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} × 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,
The University, Bristol, England

Reflectance Spectrum and Electronic States of the $CuCl_5^{3-}$ Ion in a Number of Crystal Lattices

By G. C. Allen[1] and N. S. Hush

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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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(1) Department of Chemistry, University College of South Wales and Monmouthshire, Cathays Park, Cardiff, Wales.

(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).

Some diffuse reflectance spectra of $Cr(NH_3)_6CuCl_5$ and $Co(NH_3)_6CuCl_5$ were recorded by Mori.[3] These were not very well resolved and no interpretation was attempted. Single-crystal measurements for $Co(NH_3)_6CuCl_5$ together with some point-charge crystal field calculations have been briefly reported by Day,[4] and a band observed at 9.5 kK was assigned to a $^2A_1' \rightarrow {}^2E''$ transition of $CuCl_5^{3-}$. However, additional information is required in order to assign the spectrum obtained under higher resolution which contains two bands in the near-infrared region. The temperature dependence of the spectra is found to be of use in this respect (*vide infra*).

In the present work the diffuse reflectance spectra of a number of pentachlorocuprate(II) complexes of type $M^{III}(NH_3)_6CuCl_5$ (where $M^{III} = Cr^{3+}, Co^{3+}, Ru^{3+}$, and Rh^{3+}) and $dienH_3CuCl_5$ have been measured at room and liquid nitrogen temperatures. The near-infrared bands observed have been assigned on the basis of crystal-field theory. The infrared spectra of the above pentachlorocuprate(II) complexes have been measured in the CsBr region.

Experimental Section

Preparation of Pentachlorocuprate(II) Complexes of Type $M^{III}(NH_3)_6CuCl_5$ (Where $M^{III} = Cr^{3+}, Co^{3+}, Ru^{3+}$, or Rh^{3+}).—The complexes were prepared according to the method of Mori.[5] A 2-g amount of the metal ammine $M^{III}(NH_3)_6Cl_3$ and 2 g of copper(II) chloride dihydrate were dissolved in 60 ml of water. The solution was filtered and heated to 60°; then 20 ml of 12 *N* hydrochloric acid was added. The mixture was cooled in a cold water bath for 30 min with occasional stirring and the precipitated complex was filtered, washed with ethanol, and dried under vacuum.

Anal. Calcd for $Cr(NH_3)_6CuCl_5$: N, 21.30; H, 4.90; Cl, 44.50. Found: N, 21.22; H, 4.94; Cl, 44.60. Calcd for $Co(NH_3)_6CuCl_5$: N, 20.91; H, 4.51; Cl, 44.10. Found: N, 21.05; H, 4.62; Cl, 44.30. Calcd for $Ru(NH_3)_6CuCl_5$: N, 18.92; H, 4.08; Cl, 39.91. Found: N, 18.85; H, 4.24; Cl, 40.10. Calcd for $Rh(NH_3)_6CuCl_5$: N, 18.85; H, 4.07; Cl, 39.76. Found: N, 18.75; H, 4.29; Cl, 39.90.

Preparation of Diethylenetriammonium Pentachlorocuprate(II).—$dienH_3CuCl_5$ was prepared according to the method of Mori.[6] A 10-ml amount of 12 *N* hydrochloric acid was slowly added to 2.5 g of diethylenetriamine in 3 ml of water at 0°. To the mixture was added 1 g of copper(II) chloride dihydrate dissolved in 2.5 ml of water and 10 ml of 12 *N* hydrochloric acid. When the mixture was slowly shaken two or three times and allowed to stand for several minutes, yellow crystals were deposited. The crystals were filtered, washed first with 12 *N* hydrochloric acid and then ethanol, and finally dried under vacuum.

Anal. Calcd for $(H_3NC_2H_4NH_2C_2H_4NH_3)CuCl_5$: N, 12.11; C, 13.84; H, 4.65. Found: N, 11.91; C, 14.10; H, 4.80.

