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The Crystal Structures of the Hexaamminecopper(II) Halides

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The hexaamminecopper(II) halide phases of approximate composition $Cu(NH_3)_6X_2$ (X = Cl, Br, or I) which exist in equilibrium with 1 atm of ammonia are all tetragonal at room temperature. The source of the displacement from the face-centered-cubic K_2PtCl_6 structure is the Jahn–Teller distortion of the hexaamminecopper(II) ion. The positions of the nitrogen atoms were determined in the chloride and bromide, and it was shown that there are four short (2.1 A) and two long (2.6 A) copper–nitrogen distances. The bromide undergoes a transition to the cubic form in the temperature range 70–110°.

Introduction

Octahedrally coordinated complexes of copper(II) usually show a tetragonal distortion in which there are four short and two long distances.[1] This is usually interpreted as a manifestation of the Jahn–Teller effect,[2] which occurs in copper(II) complexes because of the orbital degeneracy of the ground state $3d^9$ configuration of Cu(II) in a field of cubic symmetry. However, the compounds discussed by Orgel and Dunitz[1] are of low symmetry and the distortions arising from the Jahn–Teller effect are combined with distortions having quite different sources. On the other hand, the compounds $Cu(NH_3)_6X_2$ (X = Br, I) were reported[3] to have a face-centered-cubic structure similar to that of K_2PtCl_6. Thus, these compounds represent good tests of the applicability of the Jahn–Teller theorem to copper(II).

Recently, Elliott and Hathaway[4] have investigated hexaamminecopper(II) chloride, bromide, iodide, tetrafluoroborate, and perchlorate by X-ray diffraction, optical spectroscopy, and electron spin resonance spectroscopy. Their X-ray powder diagrams indicated that the chloride is tetragonal and the others are cubic. The electron spin resonance spectra indicated a tetragonal environment for Cu(II) in both the chloride and bromide and a cubic environment in the other salts. The purpose of this investigation is to establish quantitatively the structure of $Cu(NH_3)_6^{2+}$ ions in the halides.

Experimental Section

Preparations.—Our initial plan was to obtain X-ray diffraction intensities from single crystals of hexaamminecopper(II) halides, since, even for simple compounds, this is generally the most accurate method of structure determination. Although we were able to obtain, from aqueous solutions, crystals of the chloride which were large enough for single-crystal work, analysis indicated a molar ratio of ammonia to copper which was close to 5 rather than 6. Weissenberg photographs of one of these crystals indicated a face-centered, approximately cubic unit cell. However, each reflection was split into several closely grouped spots, some of which had different Bragg angles. Thus, the symmetry must be lower than cubic, and we could not even explain the splittings on the basis of a tetragonal cell. We therefore abandoned this approach.

Hexaamminecopper(II) chloride was prepared[5] by passing anhydrous ammonia through a solution of cupric chloride in ethyl acetate; the desired compound precipitated as a fine powder. The bromide was obtained by adding anhydrous cupric bromide to liquid ammonia, and the iodide was prepared according to the procedure of Horn.[6] These methods all yielded fine powders, and all of our work is therefore based on powder diffraction data.

X-Ray Diffraction.—Although some initial work was done with conventional film methods, with samples sealed in glass capillaries, all of the data reported herein were obtained with a Philips Electronics Co. diffractometer, X-ray source, scintillation counter, and associated counting circuitry. Copper Kα radiation, with a nickel filter, was used exclusively. A cover for the flat sample holder was devised to keep the powder in contact with anhydrous ammonia at barometric pressure. The cover had a hemicylindrical Mylar window to permit transmission of X-rays, which, because it was not located near the region of detectable scattering, did not itself contribute significantly to the diffraction pattern.

Initially, conventional strip charts were used in order to tell us the locations of the detectable powder lines. The profiles of the powder lines were then obtained by taking 1-min counts in duplicate at 0.02° intervals over each diffraction peak. The resulting curves were integrated (over the entire α_1–α_2 doublets) to obtain the corresponding intensities, and they were also analyzed to find the peak centroids, which were used to compute unit-cell parameters. To correct for misalignment and other sources of error in Bragg angles, careful measurements were made of the peak positions of the silicon reference sample which is supplied with the Philips diffractometer. These were used to compute p and q in a correction formula

$$2\theta_c = 2\theta_m + 2q\theta_m + p \qquad (1)$$

in which θ_m is the measured Bragg angle and θ_c the corrected value. This formula was then used to correct our measured peak centroids.

