Tableau 2. *Calculs de plans moyens* ($\bar{\sigma} = 0{,}003$ Å)

Equations de plans moyens ($aX + bY + cZ + d = 0$) ou X,Y,Z sont les coordonnées (en Å) dans un repère orthogonal XYZ

	a	*b*	*c*	*d*
Plan 1	−0,707755	−0,679512	−0,193248	13,464908
Plan 2	0,452253	0,860341	−0,235116	−7,850950
Plan 3	0,548596	0,789390	−0,275740	−7,757125

Distances en Å des atomes au plan moyen (les atomes marqués* ne font pas partie du calcul du plan moyen)

Plan 1		Plan 2		Plan 3	
C(7)	0,025	C(1)	0,011	C(1)	0,023
C(8)	−0,015	C(2)	0,126	C(2)	0,037
C(9)	−0,008	C(3)	−0,060	C(3)	−0,083
C(10)	0,017	O(2)	−0,101	O(2)	0,045
C(11)	−0,003	C(5)	0,333	C(4)	−0,049
C(12)	−0,030	C(4)	−0,247	C(5)*	0,582
C(13)*	0,029	O(1)*	−0,182	O(1)*	−0,295
N*	0,057	N*	0,032	N*	−0,001
C(1)*	0,666	C(6)*	−0,046	C(6)*	0,385
		C(7)*	−0,019		

que confirment les calculs de planéité (Tableau 2). Bien que l'azote soit contenu dans le même plan que le cycle benzénique, la molécule n'est pas plane. L'angle entre les plans moyens des deux cycles est 31 (1)°, conséquence d'une gêne stérique entres cycles par l'intermédiaire des hydrogènes H(C2) et H(C12) et d'un effet de conjugaison le long de la chaîne N—C(1)—C(2)—C(3)—O(2), deux phénomènes antagonistes rendus possibles par la libre rotation autour de l'atome d'azote.

La résolution de cette structure a permis, en identifiant une nouvelle dihydropyrone, de montrer que contrairement aux résultats classiques concernant les réactivités spécifiques du sommet 1 [O(2)], l'action d'une amine primaire sur l'hydroxy-4 méthyl-6 dihydro-5,6 pyrone-2, ne conduit pas à une pyridone N arylée comme le permettaient d'avancer toutes les indications spectrales précédentes.

En effet, l'action des amines sur les dihydropyrones conduit, si on envisage une désmotropie du type β dicétone (Nedjar, 1977), à deux résultats différents suivants les sites d'attaque: conservation du cycle dihydropyronique par attaque en position 4 de l'hétérocycle ou obtenion d'une dihydropyridone par attaque en position 2 de l'hétérocycle.

Cette dernière possibilité, avancée dans un article récent (Nedjar, 1977), à l'issue de l'étude de l'action de quatre amines sur l'hydroxy-4 méthyl-6 dihydro-5,6 pyrone-2, est réfutée par les résultats de cette détermination structurale.

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SHORT COMMUNICATIONS

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.*

Acta Cryst. (1980). B**36**, 2854–2855

Comments on $(4H)_2$–$4C$ *type superstructure of* $TiS_{1.46}$ *as determined by high-resolution electron microscopy* by Y. Bando, M. Saeki, Y. Sekikawa, Y. Matsui, S. Horiuchi and M. Nakahira. By

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Abstract

The reported $(4H)_2$–$4C$ superstructure [*Acta Cryst.* (1979), A**35**, 564–569] is not original. Its relationship to titanium partial ordering at lower concentration is given. New results, showing that the titanium sublattice is actually distorted, are mentioned.

According to Bando, Saeki, Sekikawa, Matsui, Horiuchi & Nakahira (1979), the $(4H)_2$–$4C$ superstructure of $TiS_{1.46}$ is original and represents the first example of interlayer titanium ordering in the Ti–S system. Actually, this superstructure had already been observed and studied by X-ray single-crystal structure analysis (Bartram, 1958). Although not published it has been mentioned several times in recent years (Wiegers & Jellinek, 1970; Tilley, 1976),

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especially in two papers quoted by the authors (Norrby & Franzen, 1970; Moret, Huber & Comès, 1976). The reason why Wiegers & 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) → 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 ...*ABCDEFA*..., according to the authors' notations, instead of ...*ABCDA*... 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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A comment on structural relationships among tris(ethylenediamine) complexes $M(en)_3X_m$.

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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 $M(en)_3X_3.xH_2O$ 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 (+)-$Cr(en)_3Br_3.0{\cdot}6H_2O$ and (−)-$Rh(en)_3Cl_3$,

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