Acta Cryst. (1995). C**51**, 1481–1483

Phase Transition of Hexaamminechromium(III) Pentachlorocuprate(II)

Shigeru Ohba and Toyoaki Fujita

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3, Kohoku-ku, Yokohama 223, Japan

Ivan Bernal

Department of Chemistry, University of Houston, University Park, 4800 Calhoun Road, Houston, Texas 77204-5641, USA

(*Received* 13 *September* 1994; *accepted* 1 *February* 1995)

Abstract

The crystal of $[Cr(NH_3)_6][CuCl_5]$ shows a phase transition at 259.2 K. An X-ray diffraction study of the cubic and tetragonal phases has been carried out at 295 and 120 K, respectively. Although the arrangement of the metal complexes remained unchanged through the phase transition, the trigonal bipyramidal $[CuCl_5]^{3-}$ ion, which has D_{3h} symmetry in the cubic phase, deformed into approximate C_{2v} symmetry in the tetragonal phase, as observed in the isomorphous $[Co(NH_3)_6][CuCl_5]$ crystal. Drastic changes were observed in the equatorial coordination plane. One of three equatorial Cu—Cl bonds was elongated and the Cl—Cu—Cl bond angle formed by the two shortened Cu—Cl bonds expanded to 143.6 (1)°.

Comment

The complex ion $[CuCl_5]^{3-}$ has a regular trigonal bipyramidal (TBP) structure in crystals of $[M(NH_3)_6][CuCl_5]$ at room temperature, where M = Cr (Mori, Saito & Watanabe, 1961; Raymond, Meek & Ibers, 1968) and Co (Bernal, Korp, Schlemper & Hussain, 1982). $[Co(NH_3)_6][CuCl_5]$ shows a first-order phase transition at 280.8 K (Epstein, Bernal & Brennan, 1976), and a single crystal of the cubic phase changes into three components of twinned tetragonal low-temperature phase (Reinen & Friebel, 1984). Aoyama, Ohba, Saito & Bernal (1992) determined the crystal structure of the tetragonal phase at 120 K and revealed that the $[CuCl_5]^{3-}$ ion deforms to a distorted square pyramidal (SP) structure, which is in good accord with the EPR, reflection and IR spectra (Reinen & Friebel, 1984).

A comparison of the Cr compound with the Co compound shows that the phase-transition temperature decreases from 280.8 to 259.2 K, and the transition enthalpy decreases from 2240 to 1056 J mol^{-1}. These facts suggest that the $[CuCl_5]^{3-}$ ion transforms from SP to TBP more easily in the $[Cr(NH_3)_6][CuCl_5]$ crystal than in the Co crystal. This may be due to the larger cavity for $[CuCl_5]^{3-}$ in the Cr crystal as the result of longer Cr—N bonds than Co—N bonds, by *ca* 0.11 Å.

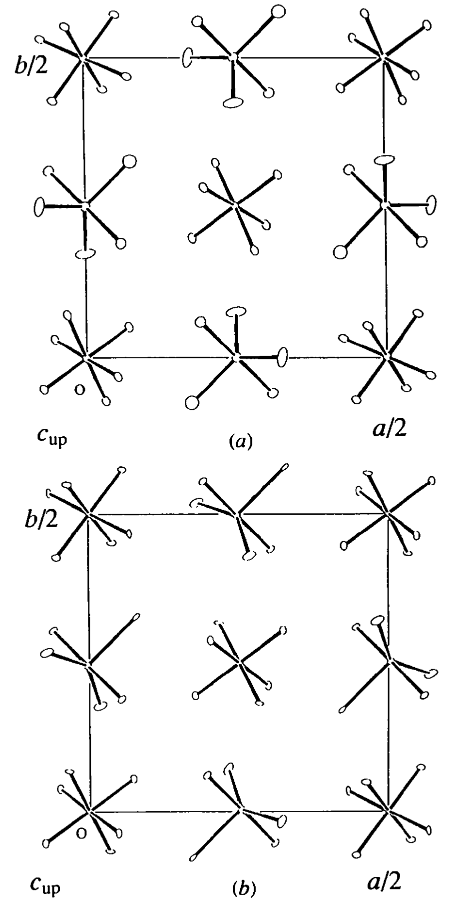

Fig. 1. Partial projection of the crystal structure of (*a*) the cubic, and (*b*) the tetragonal phase along **c**. $-\frac{1}{8} < x, y < \frac{5}{8}, -\frac{1}{8} < z < \frac{1}{8}$.

