

and under atmospheric conditions, an electron spin resonance spectrum consisting of four lines was observed. The intensity of the spectrum was arbitrarily assigned a value of 1.00.

When the same reaction was repeated in carefully degassed solvent in a vacuum apparatus a four-line electron spin resonance spectrum of relative intensity 1.79 was obtained. The origin of the paramagnetic gold(II) complex may be attributed to (1) ($R = n\text{-C}_4\text{H}_9$, $M = \text{Au}$).

The forementioned experiments demonstrate that the gold(II) *N,N*-di-*n*-butyldithiocarbamate complex is air sensitive. The values of g and $\langle a \rangle$ for this complex are displayed in Table I.

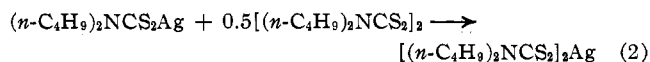
TABLE I
ESR PARAMETERS FOR SOME GOLD(II) AND SILVER(II) DITHIOCARBAMATE COMPLEXES

Complex	g	$\langle a \rangle$, G	Ref
$[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_2\text{Au}$	2.040	29.4	1
$[(n\text{-C}_4\text{H}_9)_2\text{NCS}_2]_2\text{Au}$	2.039	27.5	This work
$[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_2\text{Ag}$	2.019	28.2	1
$[(n\text{-C}_4\text{H}_9)_2\text{NCS}_2]_2\text{Ag}$	2.022	29.0	This work

When tetra-*n*-butylthiuram disulfide was added to a solution containing a mixture of gold(III) and gold(II) *N,N*-di-*n*-butyldithiocarbamate complexes, the intensity of the electron spin resonance spectrum decreased. This behavior supports equilibrium reaction 1 ($R = n\text{-C}_4\text{H}_9$, $M = \text{Au}$).

Silver(I) *N,N*-di-*n*-butyldithiocarbamate was allowed to react with 0.5 molar equiv of tetra-*n*-butylthiuram disulfide under atmospheric conditions. A blue solution formed immediately. The solution contained a paramagnetic complex which produced a two-line electron spin resonance spectrum. The intensity of the spectrum was arbitrarily assigned a value of 1.00.

The same experiment was repeated in carefully degassed solvent. The relative intensity of the resulting electron spin resonance spectrum was 1.86. The origin of the paramagnetic silver(II) complex may be attributed to (2).



The previous behavior suggests that under atmospheric conditions some of the silver(II) *N,N*-di-*n*-butyldithiocarbamate complex formed by (2) is air oxidized to a silver(III) *N,N*-di-*n*-butyldithiocarbamate species. It is possible that the silver(III) complex formed by air oxidation is a bis species of the type $[(n\text{-C}_4\text{H}_9)_2\text{NCS}_2]_2\text{Ag}^+$. This type of structure is proposed because there is not enough ligand present to form a neutral tris silver(III) complex.

When the vacuum line experiment was repeated with the same amount of silver(I) *N,N*-di-*n*-butyldithiocarbamate and 1 molar equiv of tetra-*n*-butylthiuram disulfide, a dark red color immediately appeared. The red color faded after 10 min and was replaced with a blue solution. The relative intensity of the electron spin resonance spectrum was 1.71.

The decrease in the intensity of the electron spin resonance spectrum when 1 molar equiv of tetra-*n*-butylthiuram disulfide was added can be explained as follows. If the electron spin resonance spectra obtained for the two vacuum-line silver reactions were

equal, it would indicate that the silver(I) complex is oxidized only to a silver(II) species, probably *via* (2). In the case of the silver(I) reaction with 1 molar equiv of thiuram disulfide, however, excess thiuram disulfide would remain. If this excess thiuram disulfide further oxidized the silver(II) complex to a tris silver(III) species, there should be a decrease in the intensity of the electron spin resonance spectrum. This decrease is observed experimentally.

