link the atoms into ions are further coupled, weakly, to form infinitely extended multicenter bonds. This is an extension of the four-center patterns X–X–X$\cdots$X that occur in the isostructural cesium trihalides, CsI_3 (Tasman & Boswijk, 1955), CsI_2Br (Carpenter, 1966), $CsBr_3$ (Breneman & Willett, 1969) and $CsIBr_2$ (Davies & Nunn, 1969). Along **a** and **c** the ions are well separated. The oxygen and potassium atoms occupy holes between the dibromoiodide ions.

Each oxygen atom has six neighboring bromine atoms. There are two bromine atoms in the same plane with the oxygen atom, one 3·77 Å and one 3·89 Å away. In addition, there are two sets of two bromine atoms related by a unit-cell translation in **c**, one set 3·60 Å from the oxygen atom and one at 3·64 Å. The four shorter distances are presumably hydrogen bonds although they are 0·2–0·3 Å longer than found in such hydrogen bonded systems as $NaBr.2H_2O$ (Haaf & Carpenter, 1964) or codeine hydrobromide dihydrate (Kartha, Ahmed & Barnes, 1962). This increased length may partly be due to the reduced effective negative charge on the bromine atom compared with simple bromide ions (Elema, de Boer & Vos, 1963). Hydrogen bonding to these four bromine atoms requires a disorder of the hydrogen atoms across the mirror plane, resulting in four 'half' hydrogen bonds, each somewhat longer than a whole hydrogen bond. As in $KICl_2.H_2O$ there is no hydrogen-bonded network among the water molecules, but apparently only weak hydrogen bonding between the bromine atoms and water molecules. Unlike the chlorine atoms in $KICl_2$ and $KICl_2.H_2O$ (Soled & Carpenter, 1973), the bromine atoms in $KIBr_2.H_2O$ participate as the central atoms in a multicenter bond.

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The Crystal Structure of [Co(NH₃)₆]₄Cu₅Cl₁₇: a Twinned Cubic Crystal

By PETER MURRAY-RUST

Department of Chemistry, University of Stirling, Stirling, Scotland

[Co(NH₃)₆]₄Cu₅Cl₁₇ crystallizes in the cubic space group *Fd*3, with *a* = 21·80 Å. The structure was solved and refined by standard methods to an *R* of 0·148. Although the bond lengths and angles were chemically acceptable, the poor agreement suggested that the solution was only partially correct. Analysis of the intensities at this stage suggested that the crystal used was twinned and that a correction could be made for this. The structure was then refined to a final *R* of 0·086 with a value for the twin parameter (α) of 0·323. There was no significant change in the positional parameters after this procedure but the standard deviations decreased markedly. The method used for detecting the twinning is applicable even when systematic absences or morphology give no indication that the crystal is twinned and it differentiates between twinned and disordered crystals. The structure contains [Co(NH₃)₆]³⁺ octahedra [Co–N(av) = 1·96 Å], isolated Cl⁻ ions, and [Cu₅Cl₁₆]¹¹⁻ units. The latter contain linear Cu–Cl–Cu bridges with Cu–Cl bond lengths of 2·495, 2·323 and 2·278 Å, and have 23 symmetry.

Introduction

[Co(NH₃)₆]₄Cu₅Cl₁₇ is of interest because of the unusual stoichiometry of the anion and also because of its very strong similarity to [Co(NH₃)₆]CuCl₅. The isomorphous [Cr(NH₃)₆]CuCl₅ has been investigated by Raymond, Meek & Ibers (1968) and shown to contain [CuCl₅]³⁻ trigonal bipyramids. These two compounds

can form a continuous series of solid solutions containing different ratios of monovalent to divalent copper (Mori, 1960; Day, 1968). It is clearly of interest to know the structure of the two pure phases and for this reason the title compound was investigated. A description of the structure has already appeared (Murray-Rust, Day & Prout, 1966).

Crystal data

Crystals of $[Co(NH_3)_6]_4Cu_5Cl_{17}$ were supplied by Dr P. Day. The orange crystals were well formed regular octahedra and showed no sign of anisotropy under the polarizing microscope. Rotation and Weissenberg photographs taken with copper radiation $[\lambda(Cu K\alpha_1) = 1·54051$ Å] showed the cell dimension to be 21·80 (1) Å, and that the diffraction pattern had systematic absences: hkl: $h+k = 2n+1$, $k+l = 2n+1$ and $h+l = 2n+1$; $hk0$: $h+k = 4n+1$, $4n+2$, $4n+3$. The Weissenberg photographs showed that the diffraction pattern had $m3$ and very close to $m3m$ symmetry. There appeared to be a few instances where the intensities of the reflexions hkl and khl were different but these could not be measured accurately from the photographs. It was not, therefore possible to differentiate between the space group $Fd3$ and $Fd3m$ from photographic data.

The density, determined by flotation, was 2·00 g cm⁻³, which agrees with the calculated value of 1·99 g cm⁻³ (on the basis of 8 formula units of $[Co(NH_3)_6]_4Cu_5Cl_{17}$ per cell). The absorption coefficient for Cu Kα radiation is 192 cm⁻¹ and for Mo Kα is 45 cm⁻¹. For this reason molybdenum radiation was used for data collection.