In our studies of the phase transition in $Cu(NH_3)_6Br_2$, heat was supplied to the sample holder by a small light bulb built into the diffractometer, and temperatures were measured by means of a thermocouple embedded in the sample.

Results

Unit-Cell Parameters and Space Group.—The powder patterns of all three compounds could be indexed on the basis of tetragonal unit cells with c/a approximately 0.9. Systematic absences correspond to space group D_{4h}-F4/mmm or a tetragonal subgroup of lower symmetry. We assumed the former to be

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[1] J. D. Dunitz and L. E. Orgel, *Nature*, **179**, 462 (1957).

[2] H. A. Jahn and E. Teller, *Proc. Roy. Soc.* (London), **A101**, 220 (1937).

[3] G. Peyronel, *Gazz. Chim. Ital.*, **71**, 363 (1941).

[4] H. Elliott and B. J. Hathaway, *Inorg. Chem.*, **5**, 885 (1966).

[5] A. Naumann, *Ber.*, **37**, 3600 (1904).

[6] D. W. Horn, *Am. Chem. J.*, **39**, 204 (1908).

correct and at no time during our analysis of the data was there an indication of lower symmetry.

Unit-cell parameters were obtained by a least-squares analysis of the corrected peak centroids. The largest remaining source of error is likely to be due to displacement of the sample relative to the position of the silicon standard.[7] This leads to observational equations of the form

$$\sin^2\theta_c = (h^2 + k^2)A + l^2C + D\sin\theta_c\cos^2\theta_c \qquad (2)$$

in which $A = (\lambda/2a)^2$, $B = (\lambda/2c)^2$, and D is an empirical parameter which is proportional to the sample displacement. We took the wavelength λ to be either 1.5418 A (unresolved $K\alpha_1\alpha_2$) or 1.5405 A ($K\alpha_1$ only). Considerable care in the analysis of the data was necessary because of the extensive overlapping of powder lines. A line was included in the analysis only (1) if it could be resolved from other lines or (2) if it was a dominant member of a set of unresolvable lines. By "dominant" we mean that $m|F|^2$ for the indices assigned to the line was at least 25 times as great as $m|F|^2$ for any interfering reflection. The final cell determinations were actually made after the completion of the structure determination, when all of the structure factors had been computed. The results are summarized in Table I. The observed lattice spacings for the reflections used to determine the cell edges are listed in Table III along with calculated values for all reflections used in the structure analysis.

TABLE I

LATTICE PARAMETERS, WITH STANDARD DEVIATIONS, OF HEXAAMMINECOPPER(II) HALIDES

Compound	a, A	c, A	c/a	Vol., A^3
$Cu(NH_3)_6Cl_2$	10.375 ± 0.007	9.481 ± 0.011	0.9138	1020.5
$Cu(NH_3)_6Br_2$	10.746 ± 0.002	9.675 ± 0.001	0.9003	1117.3
$Cu(NH_3)_6I_2$	11.200 ± 0.001	10.290 ± 0.001	0.9188	1290.8

The comparative inaccuracy in the cell parameters of the chloride is due to more extensive overlapping of reflections for this compound. In particular, there were few usable reflections with large l values.

Structure Determination.—Intensities were measured for both the chloride and the bromide. Since we expected the obtainable accuracy in the nitrogen position to be very low in the case of the iodide, no intensities were measured for this compound.

The structure was assumed to consist of: Cu at 0, 0, 0; X at $^1/_4$, $^1/_4$, $^1/_4$; $^3/_4$, $^3/_4$, $^3/_4$; N_1 at x, 0, 0; $\bar{x}$, 0, 0; 0, x, 0; 0, $\bar{x}$, 0; N_2 at 0, 0, z; 0, 0, $\bar{z}$; plus atoms related to these by addition of $^1/_2$, $^1/_2$, 0; $^1/_2$, 0, $^1/_2$; 0, $^1/_2$, $^1/_2$. An approximate scale factor and average temperature parameter were obtained from a least-squares fit of observed intensities to those calculated from copper and halide atoms only. The observed intensities were corrected for Lorentz and polarization factors and are, therefore, to be compared with calculated intensities

$$I_{\text{calcd}} = K\sum_i m_i|F_i|^2 \qquad (3)$$

in which i indicates a given form $\{hkl\}$ with multiplicity m_i and structure factor F_i, and K is a scale constant.