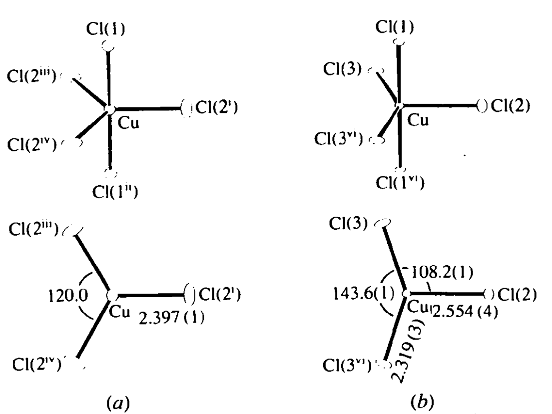

Fig. 2. *ORTEP* drawing (Johnson, 1965) of the $[CuCl_5]^{3-}$ complex in (*a*) the cubic, and (*b*) the tetragonal phase, with the displacement ellipsoids scaled at the 25% probability level. The equatorial plane of the trigonal bipyramid is also shown with the Cu—Cl bond lengths (Å) and the Cl—Cu—Cl bond angles (°).

Acta Crystallographica Section C
ISSN 0108-2701 ©1995

The distorted SP structure of $[CuCl_5]^{3-}$ in the tetragonal phase of the Cr crystal is similar to that of the Co crystal.

Experimental

For (I), crystals were prepared by the literature method (Mori, 1960). For (II), the crystal was coated with adhesive and cooled and retained at 120 K in a steam of cold nitrogen gas.

Compound (I) (cubic phase)

Crystal data

$[Cr(NH_3)_6][CuCl_5]$
$M_r = 395.0$
Cubic
$Fd\bar{3}c$
$a = 22.288$ (2) Å
$V = 11072$ (1) Å^3
$Z = 32$
$D_x = 1.90$ Mg m$^{-3$}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 12 reflections
$\theta = 10–15°$
$\mu = 3.26$ mm^{-1}
$T = 295$ K
Prism
$0.25 \times 0.25 \times 0.25$ mm
Orange

Data collection

Rigaku AFC-5 diffractometer
θ–2θ scans
Absorption correction: by integration from crystal shape
$T_{min} = 0.489$, $T_{max} = 0.525$
4004 measured reflections
859 independent reflections
345 observed reflections $[|F_o| > 3\sigma(|F_o|)]$
$R_{int} = 0.034$
$\theta_{max} = 30.0°$
$h = 0 \rightarrow 31$
$k = 0 \rightarrow 31$
$l = 0 \rightarrow 31$
5 standard reflections monitored every 100 reflections intensity decay: 4%

Refinement

Refinement on F
$R = 0.030$
$wR = 0.031$
$S = 1.82$
345 reflections
35 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(|F_o|) + (0.015|F_o|)^2]$
$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 0.5$ e Å^{-3}
$\Delta\rho_{min} = -0.4$ e Å^{-3}
Extinction correction: Type 1 Gaussian (Becker & Coppens, 1975)
Extinction coefficient: $7.4 (2) \times 10^4$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (I)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cu	1/4	1/4	1/4	2.17 (1)
Cr	0	0	0	1.47 (1)
Cl(1)	0.19040 (3)	x	x	2.53 (1)
Cl(2)	1/4	0.07603 (3)	$-y$	4.52 (3)
N	0.07136 (12)	0.05142 (15)	−0.03040 (13)	2.52 (7)

Table 2. *Selected geometric parameters* (Å, °) *for* (I)

Cu—Cl(1)	2.301 (1)	Cr—N	2.074 (3)
Cu—Cl(2^i)	2.397 (1)		
Cl(1)—Cu—Cl(1^{ii})	180.0	Cl(2^i)—Cu—Cl(2^{iii})	120.0
Cl(1)—Cu—Cl(2^i)	90.0	N—Cr—N^v	90.4 (1)

Symmetry codes: (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.