Diffuse Reflectance Measurements.—The diffuse reflectance spectra of the pentachlorocuprate(II) complexes, together with the corresponding starting metal ammines, were measured at room and liquid nitrogen temperatures for the frequency range 4.0–45.0 kK using a Beckman DK-2 spectroreflectometer with magnesium oxide as a reference.

The samples were prepared by grinding in an agate mortar and sieving the resulting powder to give a particle size not greater than 50 μ. The intensities are expressed in terms of the Kubelka–Munk function F_R,[7] defined by

$$F_R = \frac{(1 - R_{\text{diff}})^2}{2R_{\text{diff}}} = \frac{k}{s}$$

where $R_{\text{diff}} = I(\text{reflectance sample})/I(\text{reflectance standard})$ is the relative diffuse reflectance referred to a nonabsorbing standard, k is the absorption coefficient defined by $I = I_0e^{-ks}$, and s is the scattering coefficient for the substance in question.

Infrared Spectra.—The infrared spectra of the prepared pentachlorocuprate(II) complexes were recorded by Dr. P. Goggin (at the University of Oxford), using a Perkin-Elmer Model 221 spectrometer, for the range 714–250 cm^{-1}. The sample was prepared as a mull and mounted using polythene sheets between CsBr plates.

Results

The diffuse reflectance spectra of the pentachlorocuprate(II) complexes studied are listed in Table I. Some typical spectra are shown in Figures 1–3. The spectra of the complexes of type $M^{III}(NH_3)_6CuCl_5$ are very similar, as would be expected. The near-infrared bands observed in the 4–6-kK region are assigned to vibrational combinations of the fundamental region for the ligand NH_3, since they are found in practically the same position in both the $M^{III}(NH_3)_6CuCl_5$ complex and the corresponding starting metal ammine $M^{III}(NH_3)_6Cl_3$. Two very prominent bands are found in the near-infrared regions 8–10 kK at room temperature and 9–11 kK at liquid nitrogen temperature. The first of the two bands at approximately 8.3 kK (~9 kK at low temperature) is more intense than the second band which occurs at roughly 10 kK (~11 kK at low temperature). The values of the Kubelka–Munk intensity function are in the approximate ratio 1:0.85 at room temperature and 1:0.90 at liquid nitrogen temperature. For the diethylenetriammonium pentachlorocuprate(II), however, these absorption maxima are shifted to higher frequency and the relative intensity of the two bands is reversed (see Figure 3). The absorption at the higher frequency, 12.50 kK (12.99 kK at low temperature), is more intense than that of the low-frequency band at 11.36 kK. The values of the Kubelka–Munk intensity function are in the ratio 1:1.2 at both room and liquid nitrogen temperature.

The remaining bands of the $CuCl_5^{3-}$ ion in Table I are assigned to charge-transfer transitions. Three charge-transfer bands can be identified below 40 kK. For the metal hexaammine complexes, the average energies of these at 90°K are 24.2, 27.2, and 37.8 kK. For $dienH_3CuCl_5$, the corresponding values are 24.04, 28.17, and 37.04 kK. The first charge-transfer band is not well resolved, and when it is observed it is usually seen only as a shoulder.

Discussion

In a trigonal-bipyramidal crystal field the d-manifold splitting is calculated for D_{3h} symmetry. This gives three levels: $A_1' = z^2$; $E'' = xz, yz$; $E' = x^2 - y^2, xy$. The three ligands in the plane normal to the threefold axis give rise to a splitting characterized by Δ_1

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(3) M. Mori, *Bull. Chem. Soc. Japan*, **34**, 1249 (1961).

(4) P. Day, *Proc. Chem. Soc.*, 18 (1964).

(5) M. Mori, *Bull. Chem. Soc. Japan*, **33**, 985 (1960).

(6) M. Mori and S. Fujiwara, *ibid.*, **36**, 1636 (1963).

(7) G. Kortum, *Trans. Faraday Soc.*, **58**, 1624 (1962).