Experimental

Data were collected from a regular octahedron of side 0·35 mm mounted about **a** on a Hilger–Watts linear diffractometer. Levels $0kl$ to $8kl$ were collected for one octant of reciprocal space. This ensured that many reflexions were observed twice or thrice and a high proportion of the reflexions in the copper sphere were collected. Balanced Zr/Sr filters and an ω scan of 1·5° were used. Reflexions for which the two background counts differed by more than 3 e.s.d.'s were remeasured or rejected. Correction for white radiation streaks was made from the counts with balanced filters. Reflexions with an intensity of less than 6 × (standard deviation of total count) were then discarded. Lorentz and polarization corrections were applied but not absorption corrections since axial reflexions showed little variation in intensity when the crystal was rotated. Layer scale factors were calculated by comparing reflexions on different layers related by the triad axis. The discrepancy between the intensities of symmetry equivalent reflexions, defined as $R = \sum[\Delta(hkl)+(klh)+(lhk)]/\sum \bar{I}$ (hkl) was 0·098 {where $\bar{I}(hkl) = \frac{1}{3}[I(hkl)+I(klh)+I(lhk)]$ and $\Delta(hkl) = |\bar{I}-I(hkl)|$}. The intensity of the reflexion hkl was then taken as $F^2(hkl) = \bar{I}$, unless $|\Delta|$ was greater than 0·20 $\bar{I}$, when the reflexion was rejected.

This gave a set of 403 unique reflexions, of which 78 were of the type hhl and 6 of the type hhh.

To determine whether the Laue group was $m3$ or $m3m$, reflexions hkl and khl were compared. The discrepancy index

$$R = 2 \sum |F^2(hkl) - F^2(khl)|/\sum[F^2(hkl) + F^2(khl)]$$

was found to be 0·36. This is much higher than the discrepancy between symmetry-related equivalents and is clearly beyond experimental error, which shows that in general $F(hkl) \neq F(khl)$ and that the space group is $Fd3$. If, however, $F(hkl)$ and $F(khl)$ were completely unrelated, the discrepancy would be much nearer unity, which implies that the structure is close to $Fd3m$ symmetry.

Determination of the structure

The structure must be close to that of $[Co(NH_3)_6]CuCl_5$ as the cell dimensions, space groups and reflexion intensities are very similar. Moreover solid solutions are formed between these two compounds. $[Co(NH_3)_6]CuCl_5$, has 32 formula units in a cubic cell, $a = 21·85$ (1) Å, in space group $Fd3c$ (Murray-Rust, 1963; Day, 1968). The isomorphous $[Cr(NH_3)_6]CuCl_5$ (Raymond, Meek & Ibers, 1968) has atoms in the following positions [$Fd3c$, origin at $\bar{3}$, *International Tables for X-ray Crystallography* (1959)]:*

$$
\begin{aligned}
&32Cu \ (b) \ \tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4} \\
&\dagger 32Cr \ (c) \ 0,0,0 \\
&64Cl \ (e) \ 0·1904, 0·1904, 0·1904 \\
&96Cl \ (g) \ \tfrac{1}{4}, 0·0760, -0·760 \\
&193N \ (h) \ 0·0711, 0·0514, -0·0303 \ .
\end{aligned}
$$

Because of the close similarity of the structures it is likely that the Co(c), Cu(b), and N(h) atoms are in similar positions in the title compound, but places must be found for 8 more Cu atoms, and the 160 Cl atoms must be replaced by 136.

A sharpened Patterson function had a set of very strong peaks on points of a primitive sublattice with cell dimension $a/4$, which is consistent with Cu and Co atoms in the same positions as in $[Co(NH_3)_6]CuCl_5$. There were also prominent peaks related by a vector of $a/8, a/8, a/8$ which can be explained by placing the 8 extra Cu atoms at position (a) in $Fd3$. The heavy atoms were therefore placed as follows [it should be noted that position (e) (x,x,x) does not require the coordinate to be exactly $\tfrac{1}{4}$].

$$
\begin{aligned}
&16Co \ (c) \ 0,0,0 \\
&16Co \ (d) \ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2} \\
&32Cu \ (e) \ \tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4} \\
&8Cu \ (a) \ \tfrac{1}{8},\tfrac{1}{8},\tfrac{1}{8} \ .
\end{aligned}
$$

A Fourier synthesis phased on these atomic positions would have a very high degree of false symmetry.

---

* All coordinates are given relative to an origin of symmetry $\bar{3}$ in $Fd3$ and $Fd3c$.

† Corresponds to Co in $Co(NH_3)_6CuCl_5$.

An indication of one of the chlorine positions could however be obtained from the Patterson function as there was a diffuse peak at about $a/16, a/16, a/16$. This can be interpreted as a Cl atom forming a linear bridge between Cu(a) and Cu(e) in position (e) with a parameter $x = 0.1875$. This corresponds closely to the Cl atom at position (c) in $Fd3c$, although it is only 32-fold in $Fd3$, which leaves 104 Cl atoms and 196 N atoms.

