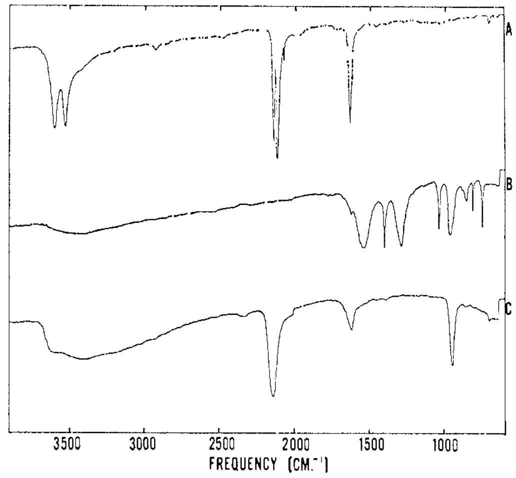

Figure 2.—Infrared spectra of (A) $K_4[Mo(CN)_8]\cdot 2H_2O$, (B) $UO_2(NO_3)_2\cdot 6H_2O$, and (C) $(UO_2)_2[Mo(CN)_8]\cdot nH_2O$ in KBr disks.

solution, the solid materials analyze as $(UO_2)_2Mo(CN)_8\cdot nH_2O$, $n \sim 6$–8. The second uranyl group in the solid is apparently required for electroneutrality. Potassium ions, present in solution, were not detected in the solids by chemical analysis. One possible structural rationalization for the stoichiometry of the solids, suggested by the solution spectral results, is represented by the formula $[UO_2(H_2O)_6]_n[UO_2(H_2O)_2Mo(CN)_8]_n$. Here the uranium atom of the cation achieves eight-coordination by bonding to six water molecules in the hexagonal plane, in the usual manner.[5b] In order to complete the hexagonal coordination belt of the uranyl group associated with the anion, the nitrogen atoms of the $[Mo(CN)_8]^{4-}$ complex might bond to the uranium atoms to form some kind of polymeric structure. Other polymeric structures in which *both* uranyl groups are bonded to the nitrogen atoms of the anion are also possible.

Evidence for the participation of the cyanide ligands in uranyl binding was obtained from infrared spectral studies of the solids. In Figure 2 are displayed the infrared spectra of $UO_2(NO_3)_2\cdot 6H_2O$, $K_4[Mo(CN)_8]\cdot 2H_2O$, and $(UO_2)_2[Mo(CN)_8]\cdot nH_2O$. From the figure it is apparent that the sharp, distinct bands in the cyanide stretching frequency region (2050–2140 cm^{-1}) of $[Mo(CN)_8]^{4-}$ are replaced by a broad envelope centered at 2140 cm^{-1} in the red-brown adduct. This result is consistent with $Mo—C\equiv N—UO_2$ binding, as proposed above. It is, moreover, evident from the infrared spectra that the oxygen atoms of the linear uranyl group interact very weakly if at all with the molybdenum atoms, since the asymmetric O–U–O stretching frequency,[19] $\sim$940 cm^{-1}, is unaltered upon adduct formation.

Infrared spectra of the red-brown adducts formed from uranyl chloride or uranyl acetate were identical with that obtained for the uranyl nitrate (Figure 2), confirming that simple anions present in solution do not coprecipitate with octacyanomolybdate(IV). When solutions of $K_4[W(CN)_8]\cdot 2H_2O$ were added to solutions of uranyl salts, a red-brown color developed. The presumably analogous tungsten system was not studied further. Attempts to examine the photochemical behavior[1] of aqueous solutions of $(UO_2)_2[Mo(CN)_8]\cdot nH_2O$ were unsuccessful because of interference from the known photoreduction[20] of the uranyl ion.

In summary, it may be concluded from the present study that the red-brown color that appears when $[Mo(CN)_8]^{4-}$ and UO_2^{2+} ions are allowed to react in aqueous solution does not correspond to an increase in the coordination number of the molybdenum atom. Instead, it has been shown that the nitrogen atoms of the cyanide ligands are bonded to the uranyl groups to form a complex which is probably polymeric.

