motion other than a simple pulling away of the hydrogen isotope."

Figure 3 shows the temperature dependence of this theoretical maximum fractionation factor. The least-squares line from Fig. 2 is included on this graph, together with the points of Johnston and Davis[3] for the reaction of several metals with liquid water and for the reaction of zinc with 3.5 M H_2SO_4. The horizontal line at $\alpha = 1.4$ represents the theoretical α at $T = \infty$. The observed fractionation factors are seen to be lower than the curve representing the theoretical upper limit.

From the results of the present investigation it is possible to evaluate the correction for incomplete conversion of water to hydrogen in the conventional analytical method for deuterium. It is shown in the Appendix that the observed separation, S, is related to the fractionation factor, α, and the fractional conversion, f, by the equation

$$S = \frac{f}{1 - (1 - f)^{1/\alpha}}$$

From Fig. 2, $\alpha = 1.6 \pm 0.1$ at 400°. Shown in Fig. 4 is a graph of the correction factor, S, as a function of $1 - f$, the fraction of water unconverted.

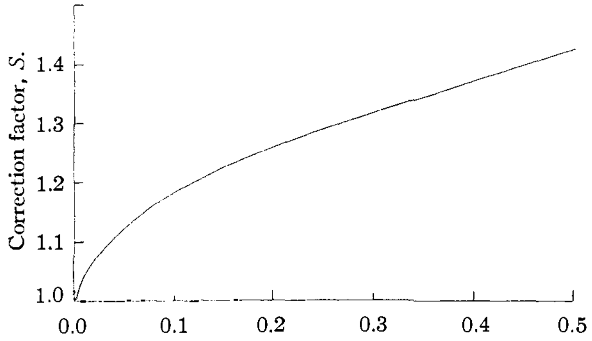

Fig. 4.—Correction factor for incomplete conversion of water to hydrogen by reaction with zinc at 400°.

Although this source of error has been generally recognized in the past (see, for example, ref. 6), quantitative data on the magnitude of the effect have been lacking. From the present results it would appear that at least 99% conversion is required in order to insure an error of <5% in the isotope ratio, (D)/(H).

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Appendix

Consider the competing isotopic reactions

$$HOH + M \longrightarrow H_2 + MO \qquad k_1$$
$$HOD + M \longrightarrow HD + MO \qquad k_2$$

Let $a_1 = (H_2O)$, $a_2 = (HOD)$, $x_1 = (H_2)$, $x_2 = (HD)$. The superscript ^{0} denotes initial concentration.

For the tracer case ($a_2 << a_1$, $x_2 << x_1$) one obtains, regardless of mechanism (see, for example, J. Bigeleisen, *Science*, **110, 14** (1949))

$$\frac{dx_1}{dx_2} = \frac{k_1 a_1}{k_2 a_2} = \alpha \frac{a_1^0 - x_1}{a_2^0 - x_2}$$

This is integrated to give

$$\frac{x_2}{a_2^0} = 1 - \left(1 - \frac{x_1}{a_1^0}\right)^{1/\alpha}$$

Introducing the expression for the observed separation factor, $S = (x_1/x_2)/(a_1^\circ/a_2^\circ)$, one obtains

$$S = \frac{x_1/a_1^0}{1 - (1 - x_1/a_1^0)^{1/\alpha}}$$

The fraction reacted is closely approximated by $f = x_1/a_1^0$ so that

$$S = \frac{f}{1 - (1 - f)^{1/\alpha}} \quad \text{or } \alpha = \frac{\log(1 - f)}{\log(1 - f/S)}$$

Chicago, Illinois

[Contribution from the Chemical Laboratories of the University of Notre Dame]

The *trans* Effect in Inorganic Coördination Compounds.[1] I. Ultraviolet and Infrared Studies of *cis*- and *trans*-Dinitrotetramminecobalt(III) Chloride

By J. Philip Faust[2] and J. V. Quagliano

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Ultraviolet and infrared spectra of *cis*- and *trans*-dinitrotetramminecobalt(III) chloride in the solid state have been measured. The use of the potassium bromide disk method for the ultraviolet and infrared studies of inorganic coördination compounds is discussed. In the absence of the solvent water, the so-called third band appears only in the ultraviolet spectrum of the *trans* isomer, in agreement with the *trans* anions hypothesis of Shibata–Tsuchida. The presence of strong absorption bands at 7.5 and 12.0 μ in the infrared spectra of the ammine complexes are explained as due to deformation of the ammonia groups coördinated to the metal atom. *cis*- and *trans*-dinitrotetramminecobalt(III) chloride are readily distinguished by their infrared spectra. Spectral evidence is presented to support the nitrogen-to-metal bonding in these nitro complexes.