At this stage it was hoped that Cu(a) and Cl(e) would be sufficient to break the false symmetry imparted by the other heavy atoms and a Fourier synthesis was calculated. The main additional features were peaks at 0·28, 0·07, -0.08 and 0·28, -0.08, 0·07, the first being twice the height of the second and of reasonable height for a chlorine atom. The positions of the two peaks are related by a mirror plane along (110) and as the atoms used for phasing the synthesis were all related by this mirror symmetry it was assumed that the smaller peak was a 'ghost' of the first produced by some incorrect phases. (It is more probable in fact that the ghost peak was produced as a result of the twinning of the crystal.) A chlorine atom was thus put in the first position (96-fold) and another Fourier synthesis calculated. This had no significant electron density where the 'ghost' had been but showed clearly the position of the nitrogen atoms [in two independent sets of 96-fold positions (g)]. All atoms had now been introduced into the structure except for 8 chlorine atoms. An 8-fold position (b) is available at $\frac{3}{8}, \frac{3}{8}, \frac{3}{8}$ and there is a large 'hole' in the structure here as there are no other atoms within 4 Å. However the electron density at this point, although positive, was not large and it was concluded that the chlorine ion (ionic radius of 1·81 Å) was vibrating with a large amplitude in this hole. It was included with a high temperature factor ($B_{iso} = 8$ Å^2) and its occupancy was varied. The structure was refined by full-matrix least-squares calculations with isotropic temperature factors until convergence was obtained with R at 0·146. The parameters obtained by this process are listed in Table 1. The structure is chemically acceptable with satisfactory bond lengths and angles,

but the temperature factors of the atoms are in general rather low [except for Cl(b)].

Detection of twinning and structure refinement

At this stage the structure might be considered as solved were it not for the high value of R. Diffractometer data should yield an R below 0·10 particularly after the collection of many symmetry-related reflexions which were only included if they agreed well. The structure is chemically acceptable and bond lengths and angles are reasonable (*e.g.* Co–N bonds are 1·98, 2·00 Å and the angles in the octahedra are all $90 \pm 1°$). A difference synthesis showed no obvious features.

An analysis of the agreement between F_o and F_c was carried out. The Co atoms and Cu atoms contribute only to some of the reflexions owing to the high symmetry of their positions and for this group of reflexions the conventional R^* was 0·066. However for the other reflexions R was 0·22, suggesting that the positions of the Cl and N atoms, particularly those lying off the (011) mirror plane, might be incorrect. An analysis was therefore made of the relationship between $F(hkl)$ and $F(khl)$. In the space group $Fd3m$ these would necessarily be equal, but in $Fd3$ there is, in general, no relationship between them. For a random distribution of equal atoms in this space group the discrepancy index $R = \sum\{[||F(hkl)| - |F(khl)|]|/\frac{1}{2}\sum[|F(hkl)| + |F(khl)|]\}$ might be expected to be about 0·8. For the observed structure factors, $R = 0.138$ whilst for the structure factors calculated from this model $R = 0.435$. This is shown graphically in Fig. 1(a) and (b), which show scatter diagrams of $|F(hkl)|$ plotted against $|F(khl)|$. Reflexions to which the heavy atoms contribute will be large and have $F(hkl)$ and $F(khl)$ approximately equal as most of the scattering material will be related by $Fd3m$ symmetry. However reflexions to which only light atoms contribute will be smaller and should show a large scatter as most of these are not related by the mirror plane and $F(hkl)$ is not related to $F(khl)$. This is clearly true for F_c [Fig. 1(b)] but not for F_o [Fig. 1(a)] where $F(hkl) \sim F(khl)$ regardless of whether the heavy atoms contribute or not. This strongly suggests that the structure is in some way disordered about the plane (110) making it approximately closer to $Fd3m$ symmetry than is suggested by the model so far proposed. There are two obvious ways in which this could arise: local disorder and twinning.

A disordered arrangement of the atoms in individual cells

Consider a certain proportion (λ) of the unit cells with atoms in positions ($x_i y_i z_i$) and the rest $(1 - \lambda)$ with the same atoms at ($y_i x_i z_i$). If these cells are totally disordered the structure factor can be written

$$F_{dis}(hkl) = \lambda[F(hkl, x_i y_i z_i)] + (1 - \lambda)[F(hkl, y_i x_i z_i)].$$
$$(1a)$$

Table 1. *Final parameters of original model* (A) *with estimated standard deviations*

Estimated standard deviations are given in parentheses, except for atoms in special positions.

	x	y	z	B_{iso} (Å^2)
Co(1)	0	0	0	0·83 (10)
Co(2)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1·08 (17)
Cu(1)	0·2509 (3)	0·2509 (3)	0·2509 (3)	2·71 (26)
Cu(2)	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	1·34 (21)
Cl(1)	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{8}$	8·00*
Cl(2)	0·1849 (4)	0·1849 (4)	0·1849 (4)	0·96 (16)
Cl(3)	0·2777 (5)	0·0713 (5)	-0.0748 (5)	2·7 (22)
N(1)	0·0621 (13)	0·0593 (13)	-0.0306 (13)	1·19 (49)
N(2)	0·5350 (16)	0·0811 (16)	-0.0269 (16)	2·62 (65)

* B_{iso} for this atom was fixed and the occupation number refined to 0·60 (10).