The color change from red to blue can be explained by assuming the formation of a red tris silver(III) complex. By considering (1) ($R = n\text{-C}_4\text{H}_9$, $M = \text{Ag}$) the silver(III) complex could participate in an equilibrium with the blue silver(II) species and 0.5 molar equiv of thiuram disulfide. This behavior would be analogous to the gold(III)-gold(II) equilibrium reactions discussed earlier.

The values of g and $\langle a \rangle$ for the silver(II) complex are displayed in Table I. It was not possible to resolve the hyperfine structure due to the silver-107 and -109 isotopes.

The g values for *N,N*-diethylthiocarbamate and *N,N*-di-*n*-butyldithiocarbamate complexes containing the same metal are nearly identical. This likely means that in solution the structures of the complexes are the same. It would be expected that the paramagnetic silver and gold complexes are square planar.

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A New Synthesis of Potassium *cis*- and *trans*-Bis(oxalato)diaquorhodate(III)

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The potassium salts of *cis*- and *trans*-bis(oxalato)diaquorhodate(III) are reported to have been prepared in crystalline form by Gillard and Wilkinson.¹ Other workers have obtained these isomers in solution from the aquation of tris(oxalato)rhodate(III) ion^{2,3} and of *cis*- and *trans*-dichlorobis(oxalato)rhodate(III) ions.⁴

In connection with our continued interest in reactions of rhodium oxalato complexes^{5,6} it became desirable to prepare pure solid salts of the *cis*- and *trans*-bis(oxalato)diaquorhodate(III) ions. In spite of several attempts, we have not been successful in repeating the synthesis as described by Gillard and Wilkinson.¹

(1) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 870 (1964).

(2) (a) D. Barton and G. M. Harris, *Inorg. Chem.*, **1**, 251 (1962); (b) K. V. Krishnamurty, *ibid.*, **1**, 422 (1962).

(3) (a) L. Damrauer, Ph.D. Dissertation, Boston University, 1969; (b) L. Damrauer and R. M. Milburn, *Proc. Int. Conf. Coord. Chem.*, **12**, 38 (1969); (c) L. Damrauer and R. M. Milburn, *J. Amer. Chem. Soc.*, **93**, 6481 (1971).

(4) S. A. Johnson, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 1741 (1963).

(5) L. Damrauer and R. M. Milburn, *J. Amer. Chem. Soc.*, **90**, 3884 (1968).

TABLE I
SPECTRAL CHARACTERISTICS OBSERVED FOR *cis*- AND *trans*-BIS(OXALATO)DIAQUORHODATE(III) IONS OBTAINED BY
AQUATION OF TRIS(OXALATO)RHODATE(III) ION

Isomer	Method of sepn	Investigators	λ_{max} , nm	Absorbancy coeff
Cis	Chloride-exchange column	Gillard and Wilkinson ¹	401	120
Trans	Chloride-exchange column	Gillard and Wilkinson ¹	403	92
Cis	Chloride-exchange column	Present study	394 ^a	198
Cis ^b	Chloride-exchange column	Present study	401	194
Trans	Chloride-exchange column	Present study	387	70.5
Cis	Fractional crystallization	Present study	394	196
Trans	Fractional crystallization	Present study	387	69
Cis-trans	Soln from aquation (solid not separated)	Damrauer and Milburn ³	394	163
Cis-trans	Soln from aquation (solid not separated)	Krishnamurty ^{2b}	~394	~183

^a Calculated from rhodium analysis on solution: I. M. Kolthoff and P. J. Elving, Ed., "Treatise on Analytical Chemistry," Part II, Vol. 8, Interscience, New York, N. Y., 1963, p 468. ^b Complex precipitated from solution with methanol. Analysis indicates impure product.

We have developed a modified procedure, however, which leads to the preparation of the pure potassium salts of the two isomeric complexes. The spectral characteristics of the isomeric complexes are different from those previously ascribed to the substances.