Acknowledgments.—We are grateful to the National Science Foundation for financial support of this work, to a reviewer for pointing out relevant literature, and to Miss S. Hoffer for experimental assistance.

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[19] J. I. Bullock, *J. Chem. Soc., A*, 781 (1969).

[20] E. Rabinowitz and R. L. Belford, Ed., "Spectroscopy and Photochemistry of Uranyl Compounds," Vol. 1, Monographs on Nuclear Energy, The Macmillan Co., New York, N. Y., 1964.

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Nuclear Magnetic Resonance Studies of the Stereochemistry of Dichlorobis(β-diketonato) Complexes of Germanium(IV)

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All of the group IV metals with the exception of lead(IV) are known to form acetylacetonate complexes of the type $M(acac)_2Cl_2$. The constitution of $Si(acac)_2Cl_2$ in solution is uncertain,[1] but the Ti(IV),[2–4] Zr(IV),[5,6] Hf(IV),[5,6] Ge(IV),[7] and Sn(IV)[7–9] complexes are monomeric and have been assigned *cis* configurations. Neither these complexes nor their known derivatives with other β-diketonato or halo ligands have been shown to adopt a *trans*-dihalo structure.[9a]

The nmr studies reported here establish the existence of both *cis* and *trans* structures for the dichlorobis(β-diketonato)germanium(IV) complexes $Ge(dpm)_2Cl_2$ and $Ge(pvac)_2Cl_2$, where dpm = $(t\text{-}C_4H_9)COCHCO(t\text{-}C_4H_9)^-$ and pvac = $(t\text{-}C_4H_9)COCHCOCH_3^-$. Also, the nmr spectrum of $Ge(acac)_2Cl_2$ has been reinvestigated, and the results indicate that the molecule adopts a

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[1] D. W. Thompson, *Inorg. Chem.*, **8**, 2015 (1969).

[2] D. C. Bradley and C. E. Holloway, *Chem. Commun.*, 284 (1965).

[3] R. C. Fay and R. N. Lowry, *Inorg. Nucl. Chem. Letters*, **3**, 117 (1967).

[4] R. C. Fay and R. N. Lowry, *Inorg. Chem.*, **6**, 1512 (1967).

[5] T. J. Pinnavaia and R. C. Fay, *ibid.*, **7**, 502 (1968).

[6] R. C. Fay and T. J. Pinnavaia, *ibid.*, **7**, 508 (1968).

[7] J. A. S. Smith and E. J. Wilkins, *J. Chem. Soc., A*, 1749 (1966).

[8] J. A. S. Smith and E. J. Wilkins, *Chem. Commun.*, 381 (1965).

[9] J. W. Faller and A. Davison, *Inorg. Chem.*, **6**, 182 (1967).

[9a] NOTE ADDED IN PROOF.—*cis* and *trans* octahedral configurations have been recently found for $Ti(acac)_2I_2$: R. C. Fay, Cornell University, personal communication, Dec 1969.

trans configuration in addition to the previously reported[7] *cis* configuration.

Experimental Section

Syntheses.—The complexes reported here were prepared in better than 50% yield by using methods similar to those described previously for $Ge(acac)_2Cl_2$.[10,11] Since the compounds are hygroscopic, all preparative reactions and subsequent manipulations of the products were conducted under an atmosphere of dry nitrogen. Germanium(IV) chloride (99.999+%) was purchased from Research Organic/Inorganic Chemicals Corp. and was used without further purification. Acetylacetone (bp 136–140°) was purchased from Matheson Collman and Bell and was freshly distilled before use. Dipivaloylmethane and pivaloylacetone were prepared in the manner described by Adams and Hauser.[12] Benzene, hexane, and dichloromethane were dried by refluxing over calcium hydride. Chloroform was freed of ethanol by treatment with activated alumina and was dried over calcium hydride.

