

Fig. 1. Projection along the *c* axis of the atomic arrangement of Yb₂P₆O₁₈·16H₂O. The PO₄ tetrahedra of the P₆O₁₈ groups are denoted by the labels of their central P atoms. The water molecules belonging to the Yb coordination are represented by the filled circles [W(1) to W(7)], the non-bonded ones by the empty circles [W(8) to W(16)].

four rare-earth polyhedra. A similar type of connection can be observed in the crystal structure of Nd₂P₆O₁₈·12H₂O (Trunov, Chudinova & Borodina, 1988). Moreover, the YbO₈ dodecahedra are isolated from each other in the sense that they do not share any O atoms. The shortest distance Yb—Yb is 5.8136 (4) Å.

The non-bonded water molecules. In addition to all the internal O atoms, three external ones O(E31), O(E52) and O(E62) as well as nine water molecules are not involved in the coordination of the rare-earth atom. These non-bonded water molecules are charac-

terized by having thermal factors larger than the others (Table 1). They are dispersed in the whole atomic arrangement. In particular, some of them fill channels centred on the 2₁ axes parallel to *c* formed by the special arrangement of the rings (Fig. 1). This type of water molecule acts as an intermediate in the hydrogen-bonding scheme which extends not only between the successive anionic layers but also, probably, inside such layers.

In conclusion, the main features to note in this structure are the absence of symmetry in the P₆O₁₈ anion, the absence of direct bonding between the Yb coordination polyhedra and the absence of bonding between the P₆O₁₈ rings of an anionic layer *via* these cationic polyhedra.

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Phase Transition of Hexaamminecobalt(III) Pentachlorocuprate(II)

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Abstract. The structures above and below the transition temperature of 280.8 K have been investigated

by single-crystal X-ray diffraction. [Co(NH₃)₆][CuCl₅], *M_r* = 401.9, λ(Mo Kα) = 0.71073 Å. A redetermination at *T* = 299 (1) K, (I), cubic, *Fd* $\bar{3}$ *c*, *a* = 22.085 (2) Å, *V* = 10772 (2) Å³, *Z* = 32, *D_x* =

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1.98 Mg m⁻³, $\mu = 3.79$ mm⁻¹, $F(000) = 6432$, $R = 0.051$ for 398 observed unique reflections. At $T = 120$ (1) K, (II), tetragonal, $F4_1adc$ ($a + b$, $b - a$, c setting of $I4_1acd$), $a = 22.008$ (3), $c = 22.087$ (4) Å, $V = 10698$ (3) Å³, $Z = 32$, $D_x = 2.00$ Mg m⁻³, $R = 0.071$ for 1457 unique reflections after the correction for twinning. Although the arrangement of the metal complexes remained unchanged through the phase transition, the trigonal bipyramidal $[\text{CuCl}_5]^{3-}$ ion, which has D_{3h} symmetry in the cubic phase, deformed into approximate C_{2v} symmetry in the tetragonal phase. Drastic changes were observed in the equatorial coordination plane. One of three equatorial Cu—Cl bonds was elongated by 0.189 (1) Å and the other two were shortened by 0.062 (2) Å from the bond length of 2.3937 (3) Å in the cubic phase. Moreover, the Cl—Cu—Cl bond angle formed by the shortened Cu—Cl bonds expanded to 145.9 (1)°.