* $R = \{\sum |F_o - |F_c||\}/\{\sum F_o\}$ with unobserved and rejected reflexions excluded.

For atoms obeying $Fd3m$ symmetry $x_i = y_i$, so that $(1a)$ can be rewritten:

$$F_{dis}(hkl) = F(hkl, \text{ atoms in } Fd3m \text{ arrangement})$$
$$+ \lambda F(hkl, \; x_i y_i z_i) + (1-\lambda)F(hkl, \; y_i x_i z_i) . \quad (1b)$$

The parameter λ thus represents an occupation factor for atoms not lying on the (110) mirror planes and will apply only to atoms in position (f), in this case one Cl and two N. This is a relatively low proportion of the scattering material and it is not impossible that a scatter diagram similar to $(1a)$ could result from it. Moreover the structure is chemically feasible as it corresponds to only small changes in the $CuCl_3$ groups and the $[Co(NH_3)_6]^{3+}$ octahedra. To test this hypothesis these atoms were put into structure factor calculations with positions as in Table 1 but with the occupation number λ; complementary atoms were simultaneously introduced at $y_i x_i z_i$ with occupancy $(1-\lambda)$. The parameter λ was then refined. Regardless of the initial value of λ (values between 0·55 and 0·8 were used) it quickly refined to about 1·0. Moreover the agreement between observed and calculated structure factors was always worse for this model than for the original solution. There appears, therefore, to be no evidence for this type of disorder.

A crystal composed of two unequal twins

The diffraction pattern is also compatible with that from a crystal composed of two unequal twins. Twinning is possible either by 90° rotation about **a** or by reflexion about the (110) plane, giving rise in either case to a diffraction pattern in which reflections hkl and khl are exactly superimposed.

The procedure for determining the twin parameter α is similar to that discussed by Britton (1972). In the seven examples given by Britton, however, twinning was known or suspected in six before the final structure had been determined. The means of detection were

either morphological, optical or from systematic absences which were inconsistent with any known space group. Only in the case of Na_2SiF_6 (Zalkin, Forrester & Templeton, 1964) was no evidence given for twinning apart from a consideration of the intensities of the observed diffraction maxima. Zalkin refined the structure for a variety of values of α, finally taking that which led to the best agreement between observed and calculated structure factors. This is a time-consuming process and unrewarding if the crystal does not turn out to be twinned after all. The use of scatter diagrams [Fig. $1a$ and (b)] is relatively quick and can be used as a routine check to determine whether or not the crystal is composed of two unequal twins, often before the start of structure analysis.

Britton gives equation $(2a)$ for the relationship between the true intensities $F^2(hkl)$ and $F^2(khl)$ (J_1 and J_2) and those observed from the twinned crystal (I_1 and I_2) where $0 < \alpha < 0\cdot50$.

$$\frac{J_2}{J_1} = \frac{I_2 - \alpha(I_1 + I_2)}{I_1 - \alpha(I_1 + I_2)} \quad (2a)$$

and if $J_2 \ll J_1$ so that $J_2/J_1 \sim 0$, then

$$I_2 = \alpha(I_1 + I_2) \quad (2b)$$

or

$$\frac{I_2}{I_1} = \frac{\alpha}{1-\alpha} . \quad (2c)$$

In the present study the structure factors F, rather than their squares, were used and $(2c)$ can be rewritten

$$\frac{F_2}{F_1} = \left(\frac{\alpha}{1-\alpha}\right)^{1/2} . \quad (2d)$$

It follows that the ratio F_2/F_1 must lie between the limits $[\alpha/(1-\alpha)]^{1/2}$ and $[(1-\alpha)/\alpha]^{1/2}$. This is shown clearly in Fig. 1 where all the points lie within a sector formed by lines through the origin of slopes 1·50 and 1/1·50. From this α is calculated to be 0·31.
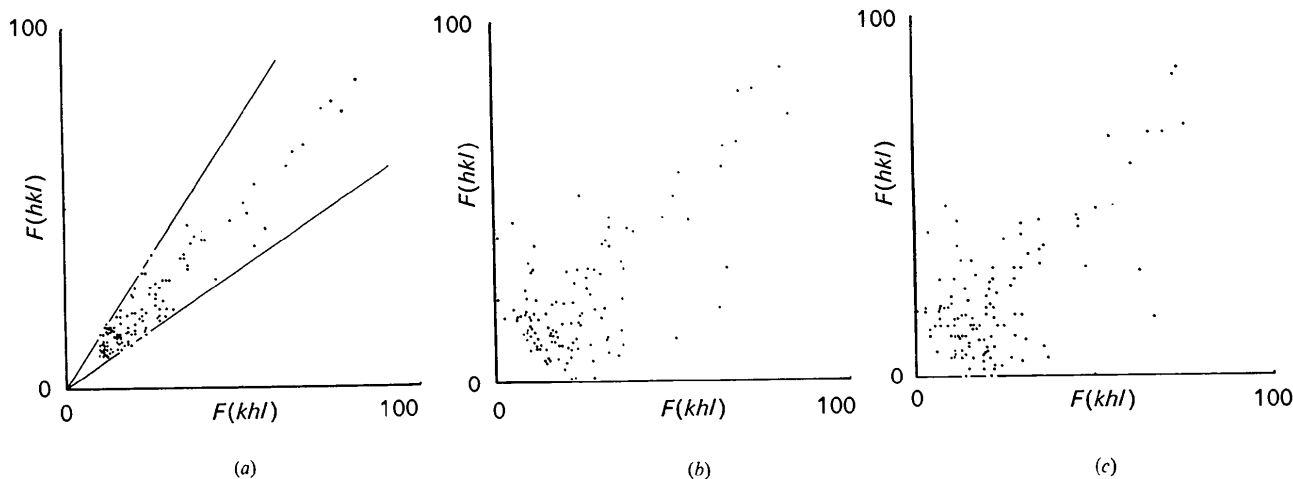

