Volume 6
Number 1
January 3, 1967

Inorganic Chemistry

CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY
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Chemistry of Polynuclear Metal Halides. II. Preparation of Polynuclear Niobium Chloride and Bromide[1]

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Received August 22, 1966

Improved preparations leading to the compounds $Nb_6X_{14}\cdot 8H_2O$ ($X = Cl, Br$) are described. High yields of $Nb_6Cl_{12}^{2+}$ were obtained by the high-temperature reaction of KCl and Nb_3Cl_8 which proceeds *via* $14KCl + 5Nb_3Cl_8 = 2K_4Nb_6Cl_{18} + 3K_2NbCl_6$. Extraction of this reaction mixture with water provides a convenient route to $Nb_6Cl_{14}\cdot 8H_2O$. The attempted formation of Nb_6Cl_{14} *via* direct reduction of $NbCl_5$ with aluminum was unsuccessful. However, aluminum reduction of $NbBr_5$ provided an unidentified anhydrous product from which yields of up to 35% $Nb_6Br_{12}^{2+}$ were extracted. Equilibration reactions involving niobium and Nb_3Br_8 at temperatures up to 975° gave no evidence for phases having $Br:Nb < 2.67$. Spectra and extinction coefficients for aqueous $Nb_6Cl_{12}^{2+}$ and $Nb_6Br_{12}^{2+}$ are given.

Introduction

The polynuclear niobium chloride was first reported in 1913 by Harned,[2] who prepared the compound by reducing $NbCl_5$ with Na(Hg) at elevated temperatures. The crystals he obtained from aqueous solution were formulated as $Nb_6Cl_{12}Cl_2\cdot 7H_2O$. The polynuclear formulation was verified much later by an X-ray study on an ethanolic solution of $Nb_6Cl_{12}^{2+}$, which was found to contain an octahedral arrangement of the niobium atoms.[3] More recent studies[4,5] have resulted in increased yields of $Nb_6Cl_{14}\cdot 7H_2O$ using a cadmium reduction of $NbCl_5$.

It was not until 1965 that the preparation of pure anhydrous Nb_6Cl_{14} was reported and the crystal structure solved by Schäfer.[6] The high-temperature equilibration of Nb_3Cl_8 and niobium to yield crystalline Nb_6Cl_{14} has been confirmed during this study. The structure of the Nb_6Cl_{12} unit in solid Nb_6Cl_{14}[6] agrees basically with that reported[8] for $Nb_6Cl_{12}^{2+}$ but has the important difference that the octahedron of niobium atoms is tetragonally compressed. A review of halide and oxide compounds which exhibit structures where metal–metal bonding is evident has recently been published by Schäfer.[7]

This work was undertaken in order to find a more convenient and efficient preparation of Nb_6Cl_{14} and to prepare the analogous Nb_6Br_{14}. Since the inception of this study, very low-yield preparations of Nb_6Br_{14} have been reported[5,8] using the method of Harned, *et al.*[4] The hydrated bromide is difficult to obtain but can now be prepared in fair yields, whereas the corresponding chloride can be prepared in nearly quantitative yield. Methods developed previously in preparing Ta_6X_{14} ($X = Br, I$)[9] have been investigated and other more satisfactory synthetic routes have been devised.

Experimental Section

Materials.—Niobium granules obtained from E. I. du Pont de Nemours and Co. were used in the preparation of niobium pentahalides. The niobium tubing (19-mm o.d.) was obtained from laboratory stock. Aluminum metal used in the reductions was either foil of *ca.* 99.9% purity or turnings prepared from ingot of very high purity (*ca.* 99.999%).

Reagent grade bromine was dried over P_4O_{10} and stored in an evacuated flask. Chlorine was used directly from lecture bottles.

Niobium pentahalides were prepared by combination of the elements in an evacuated tube at 400–450°. Aluminum tribromide obtained from Fisher Scientific Co. was sublimed under dynamic vacuum prior to use.

All compounds were stored and handled under argon in a drybox except where the contrary is obvious from the text.

Niobium trihalides[10] were used as starting materials in some

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1947.

[2] H. S. Harned, *J. Am. Chem. Soc.*, **35**, 1078 (1913).

[3] P. A. Vaughan, J. H. Sturdivant, and L. Pauling, *ibid.*, **72**, 5477 (1950).