To refine the structure, initial x and z values for nitrogen were assigned on the basis of an expected Cu–N distance of about 2.1 A. This initial structure was refined by successive least-squares determinations of parameter shifts based on the observational equations

$$I_{\text{obsd}} = I_{\text{calcd}} + \sum_k\left(\frac{\partial I_{\text{calcd}}}{\partial p_k}\right)\Delta p_k \qquad (4)$$

in which p_k is a structural parameter and Δp_k is a correction from the previous value of this parameter. From (3) we note that

$$\frac{\partial I_{\text{calcd}}}{\partial p_k} = K\sum_i m_i\frac{\partial|F_i|^2_{\text{calcd}}}{\partial p_k} \qquad (5)$$

The iteration was continued until parameter shifts were all less than 1% of the standard deviations of the corresponding parameters. Structural parameters used were isotropic temperature parameters (B) for each type of atom as well as x and z coordinates for nitrogen atoms. Since the work of Ephraim[8] shows that the chloride and bromide actually contain 5.7 and 5.8 ammonia molecules per copper atom, respectively, we assumed fractional occupancy of the nitrogen positions based on these figures. Final parameters are given in Table II, and comparisons of observed and calculated intensities are given in Table III. The final values of $R = \Sigma|I_{\text{obsd}} - I_{\text{calcd}}|/\Sigma I_{\text{obsd}}$ are 0.124 for the chloride and 0.130 for the bromide.

TABLE II

FINAL STRUCTURAL PARAMETERS FOR $Cu(NH_3)_6Cl_2$ AND $Cu(NH_3)_6Br_2$[a]

Parameter	$Cu(NH_3)_6Cl_2$	$Cu(NH_3)_6Br_2$
x (N_1)	0.200 (0.007)	0.200 (0.007)
z (N_2)	0.276 (0.012)	0.253 (0.029)
B (Cu)	6.6 (1.7)	4.7 (3.0)
B (X)	2.7 (1.3)	3.3 (1.3)
B (N)	6.1 (1.8)	−1.7 (2.1)

[a] Standard deviations given in parentheses.

Phase Transition in $Cu(NH_3)_6Br_2$.—The X-ray data reported above are in disagreement with the results of both Peyronel[3] and Elliott and Hathaway[4] in that they both report the bromide and iodide to be cubic. Peyronel apparently did not attempt to keep his material in equilibrium with ammonia, and, furthermore, he heated his sample before he produced his powder diagrams. Elliott and Hathaway state that sample preparation was carried out under an atmosphere of ammonia, but they do not state what, if any, precaution was made to maintain equilibrium with ammonia during the X-ray exposure.

To resolve the above difficulties, we observed the powder pattern of $Cu(NH_3)_6Br_2$, in contact with 1 atm of ammonia, as a function of temperature. Above 70° lines due to the previously reported cubic phase ap-

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(7) W. Parrish and A. J. C. Wilson in "International Tables for X-Ray Crystallography," Vol. II, The Kynoch Press, Birmingham, England, 1959. p 221.

(8) F. Ephraim, *Ber.*, **52**, 940 (1919).

Table III

Observed and Calculated Powder Diffraction Data

(a) $Cu(NH_3)_6Cl_2$, Scale Constant = 0.005820[a]

hkl	d_{obsd}[b]	d_{calcd}[b]	I_{obsd}[c]	I_{calcd}[c]
111		5.8020	50.8	68.2
220		3.6679	58.4	72.6
202	3.5003	3.4994	128.6	131.3
311	3.1056	3.1004	28.3	33.2
113 }		2.9025	119.7	108.0
222 }		2.9010		
400	2.5987	2.5936	130.1	122.5
004 }	2.3642	2.3703	65.2	60.4
331 }		2.3678		
313	2.2743	2.2761	40.0	39.2
422	2.0854	2.0837	102.3	98.9
224 }	1.9922	1.9908	142.6	116.6
511 }	1.9874	1.9893		
115 }	1.8375	1.8359	48.2	59.5
440 }	1.8320	1.8340		
404 }		1.7497	100.8	115.7
531 }		1.7487		
513 }	1.7112	1.7108	40.9	50.8
442 }		1.7104		
315 }		1.6417	53.3	59.7
620 }		1.6403		
602		1.6244	55.9	50.3
533 }		1.5504	23.9	30.3
622 }		1.5502		
226 }		1.4512	75.5	71.1
444 }		1.4505		
711 }	1.4497	1.4499		
551 }	1.4497	1.4499		
642	1.3774	1.3767	39.2	50.4
406 }		1.3495	62.0	56.6
624 }	1.3484	1.3487		
731 }		1.3484		