Introduction. The complex ion, $[\text{CuCl}_5]^{3-}$, exhibits D_{3h} symmetry in the crystals of $[\text{Co}(\text{NH}_3)_6]^{3+}$ (Bernal, Elliott, Lalancette & Brennan, 1968) and the $[\text{Cr}(\text{NH}_3)_6]^{3+}$ salt (Mori, Saito & Watanabe, 1961; Raymond, Meek & Ibers, 1968). Owing to the regular geometry of $[\text{CuCl}_5]^{3-}$ a variety of spectroscopic studies were carried out: laser Raman and infrared spectroscopy (Long, Herlinger, Epstein & Bernal, 1970), magnetic susceptibility (Hatfield & Jones, 1970) and diffuse reflectance spectroscopy (Allen & Hush, 1967). The crystal structure of $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$ is isomorphous with that of $[\text{Co}(\text{NH}_3)_6][\text{CdCl}_5]$ (Epstein & Bernal, 1971). During the course of a magnetic study of $[\text{CuCl}_5]^{3-}$ diluted into $[\text{Co}(\text{NH}_3)_6][\text{CdCl}_5]$, Epstein, Bernal & Brennan (1976) found that the temperature dependence of the ESR spectra suggested that the local symmetry at the Cu^{II} site was no longer D_{3h} at the low temperature. Differential thermal calorimetric measurements of $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$ indicated a first-order phase transition at 280.8 K. The geometry of the $[\text{CuCl}_5]^{3-}$ anion in the low-temperature phase was investigated by Reinen & Friebel (1984) based on single-crystal EPR and other spectroscopic measurements. The present paper reveals the deformation of the anion in the low-temperature phase.

Experimental. (I) A crystal of dimensions $0.4 \times 0.5 \times 0.6$ mm was mounted on a Rigaku AFC-5 four-circle diffractometer equipped with graphite-monochromatized Mo $K\alpha$ radiation. Laue group $m\bar{3}m$, cell parameters refined by least squares for 20 2θ values ($20 < 2\theta < 30^\circ$); intensity measurement performed to $2\theta = 55^\circ$ ($h, k, l, 0 \rightarrow 28$), θ - 2θ scan, scan speed 6° min^{-1} in θ . Variation of five standard reflections, $0.997 \leq \sum(|F_o|/|F_o|_{\text{initial}})/5 \leq 1.006$. 3369 reflections measured, 1803 observed reflections with $|F_o| >$

$3\sigma(|F_o|)$. After an analytical absorption correction by the Gaussian numerical integration method (Busing & Levy, 1957; relative transmission factors $0.24 < A < 0.33$), 398 unique reflections were obtained ($R_{\text{int}} = 0.024$). By utilizing the atomic coordinates already determined (Bernal *et al.*, 1968), non-H atoms were refined anisotropically. H atoms were located in difference syntheses and refined isotropically. $\sum w||F_o| - |F_c||^2$ minimized, $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$, $R = 0.051$, $wR = 0.055$, $S = 2.59$ for 398 unique reflections. Reflection/parameter ratio 6.75, $\Delta/\sigma < 0.3$, $-1.8 \leq \Delta\rho \leq 0.6 \text{ e \AA}^{-3}$. Complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). UNICS-III program system (Sakurai & Kobayashi, 1979), FACOM M-380R computer at Keio University.

(II) The crystal specimen used for room-temperature measurement was employed for low-temperature work. The specimen was cooled and retained at 120 K in a stream of cold nitrogen gas. Although the typical peak half-width became 0.22 from 0.12° on lowering the temperature, the cell constants did not alter appreciably. Intensity measurement was performed to $2\theta = 55^\circ$ ($h 0 \rightarrow 10, k -10 \rightarrow 10, l -10 \rightarrow 10$ for $2\theta \leq 20^\circ$, $h 0 \rightarrow 28, k 0 \rightarrow 28, l -28 \rightarrow 28$ for $20 < 2\theta \leq 55^\circ$), ω scan, $0.991 \leq \sum(|F_o|/|F_o|_{\text{initial}})/5 \leq 1.000$. 6361 reflections measured, 5222 observed, analytical absorption correction ($0.24 < A < 0.33$). Laue group appeared to be mmm based on the internal agreement factors listed in Table 1. Although $R_{\text{int}} = 0.021$ for mmm , relatively small R_{int} values of 0.029 and 0.052 were also calculated assuming the Laue symmetries $4/m$ and $4/mmm$ with the unique axis c . However, the tetragonal symmetry is apparently broken for several reflections. Tentatively, the crystal system was assumed to be orthorhombic. Systematic absences hkl , $h + k$ odd or $k + l$ odd or $h + l$ odd; $0kl$, $k + l \neq 4n$; $h0l$, $h + l \neq 4n$; $hk0$, $h + k \neq 4n$ showed that the space group was expected to be $Fddd$. Cell parameters were refined by least squares for 20 2θ values ($57 < 2\theta < 58^\circ$), $a = 21.959$ (5), $b = 21.966$ (4), $c = 22.043$ (4) Å. Supposing that the arrangement of the metal complexes was almost the same as in (I), the positions of one Cu, two Co and five Cl atoms in an asymmetric unit were derived and refined anisotropically. All six N atoms were obtained from Fourier syntheses and refined isotropically since some of them became non-positive-definite when they were refined anisotropically. The H atoms could not be located by a difference synthesis. At this stage of the refinement $R = 0.115$, $wR = 0.173$, $S = 6.45$ for 2632 unique reflections (refinement 1).