[4] H. S. Harned, C. Pauling, and R. B. Corey, *ibid.*, **82**, 4815 (1960).

[5] R. J. Allen and J. C. Sheldon, *Australian J. Chem.*, **18**, 277 (1965).

[6] A. Simon, H. G. Schnering, H. Wöhrle, and H. Schäfer, *Z. Anorg. Allgem. Chem.*, **339**, 155 (1965).

[7] H. Schäfer and H. G. Schnering, *Angew. Chem.*, **76**, 833 (1964).

[8] M. B. Robin and N. A. Kuebler, *Inorg. Chem.*, **4**, 978 (1965).

[9] P. J. Kuhn and R. E. McCarley, *ibid.*, **4**, 1482 (1965).

[10] Niobium trihalide is used as an abbreviation in the text and refers to any composition in the homogeneous phase ranges: (a) $NbCl_{2.67}(Nb_3Cl_8)$–$NbCl_{3.13}$: H. Schäfer and K. D. Dohman, *Z. Anorg. Allgem. Chem.*, **300**, 1 (1959); (b) $NbBr_{2.67}(Nb_3Br_8)$–$NbBr_{3.03}$: H. Schäfer and K. D. Dohman, *ibid.*, **311**, 134 (1964).

reactions. Niobium trichloride was prepared by allowing niobium pentachloride and aluminum to react in a sealed, evacuated tube in a temperature gradient of 450–300° for about 2 days. The aluminum trichloride was removed by sublimation at *ca.* 200° and the product was given a final heat treatment for 3 days to remove or disproportionate any remaining higher chlorides. A final treatment at 500° provided green Nb_3Cl_8 whereas a heating of 300° gave a black product with a composition of about $NbCl_3$.

Black crystals of Nb_3Br_8 were prepared by reducing $NbBr_5$ with zinc metal at 550–600° for about 3 days. In this reaction the temperature was raised slowly to the final value so that excessive pressure did not build up. Zinc bromide was removed from the very inert Nb_3Br_8 by leaching with water.

Dodeca-μ-chloro-hexaniobium Dichloride.—Niobium trichloride can be disproportionated when heated with KCl at 600–900°. It was advantageous to use Nb_3Cl_8 rather than material near the upper end of the phase range ($NbCl_{3.1}$), as indicated by the reaction

$$5Nb_3Cl_8 + 14KCl = 3K_2NbCl_6 + 2K_4Nb_6Cl_{18} \qquad (1)$$

The presence of K_2NbCl_6[11] was identified from X-ray powder pattern data; the identification of $K_4Nb_6Cl_{18}$ will be discussed under Results. At 600° the reaction can be accomplished in a sealed Vycor tube heated for 2–3 hr. In order to avoid contamination resulting from reactions involving glass at higher temperatures it was necessary to use niobium or molybdenum tubes which were sealed by electron-beam welding and enclosed in an evacuated quartz tube. When a niobium tube was used, all of the K_2NbCl_6 was reduced to $K_4Nb_6Cl_{18}$ if the reaction was continued for a few days. A typical yield of $K_4Nb_6Cl_{18}$ for the reaction at 600° was 66% of that calculated from eq 1.

An extension of the above procedure has led to a one-step preparation of $K_4Nb_6Cl_{18}$. This reaction (using excess KCl) was carried out in a niobium tube at 800–900° for 4–5 days.

$$14NbCl_5 + 20KCl + 16Nb = 5K_4Nb_6Cl_{18} \qquad (2)$$

The only precaution is that a gradual initial heating be used so that excessive pressure does not result. Starting at *ca.* 400° and raising the temperature to 800° over 18–24 hr have been found to be satisfactory. The yields of $K_4Nb_6Cl_{18}$ were less than expected from eq 2. Upon introducing such products into water, considerable hydrolysis to niobium oxide occurred. This indicated the presence of niobium(IV) (probably as K_2NbCl_6) or unreduced $NbCl_5$.

Reactions Providing the Nb_6Br_{12} Unit.—Three methods were investigated.