Experimental Section

(a) **Preliminary Approaches.**—N. S. R. and another investigator in our laboratories⁶ have tried without success to reproduce the synthesis of the potassium salts of *cis*- and *trans*-bis(oxalato)-diaquorhodate(III) as described by Gillard and Wilkinson.¹ Several points of difficulty arose. A major problem occurred in the described method of separating the *cis* complex from solution. In their procedure Gillard and Wilkinson stated that the addition of an equal volume of ethanol to the solution containing *cis*-bis(oxalato)diaquorhodate(III) ion, chloride ion, and potassium ion (arising from elution of the anion-exchange column with 10% potassium chloride solution) precipitates potassium chloride and leaves a solution from which the required *cis* salt can be crystallized. Both workers here (Rowan and Kruszyna⁶) have found that the addition of ethanol results in the separation of potassium chloride and the greater part of the rhodium as a brown oil. Difficulty was experienced in purifying the oil and also the residual solution, and the materials we have been able to isolate do not have spectral characteristics appropriate to the pure substance prepared as described in section (b) below. Difficulties were also encountered in obtaining pure *trans*-bis(oxalato)diaquorhodate(III) by the previously described¹ procedure. Likely reasons for the difficulties are suggested by the results of additional approaches to the preparation which we have pursued (see the next several paragraphs). Most significantly, the spectral characteristics reported by Gillard and Wilkinson¹ for potassium *cis*- and *trans*-bis(oxalato)diaquorhodate(III) do not correspond to those we obtain, and it is believed that the evidence we present below can leave little doubt that we have obtained the pure materials (see Experimental Section, part (b), Discussion, and Table I).

One attempted preparation, which represents a slight modification of the method of Gillard and Wilkinson¹ and which appeared to lead to potassium *trans*-bis(oxalato)diaquorhodate(III) but not potassium *cis*-bis(oxalato)diaquorhodate(III), will be described because of the information it provides. Here 100 ml of a solution 0.025 *M* in potassium tris(oxalato)rhodate(III) and 1 *M* in perchloric acid was boiled for 2.5 hr, which is about 20 half-lives for aquation to the bisoxalato species.³ The mixture was cooled to room temperature, neutralized to pH 3-4 with potassium carbonate, and then cooled in a refrigerator for several hours to maximize the precipitation of potassium perchlorate. The potassium perchlorate was removed by filtration, and the filtrate at ~30° was passed onto a Dowex 1-X8 resin in the chloride form (column 1 in. in diameter and ~4 in. long; resin 200-400 mesh).

The first yellow fraction washed right through the chloride column but was held by a cation-exchange column in the potassium ion form consistent with the properties expected for oxalatotetraaquorhodium(III) ion. In the pH range 1-4 the

visible absorption maximum occurred at 389 nm; at pH 6.5 the maximum had shifted to 397 nm suggestive of the formation of a hydroxyaquo species.

After washing the chloride column with water a second fraction, which we presumed to contain *trans*-bis(oxalato)diaquorhodate(III) ion, could be eluted with 2% potassium chloride solution. This fraction had an absorption maximum of 386-387 nm throughout the pH range 2-6.5. A yellow crystalline material which was essentially free of unbound chloride could be obtained by freezing the eluted solution, thawing, and filtering off the residual solid. Purification was possible by redissolving the solid in a minimum amount of warm water and repeating the freezing-thawing process. The solid was dried over calcium chloride; yield ~6%. *Anal.*⁷ Calcd for $\text{K}[\text{Rh}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 1.5 \text{H}_2\text{O}$: C, 12.6; H, 1.80; K, 10.3. Found: C, 12.7; H, 2.03; K, 10.6. The product had an absorption maximum at 387 nm with an absorbancy coefficient of 70.5.

Once the above "trans" fraction had been eluted, a third fraction ("cis" fraction) was eluted with 10% potassium chloride. The freshly eluted solution displayed a visible absorption maximum at 394 nm through the pH range 2-6.5. The potassium chloride was difficult to separate from the complex, although ethanol, acetonitrile, and methanol were each used. A yellow powder could be precipitated with methanol, however, and it was possible to remove most of the free chloride in several cycles of dissolving in water and reprecipitating with methanol. The resulting pale yellow solid *now* exhibited an absorption maximum at 401 nm. The material was dried over calcium chloride (yield, assuming required product, ~12%). *Anal.*⁷ Calcd for $\text{K}[\text{Rh}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$: C, 12.9; H, 1.60; K, 10.5; Cl, 0.00. Found: C, 12.73; H, 1.29; K, 19.5; Cl, 0.58. It is clear that this product did not correspond to the required substance.

