

TABLE I

Assignment	RAMAN FREQUENCIES FOR ZnX_4^{2-} SPECIES (cm^{-1}) ^e					
	Cs_2ZnCl_4	$(ZnCl_4^{2-})$ (aq)	Cs_2ZnBr_4	$(ZnBr_4^{2-})$ (aq)	Cs_2ZnI_4	(ZnI_4^{2-}) (aq)
ν_1 (A_1)	288 s	280, ^a 278, ^b 275 ^c	178 s	172, ^a 172, ^c 172 ^d	130 s	122 ^a
ν_2 (E)	116 w	82–116, ^a 110, ^b 79 ^c	80 m	61, ^a 66, ^c 63 ^d	60 w	44 ^a
ν_3 (F_2)	298 m	280, ^a 278, ^b 306 ^c	212 m	210, ^a 208, ^c 213 ^d	172 w	170 ^a
ν_4 (F_2)	130 w	82–116, ^a 110, ^b 104 ^c	89 m	82, ^a 88, ^c 81 ^d	70 w	62 ^a

^a Reference 5. ^b Reference 8. ^c Reference 6. ^d Reference 7. ^e Band description: s, strong; m, medium; w, weak.

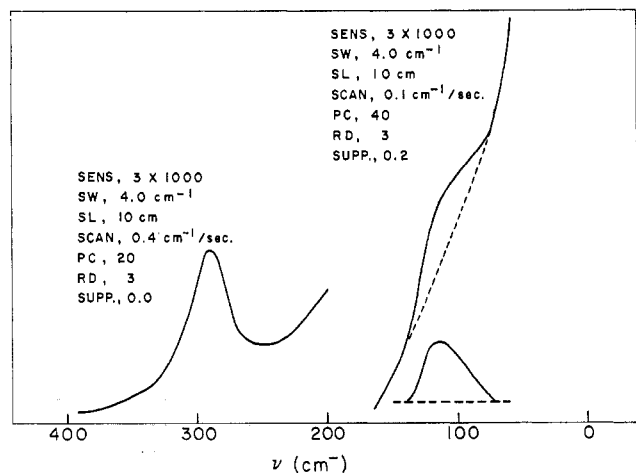


Figure 1.—Raman spectrum of 2.88 *M* $ZnCl_2$ –9.35 *M* HCl aqueous solution showing a horizontal projection of 110- cm^{-1} band. A Cary Model 81 Raman spectrophotometer and a 15-amp lamp current were used. Abbreviations: SENS = sensitivity setting, SW = slit width, SL = slit length, SCAN = scan speed, PC = period control, RD = Raman dynode setting, and SUPP = zero suppression setting.

but the difference is only 5 cm^{-1} . The low-frequency solution band for $ZnCl_4^{2-}$ is quite broad in the published spectra.^{5,8} Figure 1 shows this band as obtained in our laboratory for a solution containing 2.88 *M* $ZnCl_2$ and 9.35 *M* HCl . It is centered at 110 cm^{-1} and has a width at half-height of 40 cm^{-1} . We expect that if $ZnCl_4^{2-}$ remains tetrahedral on dissolution, the ν_2 and ν_4 frequencies should decrease by about the same amount (~ 16 and ~ 8 cm^{-1} , respectively) as for $ZnBr_4^{2-}$ and ZnI_4^{2-} . The resulting frequencies at 100 and 122 cm^{-1} could clearly both be contained in the observed solution band. It would appear that the two tetrahedral bending modes of $ZnCl_4^{2-}$ are simply broadened and merged into one envelope by interaction with the aqueous medium. A similar phenomenon has been observed for the tetrahalo complexes of thallium(III). Here also solution Raman spectra show two bands in the bending region for $TlBr_4^-$,¹¹ but only one for $TlCl_4^-$.¹²

Direct evidence that all three tetrahalo species remain tetrahedral upon dissolution is provided by the symmetric stretching frequency (ν_1), which is lowered by only 6–8 cm^{-1} in each case. Since ν_1 is primarily a measure of the $Zn-X$ stretching force constant, and therefore presumably of the $Zn-X$ bond strength, one would certainly expect a change in coordination of $ZnCl_4^{2-}$ to produce a much greater lowering of ν_1 due to weakening of the $Zn-Cl$ bonds through increased