A. Aluminum Reduction of $NbBr_5$.—Usually the reactions were performed as described previously.[9] Based on eq 3, approximately stoichiometric quantities of $NbBr_5$ and aluminum were sealed in an evacuated Pyrex tube with or without added $AlBr_3$. The tube was generally heated in a two-section electric furnace so that a temperature gradient could be used to mix the reactants by reflux. Table I summarizes the results of several such experiments.

$$16Al + 18NbBr_5 = 3Nb_6Br_{14} + 16AlBr_3 \qquad (3)$$

In reactions where no excess $AlBr_3$ was added, the product was found in two distinct sections of the tube. The small amount of green powder which formed on the aluminum at the bottom of the tube (*e.g.*, as in expt 2, Table I) contained all of the product extractable as $Nb_6Br_{12}^{2+}$. The remainder and larger part of the product was deposited farther up the tube and consisted of niobium tribromide and $NbBr_4$.

An increased yield of $Nb_6Br_{12}^{2+}$ was found when $AlBr_3$ was added at the start. It is thought that the possible solvent power or the mixing action provided by the $AlBr_3$ promotes more efficient reaction between the aluminum and the higher niobium bromides. The products of these latter reactions were uniform powders.

Table I

Reduction of $NbBr_5$ with Aluminum

Expt	Temp gradient, °C[a]	Time, days	$Nb_6Br_{12}^{2+}$ yield, %
1[b]	450–290	2	None detected
2	450–300	2	0.6[c]
3[d]	350–280	5	34
4	400–280	3	~19
5	300–350	3	23
6	300–300	14	14

[a] First listed temperature always maintained at reaction site in lower end of tube. [b] This product was given a final heat treatment at 550° for 6 hr. [c] Product separated into black and green fractions; 40% of the latter was extractable as Nb_6Br_{14}. [d] In reactions 3–6 $AlBr_3$ was added as indicated in the text.

B. Disproportionation of Niobium Tribromide in RbBr.—This type of reaction was carried out in the same manner as for the reaction between niobium trichloride and KCl. In one 3-hr reaction between Nb_3Br_8 and RbBr at 710° a yield of $Nb_6Br_{12}^{2+}$ of 6.3% was obtained.

C. Equilibrations.—In these experiments higher niobium bromides alone or in the presence of niobium granules were equilibrated in evacuated niobium or Vycor tubes at high temperature. In order to avoid loss of material by vaporization the tube was placed in the furnace so that the upper end was always at a slightly higher temperature than the section containing the reactants. The results are summarized in Table II.

Table II

Equilibration Reactions

Reactants	Container	Temp, °C	Time, days	Product
$NbBr_4$	Vycor	600	7	Nb_3Br_8, $NbBr_4$, $NbBr_5$
$NbBr_5$, Nb	Vycor	675	8	Nb_3Br_8
Nb_3Br_8, Nb	Nb	800	5	Nb_3Br_8
Nb_3Br_8, Nb	Nb	975	5	Nb_3Br_8

$Nb_6Cl_{14} \cdot 8H_2O$.—Green aqueous solutions containing the $Nb_6Cl_{12}^{2+}$ ion were made up by extracting the products of the above reactions. Any niobium oxides formed by hydrolysis or niobium trichloride, which was inert to water, could be removed by filtration. The dark green solutions were acidified with hydrochloric acid (pH $\simeq$1) and then slowly concentrated on the hot plate at 40–50°. If a higher temperature was used during evaporation, slight hydrolysis and separation of $Nb_2O_5 \cdot xH_2O$ were noticed. Black crystals of $Nb_6Cl_{14} \cdot 8H_2O$ began to separate when the solution became sufficiently concentrated to appear opaque. The crystals were collected on a frit, washed successively with water and ether, and dried *in vacuo*. *Anal.* Calcd for $Nb_6Cl_{14} \cdot 8H_2O$: Nb, 46.53; Cl, 41.44. Found: Nb, 46.57; Cl, 41.33.

$Nb_6Br_{14} \cdot 8H_2O$.—The procedure for isolating this hydrate is essentially the same as that used for the chloride. However, no acid was added to the solution. The black crystals were collected on a frit, washed successively with water and ether, and dried in air. *Anal.* Calcd for $Nb_6Br_{14} \cdot 8H_2O$: Nb, 30.60; Br, 61.49; O, 7.03. Found: Nb, 30.55; Br, 60.62; O, 7.06.