A final small fraction which could be eluted with concentrated potassium chloride had an absorption maximum at 399 nm over the pH range 2.5-6.7. It was presumed this fraction contained unreacted tris-oxalato complex and no attempt was made to purify the complex.

In summary, we found the procedure of Gillard and Wilkinson¹ and several modifications of the process to be unsatisfactory, especially for the preparation of potassium *cis*-bis(oxalato)diaquorhodate(III).

(b) **Preparation by Fractional Crystallization.**—The following successful method for the preparation of potassium *trans*- and *cis*-bis(oxalato)diaquorhodate(III) is based on the results of aquation studies³ and on fractional crystallization procedures. Here 1.00 g of $\text{K}_3\text{Rh}(\text{C}_2\text{O}_4)_3 \cdot 1.5 \text{H}_2\text{O}$ was dissolved in about 200 ml of water, 30 ml of 60-62% perchloric acid was added, and the solution was diluted to 500 ml ($[\text{H}^+] \approx 0.55 \text{M}$, $[\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}] \approx 4 \times 10^{-3} \text{M}$). The solution in a stoppered flask was maintained in a thermostat bath at 80° for 32 hr, which for the conditions represents ~12 half-lives for the aquation to the bis(oxalato)diaquo species.³ The solution was cooled and then transferred to a beaker, 0.20 g of calcium carbonate was added (the stoichiometric amount needed on the assumption that 1 mol of oxalate is lost per mole of tris-oxalato complex), and the mixture was then neutralized to pH 4 using potassium carbonate and placed in a

(6) H. G. Kruszyna, unpublished observations.

(7) Analysis by Galbraith Laboratories, Inc., Knoxville, Tenn.

refrigerator for several hours to maximize the precipitation of calcium oxalate and potassium perchlorate. The solution was filtered while cold, evaporated on a rotary evaporator to ~80 ml, and again refrigerated and filtered. The filtrate was then passed through a Dowex 50-X8 20-40 mesh resin in the potassium ion form to remove any cationic rhodium species and any excess Ca^{2+} or H^+ . The solution was then washed through the column with water, and the pH was checked to make sure it was between 6 and 7. (If too low, adjustment to that range can be made with more potassium carbonate.) The solution was evaporated to about 10-15 ml on a rotary evaporator, refrigerated for about 2 hr, and again filtered. The filtrate was then placed in an evaporating dish in the refrigerator and allowed to evaporate slowly. The trans isomer is much less soluble than the cis isomer, and after 2 days to 1 week it comes out of solution as bright yellow crystals. These crystals in aqueous solution had the same spectrum as the second fraction in the chloride column method described under section (a) above (see Table I). The yield here was about 0.15 g (~19%).

The cis isomer is more soluble, and it was necessary to evaporate to about 5 ml before any crystals would form. In the refrigerator this took anywhere from 1 week to 1 month. When a fairly large crop of these dark orange crystals had formed they were filtered off. These crystals in aqueous solution had the same spectrum as the freshly eluted solution in the third fraction in the chloride column method described under section (a) above (see Table I). The yield of complex was 0.25 g (~32%).

Both isomers were recrystallized by dissolving the crystals in about 2 ml of warm water, filtering the warm solutions, and placing the filtrates in the refrigerator to allow slow crystallization. The resulting crystals were filtered from solution, washed with minimum amounts of cold water, cold ethanol, and cold ether, and then allowed to equilibrate with the atmosphere. The final yield of trans isomer was 0.08 g (~9%). *Anal.*⁷ Calcd for $\text{trans-K}[\text{Rh}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$: C, 11.77; H, 2.45; K, 9.58; Rh, 25.24. Found: C, 11.85; H, 2.52; K, 9.55; Rh, 25.35. The final yield of cis isomer was 0.12 g (~16%). *Anal.*⁷ Calcd for $\text{cis-K}[\text{Rh}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 1.75\text{H}_2\text{O}$: C, 12.45; H, 1.95; K, 10.14; Rh, 26.69. Found: C, 12.45; H, 1.98; K, 10.21; Rh, 26.60. Characteristics for visible absorption spectra are included in Table I. Infrared absorption spectra are shown in Figure 1.