Dichlorobis(2,2,6,6-tetramethyl-3,5-heptanedionato)germanium(IV).—A mixture of germanium(IV) chloride (2.58 g, 0.0120 mol) and dipivaloylmethane (4.42 g, 0.0240 mol) in 60 ml of chloroform was heated just below reflux temperature for 120 hr. Removal of the solvent by vacuum distillation gave a white solid, which was recrystallized twice from hexane to remove any occluded free ligand. A solution of the product in dichloromethane at a concentration of *ca.* 0.2 g/ml was heated to boiling, and an equal volume of hot hexane was added. After aging 48 hr at room temperature, the solution yielded colorless prismatic crystals, which were filtered and dried *in vacuo* at room temperature for 6 hr; mp 139–140°; $\Lambda = 0.011$ ohm^{-1} cm^2 mol^{-1} (0.011 *M* soln in $C_6H_5NO_2$ at 25°).

Anal. Calcd for $Ge(C_{11}H_{19}O_2)_2Cl_2$: C, 51.81; H, 7.51; Cl, 13.90; Ge, 14.23; mol wt, 510. Found: C, 51.71; H, 7.73; Cl, 14.40; Ge, 14.65; mol wt (C_6H_6), 520.

Three additional crops of crystals were obtained from the dichloromethane–hexane mother liquor by successively removing *ca.* 40% of the solvent by vacuum distillation, adding a volume of hot hexane equal to half the volume of solvent removed by distillation, and allowing the resulting solution to age at room temperature. Each of the four crops of crystals had the same melting point and, when dissolved in benzene at 17°, gave an nmr spectrum characteristic of only the *trans* isomer. Samples crystallized within 1 hr or less from hexane or benzene exhibited nmr spectra at 17° characteristic of a mixture of *cis* and *trans* isomers.

Dichlorobis(5,5-dimethyl-2,3-hexanedionato)germanium(IV).—Pivaloylacetone (9.83 g, 0.0691 mol) and germanium(IV) chloride (6.20 g, 0.0289 mol) were allowed to react in 60 ml of hot chloroform for 120 hr. The volume of the mixture was reduced to *ca.* 15 ml, and 40 ml of hot hexane was added. The solution was refrigerated for 24 hr, and the resulting solid was recrystallized twice from hexane. The fine white crystals were dried *in vacuo* at room temperature for 6 hr; mp 177–178.5°; $\Lambda = 0.022$ ohm^{-1} cm^2 mol^{-1} (0.010 *M* soln in $C_6H_5NO_2$ at 25°).

Anal. Calcd for $Ge(C_8H_{13}O_2)_2Cl_2$: C, 45.12; H, 6.15; Cl, 16.65; Ge, 17.04, mol wt, 426. Found: C, 44.93; H, 6.18; Cl, 16.64; Ge, 17.11; mol wt (C_6H_6), 418.

Dichlorobis(2,4-pentanedionato)germanium(IV).—This compound was prepared by reaction of germanium(IV) chloride and acetylacetone as described by Ong and Prince.[11] The white crystalline product was recrystallized by dissolving in hot dichloromethane, adding hot hexane to produce a turbid solution, and cooling. The crystals were washed with hexane and dried *in vacuo* at room temperature; mp 240–242°; lit., mp 238–244,[7] 240,[11] 236–240°.[13]

Physical Measurements.—All solutions were prepared in a glove bag filled with dry nitrogen. Benzene, dichloromethane, and deuteriochloroform were dried over calcium hydride. Nitrobenzene was washed with 1:1 sulfuric acid, water, 1 *M* sodium hydroxide, and water; each washing was repeated until the wash solution was colorless. The nitrobenzene was then dried over molecular sieves and vacuum distilled.

Molar weights were determined cryoscopically. Molar conductivities were measured with a Beckman conductivity bridge, Model RC16B2. Proton magnetic resonance spectra were recorded on a Varian A56/60D analytical spectrometer (60.000 MHz) equipped with a Varian temperature controller, Model V-6040.