$Cl-Cl$ repulsion and the necessary rehybridization of the zinc orbitals. Any reasonable bonding scheme for square-planar $ZnCl_4^{2-}$ must involve the outer 5s, 5p, or 4d orbitals of zinc. Such a structure could be stabilized by the coordination of two waters at the *trans*-octahedral positions, but the $Zn-Cl$ bonds themselves would be weaker than in tetrahedral $ZnCl_4^{2-}$. There is no known precedent for the proposed $ZnCl_4^{2-}$ (T_d) \rightarrow $ZnCl_4(H_2O)_2^{2-}$ (D_{4h}) transformation. However, there are a number of transformations of the type MX_4^z (T_d) \rightarrow MX_6^{z-2} (O_h), and every case for which spectral data are available involves a marked reduction in the symmetric stretching frequency; e.g., for $SnCl_4$, $\nu_1 = 368$ cm^{-1} ,¹³ and for $SnCl_6^{2-}$, $\nu_1 = 311$ cm^{-1} .¹⁴ Part of this reduction may be due to the increase in charge, but some of it must surely arise from changes in bond type and nonbonded repulsion. It seems to us that the only reasonable interpretation for the observation that $ZnCl_4^{2-}$ undergoes the same slight shift in ν_1 on dissolution as do $ZnBr_4^{2-}$ and ZnI_4^{2-} is that the first complex also retains its tetrahedral coordination.

Acknowledgment.—This work was supported by the National Science Foundation, under Grant GP 3404.

(13) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 106.

(14) Reference 13, p 119.

CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE ED INORGANICA DELL'UNIVERSITÀ DEGLI STUDI, MILAN, ITALY

Substituted Halocarbonyl Complexes of Rhenium(I) with Ligands Having Oxygen as the Donor Atom

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The first replacement reaction of carbon monoxide on metal carbonyls with ligands having oxygen as donor atom has been done in our laboratories by allowing molybdenum and tungsten hexacarbonyls to react with tertiary phosphine oxides.¹

Hieber and co-workers² in the reaction of $H_3Mo_2(CO)_6(OH)_3$ with triphenylphosphine oxide obtained a compound which they considered $Mo(CO)_3(C_6H_5)_3$ –

(1) F. Canziani, F. Zingales, and U. Sartorelli, *Gazz. Chim. Ital.*, **94**, 841 (1964).

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(11) M. L. Delwaille, *Compt. Rend.*, **238**, 2522 (1954).

(12) T. G. Spiro, *Inorg. Chem.*, **4**, 1290 (1965).

PO; a further study of this reaction however led us to the conclusion that the binuclear compound $[\text{Mo}(\text{CO})_3((\text{C}_6\text{H}_5)_3\text{PO})(\text{H}_2\text{O})]_2$ was first formed, which at higher temperature gave $\text{Mo}(\text{CO})_3((\text{C}_6\text{H}_5)_3\text{PO})_3$.³

Recently, the analogous trisubstituted compound of molybdenum hexacarbonyl with triphenylarsine oxide has been prepared and characterized.⁴

We have now carried on the study of this substitution reaction on halopentacarbonylrhenium(I). In this note we will describe the preparations and properties of the disubstituted derivatives of formulas $\text{Re}(\text{CO})_5\text{-L}_2\text{X}$ and $\text{Re}(\text{CO})_5\text{DX}$, where X is Cl, Br, or I, L is a monodentate ligand such as triphenylphosphine oxide or pyridine N-oxide, and D is a bidentate ligand such as 1,2-bis(diphenylphosphine oxide)ethane (DPO_2) and 2,2'-bipyridine N,N'-dioxide (bipyO_2).