(b) $Cu(NH_3)_6Br_2$, Scale Constant = 0.0001019[a]

hkl	d_{obsd}[b]	d_{calcd}[b]	I_{obsd}[c]	I_{calcd}[c]
111	5.9786	5.9759	14.7	14.2
200	5.3742	5.3732	2.8	3.7
002	4.8410	4.8374	1.4	2.1
220	3.8016	3.7994	33.5	36.4
202	3.5960	3.5951	59.7	66.1
311	3.2076	3.2063	5.8	7.0
222 }	2.9888	2.9880	65.7	56.0
113 }		2.9686		
400	2.6859	2.6866	46.9	57.0
004	2.4174	2.4187	39.2	29.0
240	2.4029	2.4030		
402 }	2.3486	2.3487	16.0	13.8
313 }	2.3396	2.3393		
422	2.1520	2.1521	64.8	60.4
511 }	2.0593	2.0592	65.3	57.2
224 }	2.0402	2.0403		
440	1.8994	1.8997	18.1	30.2
404 }	1.7973	1.7975	67.8	64.1
600 }		1.7910		
442 }		1.7682	18.6	24.6
153 }		1.7642		
244 }		1.7046	44.2	46.4
260 }	1.6994	1.6992		
135 }		1.6815	36.0	36.1
602 }		1.6796		
206	1.5446	1.5444		
155 }		1.4253	42.4	44.8
642 }		1.4242		

(c) $Cu(NH_3)_6I_2$

hkl	d_{obsd}	d_{calcd}	*hkl*	d_{obsd}	d_{calcd}
111	6.2839	6.2760	420	2.5042	2.5043
200	5.6092	5.6000	402	2.4597	2.4594
002	5.1458	5.1452	204	2.3379	2.3377
220	3.9594	3.9597	422	2.2516	2.2518
202	3.7876	3.7888	224	2.1572	2.1573
311	3.3488	3.3489	440	1.9799	1.9798
222	3.1378	3.1380	244	1.7943	1.7945
400	2.7992	2.8000	624	1.4587	1.4587

[a] The scale constant, determined in the refinement, converts absolute intensities (corrected for Lorentz and polarization factors) to the listed values. [b] The observed lattice spacings, which correspond to indices on the same line, are listed for reflections used in the determination of the unit-cell edges. Calculated values are given for all reflections. [c] Observed and calculated intensities are listed for single reflections or for the set of reflections enclosed by brackets. In several cases reflections were resolved for centroid measurement but not for measurement of integrated intensities.

peared in the diffraction pattern, but even at 110° the transition was incomplete. At a given temperature within this range the proportion of cubic to tetragonal phases remained constant for periods of several hours. The time required to reach this constant proportion was of the order of minutes. Clearly the transition does not occur reversibly under these conditions since the phase rule would exclude (if we assume that the components are $CuBr_2$ and NH_3) the coexistence of two solid phases over a range of temperatures. Further evidence concerning the irreversible nature of the transition was obtained by measuring the per cent of cubic phase present as a function of temperature for both ascending and descending temperatures. This was done by measuring the integrated intensities for the (400) powder lines of the cubic and tetragonal phases. The results, which clearly show a hysteresis loop, are shown in Figure 1.

Discussion

The parameters listed in Tables I and II give the following interatomic distances with standard deviations

Compound	Four Cu–N_1, A	Two Cu–N_2, A
$Cu(NH_3)_6Cl_2$	2.07 ± 0.07	2.62 ± 0.11
$Cu(NH_3)_6Br_2$	2.15 ± 0.08	2.45 ± 0.28

If the $Cu(NH_3)_6^{2+}$ ion is assumed to have the same dimensions in both compounds, as seems likely, the best (weighted mean) distances with their standard deviations are Cu–N_1 = 2.11 ± 0.05 A and Cu–N_2 = 2.59 ± 0.10 A. Although these results are not so accurate as one might hope, they clearly demonstrate distortion from a regular octahedron in the expected manner—D_{4h} symmetry with four short and two long distances.

It may seem rather strange that the unit cell is shortened in the direction of the long Cu–N distances.

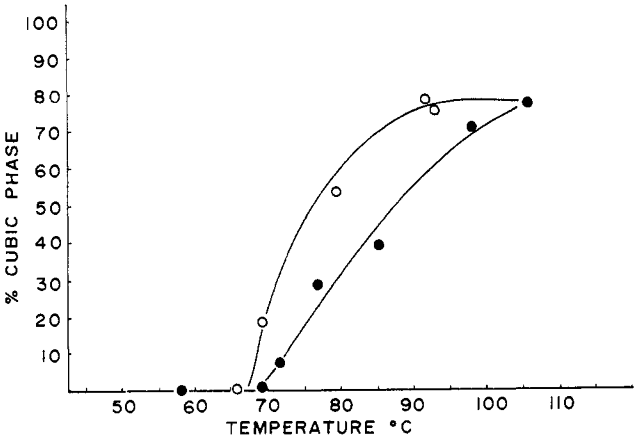

Figure 1.—Phase (cubic and tetragonal) composition as a function of temperature for $Cu(NH_3)_6Br_2$: solid circles, increasing temperature; open circles, decreasing temperature.

