From the data reported in Table III it is apparent that the CO stretching occurs at higher frequencies in $Mo(CO)_3((C_6H_5)_3PO)_3$ and $Mo(CO)_3(C_5H_5NO)_3$ than in $Mo(CO)_3$dien.[11] Therefore it seems reasonable to assume that pyridine N-oxide and triphenylphosphine oxide are more π-acceptor ligands than the halogens. These considerations lead us to assign the A′ (1) mode to the band at the lowest frequency, the A′ (2) mode to the band at the highest frequency, and the A″ mode to the band of intermediate frequency.

TABLE III

CO STRETCHING FREQUENCIES (CM^{-1})

Compound	CO in Nujol mull	
$Mo(CO)_3$dien[a]	1887	1734
$Mo(CO)_3((C_6H_5)_3PO)_3$	1897	1758
		1733
$Mo(CO)_3(C_5H_5NO)_3$	1919	1780

[a] dien = diethylenetriamine.

The comparison of the infrared spectra of our compounds with those of the analogous derivatives having tertiary phosphines and pyridines as ligands (Table II) shows that in compounds with oxygen as the donor atom the CO stretching vibrations occur at lower frequencies. This is in accord with the well-known aptitude of tricovalent phosphorus and nitrogen in the pyridine to form bonds with fairly strong π character.

The dipole moment measurements were confined to the series $Re(CO)_3((C_6H_5)_3PO)_2X$ (where X = Cl, Br, I) owing to the poor solubility of the other compounds in suitable solvents. The observed values of 8–10 D. (Table I) compared with the values of 7.6 and 3 D. observed for *cis*- and *trans*-$Re(CO)_3((C_6H_5)_3P)_2I$,[12] respectively, confirm the *cis* structure as deduced above on the basis of the infrared spectra. The higher values for $Re(CO)_3((C_6H_5)_3PO)_2X$ may be explained by the increasing of the moment from phosphine to phosphine oxide; a similar increase was observed in the dipole moments of $Ni((C_2H_5)_3P)_2(NO_3)_2$ and $Ni((C_2H_5)_3PO)_2(NO_3)_2$ reported as 8.85 and 10.51 D., respectively.[13,14]

It is interesting to note that the dipole moments increase in the series Cl, Br, I, *i.e.*, 8.15, 8.78, and 10.11 D., respectively. This may be explained as an increasing effect of back-donation from metal to the halogen atom in such a way as to overcome the normal electrostatic effect or by an increasing distortion from a regular octahedral structure by the bulkier halogens.

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Polarized Crystal Spectrum of Pentaamminecupric Ammonium Perchlorate

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The preparation and crystal structure of $Cu(NH_3)_5(ClO_4)_2NH_4ClO_4$ have been described.[1] This compound is one of the few so far characterized as containing square-planar, four-coordinated Cu(II) without z-axis ligands. $Cu(NH_3)_4^{2+}$ ions are stacked along the c axis of the tetragonal unit cell and the fifth ammonia molecule is at such a distance (3.75 A) from each of two copper atoms that we may reasonably ignore it in our considerations of metal–ligand interactions in the crystal. The compound is very suitable for the application of single-crystal polarized spectroscopy to the problem of the d-orbital energy order in $Cu(NH_3)_4^{2+}$ since the crystal structure is favorable and we might expect that the absence of axial ligands should produce a greater splitting of the one-electron levels and hence better resolution of the d–d transitions than is observed in other cuprammine species. Since the point group is D_{4h}, we should be able to assign the $d_{xy} \rightarrow d_{x^2-y^2}$ transition, since the vibronic coupling scheme outlined in Table II shows that this is forbidden in z polarization. Furthermore, we are justified in considering only σ bonding in the discussion of the electronic structure of a copper–ammonia complex.

Since the site symmetry of the copper atom is D_{2d} and there are two molecules per unit cell, site-group and factor-group perturbations should strictly be taken into account, but we shall assume that these are negligible.

Experimental Section

Preparation.—Pentaamminecupric ammonium perchlorate was prepared by adding 1 M aqueous ammonium perchlorate to 0.1 M cupric nitrate to which ammonia had been added in the molar ratio 6:1. Deep blue crystals rapidly precipitated. These included large rectangular plates, suitable for crystal spectroscopy.

