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X-ray Crystallographic Investigation of the Mixed-Valence Hexaamminocobalt(III) Chlorocuprates(I, II). II*

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Cell dimensions and space groups have been determined by single-crystal rotation photography for several mixed-valence hexaamminocobalt(III) chlorocuprates(I,II) with different ratios of Cu^I to Cu^{II}. Intensities for a crystal with a value of Cu^I/total Cu of 0·28 were collected on precession photographs with Mo $K\alpha$ radiation and measured with a microdensitometer. Structure factors were computed for a model simulating a solid solution of $Cu^{II}Cl_5^{3-}$ and $Cu^ICl_4^{3-}$ ions and the parameters were refined to give an R of 0·082. There was no evidence for a significant amount of pentanuclear chlorocuprate(I,II) species. The results are in agreement with the data and model given by Day [*J. Chem. Soc. (A)* (1968), pp. 1835–1838].

Introduction

A complex series of crystalline compounds is obtained when mixtures of Cu^I and Cu^{II} in strong hot hydrochloric acid solution are precipitated by the addition of the large hexaamminocobalt(III) or hexaamminochromium(III) cations (Mori, 1960). Further study (Mori, 1961; Mori, Saito & Watanabe, 1961) confirmed that well defined compounds derived from the pure copper halides existed with the stoichiometries $M(NH_3)_6Cu^{II}Cl_5$ and $[M(NH_3)_6]_4Cu^I_5Cl_{17}$ (where M is Co or Cr). Mori showed further that intermediate compounds which contained both Cu^I and Cu^{II} could be prepared and that these showed intense charge-transfer bands in the visible region, being either dark brown or black, in contrast to the two pure-valence compounds which were orange. The ratio of Cu^I to Cu^{II} in these mixed-valence crystals appeared to be capable of taking any arbitrary value, so that the stoichiometries are not fixed. Culpin, Day, Edwards & Williams (1968) showed that they were solid solutions containing both valence states by measurement

of the absorption spectra and conductivity of single crystals. These properties varied smoothly with change in the ratio of valence states, strongly suggesting that discrete phases of fixed stoichiometry did not occur.

The formulae of these solid solutions are not straightforward for not only does the Cu^I/Cu^{II} ratio change but the value of total Cu/Co also varies, changing from 1·0 in the pure Cu^{II} compound to 1·25 in the pure Cu^I compound. We can formulate the intermediate compounds as $[M(NH_3)_6][Cu(II)^{II}_{1-x}Cu^I_x]Cl_{3+2n-nx}$ where x, which represents the ratio of Cu^I to total Cu, lies between 0 and 1. The parameter n, which is 1 when $x=0$ and 1·25 when $x=1$. defines the ratio Co/total Cu and, if the composition of the crystals is reproducible, is presumably a function of x. Day (1968) attempted to find the relationship between n and x by chemical analysis of the precipitated solids, which he analysed for $Co(NH_3)_6$. Cu^I, total Cu and Cl. He gave a relationship for n as a function of x (here translated from his graphical presentation), with $x<0·4$: $n=1·0$; $x>0·4$: $n=1·00+0·417(x−0·4)$ although the data could also be represented by more complicated non-linear functions and there is little evidence for a discontinuity of slope at $x=0·4$. Mori noticed that both

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the bulk sample and individual crystals of the solid solutions showed signs of occasional inhomogeneity and Day attempted to overcome this by rapid cooling of the solution to induce precipitation. For this reason, and the difficulty of analysing the compounds (Day's experimental values of total Cu/Cl for both pure-valence compounds are 5% different from the calculated values), additional investigation of the stoichiometry of the solid solutions is desirable. The present study was undertaken in an attempt to find the Co/total Cu ratios crystallographically and also to investigate the structures of the mixed-valence crystals.