Table I

The Absorption Maxima for the Diffuse Reflectance Spectra of the Pentachlorocuprate(II) Complexes

Compound	Temp	Absorption max, kK									
$Cr(NH_3)_6CuCl_5$	Room temp	4.00,^{a}	4.60,^{a}	4.77^a		8.33,	10.00 sh,			27.47,	39.06
	Liq N_2 temp	3.95,^{a}	4.57,^{a}	4.85,^{a}	5.33 sh,^{a}	8.70,	10.81,	21.74 sh,^{a}	24.39 sh,	27.25,	37.31
$Co(NH_3)_6CuCl_5$	Room temp	4.08,^{a}	4.61,^{a}	4.83^a		8.40,	10.10,		27.03,	39.37	
	Liq N_2 temp	4.08,^{a}	4.58,^{a}	4.83,^{a}	5.41,^{a}	8.88,	10.81,	21.05,^{a}	27.03		
$Ru(NH_3)_6CuCl_5$	Room temp	4.04,^{a}	4.58,^{a}	4.82,^{a}	8.50,	10.20,	27.03,	39.22			
	Liq N_2 temp	4.03,^{a}	4.56,^{a}	4.82,^{a}	9.01,	10.81,	27.32,	38.46			
$Rh(NH_3)_6CuCl_5$	Room temp	4.11,^{a}	4.60,^{a}	4.84,^{a}		8.26,	9.90,	23.81 sh,	27.40,	33.33,^{a}	39.06
	Liq N_2 temp	4.10,^{a}	4.59,^{a}	4.85,^{a}	5.41,^{a}	9.01,	10.99,	24.10 sh,	27.03,	33.33 sh,^{a}	37.04
$dienH_3CuCl_5$	Room temp	4.30 sh,^{a}	4.61,^{a}		5.71,^{a}	6.10 sh,^{a}	11.36 sh,	12.50,	23.81 sh,	28.41,	35.71
	Liq N_2 temp	4.30 sh,^{a}	4.57,^{a}	4.98 sh,^{a}	5.71,^{a}	6.14 sh,^{a}	11.36 sh,	12.99,	24.04,	28.17,	37.04

[a] Absorption maxima assigned to transitions of the cation. These were measured for the chlorides $M^{III}(NH_3)_6Cl_3$ and $dienH_3Cl_3$ and were nearly identical with the values obtained for the corresponding $CuCl_5^{3-}$ complexes. For the metal ammine ions, the values are in good accord with those listed by C. K. Jørgensen," Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Inc., New York, N. Y., 1962, pp 287–295.

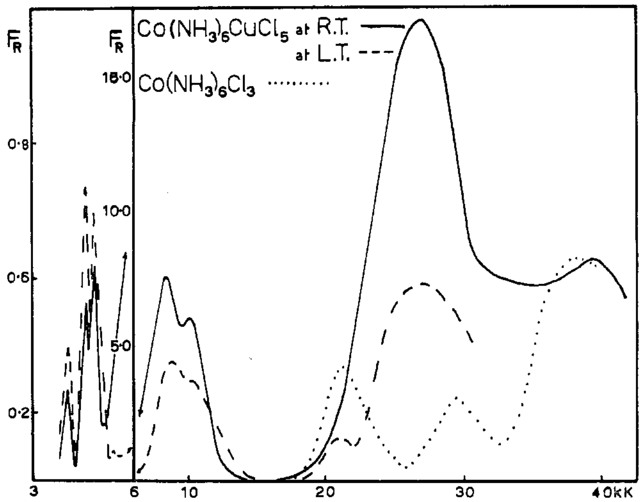

Figure 1.—Reflectance spectrum of $Co(NH_3)_6CuCl_5$ at room temperature (solid line) and liquid N_2 temperature (broken line). The reflectance spectrum of $Co(NH_3)_6Cl_3$ is shown as a dotted line.