Elliott and Hathaway[4] suggested a structure in which the elongated tetragonal axes of the $Cu(NH_3)_6^{2+}$ group occur randomly along the *a* and *b* axes. This is clearly not the case, however, and, in fact, the large separation of the $Cu(NH_3)_6^{2+}$ ions precludes any significant short-range interaction between these ions. Thus, effects on the lattice parameters would be difficult to predict.

Although we cannot be certain of the source of the discrepancy, in the cases of the bromide and iodide, between this work and that of Peyronel[3] and Elliott and Hathaway,[4] it might well be that the latter workers failed to maintain equilibrium with ammonia gas at 1 atm. It is clear that the transition of $Cu(NH_3)_6Br_2$ to the cubic form is associated with considerable loss of ammonia. Ephraim[8] reported that the ratio of ammonia to copper in the bromide in equilibrium with 1 atm of ammonia is 5.48 at 65° and 5.08 at 115°. Permanent loss of ammonia might stabilize the high-temperature cubic phase. A thorough study of the phase transition as a function of ammonia pressure would probably clarify this situation, but such a study is beyond the scope of this report.

Among the possible causes of the irreversible nature of the phase transition are (1) slow diffusion of NH_3 in the solid and (2) stresses, produced by changes in the cell dimensions, which are not annealed out at the transition temperature. The evidence would seem to favor the latter as most important. In the first place, there is no detectable change in the cubic–tetragonal phase ratio over a period of hours once the steady value has been reached within a few minutes. Secondly, marked line broadening, particularly in the tetragonal phase, indicated considerable strain and/or reduction of particle size in the phase-transition region. For example, the line widths (2θ) at half-height for the (400) tetragonal line were 0.17 (normal), 0.29, 0.40, and 0.29° at temperatures of 45, 70, 81, and 92°, respectively.

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On the Question of Autoionization in Complexes of Metal Pentafluorides

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The possibility of ionization of complexes of phosphorus, arsenic, and antimony(V) fluorides with organic donor molecules was explored by nmr techniques. No evidence of ionization in acetonitrile solution was obtained at concentrations in the range 3–12 *M*. It was established that a hexacoordinate arsenic species such as $F_5AsNCCH_3$ hydrolyzes to give significant quantities of the AsF_6^- ion, presumably due to F^- attack of the complex in either an SN1 or SN2 type of mechanism.

In earlier work[1,2] we had characterized the complexes of phosphorus, arsenic, and antimony pentafluorides with organic donor molecules as hexacoordinate, monomolecular structures of C_{4v} symmetry. These conclusions were based on analyses of the F^{19} nmr spectra of acetonitrile solutions of the complexes. Recently, Kolditz and Rehak[3,3a] have proposed that in acetonitrile the complexes MF_5NCCH_3 (M = P, As, Sb) and $MF_5N(CH_3)_3$ (M = P, Sb) undergo significant autoionization

$$2MF_5\cdot\text{donor} \rightleftarrows MF_4(\text{donor})_2^+ + MF_6^-$$

Conductivity data and hydrolysis studies comprise the experimental basis of their proposal. We wish to confirm our original observations and conclusions and to raise serious question regarding the proposal of Kolditz and Rehak.

As originally reported,[1] the F^{19} spectrum of $F_5PN(CH_3)_3$ in acetonitrile solution consists of two doublets

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(1) E. L. Muetterties, T. A. Bither, M. W. Farlow, and D. D. Coffman, *J. Inorg. Nucl. Chem.*, **16**, 52 (1960).

(2) E. L. Muetterties, "Advances in the Chemistry of the Coordination Compounds," The Macmillan Co., New York, N. Y., 1961, p 513.

(3) L. Kolditz and W. Rehak, *Z. Anorg. Allgem. Chem.*, **342**, 32 (1966).

(3a) NOTE ADDED IN PROOF.—Professor Kolditz in a personal communication to us has made the valid point that the concentration ranges examined conductometrically in his work[3] are lower (~10^2 to 10^3) than those employed in these nmr studies. Professor Kolditz has, however, reexamined these systems and is now obtaining conductivities significantly lower than those published originally.[3]