An early study of $Cr(NH_3)_6Cu^{II}Cl_5$ was made by Mori, Saito & Watanabe (1961) who collected photographic data and refined them to an R of 0·19, and this was later superseded by a much more accurate diffractometric analysis by Raymond, Meek & Ibers (1968). The structure of $[Co(NH_3)_6]_4Cu_5Cl_{17}$ was determined by Murray-Rust (1973) and although the crystal was found to be a twin, relatively accurate atomic parameters were obtained. There is a close similarity between the two structures, both of which are based on a rock-salt lattice of $M(NH_3)_6$ ions and chlorocuprate species. Day showed that $Co(NH_3)_6CuCl_5$ and $Cr(NH_3)_6CuCl_5$ had the same space group ($Fd3c$) and almost identical cell constants; it will be assumed that these two are isostructural and all further discussion and results apply to the hexaamminocobalt(III) system. Day also subjected samples of the intermediate solid solutions to powder diffractometry and determined their space groups and cell constants (Table 1). All were cubic and had either $Fd3c$ or $Fd3$ symmetry. [Day lists all these latter as having space group $Fd3m$ but the distinction between this and $Fd3$ cannot be made on the basis of powder diffraction. As the pure Cu compound has been shown to have space group $Fd3$ (Murray-Rust, 1973) this symmetry is assumed for the intermediate compounds in preference to $Fd3m$.] On the basis of the structures of the pure-valence compounds, the analytical data for the solid solutions and the space group information, Day produced a model for these intermediate compounds and the present structural study was undertaken to check its validity.

Single-crystal X-ray crystallography

A number of bulk samples of mixed-valence compounds were supplied by Dr P. Day, all of which had been analysed for Cu^I/total Cu (and some of which represent data in his 1968 paper). These samples showed no obvious inhomogeneity under the microscope and it was assumed that the bulk analyses represented the compositions of the individual crystals. Single octahedral crystals of side ca 0·1 mm were selected from these samples and photographed on a Unicam rotation camera. This was fitted with a narrow lead-glass collimator to reduce scattered radiation and the film was cut in the Straumanis setting. Rotation photographs of the crystals were taken with Cu $K\alpha$ radiation and the

Table 1. *Space group and cell dimensions* (Å) (*with e.s.d.'s in parentheses*) *of mixed-valence hexaamminocobalt*(III) *chlorocuprates*(I, II)

Values of a (powder method) are from Day (1968).

x	a (powder)	a (single crystal)	Space group
0·00	22·03 (33)	21·85 (3)	$Fd3c$
0·22	21·94 (6)		$Fd3c$
0·28		21·81 (3)	$Fd3c$
0·42	21·93 (7)	21·71 (5)	$Fd3c$
0·51	21·84 (9)		$Fd3c$
0·52	21·92 (3)		$Fd3c$
0·66	21·88 (6)		$Fd3c$
0·66	21·79 (3)		$Fd3$
0·75	21·91 (8)		$Fd3c$
0·75	21·76 (2)		$Fd3$
0·81	21·74 (12)		$Fd3$
0·83		21·77 (3)	$Fd3$
0·89	21·73 (3)		$Fd3$
0·99		21·79 (3)	$Fd3$
1·00	21·74 (3)	21·80 (3)	$Fd3$

cell dimensions were computed from the value of θ for the 0,0,28 reflexion on the zero-layer line. There is much less overlap of reflexions from cubic lattices in rotation photography than in the powder method and it was fairly straightforward to distinguish between space groups $Fd3c$ and $Fd3$ from the presence or absence of hhl (h odd) spectra. (The rotation method shares the same disadvantage of the powder method in not distinguishing between $Fd3$ and $Fd3m$.) Crystals with $0·4 \leq x \leq 0·7$ gave diffraction patterns with considerable streaking (which suggests a degree of disorder) and for these compounds the cell constants could not be obtained accurately; one crystal with $x = 0·69$ gave a poor diffraction pattern which did not extend to the limit of the Cu $K\alpha$ sphere. Cell constants and space groups obtained by this method are compared with those of Day in Table 1.