Analytical Procedures.—Niobium was always determined as the oxide, Nb_2O_5. Hydrolysis with ammonia followed by acidification, filtration, and ignition was generally used. In analyzing the inert trihalide phases, direct oxidation with HNO_3 followed by ignition was used. Bromine and chlorine were determined volumetrically with $AgNO_3$. The yield of Nb_6X_{14} was determined by extracting a sample with water and determining the soluble niobium as above, or spectrophotometrically as $Nb_6X_{12}^{2+}$. Where both methods were used, reasonable agreement in the yield was obtained. Owing to slight but varying amounts of hydrolysis of the aqueous $Nb_6X_{12}^{2+}$ species, the yield data are

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(11) B. Torp, unpublished Ph.D. Thesis, Iowa State University, Ames, Iowa.

only approximate. They are useful in that largely differing values indicate the relative utility of given reactions.

Spectra.—Visible and ultraviolet spectra were obtained on a Cary Model 14 spectrophotometer. All spectra were run against a solvent reference. Reflectance spectra were obtained on a Beckman DU spectrophotometer fitted with a Beckman 2580 reflectance attachment. The samples were diluted with KX ($X = Cl, Br$) and the same KX was used as a reference.

Results and Discussion

The aim of most of the preparative work discussed here was to develop more convenient and efficient syntheses of the hydrated cluster compounds. It has been found by others[6] and verified in this laboratory that anhydrous Nb_6Cl_{14} dissolves in most solvents only with difficulty. This is presumably a result of the extensive intercluster M–X–M binding, which is a prominent feature of the structure. The hydrated compounds, however, dissolve readily in ethanol and methanol forming about 10^{-3} *M* solutions and thus they are more suitable for further studies than the more dilute saturated aqueous solutions.

For formation of Nb_6Cl_{14} it was found that the equilibration of niobium trichloride with niobium proceeds very slowly, even at temperatures in excess of 800°. However, a more convenient and rapid reaction, the disproportionation of Nb_3Cl_8 in KCl, affords the salt $K_4Nb_6Cl_{18}$, which is readily soluble in water or alcohol to provide solutions of $Nb_6Cl_{12}^{2+}$. The formula of $K_4Nb_6Cl_{18}$ was verified through a series of experiments where KCl and Nb_6Cl_{14} in mole ratios varying from 1 to 6 were equilibrated at 800° for 3 days in niobium tubing. The following results were obtained from X-ray powder pattern data: (1) the patterns of the products resulting from the mole ratios of 1 and 2 contained lines of unreacted Nb_6Cl_{14}; (2) the pattern of the 4:1 product agreed exactly with that of the product from the equilibration of Nb_3Cl_8 with KCl in niobium; (3) there was no change in the patterns on variation of the mole ratio from 4 to 6.

Other evidence for the formation of the complex $K_4Nb_6Cl_{18}$ is derived from reflectance spectra. The reflectance spectrum of the 4:1 product (Figure 1) shows the characteristic bands of the $Nb_6Cl_{12}^{2+}$ cluster although small shifts to lower energy are observed. This reflectance spectrum also agrees almost exactly with that obtained on the product of a reaction of Nb_3Cl_8 and KCl in Vycor at 600°. Independent confirmation of the existence of $K_4Nb_6Cl_{18}$ has been obtained by Schäfer, who carried out experiments similar to the ones reported here.[12]

The corresponding reaction in the bromide system appears not to go so readily as for the chloride. Whereas the reaction of Nb_3Br_8 and RbBr at 710° for 3 hr produced about 6% $Nb_6Br_{12}^{2+}$, a subsequent equilibration of $NbBr_5$, RbBr, and Nb in a niobium tube at 800° for 10 days provided only *ca.* 1% yield. Other products of the latter reaction were not identified. By analogy to the chloride system, the $Nb_6Br_{12}^{2+}$ species obtained in these reactions is probably $Rb_4Nb_6Br_{18}$.