Results and Discussion

Dichlorobis(dipivaloylmethanato)germanium(IV), $Ge(dpm)_2Cl_2$, and dichlorobis(pivaloylacetonato)germanium(IV), $Ge(pvac)_2Cl_2$, are monomeric in benzene and very weak electrolytes in nitrobenzene. The acetylacetonate derivative, $Ge(acac)_2Cl_2$, has been previously reported to be a monomer[13] and a weak electrolyte[11] in ionizing solvents. Dissociated species of the type $Ge(dik)_2Cl^+$, which have been postulated by Osipov and coworkers[14] in attempting to account for the dipole moment of $Ge(acac)_2Cl_2$ in chloroform, cannot be present in solution in an appreciable amount.

Nmr spectra for $Ge(dpm)_2Cl_2$ in benzene are shown in Figure 1. A fresh solution at 17° exhibits a single t-C_4H_9 proton resonance line and a single –CH= line, which is in accord with the result expected for a *trans* structure (symmetry D_{2h}). At 37° isomerization of the complex occurs within 2.5 hr, and two new lines at τ 9.00 and 4.15 appear in the spectrum of the equilibrium mixture. The line at τ 9.00 represents one of the two equally intense t-C_4H_9 resonances expected for the *cis* isomer (symmetry C_2). The other t-C_4H_9 resonance component of the *cis* isomer has the same chemical shift value as the t-C_4H_9 line of the *trans* isomer. The line at τ 4.15 is assigned to the –CH= resonance of the *cis* isomer.

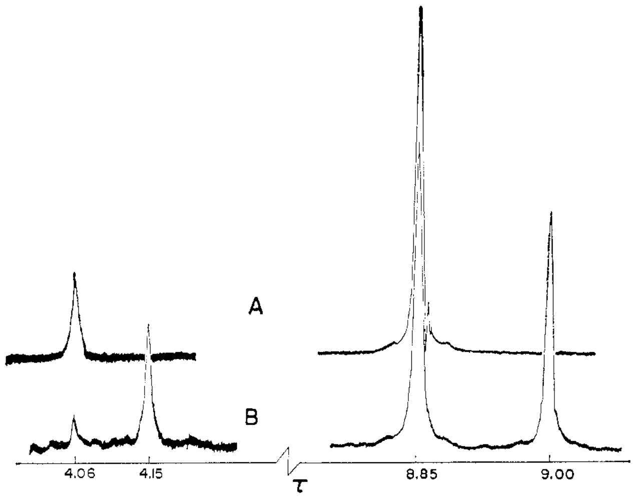

Figure 1.—Nmr spectra for (A) *trans*-$Ge(dpm)_2Cl_2$ in benzene at 17° and (B) an equilibrium mixture of *cis*- and *trans*-$Ge(dpm)_2Cl_2$ in benzene at 40°. Concentrations are *ca.* 2.0 and 5.0 g/1000 ml of solvent, respectively. Spectrum A was recorded within 5 min after preparation of the solution at 17°.

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(10) G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, **125**, 1261 (1924).

(11) W. K. Ong and R. H. Prince, *J. Inorg. Nucl. Chem.*, **27**, 1037 (1965).

(12) J. T. Adams and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1220 (1944).

(13) M. Cox, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 6113 (1964).

(14) O. A. Osipov, V. L. Shelepina, and O. E. Shelepin, *J. Gen. Chem. USSR*, **36**, 274 (1966).

Further evidence for the existence of both *cis*- and *trans*-dichloro configurations is obtained from the nmr spectrum of Ge(pvac)$_2$Cl$_2$. Because of the asymmetry of the diketonate ligand, a *cis*-dichloro configuration should give rise to three geometric isomers. Two of the isomers have C_2 symmetry, and the third has C_1 symmetry. A *trans*-dichloro configuration should give two isomers with point group symmetries of C_{2h} and C_{2v}. If all five isomers were present in an equilibrium mixture, then the t-C_4H_9, CH_3, and –CH= regions of the nmr spectrum each should contain six resonance lines. As shown in Figure 2, six t-C_4H_9 lines (τ 8.86–9.03) and six CH_3 lines (τ 8.31–8.41) are indeed observed in benzene solution. The presence of only five –CH= lines in the region τ 4.42–4.52 is probably due to a coincidence of chemical shifts for two of the lines.