Fig. 1. Diagrams of $|F(hkl)|$ plotted against $|F(khl)|$. (a) Observed structure amplitudes for $[Co(NH_3)_6]_4Cu_5Cl_{17}$. (b) Calculated structure amplitudes for the same compound. (c) Observed structure amplitudes corrected for twinning. The lines in (a) enclose all the observed reflexions and lead to a value of the twinning parameter.

Since what have been observed are I_1 and I_2 it is possible to calculate the 'true' values of $F^2(hkl)$ and $F^2(khl)$ from (2a). These 'detwinned' values of $F^2(hkl)$ and hence $F(hkl)$ can be used in the normal refinement of the structure. This procedure was adopted and a set of 'detwinned' $F'(hkl)$ was produced. [In a few cases negative or zero values of J_1 and J_2 were obtained. This is due to experimental error and the value of $F(hkl)$ in these cases was set equal to half the observable minimum]. In several cases one reflexion of a pair $F(hkl)$ and $F(khl)$ had been rejected as being too inaccurate and the correction procedure could not therefore be applied. The absolute values of J_1 and J_2 are highly dependent on the accuracy of I_1 and I_2 so that any inaccuracy in either $F(hkl)$ or $F(khl)$ results in a large error in $F'(hkl)$. No modification needs to be made to reflexions of the type $F(hhl)$ and $F(hhh)$. A scatter diagram of the corrected intensities has a very much more satisfactory distribution [Fig. 1(c)], very similar to Fig. 1(a). The parameters obtained at the end of the first refinement (Table 1) were used to calculate the structure factors and agreement was much better. After one cycle of least-squares refinement the isotropic temperature factors were much more satisfactory and R was 0·095.

Refinement of the twinned structure

At this stage α was varied slightly to find the value which gave the best agreement between F_o and F_c (the procedure adopted by Zalkin). This is shown in Table 2 where a value of 0·323 gives marginally better agreement than the original 0·31. This new value was used to procedure the final set of 'detwinned' F_o' which appear in Table 3. Anisotropic temperature factors were then applied to all atoms and 4 cycles of least-squares refinement led to convergence at an R of 0·085. The weighting scheme was: $w=1$, $F<90$; $w=1/[1+(F-90)^2/225]$, $F>90$, and the quantity minimized was $\sum w[F_o(hkl) - F_c(hkl)]^2$, the summation being over the reflexions given in Table 3. The method of refinement was based on the full-matrix procedure and the scattering factors used were those tabulated by Ibers (1968), the atoms being assumed to be Co^{3+}, Cu^+ and Cl^-. No correction was made for anomalous dispersion. The estimated standard deviations of the positional and thermal parameters were derived from the inverted normal matrix, and refinement was terminated when all shifts were less than one-third of the estimated deviations. The final positional and thermal parameters are given in Table 4.

Table 2. *Variation of R with* α

Values computed at limit of isotropic refinement.

α	R
0·30	0·1000
0·31	0·0951
0·32	0·0927
0·323	0·0926
0·33	0·0935
0·34	0·0968

Discussion of twinning in space groups of high symmetry

It seems clear that the model of a crystal containing two unequal twins is a satisfactory solution of the present problem. It is disturbing to realize however that there was no other indication of twinning (and the preliminary publication of the structure was made with no thought of this phenomenon!). This state of affairs seems very possible for a number of crystals in tetragonal, trigonal or cubic space groups. If $\alpha = 0·50$, a fairly common occurrence, then there may be no means whatever of detecting twinning and the structure would be 'solved' in a space group of higher symmetry, possibly with 'disorder'. It is therefore interesting to compare the 'detwinning' structure (*B*) with the original one (*A*), where it might be thought that the poor agreement between F_o and F_c would have led to an incorrect structure. However comparison of the two structures (Table 5) shows that this is not the case. If

Table 3. *Observed (before and after correction) and calculated structure factors*