There are two chains of maximal subgroups for $Fd\bar{3}c$ connected with $Fddd$ (*International Tables for Crystallography*, 1983, Vol. A): $Fd\bar{3}c > Fd\bar{3} > Fddd$

Table 1. Internal agreement factors of the low-temperature phase assuming possible Laue symmetry without the correction for twinning

Laue symmetry	R_{int}	NG*	Number of unique reflections
<i>mmm</i>	0.021	0	2343
<i>4/m</i>	unique <i>a</i> 0.146	61	2163
	unique <i>b</i> 0.175	77	2070
	unique <i>c</i> 0.029	2	2278
<i>4/mmm</i>	unique <i>a</i> 0.144	37	1461
	unique <i>b</i> 0.167	48	1509
	unique <i>c</i> 0.052	1	1364
$m\bar{3}$	0.192	50	988
$m\bar{3}m$	0.193	34	595

* NG stands for the number of reflections showing the internal difference greater than $50\sigma(|F_o|)$.

and $Fd\bar{3}c > F4_1/adc$ ($I4_1/acd$) $> Fddd$. Further reduction of the space-group symmetries may be meaningless because of the unsuccessful refinements for the space groups $Fdd2$, $Fd2d$ and $F2dd$. In view of the small difference in the cell edges *a* and *b* and the pseudo- $4/mmm$ Laue symmetry, the possibility of partial submicroscopic twinning could by no means be excluded. The extensive twinning of the crystals below the phase-transition temperature was indicated by the single-crystal EPR measurement and the space group was assigned to be $I4_1/acd$ based on powder X-ray diffraction (Reinen & Friebel, 1984). The $|F_c|$ values showed approximate $4/mmm$ Laue symmetry and the atomic coordinates could be transferred to fit with the space group $F4_1/adc$ (*a* + *b*, *b* - *a*, *c* setting of $I4_1/acd$), where the $[\text{CuCl}_5]^{3-}$ anion has crystallographic twofold symmetry. The coordinates of the equivalent positions of $F4_1/adc$ are listed in Table 2. The N atoms could be refined anisotropically with positive-definite values, $R = 0.117$, $wR = 0.175$, $S = 6.52$ for 2632 reflections (refinement 2).

Thus, the crystal was expected to have three twin components of different orientations. We labelled the *a*, *b* and *c* directions of the predominate twin component as *x*, *y* and *z*. P_x and P_y are the populations of the twin components which have their tetragonal unique axis parallel to *x* and *y*, respectively. The X-ray intensity was observed as a superposition of the reflections from the three twin components since the lattice constants are nearly cubic: $I_{\text{total}}(hkl) = (1 - P_x - P_y)I(hkl) + P_xI(lhk) + P_yI(klh)$. Taking account of the scale factor *K*, the function $\sum [I_{\text{obs}}(hkl) - KI_{\text{total}}(hkl)]^2$ was minimized. $F_c^2(hkl)$ values of refinement 2 were used for $I(hkl)$ in an approximation. Since P_y was evaluated to be -0.024 (2), it was fixed at zero. After the correction for twinning, $I'_{\text{obs}}(hkl) = I_{\text{obs}}(hkl) - KP_xI(lhk)$ with $P_x = 0.143$ (2), 1457 unique reflections with $|F_o| > 3\sigma(|F_o|)$ were obtained; $R_{\text{int}} = 0.026$ for 1146 reflections. Atomic coordinates and anisotropic thermal parameters were further refined. H atoms were not included in the calculation. Final $R = 0.071$, $wR = 0.107$, $S = 4.4$ for