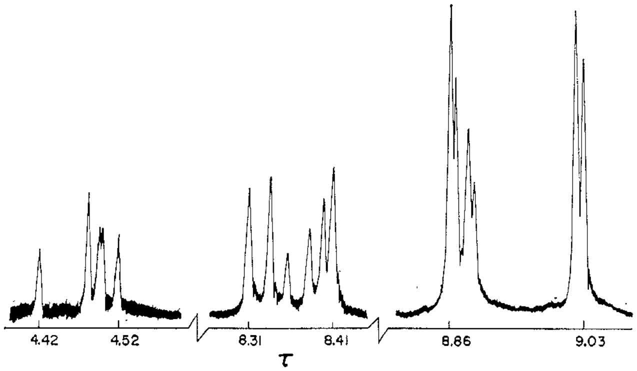

Figure 2.—Nmr spectrum of Ge(pvac)$_2$Cl$_2$ in benzene at 40°; concentration is 12.0 g/100 ml of solvent.

In the case of Ge(acac)$_2$Cl$_2$, nmr studies by Smith and Wilkins[7] indicate that the molecule adopts the *cis* configuration in deuteriochloroform solution. The large dipole moment reported for the compound in chloroform (7.4 D)[14] also supports a *cis* structure.[15] In view of the results obtained for Ge(dpm)$_2$Cl$_2$ and Ge(pvac)$_2$Cl$_2$, we reinvestigated the nmr spectrum of Ge(acac)$_2$Cl$_2$. The spectrum in dichloromethane is shown in Figure 3. The two equally intense CH_3 resonances at τ 7.82 and 7.93 and the –CH= resonance of appropriate intensity at τ 4.25 indicate that the molecule does indeed adopt primarily the *cis* configuration. However, the remaining CH_3 and –CH= lines at τ 7.84 and 4.22, respectively, strongly suggest the presence of an appreicable equilibrium amount of the *trans* isomer (*ca.* 15–20%). A qualitatively similar spectrum was obtained in deuteriochloroform solution. Apparently, the presence of free acetylacetone as an impurity in the sample investigated by Smith and Wilkins prevented them from detecting the *trans* isomer.

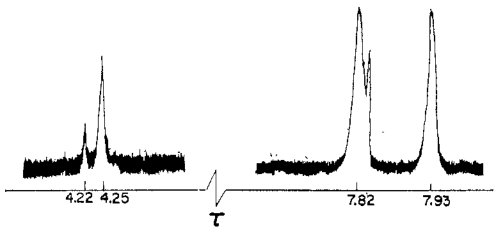

Figure 3.—Nmr spectrum of Ge(acac)$_2$Cl$_2$ in dichloromethane at 40°; concentration is *ca.* 2.0 g/100 ml of solvent.

Previous discussions of the stereochemistry of dihalobis(β-diketonato) complexes of titanium(IV)[2,16] and tin(IV)[17] have pointed out that differences in the π-bonding abilities of the donor oxygen atoms on the diketonate ligands and the halogen ligands should lead to stabilization of the *cis* configuration. Any difference in the ability of oxygen and chlorine to π bond to germanium(IV) may not be very important in influencing the stereochemistry of the complexes studied here. For Ge(dpm)$_2$Cl$_2$ in benzene at 40°, the value of the equilibrium constant, $K = [cis]/[trans]$, is 6.60 ± 0.10, as determined by planimetric integration of five spectral copies of the t-C_4H_9 resonances for the equilibrium mixture (*cf.* Figure 1, spectrum B). The statistical value of K expected on the basis of symmetry considerations alone is 4.00. Thus an exothermic enthalpy change of only 0.31 kcal/mol, whether due to more favorable π bonding in the *cis* isomer or to some other effect, such as differences in solvation enthalpies, is sufficient to account for the deviation of K from the statistical value.