FO is the observed structure factor and FO' is its value after correction for twinning. FC is the structure factor calculated from the parameters in Table 4. Reflexions of the types hhh and hhl are not affected by the twinning and have been placed at the beginning of the table. Reflexions hkl and khl are grouped together.

the positional parameters (p_i) of these two models are compared, the quantity $\Delta(p_i) = |p_{iA} - p_{iB}|$ can be calculated, with an estimated standard deviation $[\sigma(p_i)]$ of

$$[\sigma^2(p_{iA}) + \sigma^2(p_{iA})]^{1/2}$$

where $\sigma(p_{iA})$ and $\sigma(p_{iA})$ are the standard deviations of the relevant parameters derived from the inverse normal matrix. The quantity

$$t(p_i) = \Delta(p_i)/\sigma(p_i)$$

is a measure of the likelihood of $\Delta(p_i)$ being insignificant, for if $t(p_i) > 3 \cdot 0$ it is likely that $\Delta(p_i)$ is significant. There are no values of Δ greater than $3 \cdot 0$ so that the parameters are not appreciably different. The quantity

$\sum t_i^2$ can also be used and this falls well below the value (27·7) which would show that the models were significantly different (*International Tables for X-ray Crystallography*, 1959).

Table 5. *Comparison between positional parameters before and after correction for twinning*

The absolute difference (Δp) between parameters ($\times 10^4$) is compared with the estimated standard deviation (σ) of this difference ($\times 10^4$). The ratio between these ($\Delta p/\sigma$) is t. Parameters were compared at the limit of isotropic refinement.

		Δp	σ	t	t^2
Cu(1)	(x)	6	3·3	1·8	3·2
Cl(2)	(x)	4	4·5	0·9	0·8
Cl(3)	(x)	5	5·6	0·9	0·8
Cl(3)	(y)	4	5·6	0·7	0·5
Cl(3)	(z)	2	5·6	0·3	0·1
N(1)	(x)	25	14·8	1·7	2·8
N(1)	(y)	1	14·8	0·1	0·0
N(1)	(z)	16	14·8	1·1	1·2
N(2)	(x)	1	18·9	0·1	0·0
N(3)	(y)	35	18·9	1·9	3·5
N(2)	(z)	9	18·9	0·5	0·2

$$\sum_{11} t^2 = 13 \cdot 1 \qquad \chi_{11}^2 = 27 \cdot 2$$

The positional parameters of the atoms have thus been changed negligibly by the correction of F_o, and the main effect has been to reduce the e.s.d.'s by 40%. The same effect was noticed by Zalkin who stated that no atom moved as much as 0·1 Å as a result of this correction. This suggests that in these two cases, which have moderately large values for α (0·32 and 0·41), the structure can be satisfactorily solved before twinning is detected. Moreover it appears that it is unlikely that the effect will be misinterpreted, as disorder was not suggested by a difference synthesis.

Discussion of the structure

The structure (Fig. 2) consists of [Co(NH₃)₆]³⁺, [Cu₅Cl₁₆]¹¹⁻ and isolated Cl⁻ ions. It is closely related to [Co(NH₃)₆]CuCl₅ (Fig. 3), which can be described as a rock-salt lattice of alternate [Co(NH₃)₆]³⁺ and trig-

Fig. 2. The structure of [Co(NH₃)₆]₄Cu₅Cl₁₇. One eighth of the unit cell is shown. [Co(NH₃)₆]³⁺ ions are represented by octahedra, copper atoms by filled circles and chlorine atoms by open circles, the largest of which is the chloride ion at ⅜,⅜,⅜. The octahedron at ¼,¼,¼ has been omitted for clarity.

Table 4. *Final parameters with estimated standard deviations*

The temperature factor is given by exp $[-10^6(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	0	0	0	516 (66)	516 (66)	516 (66)	*	*	*
Co(2)	½	½	½	989 (85)	989 (85)	989 (85)	*	*	*
Cu(1)	0·2515 (2)	0·2515 (2)	0·2515 (2)	1708 (2)	1708 (60)	1708 (60)	90 (65)	90 (65)	90 (65)
Cu(2)	⅛	⅛	⅛	1312 (115)	1312 (115)	1312 (115)	*	*	*
Cl(1)	⅜	⅜	⅜	3837 (†)	3837 (†)	3837 (†)	*	*	*
Cl(2)	0·1853 (2)	0·1853 (2)	0·1853 (2)	905 (98)	905 (98)	905 (98)	−42 (98)	−42 (98)	−42 (98)
Cl(3)	0·2782 (3)	0·0709 (3)	−0·0750 (3)	1528 (126)	1122 (111)	1026 (116)	−26 (105)	73 (106)	61 (105)
N(1)	0·0637 (8)	0·0568 (7)	−0·0305 (7)	1381 (354)	1307 (376)	636 (400)	−284 (341)	−157 (330)	−516 (323)
N(2)	0·5351 (10)	0·0776 (10)	−0·0278 (9)	1865 (528)	918 (554)	2829 (545)	152 (489)	609 (458)	−176 (474)

* Required by symmetry to be zero.
† The temperature factor of this atom was not refined and the occupancy was refined to 0·62 (4).

onal bipyramidal $[CuCl_5]^{3-}$ ions, both of which lie on triad axes. It might be expected that the corresponding copper(I) compound would contain a similar arrangement of $[Co(NH_3)_6]^{3+}$ ions and $[CuCl_4]^{3-}$ tetrahedra and the present structure does indeed contain these units. In addition, however, it contains one extra Cu^+ ion for each four $[CuCl_4]^{3-}$ groups (and necessarily an extra Cl^- ion to maintain the stoichiometry). The extra Cu atom joins up the four $CuCl_4$ tetrahedra to form a $[Cu_5Cl_{16}]^{11-}$ ion and the extra chloride ion is located in a large hole in the lattice.