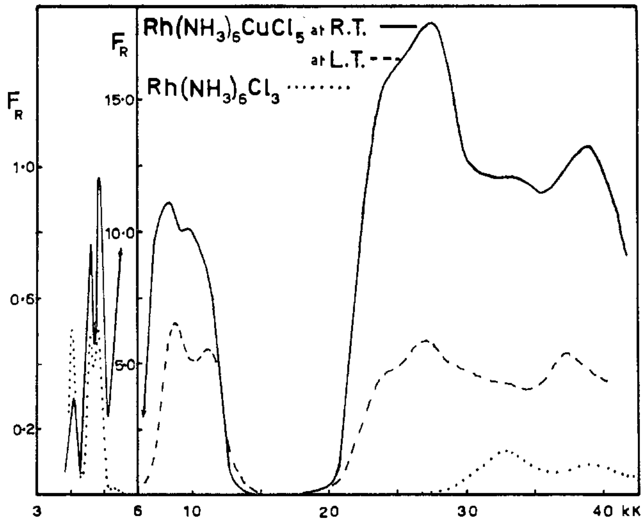

Figure 2.—Reflectance spectrum of $Rh(NH_3)_6CuCl_5$ at room temperature (solid line) and liquid N_2 temperature (broken line). The reflectance spectrum of $Rh(NH_3)_6Cl_3$ is shown as a dotted line.

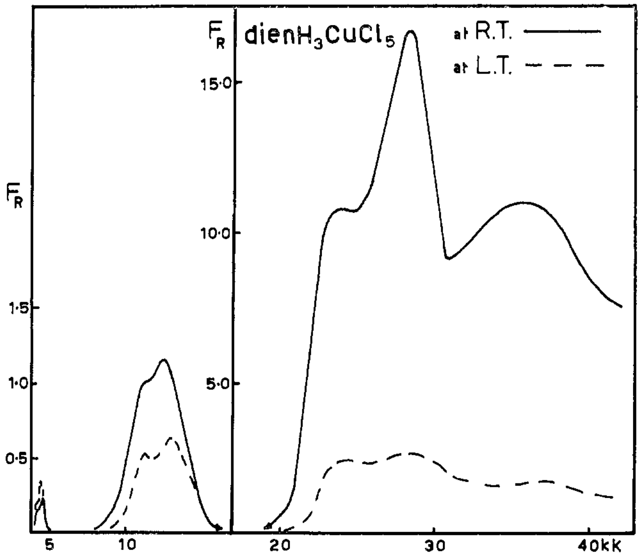

Figure 3.—Reflectance spectrum of $dienH_3CuCl_5$ at room temperature (solid line) and liquid N_2 temperature (broken line).

and the two ligands on the z axis give rise to a splitting characterized by Δ_2. The energy formulas are calculated to be

$$E[z^2] = E[A_1'] = 6\Delta_1 + 2\Delta_2$$

$$E\begin{bmatrix} xy \\ x^2 - y^2 \end{bmatrix} = E[E'] = \Delta_1 - 2\Delta_2 \qquad (1)$$

$$E\begin{bmatrix} xz \\ yz \end{bmatrix} = E[E''] = -4\Delta_1 + \Delta_2$$

Assuming provisionally that $\Delta_1 \geqslant \Delta_2$, the 3d–3d transitions for the Cu^{II} $3d^9$ ion are (a) for the lower frequency band

$$\Delta E_1 = 5\Delta_1 + 4\Delta_2 \quad (^2A_1' \longrightarrow {}^2E') \qquad (2)$$

and (b) for the higher frequency band

$$\Delta E_2 = 10\Delta_1 + \Delta_2 \quad (^2A_1' \longrightarrow {}^2E'') \qquad (3)$$

On this assumption, the values of Δ_1 and Δ_2 were deduced for each pentachlorocuprate(II) complex studied. The values obtained, together with the frequencies of the observed bands assigned to 3d–3d transitions at both room and liquid nitrogen temperatures, are listed in Table II. For complexes of type $M^{III}(NH_3)_6CuCl_5$ the values of Δ_1 and Δ_2 are very similar. On this assignment, the splitting due to the equatorial ligands is on the average 5% higher than that due to the axial