Table 2. Coordinates of the equivalent positions of $F4_1/adc$ (*a* + *b*, *b* - *a*, *c* setting of $I4_1/acd$; No. 142) and the corresponding numbers of the positions in space groups $Fd\bar{3}c$ (No. 228) and $Fddd$ (No. 70) listed in International Tables for Crystallography (1983, Vol. A)

The origin is at the centre of symmetry and half of the positions, which are related by a centre of symmetry, are omitted from this table. Representative coordinates of special positions are also given with (*a*) multiplicity, Wyckoff letter and (*b*) site symmetry.

(a)	(b)	$F4_1/adc$	$Fd\bar{3}c$	$Fddd$
64(g)	1	<i>x</i> , <i>y</i> , <i>z</i>	(1)	(1)
		$\frac{1}{4} - x$, $\frac{3}{4} - y$, $\frac{1}{2} + z$	(2)	(2)
		$\frac{1}{2} - y$, $\frac{3}{4} + x$, $\frac{3}{4} + z$	(16)	—
		$\frac{3}{4} + y$, $-x$, $\frac{3}{4} + z$	(15)	—
		$\frac{1}{4} + y$, $\frac{3}{4} + x$, $-z$	(13)	—
		$-y$, $-x$, $\frac{3}{4} - z$	(14)	—
		$\frac{1}{2} + x$, $\frac{1}{4} - y$, $\frac{3}{4} - z$	(4)	(4)
		$\frac{1}{4} - x$, <i>y</i> , $\frac{3}{4} - z$	(3)	(3)
32(f)	2	<i>x</i> , $\frac{1}{2}$, $\frac{1}{2}$	—	—
32(e)	2	<i>x</i> , $\frac{1}{2} - x$, $\frac{1}{2}$	—	—
32(d)	2	$\frac{1}{2}$, $\frac{1}{2}$, <i>z</i>	—	—
32(c)	1	0, 0, 0	0	0
16(b)	222	$\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$	—	—
16(a)	4	$\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$	—	—

1457 unique reflections (refinement 3). * Reflection/parameter ratio 23.1, $\Delta/\sigma < 0.03$, $-1.7 \leq \Delta\rho \leq 1.5 \text{ e } \text{\AA}^{-3}$.

Differential scanning calorimetry

In order to document further the behaviour of these compounds, differential scanning calorimetry (DSC) measurements of pure $[\text{Co}(\text{NH}_3)_6][\text{CdCl}_5]$ in the temperature range 123 to 473 K were carried out and no evidence of a phase transition was found, suggesting that the $[\text{CuCl}_5]^{3-}$ ion alone is responsible for the temperature dependence of the ESR spectra of the copper-doped crystals of $[\text{Co}(\text{NH}_3)_6][\text{CdCl}_5]$. The DSC measurements were recorded with a Seiko Robotic DSC Model RDC-220 instrument. The sample size was 12.82 mg and the atmosphere was pre-purified flowing nitrogen. The scanning rate was 10 K min^{-1} . Similar results were obtained with a General V4.1C DuPont 2100 differential scanning calorimeter.