The bond distances and angles are given in Table 6. The two independent $[Co(NH_3)_6]^{3+}$ ions are nearly perfect octahedra and the Co–N distances are in excellent agreement with the value of 1·96 (2) Å found by Barnet, Craven, Freeman, Kime & Ibers (1966). The hitherto unreported $[Cu_5Cl_{16}]^{11-}$ ions can be thought of as five vertex-linked $CuCl_4$ tetrahedra. The Cu–Cl bond distances and angles are not equal however and an alternative description is that of four nearly planar $[CuCl_3]^2$ ions coordinated to a central $CuCl_4$ tetrahedron. This is suggested by the relatively long Cu(1)–Cl(3) bond, and the small Cl(2)–Cu(1)–Cl(3) angle, which is markedly less than tetrahedral. The $[Cu_5Cl_{16}]^{11-}$ ion has 23 symmetry and is rotated by about 20° from a completely staggered ($\bar{4}3m$) conformation.

A comparison of the structure with $[Cr(NH_3)_6]CuCl_5$ shows that most of the atoms are in nearly identical positions. The Co atoms are necessarily the same and the Cu(1) atoms are displaced by only 0·05 Å. It is not strictly fair to compare the nitrogen positions as the
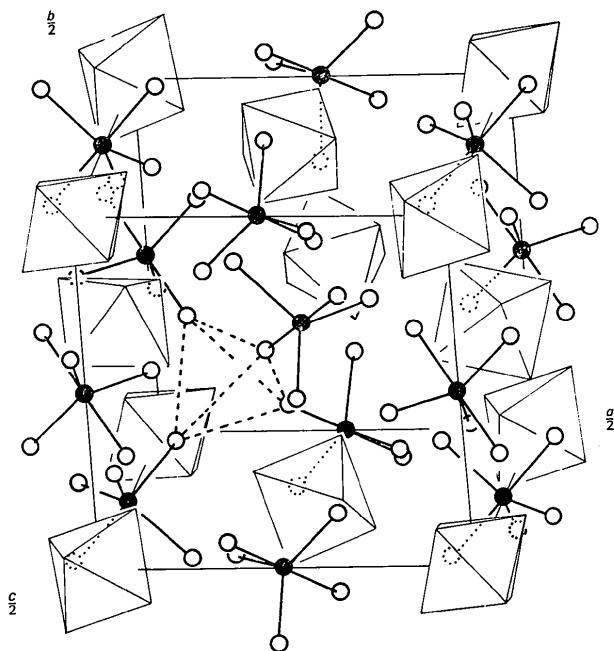
Table 6. Distances and angles in the structure with estimated standard deviations

Distances (Å)

Co(1)–Cu(1)	5·480 (6)
Co(1)–Co(1)	7·707 (9)
Cu(1)–Cl(2)	2·495 (6)
Cu(1) –Cl(3)	2·323 (7)
Cu(2)–Cl(2)	2·278 (5)
Co(1)–N(1)	1·953 (16)
Co(2)–N(2)	1·972 (21)
Cu(1)–Cl(1)	4·667 (6)
Cl(3) –Cl(1)	4·888 (8)

Angles (°)

N(1)–-Co(1)–N(1')	90·3 (3)
N(1)–-Co(1)–N(1'')	89·7 (3)
N(2)–-Co(2)–N(2')	92·9 (4)
N(2)–-Co(2)–N(2'')	87·1 (4)
Cu(1)–Cl(2) –Cu(2)	18·0 (0)
Cl(2) –Cu(1)–Cl(3)	98·7 (2)
Cl(3) –Cu(1)–Cl(3)	117·7 (2)

parameters for the chlorocuprate(II) are for Cr rather than Co, but the positions differ by less than 0·3 Å. The bridging chloride ion, Cl(2), is within 0·2 Å of one of the axial Cl(c) atoms in the chlorocuprate(II) bipyramid but the other axial atom has no equivalent in the present structure. The equatorial Cl(g) atoms of the $[CuCl_5]^{3-}$ ion correspond to the terminal Cl(3) atoms in the present structure but here the difference in positions is about 0·63 Å. Atoms Cu(2) and Cl(1) have no equivalent in the chlorocuprate(II).