The proton chemical shifts for *cis*- and *trans*-Ge(acac)$_2$Cl$_2$ are of special interest. Calculations by Smith and Wilkins[7] and Serpone and Fay[15] indicate that electric field effects arising from the dipole moment of a *cis*-M(acac)$_2$Cl$_2$ molecule can be expected to shift the proton resonances to lower field relative to neutral, nonpolar M(acac)$_n$ complexes. For the *cis* isomer of Ge(acac)$_2$Cl$_2$ in dichloromethane, the average chemical shift of the nonequivalent CH_3 protons and the chemical shift of the equivalent –CH= protons lie in the ranges expected in the presence of an electric field effect. However, the proton resonances of the *trans* isomer occur at slightly lower values of magnetic field strength than those of the *cis* isomer. An electric field model would predict that the CH_3 and –CH= resonances of the nonpolar *trans* isomer should occur upfield from the *cis* isomer by *ca.* 0.1 and 0.25 ppm, respectively.[15] As pointed out by Serpone and Fay, although a through space electric field model permits quantitative estimates of the low-field shifts of *cis*-M(acac)$_2$X$_2$ complexes, the shifts can be interpreted in terms of inductive effects acting through bonds. The results obtained here for *trans*-Ge(acac)$_2$Cl$_2$ suggest that the low-field shifts are indeed due to inductive effects of the chlorine atoms. The nearly equal chemical shifts observed for *cis*- and *trans*-Ge(dpm)$_2$Cl$_2$ in benzene also favor an inductive model over an electric field model. Thompson[18] has recently cited –CH= proton chemical shift data for *cis* and *trans* isomers of Si(acac)$_2$(OOCCH$_3$)$_2$

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[15] N. Serpone and R. C. Fay, *Inorg. Chem.*, **8**, 2379 (1969).

[16] D. C. Bradley and C. E. Holloway, *J. Chem. Soc., A*, 282 (1969).

[17] W. H. Nelson, *Inorg. Chem.*, **6**, 1509 (1967).

[18] D. W. Thompson, *J. Magn. Resonance*, **1**, 606 (1969).

and for $Al(acac)_2(DMF)_2^+$, along with data for other metal acetylacetonates suspected of having either exclusively *cis* or *trans* structures in solution, which also indicate that factors other than electric field effects are important in determining ring proton shifts.

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Carbon Monoxide Exchange Reaction of *o*-Phenanthrolinechromium Tetracarbonyl

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Early carbon monoxide exchange studies of the compounds $Mn(CO)_5X$ (X = Cl, Br, I)[1,2] were interpreted as indicating that the four equatorial carbonyl groups exchanged at a much faster rate than did the axial group. More recently infrared techniques have been employed to examine the rate of ^{13}CO or $C^{18}O$ incorporation into $Mn(CO)_5X$ compounds.[3,4] Under these conditions no significant difference in the rate constants for equatorial and axial substitution was detected, and mechanisms based on the equivalence of these rate constants have been postulated.[4] However, Brown[5] has questioned the validity of these mechanisms and suggested that intermolecular exchange at the axial and equatorial positions may occur at different rates but that equilibration, either by a nondissociative twist mechanism or by halide exchange *via* an acyl halide intermediate, may offer an alternate explanation for the observed similarity of the rate constants.

In continuing our examination of the possibility of different exchange rates for stereochemically different CO ligands in substituted carbonyl compounds, we have examined the exchange reaction of $Cr(CO)_4$(*o*-phen) with $C^{18}O$. Evidence is presented that the rate constants for exchange of the axial and equatorial[6] CO groups are significantly different.

Experimental Section

$Cr(CO)_4$(*o*-phen) was prepared and purified by the literature method.[7] 1,2-Dichloroethane was dried by refluxing over P_2O_5 and was freshly distilled before use. $C^{18}O$ was supplied by Miles Laboratory, Inc., Elkhart, Ind.

The apparatus used for the exchange experiments was essentially the same as has been previously described.[8] All exchange reactions were carried out in 1,2-dichloroethane. Under an atmosphere of carbon monoxide, the decomposition of the substrate at the temperature of the experiments was effectively zero. A large number of other solvents were tested but poor solubility or rapid decomposition of the substrate precluded their use.

