model named pentagonal'. The authors point out that in this last type of packing, exhibited by (+)- $Cr(en)_3Br_3 \cdot 0.6H_2O$ and (-)- $Rh(en)_3Cl_3$,

Table 1. Correspondence between the coordinates of the Cr atoms in (+)-Cr(en)₃Br₃·0.6H₂O, transformed to a pseudo-cubic cell (see text), and the coordinates of the A and B atoms in C15-type structures

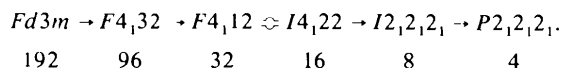
	Cr ^{III} complex			MgCu ₂			
	x'	y'	z'	x	y	z	
Cr(1)	0.1145	0.0981	0.1068	0.125	0.125	0.125	A in 8(a)
Cr(2)	0.2538	0.7605	0.0046	0.25	0.75	0	} B in 16(d)
Cr(3)	0.4920	0.0113	0.0103	0.50	0	0	

there are spheres with different environments, one kind [Cr(2) and Cr(3) in the first compound] with 12 neighboring spheres, and the other kind [Cr(1)] with 16. The Rh complex is cubic ($a_0 = 21.675 \text{ \AA}$, space group $F4_132$); the Cr complex is orthorhombic [$a_0 = 21.019(4)$, $b_0 = 16.460(3)$, $c_0 = 15.346(3) \text{ \AA}$; space group $P2_12_12_1$] and is pseudo-cubic (Spinat, Whuler & Brouty, 1979). The description of this packing by Spinat *et al.* clearly shows that it corresponds to the packing found in many alloys possessing the cubic structure type MgCu₂ (*Strukturbericht* type C15, space group $Fd3m$); these alloys are known as the cubic Friauf-Laves phases. The relationship becomes apparent on comparing Fig. 7 of Spinat *et al.* (1980) with Fig. 3(c) of Shoemaker & Shoemaker (1967) which gives the normal projection of MgCu₂ on (110). (It should be noted that a and c in the first figure correspond to c and $|110|$ respectively in the second figure.)

The MgCu₂ structure type belongs to a group of structures formed by metal atoms of somewhat different sizes (Frank & Kasper, 1959). We have called these structures 'tetrahedrally close-packed' or 't.c.p.' (Shoemaker & Shoemaker, 1971) because all interstices are tetrahedral. These structures represent very compact packings of atoms of different sizes: A atoms with CN 14, 15 and/or 16 (only 16 for Mg in MgCu₂) and somewhat smaller B atoms with CN 12 (icosahedral). The packings would be less compact if regarded as being of spheres all of the same size, as do Spinat *et al.* (1980) in describing their 'empilement pentagonal' which they regard as less compact than the c.c.p. and h.c.p. packings. Actually, not only are the atoms of different sizes but, in addition, the A atoms are not spherical. The Mg atom (CN 16) in MgCu₂ can be regarded as having two different radii (Shoemaker & Shoemaker, 1964), representing a sphere with tetrahedrally placed dimples.

The positions of the Cr^{III} ions in (+)-Cr(en)₃Br₃·0.6H₂O are very close to the positions of the metal atoms in the MgCu₂ structure type as may be seen in Fig. 6 of Spinat *et al.* (1979), where the distances of the Cr^{III} ions to the intersections of the dashed lines represent the deviations. The transformed pseudo-cubic cell ($a' = a$, $b' = b - c$, $c' = b + c$) has cell dimensions: $a' = 21.0$, $b' = c' = 22.5 \text{ \AA}$, $\alpha = 86$, $\beta = \gamma = 90^\circ$, and contains 24 formula units. This is twice the number of formula units (12) in the orthorhombic cell, and corresponds to 8 formula units in the MgCu₂ cubic cell. We show the correspondence between the positions of Cr(1) and the A atom (CN 16) and of Cr(2), Cr(3) and the B atom (CN 12) in Table 1, where the coordinates of the Cr atoms have been obtained by the following transformation of the coordinates that are given by Spinat *et al.* (1979): $x' = x$, $y' = \frac{1}{2}(y - z)$, $z' = \frac{1}{2}(y + z) - \frac{1}{2}$. Only the correspondences for one set of AB_2 atoms have to be considered since the 2_1 axes and lattice translations of $P2_12_12_1$ generate the other seven sets in the unit cell of the C15 arrangement of atoms; apart

from the distortion, the space group $P2_12_12_1$ is effectively a subgroup of space group $Fd3m$, as is also $F4_132$, the space group of the Rh complex. A sequence of maximal subgroups leading from $Fd3m$ to the two lower space groups, with their multiplicities, follows:



The chirality of the Rh complex leads immediately to the first maximal subgroup by loss of the center of symmetry. The equivalence of $F4_112$ and $I4_122$ corresponds to the transformation of axes here described, apart from the shift of $\frac{1}{4}$ in z' which arises from the different choice of origin in $Fd3m$ and $P2_12_12_1$.

The negative ions and H₂O molecules are located in the tetrahedral interstices between the spherical complex ions somewhat as H atoms are placed in the interstices between the metal atoms in the hydrides of alloys of the MgCu₂-type structures (Shoemaker & Shoemaker, 1979). We have demonstrated that there are, per AB_2 , 17 tetrahedral interstices in the MgCu₂-type structures. In (+)-Cr(en)₃Br₃·0.6H₂O there are nine Br⁻ ions and three H₂O molecules (with partial occupancies) present in these tetrahedral interstices, for a total of 12 'interstitials' per Cr₃. However, the interstitials are generally not located very close to the centers of the tetrahedra; for example, atoms Br(1), Br(2) and Br(4) are close to triangles formed by Cr(2) and Cr(3) ions. The placement of the Br⁻ ions and the H₂O molecules is determined by their ability to form hydrogen bonds of the type N-H...Br, N-H...O, O-H...Br or O-H...O. Therefore, their positions are determined by the individual orientations and relative chiralities of the complex ions, which were not considered when their gross packing together was examined. The 'interstitials' presumably have an important role in determining the type of packing achieved by the complex ions, but this is not a simple function of their size, shape, and number.

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