Complexes.— $\text{Re}(\text{CO})_5\text{X}$ (1 mmole) in 10 ml of light petroleum and pyridine N-oxide (2 mmoles) dissolved in 5 ml of ethanol were refluxed under nitrogen for 6 hr. The ivory white crystalline products were collected on a filter under nitrogen, washed with ethanol, and dried under vacuum.

Halotricarbonyl(2,2'-bipyridine N,N'-dioxide)rhenium(I) complexes were similarly prepared by reaction between $\text{Re}(\text{CO})_5\text{X}$ (1 mmole) and 2,2'-bipyridine N,N'-dioxide (1 mmole).

Preparation of Tricarbonyltris(pyridine N-oxide)molybdenum.—Tricarbonyl(cycloheptatriene)molybdenum (0.6 g, 2.2 mmoles) and pyridine N-oxide (0.63 g, 6.6 mmoles) were heated at 40°, in 25 ml of benzene, for 1 hr under nitrogen. The orange-yellow crystalline product was collected on a filter under nitrogen, washed with a few milliliters of benzene, and dried under vacuum. It decomposed readily in the air.

Elemental analyses and other data on the complexes are given in Table I.

Halopentacarbonylrhenium complexes were prepared according to Kirkham, *et al.*⁵

TABLE I

Complex	Color	Mp, °C ^a	Dipole moment, D. ^b	Mol wt ^c	Analyses, %				
					C	H	N	Halogen	
$\text{Re}(\text{CO})_5((\text{C}_6\text{H}_5)_3\text{PO})_2\text{I}$	White	189	10.1	Calcd	954	49.11	3.17	...	13.31
				Found	915	49.21	3.23	...	13.05
$\text{Re}(\text{CO})_5((\text{C}_6\text{H}_5)_3\text{PO})_2\text{Br}$	White	178	8.7	Calcd	907	51.66	3.33	...	8.81
				Found	870	53.75	3.48	...	8.58
$\text{Re}(\text{CO})_5((\text{C}_6\text{H}_5)_3\text{PO})_2\text{Cl}$	White	157	8.1	Calcd	862	54.32	3.51	...	4.11
				Found	820	53.2	3.76	...	4.21
$\text{Re}(\text{CO})_5(\text{DPO}_2)\text{I}^d$	Ivory white	222	...	Calcd	...	42.08	2.92	...	15.33
				Found	...	42.87	3.27	...	15.45
$\text{Re}(\text{CO})_5(\text{DPO}_2)\text{Br}$	Ivory white	268	...	Calcd	...	44.62	3.10	...	10.24
				Found	...	44.96	3.21	...	10.11
$\text{Re}(\text{CO})_5(\text{DPO}_2)\text{Cl}$	Ivory white	287	...	Calcd	...	47.32	3.28	...	4.82
				Found	...	47.68	3.47	...	4.65
$\text{Re}(\text{CO})_5(\text{C}_5\text{H}_5\text{NO})_2\text{I}$	Ivory white	170	...	Calcd	587	26.58	1.72	4.77	21.61
				Found	560	26.74	1.80	4.87	21.52
$\text{Re}(\text{CO})_5(\text{C}_5\text{H}_5\text{NO})_2\text{Br}$	Ivory white	165	...	Calcd	540	28.89	1.86	5.18	...
				Found	530	29.08	1.81	5.38	...
$\text{Re}(\text{CO})_5(\text{C}_5\text{H}_5\text{NO})_2\text{Cl}$	Ivory white	162	...	Calcd	496	31.48	2.03	5.65	7.15
				Found	440	30.98	1.82	6.02	7.28
$\text{Re}(\text{CO})_5(\text{bipyO}_2)\text{I}^e$	Yellow	190	...	Calcd	...	26.67	1.38	4.79	21.68
				Found	...	26.77	1.50	5.30	21.93
$\text{Re}(\text{CO})_5(\text{bipyO}_2)\text{Br}$	Yellow	196	...	Calcd	...	29.00	1.50	5.21	...
				Found	...	30.36	1.55	5.71	...
$\text{Re}(\text{CO})_5(\text{bipyO}_2)\text{Cl}$	Yellow	207	...	Calcd	...	31.61	1.63	5.67	...
				Found	...	32.46	1.28	6.03	...
$\text{Mo}(\text{CO})_5(\text{C}_5\text{H}_5\text{NO})_3$	Orange-yellow	Calcd	...	46.56	3.23	9.06	...
				Found	...	46.02	3.54	8.97	...