TABLE II

THE FREQUENCIES (kK) AND CALCULATED VALUES OF Δ_1 AND Δ_2 FOR THE $CuCl_5^{3-}$ ION

Complex	First C–F transition		Second C–F transition		Δ_1		Δ_2	
	Room temp	Low temp	Room temp	Low temp	Room temp	Low temp	Room temp	Low temp
$Cr(NH_3)_6CuCl_5$	8.33	8.70	10.00	10.81	0.91	0.99	0.95	0.94
$Co(NH_3)_6CuCl_5$	8.40	8.88	10.10	10.81	0.91	0.98	0.96	0.99
$Rh(NH_3)_6CuCl_5$	8.26	9.01	9.90	10.99	0.90	1.00	0.95	1.00
$Ru(NH_3)_6CuCl_5$	8.50	9.01	10.20	10.81	0.92	1.03	0.97	0.98
$dienH_3CuCl_5$	11.36	11.36	12.50	12.99	1.10	1.16	1.46	1.39

TABLE III

THE FREQUENCIES, HALF-WIDTHS (WHERE MEASURABLE), AND ASSIGNMENTS OF THE FAR-INFRARED BANDS FOR THE PENTACHLOROCUPRATE(II) COMPLEXES AND STARTING METAL AMMINES

Complex	T_{1u} $M^{3+}\cdots N$ str, cm^{-1}	T_{1u} $M^{3+}\cdots N$ def, cm^{-1}	E' $Cu(II)\cdots Cl$ str, cm^{-1}
$Cr(NH_3)_6Cl_3$	468 (Δ = 28), 457 (Δ = 16)	291 sh, 283 (Δ = 30), 273	. . .
$Cr(NH_3)_6CuCl_5$	. . . 461 (Δ = 15)	. . . 280 (Δ = 37), . . .	270 (Δ = 35)
$Co(NH_3)_6Cl_3$	(498)	339 sh, 328 (Δ = 60), 291 sh	. . .
$Co(NH_3)_6CuCl_5$	483 (Δ = 12), 463 (Δ = 12)	. . . 333 (Δ = 28), . . .	273 (Δ = 30)
$Rh(NH_3)_6Cl_3$	477 (Δ = 22)	333 sh, 308 sh, 299, 293 sh	. . .
$Rh(NH_3)_6CuCl_5$	467 (Δ = 10)	339 sh, 312 sh, 299, 282 sh	274 sh
$Ru(NH_3)_6Cl_3$	463 (Δ = 32), 453 (Δ = 12)	294 sh, 286	. . .
$Ru(NH_3)CuCl_5$	. . . 455 (Δ = 13)	294 (Δ = 18), 283 (Δ = 26)	267 sh

ligands for metal hexaammine complexes at room temperature. No significant variations in the values of Δ_1 and Δ_2 with properties of the cation were observed for cations of type $M^{III}(NH_3)_6^{3+}$ where M^{III} = Co, Cr, Rh, or Ru. However, for the diethylenetriammonium complex, Δ_1 and Δ_2 were found to be markedly different, Δ_1 being approximately equal to $^2/_3\Delta_2$. This may be interpreted as indicative of some distortion of the $CuCl_5^{3-}$ ion in this compound and one might expect corresponding alterations in the Cu–Cl distances.

The temperature dependence of the frequency maxima is particularly interesting. Both band maxima shift to higher frequencies as the temperature decreases, as would be expected for ligand-field or crystal-field transitions if the lattice vibrations are appreciably anharmonic. If we denote the increase in Δ_1 and Δ_2 on passing from room temperature (~300°K) to 90°K as δ_1 and δ_2, respectively, the ratios of the band shifts predicted by eq 1 are

$$\left.\begin{aligned} \frac{\delta E(^2A_1' \longrightarrow {}^2E')}{\delta E(^2A_1' \longrightarrow {}^2E')} &= 2 \qquad (\delta_1 \gg \delta_2) \\ \frac{\delta E(^2A_1' \longrightarrow {}^2E')}{\delta E(^2A_1' \longrightarrow {}^2E')} &= \frac{1}{4} \qquad (\delta_1 \ll \delta_2) \end{aligned}\right\} \qquad (4)$$