For detailed analysis of the structure of a solid-solution crystal an octahedral crystal of side ca 0·2 mm was selected from Day's sample with $x = 0·28$. [The density, 2·00 (2) g cm^{-3} by flotation, is relatively insensitive to the value of x and no undue emphasis is given to the exact value of this parameter for the crystal selected.] The cell constant a had already been determined by rotation photography as 21·81 (3) Å and the precession photographs were consistent with this value. These photographs were taken with Mo $K\alpha$ radiation and the systematic absences (hkl: $h + k = 2n + 1$, $k + l = 2n + 1$, $h + l = 2n + 1$; $hk0$: $h + k = 4n + 1$, $4n + 2$, $4n + 3$ and hhl: $h = 2n + 1$) confirmed the space group as $Fd3c$. Intensities were collected by precession photography with exposures of varying times for each layer; five layers about [110] and three about [100]. The peak heights of these reflexions were measured with a Joyce-Loebl Mark II microdensitometer and these were used as the intensities. Lorentz and polarization corrections were applied but none for absorption ($\mu = 45$ cm^{-1} for Mo $K\alpha$ radiation) and layer scale factors were obtained from comparison of common reflexions. The merging

R for multiply-observed reflexions [defined as $R = \sum |F^2(hkl) - F^2(hkl)_i|/\sum F^2(hkl)]$ was 0·14. A set of 171 unique structure factors, F_o, is given in Table 2.*

Structures of the intermediate compounds

Table 1 shows that the intermediate solid solutions appear to form a continuous transition between the two pure-valence compounds, with little variation in the cell dimension a, roughly constant at $21·85 \pm 0·10$ Å. The present study gives slightly lower values of a for compounds with $x < 0·5$ than does Day but the differences are only just significant and may well be due to errors in the methods and variation in composition of the sample selected. Day's powder results show a slight overall decrease in a with increasing x but the rotation data do not support this. As $Fd3$ (but not $Fd3m$) is a subgroup of $Fd3c$ a smooth transition from one space group to the other is possible by infinitesimal movements of atoms related by the c glide, and this appears to occur somewhere about $x = 0·68$. This transition from $Fd3$ to $Fd3c$ will involve a gradual decrease in the intensities of the hhl (h odd) reflexions and it is possible that some compounds with $x < 0·69$ may be in $Fd3$ but with reflexions of this type too weak to be observed.

The structures of the mixed-valence solid solutions are almost certain to be intermediate between those of the two pure-valence compounds and the differences between these two structures are given in Table 3. Parameters in this table for $Co(NH_3)_6CuCl_5$, for which no accurate atomic coordinates exist, have been estimated from those of $Cr(NH_3)_6CuCl_5$ assuming reasonable bond lengths. Graphical representations of the

* Table 2 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30764 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

two structures (on the same scale and in identical orientations) are given by Murray-Rust (1973). The most important problem in the mixed-valence species is the occupancy of $Cu(2)$ sites and the average coordination of Cu in the $Cu(1)$ sites. Assuming that the total Cu/Co ratio (n) never lies outside the limits set by the two pure-valence compounds (*i.e.* $1·0 \leq n \leq 1·25$) two extreme variations of n as a function of x are possible.

Model A: $0 \leq x \leq 0·5$; $n = 1$; $0·5 \leq x \leq 1$: $n = 1 + 0·5$ $(x - 0·5)$. This corresponds to the initial replacement of $Cu^{II}Cl_5$ species in (1) sites by Cu^ICl_4 groups and was favoured by Day on the basis of his spectral and analytical data. It leads to a formula $[Co(NH_3)_6]_4Cu^I_2Cu^{II}_2Cl_{18}$ when $x = 0·5$ when half of the $Cu^{II}Cl_5$ bipyramids have been replaced by Cu^ICl_4 tetrahedra (disordered in both location and orientation). When x increases further, filling of the $Cu(2)$ sites will begin and the formation of Cl–Cu–Cl bridges (as in the Cu_5Cl_{16} species of the pure Cu^I compound) will initiate the necessary ordering of the orientation of the Cu^ICl_4 tetrahedra. The exact point at which n becomes greater than unity is arbitrary and Day's analysis gave a value of ca 0·4. He developed a statistical model for the filling of $Cu(2)$ sites and derived a non-linear variation of n with x for $x > 0·5$ which showed slightly better agreement with the chemical analyses. This model requires all intermediate compounds to be disordered to some extent.