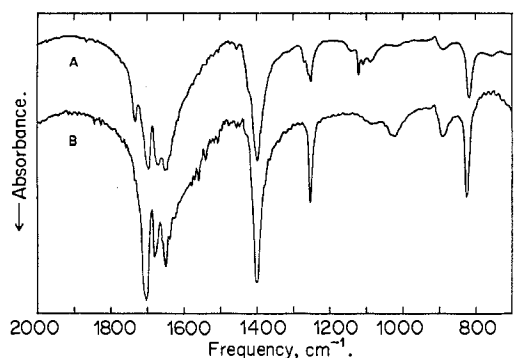


Figure 1.—Infrared spectra (KBr pellets) for (A) potassium *cis*-bis(oxalato)diaquorhodate(III) and (B) potassium *trans*-bis(oxalato)diaquorhodate(III).

A variation of this method, which was not pursued in detail, used $\text{K}_3[\text{Rh}(\text{C}_2\text{O}_4)_2\text{Cl}_2]$ ⁸ as a starting material. Heating a 3.0×10^{-3} M solution of potassium dichlorobis(oxalato)rhodate(III) for 80-90 hr at 80° produces the same *cis*- $\text{Rh}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$ /*trans*- $\text{Rh}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$ mixture as one obtains from the $\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}$ aquation. This solution was then cooled to room temperature and treated with the stoichiometric amount of silver perchlorate to remove the chloride ion and excess potassium ion. The solution was then evaporated to ~80 ml and cooled, and further AgCl and KClO_4 were filtered off. This leaves a filtrate which may be treated in exactly the same way as the corresponding filtrate of the same volume in the above described fractional crystallization method.

Visible spectra were taken on a Cary 14 spectrophotometer,

(8) J. P. Collman and H. F. Holtzclaw, Jr., *J. Amer. Chem. Soc.*, **80**, 2054 (1958).

and infrared spectra were taken as KBr pellets on a Perkin-Elmer Model 237B grating spectrometer.

Discussion

The methods of preparation, the solubility, ion-exchange and spectral characteristics, and the results of elemental chemical analysis can leave little doubt that the materials obtained by our fractional crystallization procedure correspond to pure potassium *trans*- and *cis*-bis(oxalato)diaquorhodate(III). The potassium salt of the trans isomer has a lower solubility in water, consistent with expected behavior (compare with *trans*- and *cis*- $\text{K}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$).⁹ Also, because of its greater symmetry, the trans isomer has a smaller affinity for an anion-exchange column and a lower molar absorptivity coefficient for the observed ligand field absorption band. Both the cis and trans isomers exhibit only one absorption maximum in the visible region.^{10,11}

The positions of the absorption maxima and the magnitudes of the absorptivity coefficients in water observed for our pure samples of the cis and trans isomers are consistent with results obtained earlier in studies of the acid-promoted aquation of $\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}$ ion.^{2,3} Accumulated evidence on the aquation^{2,3} has made it clear that the reaction proceeds almost stoichiometrically to $\text{Rh}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$, although the distribution between cis and trans isomers had remained uncertain. The column studies in the present work and also spectral comparisons (Table I) indicate that the predominant end product of the aquation is the *cis*- $\text{Rh}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$ ion.

It is difficult to reconcile the results of Gillard and Wilkinson¹ with those obtained in the present study. Besides the difficulties which we experienced in trying to reproduce their preparative procedure, it seems clear that the materials which they obtained do not correspond to the *cis*- and *trans*-bis(oxalato)diaquorhodate(III) salts as prepared by our fractional crystallization method. The absorption maxima do not agree¹² and the absorptivity coefficients are widely divergent. In addition, the infrared maxima which Gillard and Wilkinson reported show some features of disagreement with our observations (compare data in ref 1 with our Figure 1).