For the four metal hexaammine complexes, the average value of the ratios of the shifts of the higher and lower frequency bands is 1.6. This is in reasonable accord with the assignment of them to transitions to $^2E''$ and $^2E'$ levels, respectively, with $\delta_1 > \delta_2$, and implies that lattice contraction accompanying temperature decrease affects the equatorial Cu···Cl distances more than the axial Cu···Cl distances. This is in agreement with the crystal structure proposed by Mori, *et al.*,[2b] as the axial ligands are directed along the body diagonal of the unit cell, while the equatorial ligands are directed along the shorter face diagonal (*cf.* Figure 4). We would therefore expect that the increase of Δ_1 on cooling will considerably exceed that of Δ_2. This qualitative argument is the basis of the assignments proposed above.

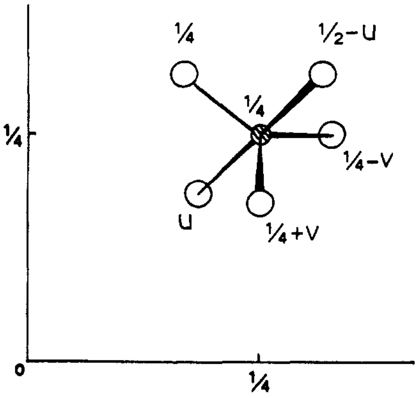

Figure 4.—The structure of the $CuCl_5^{3-}$ ion according to Mori, *et al.*,[2b] (Cu at $^1/_4$, $^1/_4$, $^1/_4$).

This interpretation of the temperature dependence of the band maxima assumes that variations in the splitting can be explained, in first-order approximation, in terms of crystal-field theory. It is not yet known how this would be modified in a more general ligand-field approach. However it should be borne in mind that the crystal-field approximation has been used with some success in interpreting the trends of equilibrium internuclear distances in transition metal complexes and in a number of qualitative interpretations of the temperature dependence of band maxima.[8]

It is of interest that the two infrared bands of the $CuCl_5^{3-}$ ion are of comparable intensity. If the transitions were made partially allowed by d–p mixing in the D_{3h} field, only one excited state ($^2E'$) would be accessible by an electric dipole transition. This suggests that the dipole moment is in fact generated by a different mechanism, possibly by vibronic coupling to charge-transfer states.

Far-Infrared Spectra.—The infrared spectra in the CsBr region for the pentachlorocuprate(II) complexes and the appropriate starting metal ammine complexes are listed and assigned in Table III.

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(8) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Inc., New York, N. Y., 1962, pp 287–295.

The relatively weak bands observed in the 500–450-cm^{-1} region are assigned to the T_{1u} metal–nitrogen (M–N) stretching vibrations which are split in the solid state owing to the low-site symmetry of the metal atom in the crystal.[9] There appears to be evidence for hydrogen bonding between the N–H of the ammine complex ions and anions such as halogens. It is noted that the relatively weak M–N stretching vibrations are significantly shifted, intensified, and sharpened on going from the $M^{III}(NH_3)_6Cl_3$ compound to the corresponding pentachlorocuprate(II) complex. This may indicate that complexing the $M^{III}(NH_3)_6{}^{3+}$ ion (where M^{III} = Cr, Co, Rh, or Ru) in a compound of type $M^{III}(NH_3)_6CuCl_5$ decreases the broadening of the M–N stretching vibration which results from hydrogen bonding in compounds of type $M^{III}(NH_3)_6Cl_3$.

The bands observed in the 340–270-cm^{-1} region are assigned to the $NM^{III}N$ deformation vibration. The resolution of these bands is considerably improved for the pentachlorocuprate(II) complexes. The $CuCl_5{}^{3-}$ ion has two fundamental species A_1' and E', respectively. The selection rules for D_{3h} show that both of these are Raman active since A_1' and E' are both contained in Γ_α but that only the E' fundamental is infrared active since Γ_t contains E' but not A_1'.