It might have been expected that the complex formed between $[Co(NH_3)_6]^{3+}$, Cu^+ and Cl^- would have the formula $[Co(NH_3)_6]CuCl_4$. It is somewhat surprising therefore to find the title compound formed instead and also that with its complex stoichiometry it is so similar to $[Co(NH_3)_6]CuCl_5$. These facts can be explained if it is assumed that the effectively spherical $[Co(NH_3)_6]^{3+}$ ions are nearly but not quite in contact with each other in an almost close-packed lattice. This leads to an almost constant Co–Co distance regardless of anion size and hence to the very similar cell dimensions. If the cations are thought of as approximately spherical they will have a van der Waals radius of about 3·7 Å (the Co–N distance and half the intermolecular NH_3–NH_3 distance). This leads to a Co–Co distance of 7·4 Å, slightly less than the experimental value of 7·71 Å, suggesting that although the cations are not quite in contact, they are much larger than the anions.

Confirmation of this is provided by the difference in cell dimensions between the cobalt and chromium chlorocuprate(II) complexes. The cell dimension of $[Co(NH_3)_6]CuCl_5$ is 21·85 (1) Å (Murray-Rust, 1963) whereas the corresponding chromium complex has $a =$ 22·24 (1) Å, corresponding to a difference in the cation-anion distance of 0·10 (1) Å. The Co–N bond length is 1·96 (2) Å and the Cr–N bond length was found to be 2·06 Å, suggesting strongly that the cations are in contact with the anions. The $[CuCl_4]^{3-}$ ion would certainly be considerably smaller than the $[CuCl_5]^{3-}$ ion and

Fig. 3. The structure of $Co(NH_3)CuCl_5$ on the same scale as Fig. 2. The atoms are represented by identical symbols, and the octahedron at $\frac{1}{4},\frac{1}{4},\frac{1}{2}$ is omitted.

this diminution in the size of anion would lead to a less stable structure as the cations would then be in contact with each other. In the present compound the empirical formula of the anion $[Cu_{1.25}Cl_{4.25}]$ leads to a greater effective volume for the anion which will be much nearer to the volume of the $[CuCl_5]^{3-}$ ion.

The structure shows clearly how twinning can occur since over 60 % of the scattering material (based on f^2) lies on the diagonal (110) plane $(x=y)$ conforming to the higher symmetry $Fd3m$. Two twin fragments related by reflexion across (110) differ only in the arrangement of the nitrogen atoms and the terminal Cl(3) atoms, corresponding to rotations of the $CuCl_3$ groups and $[Co(NH_3)_6]^{3+}$ ions. These rotations are unlikely to have much effect on the rest of the structure so that this form of twinning is highly probable.

The structure also gives insight into the possible formulae and structures of the solid solutions formed between $[Co(NH_3)_6]CuCl_5$ and the title compound. A single crystal of an intermediate phase has been in-vestigated and it is hoped to publish the structure in a future paper.

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The Crystal and Molecular Structure of the Diterpenoid Baccatin V, a Naturally Occurring Oxetan with a Taxane Skeleton

BY E. E. CASTELLANO AND O. J. R. HODDER

Chemical Crystallography Laboratory, South Parks Road, Oxford OX1 3QS, England

The structure of a new diterpenoid, baccatin V, $C_{31}H_{38}O_{11}$, isolated from *Taxus baccata* L., has been determined by X-ray diffraction techniques. The crystals are orthorhombic, space group $P2_12_12_1$ with cell dimensions $a=25.75\pm0.01$, $b=9.31\pm0.01$, $c=12.34+0.02$ Å and $Z=4$. The structure was solved by application of the symbolic addition procedure for phase determination. The molecule has been shown to contain an oxetan ring and to be $5\beta,20$-epoxy-$1\beta,2\alpha,4\alpha,7\alpha,10\beta,13\alpha$-hexahydroxytax-11-en-9-one $4\alpha,10\beta$-diacetate 2α-benzoate. The final R value is 9·14% for 2459 observed reflexions, refining positional and anisotropic thermal parameters of non-hydrogen atoms and including 28 hydrogen positions, obtained from a ΔF synthesis, in the final structure-factor calculations.

Introduction

In recent structure investigations on a series of taxane derivatives, a new diterpenoid, baccatin V, $C_{31}H_{38}O_{11}$, was isolated from *Taxus baccata* L. An insufficient amount of substance was available for detailed chemical studies, so an X-ray three-dimensional crystal-structure determination was carried out. The present paper reports on the structural characteristics of the compound. Details of its n.m.r. spectrum have been published elsewhere (Della Casa de Marcano, Halsall, Castellano & Hodder, 1970).

Experimental

Unit-cell dimensions were measured on oscillation and Weissenberg photographs and refined later on a Hilger and Watts linear diffractometer. Crystal data are as follows: $a=25.75\pm0.01$, $b=9.31\pm0.01$, $c=12.34\pm0.02$ Å; $U=2958.3$ Å^3; $D_m=1.308$ g cm^{-3} (by flotation), $D_c=1.317$ g cm^{-3}; $Z=4$. Systematic absences, $h00$ when $h\neq 2n$, $k00$ when $k\neq 2n$, and $l00$ when $l\neq 2n$; space group $P2_12_12_1$.

From a crystal mounted along the c axis 3364 reflexions of the layers zero to 12 were collected on a Hilger