^a Uncorrected values determined in evacuated tubes. ^b Dielectric constants in benzene at 25° measured with a W.T.W. Dipolmeter, Model DM 01. ^c Determined in chloroform using a Mechrolab osmometer, Model 301 A. ^d DPO_2 = 1,2-bis(diphenylphosphine oxide)ethane. ^e bipyO_2 = 2,2'-bipyridine N,N'-dioxide.

Experimental Section

Preparation of Halotricarbonylbis(triphenylphosphine oxide)rhenium(I) Complexes.— $\text{Re}(\text{CO})_5\text{X}$ (1 mmole) and $(\text{C}_6\text{H}_5)_3\text{PO}$ (2 mmoles) in 15 ml of light petroleum (bp 70–120°) were refluxed under nitrogen for 6 hr. The warm solution was filtered to remove the white crystalline products which were washed with hot ethanol and dried under vacuum. These compounds are soluble in chloroform and methylene chloride and are slightly soluble in benzene and carbon disulfide.

Halotricarbonyl-1,2-bis(diphenylphosphine oxide)ethanerhenium(I) complexes were similarly prepared by reaction between $\text{Re}(\text{CO})_5\text{X}$ (1 mmole) and 1,2-bis(diphenylphosphine oxide)ethane (1 mmole).

Preparation of Halotricarbonylbis(pyridine N-oxide)rhenium(I)

Iodotricarbonylbis(pyridine)rhenium(I) and iodotricarbonyl(2,2'-bipyridine)rhenium(I) were prepared as reported.^{6,7}

Triphenylphosphine oxide and 1,2-bis(diphenylphosphine oxide)ethane were prepared following the method previously reported.¹

The 2,2'-bipyridine N,N'-dioxide was obtained by oxidation of 2,2'-bipyridine with hydrogen peroxide in acetic acid.

Pyridine N-oxide was a Fluka reagent grade product.

Results and Discussion

The reaction of halopentacarbonylrhenium(I) with the ligands reported above led to the replacement of

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(5) W. J. Kirkham, A. G. Osborne, R. S. Nyholm, and M. H. Stiddard, *J. Chem. Soc.*, 550 (1965).

(6) E. W. Abel, G. B. Hargreaves, and G. Wilkinson, *ibid.*, 3149 (1958).

(7) E. W. Abel and G. Wilkinson, *ibid.*, 1501 (1959).

TABLE II
 CO, PO, AND NO STRETCHING FREQUENCIES (CM⁻¹)