Discussion. Final atomic coordinates and interatomic distances and bond angles are presented in Tables 3 and 4. The packing of the ions is displayed in Fig. 1 and the stereochemistries of the $[\text{CuCl}_5]^{3-}$ anion are shown in Fig. 2. The crystal structure at room temperature is essentially the same as reported pre-

* List of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54524 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Positional parameters and equivalent isotropic temperature factors (Hamilton, 1959)

	x	y	z	$B_{eq}(\text{\AA}^2 \times 10)$
(I) $T = 299$ K				
Cu	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	20
Co	0	0	0	13
Cl(1)	0.18986 (2)	(= x)	(= x)	23
Cl(2)	$\frac{1}{4}$	0.07664 (2)	(= -y)	44
N	0.0691 (2)	0.0483 (2)	-0.0288 (2)	22
(II) $T = 120$ K				
Cu	0.25334 (4)	(= $\frac{1}{2} - x$)	$\frac{1}{4}$	9
Co	0	0	0	6
Cl(1)	0.19593 (8)	0.18942 (8)	0.18431 (7)	11
Cl(2)	0.17034 (3)	(= $\frac{1}{2} - x$)	$\frac{1}{4}$	15
Cl(3)	0.22931 (10)	0.17868 (8)	0.32734 (8)	16
N(1)	0.0719 (3)	0.0490 (3)	-0.0198 (2)	9
N(2)	-0.0314 (3)	0.0650 (3)	0.0532 (3)	11
N(3)	0.0448 (3)	-0.0373 (3)	0.0680 (3)	12

Table 4. Interatomic distances (\AA) and angles ($^\circ$)

(I) $T = 299$ K				
Cu—Cl(1)	2.3005 (3)	Cl(1)—Cu—Cl(1 ^{iv})	180.00 (1)	
Cu—Cl(2)	2.3937 (3)	Cl(1)—Cu—Cl(2')	90.00 (1)	
Co—N	1.968 (4)	Cl(2')—Cu—Cl(2 ^{vi})	120.00 (1)	
		N—Co—N ^v	90.3 (2)	
(II) $T = 120$ K				
Cu—Cl(1)	2.300 (2)	Co—N(1)	1.964 (7)	
Cu—Cl(2)	2.583 (1)	Co—N(2)	1.976 (7)	
Cu—Cl(3)	2.332 (2)	Co—N(3)	1.975 (7)	
Cl(1)—Cu—Cl(1 ^{iv})	179.9 (1)	Cl(3)—Cu—Cl(3 ^{vi})	145.9 (1)	
Cl(1)—Cu—Cl(2)	89.9 (1)	N(1)—Co—N(2)	91.0 (3)	
Cl(1)—Cu—Cl(3)	89.2 (1)	N(1)—Co—N(3)	89.7 (3)	
Cl(2)—Cu—Cl(3)	107.1 (1)	N(2)—Co—N(3)	91.3 (3)	

Symmetry code: (i) $\frac{1}{4} - y, \frac{1}{4} - z, x$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$; (iii) $\frac{1}{4} + y, \frac{1}{2} - x, \frac{1}{4} + z$; (iv) $x, \frac{1}{4} - y, \frac{1}{4} - z$; (v) y, z, x ; (vi) $\frac{1}{2} - y, \frac{1}{2} - x, \frac{1}{2} - z$.

viously (Bernal *et al.*, 1968). Although the packing mode of the complex ions was not changed drastically by the phase transition from cubic to tetragonal as shown in Fig. 1, the site symmetries of the metal atoms were reduced $\text{Co } \bar{3} \rightarrow \bar{1}$, $\text{Cu } 32 \rightarrow 2$. As seen in Fig. 2, the geometry of $[\text{CuCl}_5]^{3-}$ changes from D_{3h} to approximately C_{2v} on passing through the transition temperature. At 120 K, one equatorial Cl atom, Cl(2), moves away from the central Cu atom by 0.189 (1) \AA , whereas the remaining two, Cl(3) and Cl(3^{vi}), approach the Cu atom by 0.062 (2) \AA with respect to the structure of the high-temperature phase. The apical Cu—Cl(1) bond lengths remain unchanged within experimental error. The interbond angles of the equatorial plane in the tetragonal phase are 145.9 (1) and 107.1 (1) $^\circ \times 2$. Consequently, such coordination about Cu^{II} may be described as an intermediate stage of a transition from a trigonal bipyramid (TBP) to an axially elongated square pyramid (SP). The EPR, reflection and IR spectra for the low-temperature phase of $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$ reported by Reinen & Friebel (1984) are in good accord with the intermediate structure of $[\text{CuCl}_5]^{3-}$ between the SP and the TBP forms. The TBP \rightarrow SP