The infrared spectrum of $Cr(CO)_4$(*o*-phen) exhibits four C–O stretching absorptions. They have been assigned[9] as 2008 cm^{-1} (a_1, axial CO), 1907 cm^{-1} (b_1, axial CO), 1883 cm^{-1} (a_1, equatorial CO), and 1831 cm^{-1} (b_2, equatorial CO). Upon substitution with $C^{18}O$ new bands were observed at 1986, 1888, 1875, and 1822 cm^{-1}. Spectra before and after exchange are shown in Figure 1. Since there was no overlap with bands due to the isotopically substituted products, the intensities of the bands at 2008 and 1831 cm^{-1} were measured as they decreased with increasing substitution. The extinction coefficients of these two bands were measured for solutions from 1.0×10^{-4} to 5.0×10^{-3} M (the maximum concentration range). Beer's law was confirmed and the effective molar extinction coefficient for the axial a_1 band was found to be 1.8×10^3 l. mol^{-1} cm^{-1} and for the equatorial b_2, 3.1×10^3 l. mol^{-1} cm^{-1}. The solubility of carbon monoxide in 1,2-dichloroethane was measured by a tensimetric technique.[10]

Carbon Monoxide Exchange Calculations.—The reaction sequence to be studied is shown in Figure 2. Let C_{ij} represent the concentration of each particular species, where i refers to the number of equatorial CO groups that have been substituted by $C^{18}O$, and similarly j is the number of axial CO groups that have become labeled. It was assumed and verified under the conditions of the experiments that

$$C_{02} + C_{12} + C_{22} = C_{20} + C_{21} + C_{22} = 0 \qquad (1)$$

In order to treat the data, the simplification was made that coupling between *cis* CO groups is negligible. Then if we let $C_{00} + C_{10} = x$ and $C_{00} + C_{01} = y$, the intensity of the axial a_1 band is proportional to x and that of the equatorial b_2 band is proportional to y. Now if we consider a system containing a mol of $Cr(CO)_4$(*o*-phen) and b mol of free CO, it can be shown[11] that

$$\frac{-dx}{dt} = R_{ax}\left[\frac{z}{b}\frac{2x}{2a} - \frac{b-z}{b}\frac{a-x}{2a}\right] \qquad (2)$$

$$\frac{-dy}{dt} = R_{eq}\left[\frac{z}{b}\frac{2y}{2a} - \frac{b-z}{b}\frac{a-y}{2a}\right] \qquad (3)$$

where z is the concentration of $C^{18}O$ at time t, and R_{ax} and R_{eq} are the gross rates of exchange at the axial and equatorial positions, respectively. From an examination of mass balance

$$z = d - C_{01} - C_{10} - 2C_{11} \qquad (4)$$

where d is the concentration of $C^{18}O$ at time $t = 0$. Substituting for C_{01} and C_{10}, the term C_{11} cancels, and thus

$$z = d - 2a + x + y \qquad (5)$$

Hence for a first-order reaction

$$\frac{-dx}{dt} = \frac{k_{ax}}{2b}[a(d - 2a - b) + (d - a + b)x + ay + xy + x^2] \qquad (6)$$

$$\frac{-dy}{dt} = \frac{k_{eq}}{2b}[a(d - 2a - b) + (d - a - b)y + ax + xy + y^2] \qquad (7)$$

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[1] A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, **83**, 525 (1961).

[2] W. Hieber and K. Wollmann, *Chem. Ber.*, **95**, 1552 (1962).

[3] H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Am. Chem. Soc.*, **89**, 2844 (1967).

[4] B. F. G. Johnson, J. Lewis, J. R. Miller, B. H. Robinson, P. W. Robinson, and A. Wojcicki, *J. Chem. Soc., A*, 522 (1968).

[5] T. L. Brown, *Inorg. Chem.*, **7**, 2673 (1968).

[6] The 1,10-phenanthroline ligand is assumed to be in the equatorial plane. The two CO ligands *trans* to the amine are the equatorial CO groups. The two mutually *trans* CO groups are in the axial positions.

[7] R. J. Angelici and J. R. Graham, *Inorg. Chem.*, **6**, 988 (1967).

[8] J. P. Day, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **90**, 6927 (1968).

[9] C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

[10] D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1969, p 58.

[11] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, New York, N. Y., 1961, p 192.