The $Cu(II)\cdots Cl$ E' stretching vibration observed at 273 cm^{-1} ($\Delta = 30$) is clearly resolved in the $Co(NH_3)_6CuCl_5$ complex only. The tail of the $N\cdots M^{III}\cdots N$ bending modes for the $Cr(NH_3)_6{}^{3+}$, $Rh(NH_3)_6{}^{3+}$, and $Ru(NH_3)_6{}^{3+}$ cations extends into the 280–270-cm^{-1} region. As a result, in the corresponding pentachlorocuprate(II) complexes the $Cu(II)\cdots Cl$ stretching vibration is observed only as a strong shoulder to one side of the stronger $N\cdots M^{III}\cdots N$ deformation. The appearance of a single band at closely similar frequencies in this region is good evidence that the $CuCl_5{}^{3-}$ ion has the same symmetry in all the metal hexaammine complexes.

For the complex formulated as $dienH_3CuCl_5$, however, the presence of the $CuCl_5{}^{3-}$ ion could not be demonstrated unambiguously since the infrared spectrum, although similar to those of the corresponding metal hexaammine complexes, was not sufficiently well resolved. The observed absorption maxima have not, therefore, been included in Table III.

Acknowledgment.—We wish to thank the Science Research Council for a maintenance grant to G. C. A., and we thank Dr. P. Goggin (University of Bristol) for measurements of infrared spectra.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF UTAH, SALT LAKE CITY, UTAH 84112

Fluorine-19 Nuclear Magnetic Resonance Study of Mixed Adducts of Titanium Tetrafluoride

BY DANIEL S. DYER AND RONALD O. RAGSDALE

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A new $TiF_4\cdot 2$(donor) complex in which the two donor molecules are nonidentical is reported. $TiF_4\cdot 2CH_3C(O)N(CH_3)_2$ was found to undergo exchange reactions in which one of the N,N-dimethylacetamide molecules is replaced by a *para*-substituted pyridine 1-oxide. Seven complexes of general formula $TiF_4\cdot CH_3C(O)N(CH_3)_2,4\text{-}ZC_5H_4NO$, where Z represents a *para*-substituent, were studied by F^{19} nmr. The chemical shifts were correlated with appropriate Hammett substituent constants.

Introduction

The behavior of titanium tetrafluoride toward a variety of organic donor molecules has been described.[1] Monofunctional donors coordinating through oxygen form octahedral complexes of the type $TiF_4\cdot 2$(donor), reflecting the tendency of titanium to achieve sixfold coordination. Nmr data showed that in these complexes the donor molecules coordinate at positions *cis* to each other.[1,2] In this paper a new $TiF_4\cdot 2D$ (D = donor) complex is reported in which the two donor molecules in the octahedron are nonidentical. A series of $TiF_4\cdot D,D'$ complexes was studied, where D is N,N-dimethylacetamide (DMA) and D′ is a *para*-substituted pyridine 1-oxide. The compounds investigated have the general formula $TiF_4\cdot DMA,4\text{-}ZC_5H_4NO$, where Z represents CH_3O, CH_3, H, Cl, Br, $CH_3OC(O)$, and NO_2. The structure of these complexes was established by a study of the nuclear magnetic resonance spectra.

Experimental Section

Materials.—Practical grade chloroacetonitrile and N,N-dimethylacetamide were purified by standard literature procedures. Titanium tetrafluoride obtained from Allied Chemical Corp. was used without further purification. $TiF_4\cdot 2DMA$ was prepared by the method of Muetterties.[1] All pyridine 1-oxides except 4-chloro- and 4-bromopyridine 1-oxides and methyl pyridine-4-carboxylate 1-oxide were obtained from Aldrich Chemical Co. Pyridine 1-oxide was purified by vacuum sublimation. 4-Methoxypyridine 1-oxide was purified by recrystalliza-

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(1) E. L. Muetterties, *J. Am. Chem. Soc.*, **82**, 1082 (1960).

(2) R. O. Ragsdale and B. B. Stewart, *Inorg. Chem.*, **2**, 1002 (1963).