Analysis.—Perchlorate was determined gravimetrically as $KClO_4$, while copper was weighed as $Cu(py)_2(SCN)_2$. *Anal.* Calcd for $CuNH_4(ClO_4)_3(NH_3)_5$: Cu, 13.7; ClO_4, 62.4. Found· Cu, 13.4; ClO_4, 62.8.

Spectra.—Crystal spectra were measured at room temperature by means of a microspectrophotometer constructed in this laboratory.[2] The plane of polarization of the incident beam was polarized parallel to or perpendicular to the ionic planes, these being normal to the c axis. The spectra obtained are shown in Figure 1, and their features are summarized in Table I. The dimensions of the crystals employed were approximately 250 × 100 × 20 μ and extinction coefficients were calculated from the measured thickness and the crystallographic density of 1.84 g/ml. The thickness was obtained by means of a microscope with a micrometer attachment, the estimated error being ±10%.

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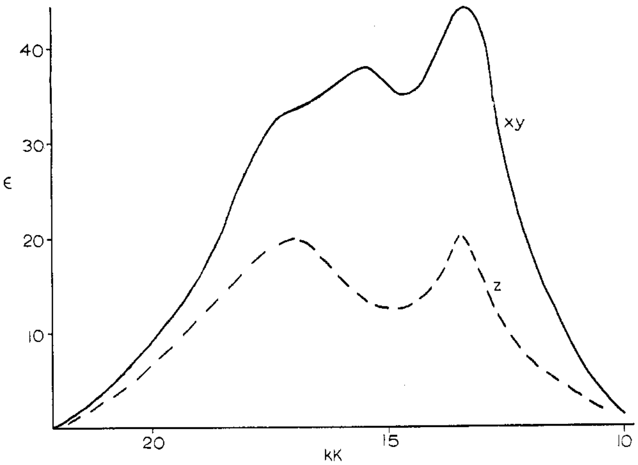

Figure 1.—Crystal spectrum of $Cu(NH_3)_5(ClO_4)_2NH_4ClO_4$, with incident light polarized parallel (z) or perpendicular (xy) to the c axis. ϵ is in units of M^{-1} cm^{-1}; 1 kK = 10^3 cm^{-1}.

Results and Discussion

In a field of tetragonal symmetry, the d orbitals are split into four levels: b_{1g} ($d_{x^2-y^2}$), a_{1g} (d_{z^2}), b_{2g} (d_{xy}), and e_g ($d_{xz,yz}$). The evidence suggests that the b_{1g} level is highest in energy,[3] in agreement with the predictions of the crystal field and molecular orbital theories. The relative energies of the remaining one-electron levels are not predictable and are probably variable, depending on the metal and ligands. Studies of solution spectra, and particularly of the effects of axial solvation, of planar complexes have provided evidence for a number of possible orders.[4-6] Polarized crystal spectra of square-planar d^8 systems have been difficult to interpret,[7-9] partly because of the presence of spin-forbidden bands. Studies of d^9 complexes have usually involved bis chelates[10,11] which belong to the D_{2h} point group where the selection rules are unfavorable.[12]

The crystal spectrum of pentaamminecupric ammonium perchlorate is shown in Figure 1 and detailed in Table I.

Table I

Observed Bands, Polarizations, and Assignments

E, kK[a]	Direction of polarization[b]	Assignment (D_{4h} point group)
17.0	xy	$^2B_{1g} \rightarrow {}^2E_g$
17.0	z	$^2B_{1g} \rightarrow {}^2E_g$
15.5	xy	$^2B_{1g} \rightarrow B_{2g}$
13.4	xy	$^2B_{1g} \rightarrow {}^2A_{1g}$
13.5	z	$^2B_{1g} \rightarrow {}^2A_{1g}$

[a] 1 kK = 10^3 cm^{-1}. [b] The x and y axes are directed along the Cu–N directions.