transformation occurs for $[\text{CuCl}_5]^{3-}$ but not for $[\text{CdCl}_5]^{3-}$ because of a slight energetic preference for an elongated SP with respect to a compressed TBP for d^9 cations (Reinen & Friebel, 1984). Thus, the low-temperature ESR spectra of $[\text{CuCl}_5]^{3-}$ diluted into $[\text{Co}(\text{NH}_3)_6][\text{CdCl}_5]$ showing that $g_{xx} \neq g_{yy} \neq g_{zz}$ (Epstein *et al.*, 1976) is now clarified. The Cu^{II} site does not have a principal axis of order higher than two as expected. Since pure $[\text{Co}(\text{NH}_3)_6][\text{CdCl}_5]$ does not display the phase transition in the DSC measurement, dilute $[\text{CuCl}_5]^{3-}$ anions must distort inside the Cd-host lattice at low temperature. This is readily

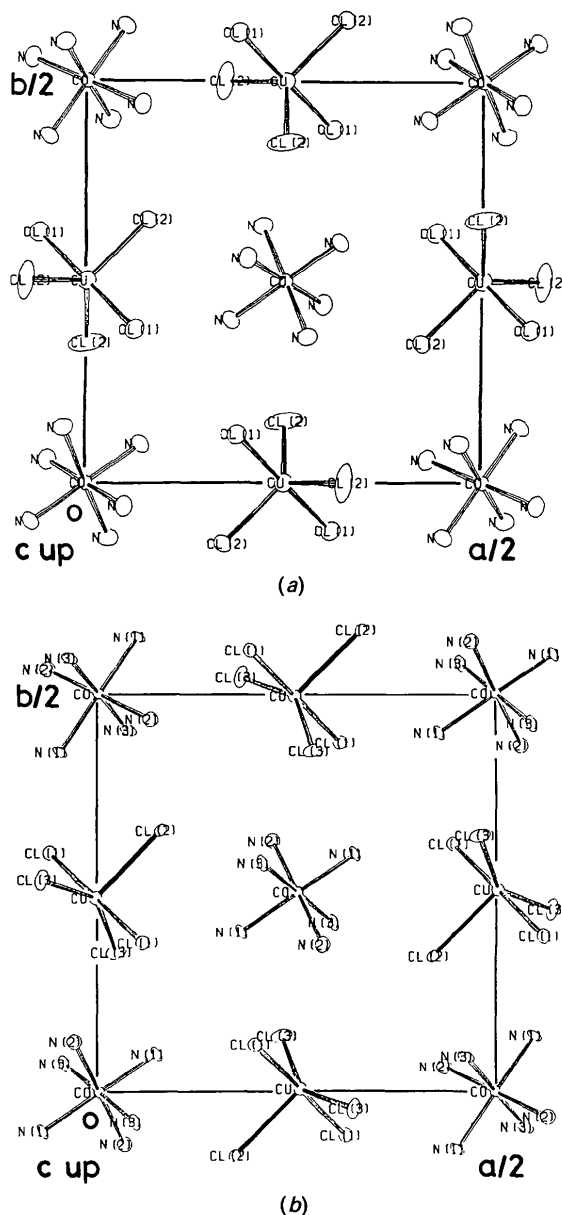


Fig. 1. Partial projection of the crystal structure of the (a) cubic and (b) tetragonal phase along c . — $\frac{1}{4} < x, y < \frac{1}{2}$, $-\frac{1}{4} < z < \frac{1}{4}$.