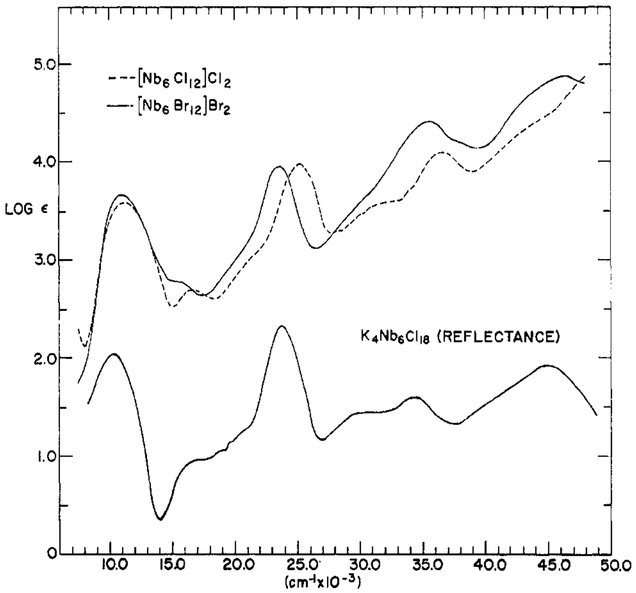

Figure 1.—Spectra of the ions $Nb_6X_{12}^{2+}$ in aqueous solution and reflectance spectrum of $K_4Nb_6Cl_{18}$.

Reduction of the niobium pentahalides with aluminum which was successful for preparing the polynuclear tantalum halides[9] has been relatively unsuccessful. In the case of the chloride, Nb_3Cl_8 is the major product and only faint traces of $Nb_6Cl_{12}^{2+}$ have been observed when a reaction product is extracted with water. It is not clear why the aluminum reduction does not work in this case since Nb_6Cl_{14} is known to be the lowest equilibrium phase.

Better yields of Nb_6Br_{14}[13] can be obtained *via* the aluminum reduction technique (Table I) and this is the most satisfactory synthetic route found, although the disproportionation of Nb_3Br_8 in RbBr shows promise (see above). It is noted in Table I that the maximum yield of Nb_6Br_{14} is obtained when the reaction mixture is maintained in a 350–280° temperature gradient. Other experiments in which separate portions of the product of an aluminum reduction were given heat treatments have shown that the amount of Nb_6Br_{14} in the product remains unaffected by heating at up to 350°, but begins to decrease at 400°.

The Br:Nb ratios in the products from the aluminum reduction reactions where $t \leq 400°$ were in the range 2.9–3.3. From the behavior on hydrolysis some $NbBr_4$ appeared to be in these mixtures, even though its presence was not detected in the X-ray patterns. The X-ray patterns indicated the principal component to be the trihalide phase, which remained unaffected by treatment with water. On the basis of these data, it appears that two over-all reactions, (3) and (4), occur simultaneously.

$$3NbBr_5 + 2Al = 3NbBr_3 + 2AlBr_3 \qquad (4)$$

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[12] H. Schäfer, Symposium on the Metal–Metal Bond in Inorganic Chemistry, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

[13] For the purposes of discussion it is assumed that Nb_6Br_{14} is formed as the anhydrous cluster species. Actually, it is possible that another cluster-containing species could be present since the evidence for Nb_6Br_{14} is the observation of $Nb_6Br_{12}^{2+}$ in aqueous solution. See ref 9 for a discussion of a similar problem regarding Ta_6Cl_{14}.

Once $NbBr_3$ is formed, it evidently cannot be transformed into Nb_6Br_{14} by further reaction.

It has not been possible to identify Nb_6Br_{14} by X-ray powder patterns although patterns of the reaction products containing significant amounts of this compound have unassignable lines in them. It is probable that the presumed Nb_6Br_{14} in these mixtures is very finely divided, and it may be amorphous. A reflectance spectrum of the product of one reaction (*viz.* expt 2) showed well-resolved bands at 23,600, 33,600, and 43,300 cm^{-1} and a very broad band centered at *ca.* 11,000 cm^{-1} which confirmed the presence of the Nb_6Br_{12} unit.

It is important to note that equilibration reactions (Table II) have not been successful in preparing Nb_6Br_{14} as they have been in the case of Nb_6Cl_{14}. The recent observation of Nb_6I_{11}[14,15] as the lowest niobium iodide phase and the work on Nb_6Cl_{14}[6] suggest that a niobium bromide lower than the Nb_3Br_8 phase should exist. The reasons for this apparent anomaly are unknown presently.