Model B: $0 \leq x \leq 0·4$: $n = 1 + 0·625x$; $0·4 \leq x \leq 1$: $n = 1·25$. This corresponds to an initial filling of the $Cu(2)$ sites without loss of Cl^- ions and for $x \leq 0·4$ the stoichiometry can be rationalized as $[Co(NH_3)_6]_4Cu^I_{5x}Cu^{II}_{4-5x}Cl_{20}$. When $x = 0·4$ the stoichiometry is $[Co(NH_3)_6]_4Cu^I_2Cu^{II}_2Cl_{20}$ and the structure might contain discrete mixed-valence $Cu_5Cl_{20}^{12-}$ ions, which would be disordered in $Fd3c$ (but could be ordered in $Fd3$). Increase of x above this value leads to loss of Cl^- ions from the structure until it contains

Table 3. *Comparison of the structures of the two pure-valence compounds*

Parameters for $Co(NH_3)_6CuCl_5$ are estimated from those for $Cr(NH_3)_6CuCl_5$ (see text).

	$Co(NH_3)_6CuCl_5$ (in $Fd3c$)				$[Co(NH_3)_6]_4Cu_5Cl_{17}$ (in $Fd3$)				
Atom	Number in cell	x/a	y/b	z/c	x/a	y/b	z/c	Number in cell	Difference
Co	32	0	0	0	$\begin{cases} 0 \\ \frac{1}{2} \end{cases}$	$\begin{matrix} 0 \\ \frac{1}{2} \end{matrix}$	$\begin{matrix} 0 \\ \frac{1}{2} \end{matrix}$	$\begin{matrix} 16 \\ 16 \end{matrix}$	None
Cu(1)	32	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0·2515	0·2515	0·2515	32	Note 1
Cu(2)		Not present			$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	8	Note 2
Cl(1)	64	0·1892	0·1892	0·1892	$\begin{cases} 0·1853 \\ \text{Not present} \end{cases}$	0·1853	0·1853	32	Note 3
Cl(2)	96	$\frac{1}{4}$	0·0768	−0·0768	0·2782	0·0709	−0·0750	96	Note 4
Cl(3)		Not present			$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{8}$	8	Note 2
N	192	0·0700	0·0504	−0·0301	$\begin{cases} 0·0637 \\ 0·0776 \end{cases}$	$\begin{matrix} 0·0568 \\ 0·5351 \end{matrix}$	$\begin{matrix} −0·0305 \\ −0·0278 \end{matrix}$	$\begin{matrix} 96 \\ 96 \end{matrix}$	Note 5

Notes: (1) This atom is fixed in $Fd3c$ but has moved along (111) by 0·03 Å to its position in $Fd3$. (2) These positions together are 16-fold (and unoccupied) in the Cu^{II} compound. They degenerate into two independent positions in $Fd3$, occupied by Cu(2) and Cl(3) in the Cu^I compound. (3) The 64-fold positions in $Fd3c$ degenerate into two independent 32-fold positions in $Fd3$, only one of which is occupied in the Cu^I structure. The difference in the occupied sites is 0·07 Å. (4) This position lies on a diad in $Fd3c$ but this axis disappears in $Fd3$ and the Cl(2) atoms have moved off it by 0·61 Å. (5) The 192-fold position degenerates into two 96-fold positions and the nitrogen atoms move by 0·29 and 0·40 Å. This corresponds to rotations of the cobalthexaammine octahedra about the triad axis of ca 11 and 15°.

only the Cu_5Cl_{16} species of the pure Cu^I compound.