The spectrum shows three bands in xy polarization at 17.0, 15.5, and 13.4 kK. In z polarization there are only two bands, at 17.0 and 13.5 kK. This is in agreement with the vibronic coupling scheme shown in Table II, which predicts that one band should be forbidden in z polarization.

Table II

Vibronic Coupling Scheme in D_{4h} Microsymmetry[a]

d–d transition	Perturbing vibration	u excited state
$^2B_{1g} \rightarrow {}^2A_{1g}$	E_u	^2E_u (xy)
	B_{2u}	$^2A_{2u}$ (z)
$^2B_{1g} \rightarrow {}^2B_{2g}$	E_u	^2E_u (xy)
$^2B_{1g} \rightarrow {}^2E_g$	E_u	$^2A_{2u}$ (z)
	$\left.\begin{matrix}A_{2u}\\B_{2u}\end{matrix}\right\}$	^2E_u (xy)

[a] Only modes of the CuN_4 chromophore have been considered.

The central band in xy polarization is thus assigned to the $d_{xy} \rightarrow d_{x^2-y^2}$ transition. The spectrum is compatible with two possible orderings of the d-orbital energies: (i) $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz,yz}$ and (ii) $d_{x^2-y^2} > d_{xz,yz} > d_{xy} > d_{z^2}$.

Both crystal field and molecular orbital arguments favor order i since the d_{xy} orbital should lie higher in energy than the $d_{xz,yz}$ when the axial field is negligible, and the σ-antibonding d_{z^2} orbital would not be expected to be lower in energy than the nonbonding orbitals in the absence of π interaction, as appears to be the case in $PtCl_4^{2-}$.[7]

The esr measurements on $Cu(NH_3)_4PtCl_4$[13] provide experimental evidence for order i. The powder reflectance spectrum of this compound[7] suggests that the Cu(II) ligand field absorption is essentially similar to that of $Cu(NH_3)_5(ClO_4)_2NH_4ClO_4$. The values of $g_{\|}$ and $g_{\perp}$ in $Cu(NH_3)_4PtCl_4$ were 2.217 and 2.051, respectively. In a tetragonal d^9 system the g values are given[14] by $g_{\|} = 2.0023(1 + 4\sigma\lambda_0/\Delta_1)$ and $g_{\perp} = 2.0023(1 + \sigma\lambda_0/\Delta_2)$, where λ_0 is the spin–orbit coupling constant for the free metal ion, Δ_1 is the energy difference between the d_{xy} and $d_{x^2-y^2}$ orbitals, Δ_2 is the energy difference between the $d_{xz,yz}$ and $d_{x^2-y^2}$ orbitals, and σ is the spin–orbit reduction factor.[15]

Using the g values reported by Fritz and Keller,[13] these expressions yield $\Delta_1/\Delta_2 = 0.91$, the same as the value we obtain from our spectrum on the basis of order i. Order ii would require $\Delta_1/\Delta_2 = 1.16$. Taking $\lambda_0 = 829$ cm^{-1}, we obtain $\sigma = 0.50$.

Measurements at liquid hydrogen temperature will shortly be made in the hope that these may help to resolve any uncertainties which our neglect of site-group and factor-group perturbations and of spin–orbit coupling may have introduced.

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Free Rotation of Methyl Groups in Dimethyltin Difluoride[1a]

BY J. J. RUSH[1b] AND WALTER C. HAMILTON[1c]

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The structure of dimethyltin difluoride, $(CH_3)_2SnF_2$, has recently been determined by X-ray diffraction[2] to be tetragonal, with $a = 4.24$ and $c = 14.16$ A and two "molecules" per unit cell. The crystal arrangement consists of an infinite two-dimensional network of tin atoms and bridging fluorine atoms, with the methyl groups above and below the plane, completing octahedral coordination of the tin. The structural data, however, yielded little information on the methyl-group hydrogen atoms, owing to the small contribution of the hydrogen to the X-ray scattering. Since the methyl groups lie on a fourfold symmetry axis, it is reasonable to assume that they are either rotating or at least fourfold disordered.