explained by the observation that the Cd—Cl bond lengths are 2.526 (1) (axial) and 2.561 (2) Å (equatorial) in $[\text{Co}(\text{NH}_3)_6][\text{CdCl}_5]$ (Epstein & Bernal, 1971). $[\text{CuCl}_5]^{3-}$, whose mean radius at room temperature is 2.356 Å, is placed in a cavity with a mean radius of 2.544 Å. When the $[\text{CuCl}_5]^{3-}$ anion distorts, the longest Cu—Cl distance of 2.583 (1) Å, which we observed along one of the original equatorial bonds, can just about fit along the longest (equatorial) Cd—Cl bond direction. Thus, one can now understand why the Cu^{II} -doped $[\text{Co}(\text{NH}_3)_6][\text{CdCl}_5]$ allows distortion of the $[\text{CuCl}_5]^{3-}$ anion inside the Cd lattice, which itself undergoes no phase change.

The deformed conformation of the $[\text{CuCl}_5]^{3-}$ anion produced by the thermal rearrangement in the title crystal is not unusual. The stereochemistry is in close agreement with the structure of a related dimeric species in $[\text{Co}(\text{en})_3]_2[\mu\text{-dichloro-Cu}_2\text{Cl}_8]\cdot\text{Cl}_2\cdot 2\text{H}_2\text{O}$ (Hodgson, Hale & Hatfield, 1971). This compound contains discrete $[\text{Cu}_2\text{Cl}_8]^{4-}$ anions consisting of two identical, pentacoordinated $[\text{CuCl}_5]$ moieties related by an inversion centre. Their geometries are also best described as being part way between a trigonal bipyramid and a square pyramid: Cu—Cl(axial) = 2.325 (4), 2.262 (4) Å; Cu—Cl(equatorial) = 2.319 (5), 2.273 (5), 2.703 (5) Å; Cl—Cu—Cl(axial) = 172.6 (2)°; Cl—Cu—Cl(equatorial) = 89.2 (2), 96.3 (2), 145.3 (2)°. Note that the large angle (*ca* 145°) in the equatorial plane is

essentially identical to our result. The typical features of small and large angles in the trigonal base of the bipyramidal array of ligands are also observed in the pentacoordinated Cu^{II} cations containing hetero ligands (Lindroos & Lumme, 1990; Haanstra, van der Donk, Driessen, Reedijk, Drew & Wood, 1990).

Reinen & Friebel (1984) proposed in their paper that the TBP structure of $[\text{CuCl}_5]^{3-}$ in the high-temperature phase can be understood as the dynamic average of three SP orientations. However, the temperature dependence of the thermal parameters listed in Table 3 disagrees with this proposal. The B_{eq} values at 299 K are ≈ 2.1 – 2.2 times those of the corresponding atoms at 120 K except for the equatorial Cl atoms. If there is dynamic disorder of $[\text{CuCl}_5]^{3-}$ in the high-temperature phase, the equatorial Cl atoms would have much larger B values and longer thermal amplitudes along the Cu—Cl bond axis than the observed values.

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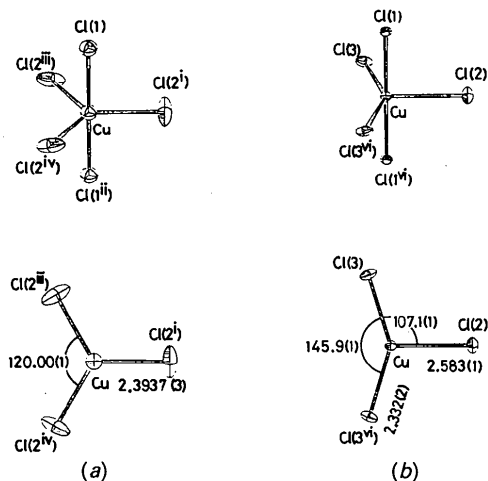


Fig. 2. Molecular structure of the $[\text{CuCl}_5]^{3-}$ complex in the (a) cubic and (b) tetragonal phase. The equatorial plane of the trigonal bipyramid is also shown with the Cu—Cl bond distances (Å) and Cl—Cu—Cl bond angles (°).