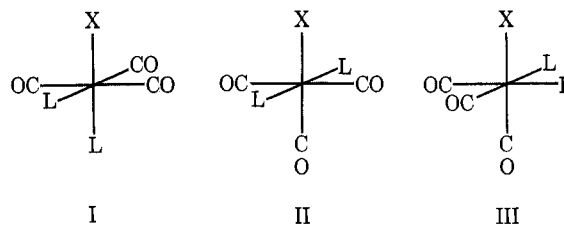
Compound	CO stretches	PO or NO stretches
(C ₆ H ₅) ₃ PO		1190 s ^a 1201 s ^b
Re(CO) ₅ ((C ₆ H ₅) ₃ PO) ₂ I	2013 vs, 1891 vs, 1876 vs ^a 2019 s, 1909 vs, 1902 vs ^b	1209 s, 1187 w, 1152 s ^a 1201 m, 1187 w, 1150 m ^b
Re(CO) ₅ ((C ₆ H ₅) ₃ PO) ₂ Br	2014 vs, 1890 vs, 1873 vs ^a 2022 s, 1909 vs, 1900 vs ^b	1211 s, 1187 w, 1153 s ^a 1201 m, 1185 w, 1151 m ^b
Re(CO) ₅ ((C ₆ H ₅) ₃ PO) ₂ Cl	2013 vs, 1887 vs, 1870 vs ^a 2021 s, 1908 vs, 1900 vs ^b	1210 s, 1187 w, 1153 s ^a 1201 m, 1185 w, 1152 m ^b
DPO ₂ ^d		1187 s, 1175 s ^a
Re(CO) ₅ (DPO ₂)I	2016 vs, 1895 vs, 1879 vs ^a	1181 s, 1161 s ^a
Re(CO) ₅ (DPO ₂)Br	2018 vs, 1892 vs, 1878 vs ^a	1181 s, 1161 s ^a
Re(CO) ₅ (DPO ₂)Cl	2021 vs, 1894 vs, 1878 vs ^a	1181 s, 1161 s ^a
C ₅ H ₅ NO		1242 s ^a
Re(CO) ₅ (C ₅ H ₅ NO) ₂ I	2006 vs, 1886 vs, 1857 vs ^a	1206 s, 1194 s ^a
Re(CO) ₅ (C ₅ H ₅ NO) ₂ Br	2011 vs, 1891 vs, 1849 vs ^a	1203 s, 1196 sh ^a
Re(CO) ₅ (C ₅ H ₅ NO) ₂ Cl	2011 vs, 1889 vs, 1847 vs ^a	1205 s, 1200 sh ^a
bipyO ₂ ^e		1262 s, 1254 s ^a
Re(CO) ₅ (bipyO ₂)I	2001 vs, 1880 vs, 1864 vs ^a	1204 vs, 1184 s ^a
Re(CO) ₅ (bipyO ₂)Br	2004 vs, 1879 vs, 1860 vs ^a	1208 vs, 1186 s ^a
Re(CO) ₅ (bipyO ₂)Cl	2004 vs, 1880 vs, 1860 vs ^a	1206 vs, 1185 s ^a
Re(CO) ₅ ((C ₆ H ₅) ₃ P) ₂ I	2020, 1942, 1887 ^{a,c}	
Re(CO) ₅ (DP)I	2032, 1945, 1885 ^{a,c}	
Re(CO) ₅ (C ₅ H ₅ N) ₂ I	2012, 1913, 1890 ^a	
Re(CO) ₅ (bipy)I	2013, 1909, 1887 ^a	

^{a,b} All spectra were recorded using a Perkin-Elmer Model 621 spectrophotometer: ^a obtained in Nujol mull; ^b obtained in carbon disulfide solution. ^c From ref 12. ^d DPO₂ = 1,2-bis(diphenylphosphine oxide)ethane. ^e bipyO₂ = 2,2'-bipyridine N,N'-dioxide.

two carbon monoxide molecules. The halotricarbonylrhenium(I) complexes were isolated as crystalline solids which appeared to be diamagnetic in the solid state, nonelectrolytic in acetone solution, and monomeric in chloroform.

The tertiary phosphine oxide derivatives are air stable and not decomposed by light; conversely, the compounds containing pyridine N-oxide and 2,2'-bipyridine N,N'-dioxide are decomposed readily in the air. Owing to their poor solubility in certain solvents, the infrared spectra of all compounds have been recorded in Nujol mulls; however, measurements on the complexes containing triphenylphosphine oxide have been taken also in carbon disulfide. The data reported in Table II show that the stretching frequencies of phosphorus-oxygen and nitrogen-oxygen bonds are lowered compared to the free ligand, indicating that, as previously observed,^{1,8,9} the ligands are coordinated to the metal through the oxygen. Further evidence is given by the fact that the dipole moment value observed for Re(CO)₅((C₆H₅)₃PO)₂I is higher than that of the analogous triphenylphosphine derivative Re(CO)₅((C₆H₅)₃P)₂I. When the substituent is a monodentate ligand, the octahedral structures I-III can be envisaged.