In this note we report a study of the rotation of the methyl groups in $(CH_3)_2SnF_2$ by total cross-section measurements with subthermal neutrons. The neutron cross-section method has been shown to be quite useful for the investigation of the motions of hydrogen atoms in solids and liquids.[3-6] At "cold" neutron energies ($E_n \ll 0.025$ ev) the total scattering cross section, σ_s, has the form σ_s (barns) $= a + c\lambda_n$, where λ_n is the neutron wavelength (A). The slope c (barns/A) is a direct measure of the change in the inelastic scattering with wavelength and basically depends on the population of excited rotational and vibrational states available for exchange of energy with the cold neutrons incident on the scattering sample. Owing to the large, incoherent proton-scattering cross section, the slopes for hydrogenous compounds will primarily be a measure of the freedom of motion of the hydrogen atoms.

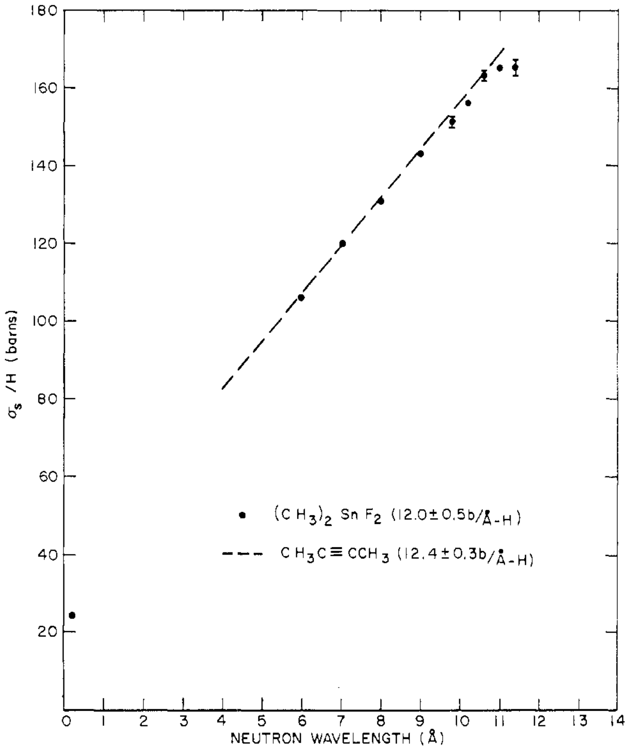

Figure 1.—Neutron-scattering cross sections per hydrogen atom for $(CH_3)_2SnF_2$ at 23°. Previous cross-section results for $CH_3C\equiv CCH_3$ are also shown (dashed line). The error bars represent the statistical errors due to counting ($\lesssim 1\%$). The errors on the slopes include statistical errors, as well as the estimated systematic uncertainties due to sample-packing and Bragg-scattering effects.

The total cross sections for polycrystalline, reagent grade $(CH_3)_2SnF_2$ were obtained by neutron transmission measurements, using the Columbia crystal spectrometer at the Brookhaven graphite reactor.[7] The technique of sample preparation has been described elsewhere.[4-6] Cross sections per molecule were corrected for neutron absorption and divided by the number of hydrogen atoms to obtain cross sections per hydrogen atom (σ_s/H). The results are plotted in Figure 1. Also shown in the figure are cross-section results previously measured for dimethylacetylene[5] (dashed line), a compound for which the barrier to rotation of the methyl groups is considered to be negligible.[8] The scatter of the points above 10 A in the $(CH_3)_2SnF_2$ results probably arises from intense Bragg scattering of the long-wavelength neutrons.

The cross-section slope for $(CH_3)_2SnF_2$ is 12 barns/A H, with an estimated error of ±0.5, quite close to the value of 12.0 ± 0.4 for $CH_3C\equiv CCH_3$. The similarity of these results is evidence for a low barrier to rotation in $(CH_3)_2SnF_2$, with only slight interaction of the methyl groups with other methyl groups and atoms in the crystal lattice. It is interesting to note that the C–Sn–C distance (4.2 A)[2] is also very close to the distance between methyl groups in $CH_3C\equiv CCH_3$ (4.3 A).

The slope of 12 is also quite similar to those measured for nonadjacent methyl groups in methylbenzenes

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