The hydrated cluster compounds are readily prepared from the raw reaction products by extraction with water and evaporation as discussed above. It is fairly certain that these compounds are eight hydrates, and this formulation agrees with recent work by Schäfer,[16] who found $Ta_6Cl_{14}\cdot 8H_2O$ and similarly $Nb_6X_{14}\cdot 8H_2O$ (X = Cl, Br). The original formulation of these compounds as seven hydrates probably resulted from a less accurate preparation and analysis than is now possible.

The visible and ultraviolet spectra of aqueous solutions of these compounds are shown in Figure 1. These spectra in general agree with those reported by Allen and Sheldon[5] except that the extinction coefficients obtained here for $Nb_6Cl_{12}^{2+}$ are higher by 15–50%. Extinction coefficients for $Nb_6Br_{12}^{2+}$ are reported here for the first time (Table III). Allen and Sheldon have discussed the assignment of these spectra on the basis of the MO description given by Cotton and Haas.[17] A detailed study of the spectra and magnetic susceptibilities of a whole family of $M_6X_{12}^{n+}$ derivatives is underway in this laboratory and will be reported at a later date.

Table III

Ion	Absorption bands, $cm^{-1} \times 10^{-3}$ ($10^{-3}\epsilon$ in parentheses)
$Nb_6Cl_{12}^{2+}$	11.1 (3.8), 16.7 (0.48), 25.2 (9.5), 36.3 (12.6)
$Nb_6Br_{12}^{2+}$	11.0 (4.7), 15.5 (0.59), 23.6 (8.9), 35.4 (27.6)

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[14] H. Schäfer, *et al.*, *J. Less-Common Metals*, **10**, 154 (1965).

[15] L. R. Bateman, J. F. Blount, and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1082 (1966).

[16] H. Schäfer and D. Bauer, *Z. Anorg. Allgem. Chem.*, **340**, 62 (1965).

[17] F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 10 (1964).

Contribution from the Department of Inorganic Chemistry,
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Reflectance Spectrum and Electronic States of the $CuCl_5^{3-}$ Ion in a Number of Crystal Lattices

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Received May 2, 1966

The electronic spectrum of the pentachlorocuprate(II) ion has been studied by diffuse reflection in salts of the type $M^{III}(NH_3)_6CuCl_5$ [M = Co, Cr, Rh, or Ru] and $dienH_3CuCl_5$. On the basis of the temperature dependence of their positions, two bands observed in the near-infrared region with average frequency 8.3 and 10.0 kK are assigned, respectively, to the $^2A_1 \rightarrow {}^2E'$ and $^2A_1 \rightarrow {}^2E''$ ligand-field transitions of the Cu^{II} ion in a D_{3h} ligand field. Three charge-transfer bands are observed in the ultraviolet region with average frequency 24.2, 27.2, and 37.8 kK. Far-infrared measurements of the $Cu^{II}\cdots Cl$ stretching frequency indicate that the microsymmetry around the five-coordinated Cu^{II} ion is identical, within experimental limits, in all the metal hexaammine compounds studied.

Introduction

There has been considerable recent interest in transition metal complexes with a central ion coordination number of five. Complexes of this type have proved to be more common than had previously been supposed.[2a] An interesting group of compounds of this type is the series with general formula $M^{III}(NH_3)_6CuCl_5$ (where M^{III} = trivalent transition ion) and $dienH_3CuCl_5$. The crystal lattice of $Co(NH_3)_6CuCl_5$[2b] was found to contain the octahedral complex ion $Co(NH_3)_6^{3+}$ and the trigonal-bipyramidal complex ion $CuCl_5^{3-}$ arranged in a structure of the sodium chloride type. An important feature of the trigonal-bipyramidal structure of $CuCl_5^{3-}$ is that the distance between the copper atom and the two axial chlorine atoms (2.32 A) is of the same order as the distance between the copper atom and the three equatorial chlorine atoms (2.35 A).

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[2] (a) See for example: G. Dyer and D. W. Meek, *Inorg. Chem.*, **4**, 1398 (1965); M. Ciampolini, *ibid.*, **5**, 41, 45 (1966); (b) M. Mori, Y. Saito, and T. Watanabe, *Bull. Chem. Soc. Japan*, **34**, 245 (1961).