It is known that in the halopentacarbonylrhenium(I) the CO group *trans* to the halogen, being more strongly bound to the metal, is less easily replaced than the other four. We may therefore assume that the formation of a compound having a structure such as I is very unlikely. Structure II has C_{2v} symmetry and it is



expected to produce three normal vibration modes (A₁ (1), A₁ (2), B₁), which correspond to two strong bands and a weak one in the infrared spectrum. Structure III has symmetry C_s and it is expected to produce three normal vibration modes (A' (1), A' (2), A'') corresponding to three strong absorption bands in the infrared spectrum.

In our spectra, three strong absorption bands do appear in the carbonyl stretching region between 2030 and 1850 cm⁻¹; therefore, we suggest that the disubstituted compounds Re(CO)₅L₂X have a structure such as III, the same as the chelated compounds Re(CO)₅DX. This interpretation is also supported by the dipole moment values reported in Table I.

The band at the lowest frequency could be assigned to the stretching of the CO group *trans* to the halogen if the ligands have more π-acceptor abilities than the halogen atoms.

To prove this we have prepared the trisubstituted derivatives of Mo(CO)₆ with triphenylphosphine oxide and pyridine N-oxide and compared their spectra with that of Mo(CO)₅dien. It is known that the amines are ligands with a very weak π-acceptor ability, comparable with the π-acceptor ability of the halogens.¹⁰

(8) F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960).

(9) S. M. Horner and S. Y. Tyree, Jr., *Inorg. Chem.*, **1**, 122 (1962).

(10) F. A. Cotton, *ibid.*, **3**, 702 (1964).

From the data reported in Table III it is apparent that the CO stretching occurs at higher frequencies in $\text{Mo}(\text{CO})_3((\text{C}_6\text{H}_5)_3\text{PO})_3$ and $\text{Mo}(\text{CO})_3(\text{C}_5\text{H}_5\text{NO})_3$ than in $\text{Mo}(\text{CO})_3\text{dien}$.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—	
$\text{Mo}(\text{CO})_3\text{dien}^a$	1887	1734
$\text{Mo}(\text{CO})_3((\text{C}_6\text{H}_5)_3\text{PO})_3$	1897	1758
		1733
$\text{Mo}(\text{CO})_3(\text{C}_5\text{H}_5\text{NO})_3$	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 $\text{Re}(\text{CO})_3((\text{C}_6\text{H}_5)_3\text{PO})_2\text{X}$ (where $\text{X} = \text{Cl}, \text{Br}, \text{I}$) 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*- $\text{Re}(\text{CO})_3((\text{C}_6\text{H}_5)_3\text{P})_2\text{I}$,¹² respectively, confirm the *cis* structure as deduced above on the basis of the infrared spectra. The higher values for $\text{Re}(\text{CO})_3((\text{C}_6\text{H}_5)_3\text{PO})_2\text{X}$ may be explained by the increasing of the moment from phosphine to phosphine oxide; a similar increase was observed in the dipole moments of $\text{Ni}((\text{C}_2\text{H}_5)_3\text{P})_2(\text{NO}_3)_2$ and $\text{Ni}((\text{C}_2\text{H}_5)_3\text{PO})_2(\text{NO}_3)_2$ reported as 8.85 and 10.51 D., respectively.^{13,14}

It is interesting to note that the dipole moments increase in the series $\text{Cl}, \text{Br}, \text{I}$, *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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CONTRIBUTION FROM THE INORGANIC
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Polarized Crystal Spectrum of Pentaamminecupric Ammonium Perchlorate

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The preparation and crystal structure of $\text{Cu}(\text{NH}_3)_5(\text{ClO}_4)_2\text{NH}_4\text{ClO}_4$ 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. $\text{Cu}(\text{NH}_3)_4^{2+}$ ions are stacked along the *c* axis of the tetragonal unit cell and the fifth ammonia molecule is at such a distance (3.75 Å) 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 $\text{Cu}(\text{NH}_3)_4^{2+}$ 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 $\text{Cu}(\text{py})_2(\text{SCN})_2$. *Anal.* Calcd for $\text{CuNH}_4(\text{ClO}_4)_2(\text{NH}_3)_5$: 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 $250 \times 100 \times 20 \mu$ 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 $\pm 10\%$.

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