Although models intermediate between A and B are conceivable, these two represent the simplest structures with small values of x and the distinction between them can be made by investigating the occupancy of the site at $\frac{1}{8},\frac{1}{8},\frac{1}{8}$, for a structure with $x \leq 0.4$. Model A requires an occupancy of 0 whereas model B has an average occupancy of $1.25x$ (for space group $Fd3c$), and moderately accurate values should be obtainable for an atom of atomic number 29. Additional evidence can come from the temperature factors or occupancies for the Cl(1) and Cl(2) sites which for model B should be similar to those of the pure Cu^{II} compound. Model A, however, will have a low occupancy for Cl(1) and positional disorder for Cl(2) and Cu(1) giving rise to spuriously high temperature factors for these atoms.

The parameters of the pure Cu^{II} compound (Table 3) were used to approximate the structure of the mixed-valence compound with $x=0.28$. These parameters were refined by least-squares techniques to fit the observed intensities of the mixed-valence compound (given in Table 2). R^* was 0.11 and the parameters derived by this process are given in Table 4(a). The temperature factors of Cu(1), Cl(1) and Cl(2) are unusually high for this type of compound (cf. Murray-Rust, 1973) and show the predicted effect of structure A. The phases from these parameters were used in the calculation of a difference synthesis which showed no significant difference density at $\frac{1}{8},\frac{1}{8},\frac{1}{8}$ but a peak of about 3 e Å^{-3} on the triad axis at 0.3 Å from Cu(1) which is more likely to be due to disorder than anisotropic vibration. A larger peak (6 e Å^{-3}) was found near Cl(2), 0.6 Å from the diad axis, in almost the same position as this atom in the pure Cu^I compound (Table 3) and of about the height expected for a partially occupied site.

This synthesis strongly supports the essential correctness of model A and an attempt was made to describe the structure by the parameters of Table 4(b) where Cu(1) and Cl(2) have been allowed extra degrees of freedom and the occupancy of Cu(2) has been refined. R for this calculation was 0.082. The amount of interstitial Cu(2) is not significantly different from zero and Cu(1) and Cl(2), which now have more reasonable temperature factors, are presumably in the average of the positions found in the $CuCl_5$ and $CuCl_4$ groups.

The analysis supports Day's formulation of the structures of the intermediates with $x < 0.4$ but little

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* Defined as $\sum ||F_o| - |F_c||/\sum |F_o|$.

Table 4. *Models simulating the structure of the mixed-valence compound* ($x=0.28$)

All the refinement was by full-matrix least-squares analysis with isotropic temperature factors. Scattering factors were taken from *International Tables for X-ray Crystallography* (1968).

(a) Refinement of parameters for $Co(NH_3)_6CuCl_5$ taken from Table 2.

	x/a	y/b	z/c	U_{iso}	Occupancy
Co	0*	0*	0*	0.0179	1.0*
Cu(1)	$\frac{1}{4}$*	$\frac{1}{4}$*	$\frac{1}{4}$*	0.0487	1.0*
Cl(1)	0.1880	0.1880	0.1880	0.0540	1.0*
Cl(2)	$\frac{1}{4}$*	0.0760	-0.0760	0.0590	1.0*
N	0.0704	0.0510	-0.0299	0.0216	1.0*

(b) Simulation of disordered $CuCl_5$ and $CuCl_4$ groups

	x/a	y/b	z/c	U_{iso}	Occupancy
Co	0*	0*	0*	0.0170	1.0*
Cu(1)	0.2550	0.2550	0.2550	0.0346	0.5*
Cl(1)	0.1880	0.1880	0.1880	0.0523	1.0*
Cl(2)	0.2621	0.0768	-0.0756	0.0346	0.5*
N	0.0707	0.0511	-0.0298	0.0292	1.0*
Cu(2)	$\frac{1}{8}$*	$\frac{1}{8}$*	$\frac{1}{8}$*	0.0300*	0.08†

* These parameters were not refined.
† This parameter was set at 0.25 at the start of the refinement and dropped to the value given.

can be deduced for those with high concentrations of Cu^I. These would almost certainly show the same type of twinning as in the pure Cu^I compound which greatly reduces the possibility of satisfactory X-ray structural analysis.

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