The position of the absorption maximum which Gillard and Wilkinson observed for their "cis" isomer (401 nm) is the same as we found for our "cis" preparation which made use of the chloride column followed by precipitation with methanol (see Table I). The analysis reported for their "cis" isomer is as follows: C, 12.7%; H, 2.0%; Rh, 28.1%. Where this analysis overlaps with ours the agreement is fair, but we found our sample to contain 19.5% potassium which is nearly twice the expected value. It is obvious from analysis that our main contaminant is not potassium chloride, but it could possibly be $\text{K}_2[\text{Rh}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})(\text{OH})]$

(9) R. E. Hamm, *J. Amer. Chem. Soc.*, **75**, 609 (1953).

(10) Water and oxalate cause approximately the same crystal field splitting, and one would not expect the ${}^1\text{A} \rightarrow {}^1\text{T}_{1g}$ band to be split, the central rhodium being in an approximately O_h field. The chromium(III)-aquo-oxalato complexes exhibit similar behavior.^{9,11}

(11) K. L. Stevenson, M. S. Matson, and R. D. Patrick, *J. Inorg. Nucl. Chem.*, **33**, 147 (1971).

(12) It might be suggested that the discrepancies in the λ_{max} values could be due to the wavelength scales on spectrophotometers for one or both research groups being out of alignment. This idea seems unlikely since both groups have observed in their respective studies a λ_{max} for $\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}$ at 400 nm.

and/or $K_2[Rh(C_2O_4)_2(H_2O)(Cl)]$. For the anions of the latter complex salts one would expect spectral shifts toward longer wavelengths relative to the corresponding isomers of $Rh(C_2O_4)_2(H_2O)_2^-$.

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Covalency in Cesium Vanadyl Chloride Monohydrate as Measured by Nuclear Quadrupole Resonance Spectroscopy

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Oxyhalides of transition elements, of the type MO^{n+} where $M^{(n+2)+}$ is Cr^{5+} , W^{5+} , or V^{4+} , containing a d^1 configuration, have been of much recent interest. The relatively simple optical and magnetic properties which arise from a single unpaired electron have made these systems particularly appealing for electron spin resonance studies. The halide complexes of these ions have been studied and it is well established that there is substantial π bonding between the metal and oxygen atoms.¹⁻⁵ Such studies have also shown that in chloride systems there is delocalization of unpaired spin density into the ligand chloride σ and π atomic orbitals. This can be confirmed in favorable cases where chlorine hyperfine splittings have given similar results for spin densities.¹ Nuclear quadrupole resonance data, as interpreted in terms of p-electron covalency, have also been used in evaluating metal-halogen covalency.⁶ The similarity in the relationship of the spectroscopic observables in esr and nqr spectra⁷ to electron orbital population prompts a comparison of the data obtained for complexes which have been studied by both methods.⁸

Theoretical Section

The bonding and molecular orbitals of interest in oxyhalide systems have been discussed in detail by various authors.¹⁻⁵ In a complex with C_{4v} symmetry where π bonding between the metal and ligand is considered, the molecular orbitals are antibonding in character and of the forms

(1) L. A. Dalton, R. D. Bereman, and C. H. Brubaker, Jr., *Inorg. Chem.*, **8**, 2477 (1969).

(2) (a) P. T. Monoharan and M. T. Rogers, *J. Chem. Phys.*, **49**, 3912 (1968); (b) P. T. Monoharan and M. T. Rogers, *ibid.*, **49**, 5519 (1968).

(3) H. Kon and N. Sharpless, *J. Phys. Chem.*, **70**, 105 (1966).

(4) K. DeArmond, B. B. Garrett, and H. S. Gutowski, *J. Chem. Phys.*, **42**, 1019 (1965).

(5) B. R. McGarvey, *J. Phys. Chem.*, **71**, 51 (1967).

(6) T. L. Brown, W. G. McDugle, and L. G. Kent, *J. Amer. Chem. Soc.*, **92**, 3645 (1970), and references therein.