Compound (II) (tetragonal phase)

Crystal data

$[Cr(NH_3)_6][CuCl_5]$
$M_r = 395.0$
Tetragonal
$F4_1/adc$ ($a+b, b-a, c$ setting of $I4_1/acd$)
$a = 22.155$ (3) Å
$c = 22.181$ (6) Å
$V = 10887$ (2) Å^3
$Z = 32$
$D_x = 1.93$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 16 reflections
$\theta = 10–15°$
$\mu = 3.32$ mm^{-1}
$T = 120$ K
Prism
$0.25 \times 0.25 \times 0.25$ mm
Orange

Data collection

Rigaku AFC-5 diffractometer
ω scans
Absorption correction: by integration from crystal shape
$T_{min} = 0.489$, $T_{max} = 0.526$
6833 measured reflections
1668 independent reflections
1327 observed reflections $[|F_o| > 3\sigma(|F_o|)]$
$R_{int} = 0.027$ (after correction for twinning)
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 28$
$k = -13 \rightarrow 28$
$l = -28 \rightarrow 28$
5 standard reflections monitored every 100 reflections intensity decay: 3%

Refinement

Refinement on F
$R = 0.100$
$wR = 0.092$
$S = 6.73$
1327 reflections
62 parameters
H atom not introduced
$w = 1/[\sigma^2(|F_o|) + (0.015|F_o|)^2]$
$(\Delta/\sigma)_{max} = 0.2$
$\Delta\rho_{max} = 1.2$ e Å^{-3}
$\Delta\rho_{min} = -1.0$ e Å^{-3}
Extinction correction: Type 1 Gaussian (Becker & Coppens, 1975)
Extinction coefficient: $0.6 (3) \times 10^4$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (II)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cu	0.2534 (1)	$1/2-x$	1/4	0.99 (4)
Cr	0	0	0	0.74 (5)
Cl(1)	0.1958 (1)	0.1899 (1)	0.1855 (1)	1.21 (5)
Cl(2)	0.1719 (2)	$1/2-x$	1/4	1.95 (9)
Cl(3)	0.2320 (1)	0.1790 (1)	0.3269 (1)	2.18 (6)
N(1)	0.0737 (4)	0.0544 (4)	−0.0236 (3)	1.2 (2)
N(2)	−0.0335 (4)	0.0673 (3)	0.0551 (3)	1.1 (2)
N(3)	0.0484 (4)	−0.0374 (4)	0.0713 (4)	1.4 (2)

Table 4. *Selected geometric parameters* (Å, °) *for* (II)

Cu—Cl(1)	2.292 (3)	Cr—N(1)	2.096 (9)
Cu—Cl(2)	2.554 (4)	Cr—N(2)	2.066 (7)
Cu—Cl(3)	2.319 (3)	Cr—N(3)	2.083 (9)
Cl(1)—Cu—Cl(1^{vi})	179.3 (1)	Cl(3)—Cu—Cl(3^{vi})	143.6 (1)
Cl(1)—Cu—Cl(2)	89.6 (1)	N(1)—Cr—N(2)	90.7 (3)
Cl(1)—Cu—Cl(3)	89.5 (1)	N(1)—Cr—N(3)	91.0 (3)
Cl(2)—Cu—Cl(3)	108.2 (1)	N(2)—Cr—N(3)	91.3 (3)

Symmetry code: (vi) $\frac{1}{2} - y, \frac{1}{2} - x, \frac{1}{2} - z$.

For (I), X-ray intensities were measured at room temperature and the structure was refined to check the crystal specimen before the low-temperature measurement. Secondary extinction correction was applied. The smallest (F_o^2/F_c^2) value is 0.20 for 400. $R = 0.041$ and $wR = 0.047$ for 1437 observed reflections. After averaging symmetry-related reflections corrected for extinction, $R = 0.030$ and $wR = 0.031$ for 345 unique reflections.

For (II), the typical peak half-width became 0.18 from 0.12° on lowering the temperature. The X-ray intensity was measured by ω scans as a superposition of the reflections from the three twin components since the lattice constants are almost cubic:

$$I_{\rm total}(hkl) = (1 - P_x - P_y)I(hkl) + P_xI(lhk) + P_yI(klh) \quad (1)$$

where P_x and P_y are the populations of the twin components which have their tetragonal unique axes parallel to x and y, respectively. For $2\theta({\rm Mo}\,K\alpha) \leq 25°$, $+h$ $\pm k$ $\pm l$ reflections were measured. For $25 < 2\theta \leq 55°$, $+h$ $+k$ $\pm l$ reflections were measured. The space group was assumed to be the same as that of [Co(NH$_3$)$_6$][CuCl$_5$] in the low-temperature phase. Coordinates of the equivalent positions of $F4_1/adc$ were listed in Table 2 of the previous paper (Aoyama *et al.*, 1992). Atomic coordinates of [Co(NH$_3$)$_6$][CuCl$_5$] at 120 K were utilized as initial parameters and the structure was refined at first in single-domain approximation; $R(F) = 0.21$. Then the function $\Sigma[I_{\rm obs}(hkl) - KI_{\rm total}(hkl)]^2$ was minimized, taking account of the scale factor K. $F_c^2(hkl)$ values of the preceding refinement were used for $I(hkl)$ in equation (1). With the refined P_x, P_y and K values, the X-ray intensities were corrected for twinning:

$$I_{\rm corr}(hkl) = [I_{\rm obs}(hkl)/K - P_xF_c^2(lhk) - P_yF_c^2(klh)]/(1 - P_x - P_y). \quad (2)$$

The structure was further refined based on the corrected structure factors. After two cycles of the correction for twinning and refinement, $R(I) = \Sigma|I_{\rm corr}(hkl) - I_c(hkl)|^2/\Sigma[I_{\rm corr}(hkl)]^2 = 0.014$, $P_x = 0.208\,(1)$, $P_y = 0.210\,(1)$ and $K = 0.901\,(1)$. The smallest ($F_o{}^2/F_c^2$) value in the extinction correction is 0.58 for 400. Final $R(F) = 0.100$, which is larger than that of the low-temperature study of [Co(NH$_3$)$_6$][CuCl$_5$] with $P_x = 0.143\,(2)$, $P_y = 0$, $R(F) = 0.071$. The larger R value of the present study may be due to the larger population of twin components, P_x and P_y.

Refinement was performed by the full-matrix least-squares program *RADIEL* (Coppens *et al.*, 1979) on a FACOM M-780/10 computer at Keio University. The DSC measurements of [Cr(NH$_3$)$_6$][CuCl$_5$] were carried out with a calibrated General V4.1C DuPont 2100 DSC instrument.

This work was supported by a Grant-in-Aid for Scientific Research (No. 04303010) from the Japanese Ministry of Education, Science and Culture.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving H atoms have been deposited with the IUCr (Reference: OH1078). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Aoyama, T., Ohba, S., Saito, Y. & Bernal, I. (1992). *Acta Cryst.* C**48**, 246–250.

Becker, P. J. & Coppens, P. (1975). *Acta Cryst.* A**31**, 417–425.

Bernal, I., Korp, J. D., Schlemper, E. O. & Hussain, M. S. (1982). *Polyhedron*, **1**, 365–369.

Coppens, P., Guru Row, T. N., Leung, P., Stevens, E. D., Becker, P. J. & Yang, Y. W. (1979). *Acta Cryst.* A**35**, 63–72.

Epstein, E. F., Bernal, I. & Brennan, W. P. (1976). *Inorg. Chim. Acta*, **20**, L47–L49.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Mori, M. (1960). *Bull. Chem. Soc. Jpn*, **33**, 985–988.

Mori, M., Saito, Y. & Watanabe, T. (1961). *Bull. Chem. Soc. Jpn*, **34**, 295–296.

Raymond, K. N., Meek, D. W. & Ibers, J. A. (1968). *Inorg. Chem.* **7**, 1111–1117.

Reinen, D. & Friebel, C. (1984). *Inorg. Chem.* **23**, 791–798.

Acta Cryst. (1995). C**51**, 1483–1485

Synthetic Copper Monophosphate

A. Yamashita and A. Kawahara

Department of Earth Sciences, Faculty of Sciences,
Okayama University, Tsushima-Naka 3-1-1,
Okayama 700, Japan

N. Sasaki

Department of Chemistry, Faculty of Education,
Kagawa University, Saiwai-cho, Takamatsu 760,
Japan

(*Received* 24 September 1994; *accepted* 27 *March* 1995)

Abstract

$Cu_9O_2(PO_4)_4(OH)_2$ belongs to the monophosphate group and contains five kinds of copper coordination polyhedron. One Cu atom is at the center of symmetry and has square-planar coordination, the others occupy distorted square-pyramidal sites. Three kinds of copper–oxygen polyhedra are connected to each other by edge sharing to form zigzag double chains along [110] and these chains are connected by PO_4 tetrahedra to form sheets parallel to $(1\bar{1}0)$. H atoms are connected to O atoms, which are shared by three copper polyhedra, to form hydroxyl ions. H atoms are also connected to O atoms shared by both Cu and P polyhedra to form hydrogen bonds.

Acta Crystallographica Section C
ISSN 0108-2701 ©1995