(7) R. Bersohn and R. G. Shulman, *J. Chem. Phys.*, **45**, 2298 (1966).

(8) This correlation check is not possible for a d^1 complex with pure O_h symmetry since data are not available for such systems.

$$|B_2\rangle^* = N_{\pi_2}(d_{xy} - \lambda_{\pi_2}\phi_{\pi_2}^L) \quad (1)$$

$$|B_1\rangle^* = N_{\sigma_2}(d_{x^2-y^2} - \lambda_{\sigma_2}\phi_{\sigma_2}^L) \quad (2)$$

$$|E\rangle^* = N_{\pi_1}((d_{xz} \text{ or } d_{yz}) - \lambda_{\pi_1}^e\phi_{\pi_1}^e - \lambda_{\pi_1}^a\phi_{\pi_1}^a) \quad (3)$$

where

$$\phi_{\pi_2}^L = 1/2(p_x(1) + p_y(2) + p_y(3) + p_x(4)) \quad (4)$$

$$\phi_{\sigma_2}^L = 1/2(\sigma(1) + \sigma(2) + \sigma(3) + \sigma(4)) \quad (5)$$

$$\phi_{\pi_1}^e = (1/\sqrt{2})(p_y(1) + p_x(3)) \quad (6)$$

$$\sigma_{\pi_1}^a = (1/\sqrt{2})(-p_x(5) + p_y(6)) \quad (7)$$

and $\lambda_{\pi_1}^e$ and $\lambda_{\pi_1}^a$ are the $|E\rangle^*$ molecular orbital coefficients for the equatorial and axial ligands, respectively. The ligand orbitals of the chlorine and oxygen involved in π bonds are pure p orbitals while the σ ligand orbitals are usually taken as sp_z hybrids. However, as noted by Bersohn and Shulman,⁷ sp hybridization is not necessary to explain the observed results for the quadrupole coupling constants for I and Cl in ICl. For the discussion here, therefore, the σ orbitals on the halogens will be taken as pure p_z in character.

If we follow the convention of Townes and Dailey⁹ that the p-orbital electron contribution to the quadrupole interaction dominates, then the quadrupole coupling constant for the chloride, eQq_{mol} , can be related to the quadrupole coupling constant for the free halogen atom, $|eQq|_{\text{atomic}}$,⁶ as in

$$|eQq|_{\text{mol}} = U_p|eQq|_{\text{atomic}} \quad (8)$$

where

$$U_p = 1/2[N_{p_x} + N_{p_y}] - N_{p_z} \quad (9)$$

and the N 's refer to the electron populations in the chlorine 3p orbitals. The p_z orbital is directed along the bond axis; the p_x and p_y orbitals are normal to it. Thus, U_p is a measure of the *difference* in p-orbital population. The orbital populations can be expressed as

$$N_{p_x} = 2 - \pi_x \quad (10)$$

$$N_{p_y} = 2 - \pi_y \quad (11)$$

$$N_{p_z} = 2 - \sigma_z \quad (12)$$

For the equatorial halides in a paramagnetic complex with C_{4v} symmetry, the terms σ_z , π_x , and π_y can be related directly to the unpaired spin density in each ligand p orbital. Thus, making use of Mulliken's population analysis¹⁰

$$\sigma_z \equiv \frac{N_{\sigma_2}^2\lambda_{\sigma_2}^2 - N_{\sigma_2}^2\lambda_{\sigma_2}S_{b_2}}{4} \quad (13)$$

$$\pi_x \equiv \frac{N_{\pi_2}^2\lambda_{\pi_2}^2 - N_{\pi_2}^2\lambda_{\pi_2}S_{b_2}}{4} \quad (14)$$

$$\pi_y \equiv \frac{N_{\pi_1}^2\lambda_{\pi_1}^2 - N_{\pi_1}^2\lambda_{\pi_1}S_e}{4} \quad (15)$$

where S_{b_2} , S_{b_1} , and S_e are the group overlap terms for the respective molecular orbitals. Following the method of Bersohn and Shulman, U_p may then be evaluated as

(9) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).

(10) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).