Directive influences in reactions of inorganic coördination compounds are well known.[3] Werner[4] was able to explain the chemical evidence of directive influences in complexes on the basis of the straightforward and simple assumption that elimination of ligands, *trans* to each other in the coördi-

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[1] Contribution from the Radiation Project operated by the University of Notre Dame and supported in part under Atomic Energy Commission Contract AT(11-1)-38.

[2] Abstracted from the Ph.D. thesis of John P. Faust, Notre Dame, July, 1952. Presented before the Physical and Inorganic Division of the 124th National Meeting of the American Chemical Society, Chicago, Ill., September, 1953.

[3] J. V. Quagliano and Leo Schubert, *Chem. Revs.*, **50**, 201 (1952).

[4] A. Werner, *Z. anorg. allgem. Chem.*, **3**, 267 (1893).

nation sphere of the complex, takes place. The *trans* effect, a designation first proposed by Chernyaev,[5] stipulates that an electronegative or other labilizing group coördinated to a metal ion loosens the bond of any other ligand *trans* to it. This *trans* group, for example, is the first to be removed in substitution reactions, and by this means *cis* and *trans* isomers of planar and octahedral coördination complexes can be differentiated.[3] Of special interest are the extensive studies of absorption spectra by Shibata[6] and Tsuchida[7] dealing with the occurrence of a third absorption band in the ultraviolet region of metal coördination compounds with anions in the *trans* positions.

Although several studies of the absorption spectra of inorganic coördination compounds in solutions have been made, an examination of the literature reveals few spectral investigations of complexes in the crystalline state. It seems desirable to investigate the spectroscopic properties of solid inorganic coördination compounds. For example, the analysis of solids is of great importance in cases where fundamental changes take place upon solution of solids and in cases where solids are insoluble in suitable solvents.[8] Recently an extremely interesting and important method for qualitative and quantitative studies of absorption spectra of organic compounds in the solid state using potassium bromide disks was introduced by Stimson and O'Donnell.[9] We adopted this technique for the study of solid inorganic coördination compounds to investigate the structural properties of ligands and their directive influences about the central metal ion of the complex. Furthermore, comparisons of spectra of solid inorganic coördination compounds with solutions of these complexes can be made, for it is well known that the state of aggregation in which the substance is measured is of importance and the frequencies may alter significantly on passage from the solid state to solution. Thus, investigations of the nature of the bonding of the coördination centers of complex compounds in the solid state as well as in solutions can be made. There is, however, some evidence that structural changes occur when some complexes are dispersed in potassium bromide.

It is the purpose of this investigation to determine the ultraviolet spectra of the *cis*- and *trans*-dinitrotetrammine isomers using the solid disk method and to compare their solid and solution spectra. Also, it is desirable from theoretical considerations to determine the validity of the Shibata–Tsuchida *trans* theory and to develop a general method for the study of the spectroscopic properties of solid inorganic coördination compounds. Furthermore, it is useful to extend these solid spectra studies to the infrared region of the spectrum, since on the basis of the *trans* effect and the differences in symmetry of *cis* and *trans* isomers differences in absorption spectra should also appear in this region.

Experimental

Preparation of Compounds.—*cis* and *trans*-dinitrotetramminecobalt(III) chloride was prepared by the method of Biltz.[10]

Anal. Calcd. for $[Co(NO_2)_2(NH_3)_4]Cl$: Cl, 13.93. Found: *cis*, Cl, 14.10; *trans*, Cl, 14.30.

The hexamminecobaltic chloride was prepared and recrystallized according to the methods of Bjerrum and McReynolds.[11]

Anal. Calcd. for $[Co(NH_3)_6]Cl_3$: N, 31.42; Cl, 39.76. Found: N, 31.43; Cl, 39.66.

Sodium hexanitrocobaltate(III) was prepared according to the method of Biltz,[12] and the infrared spectrum was identical to that of a sample kindly supplied by Dr. Henry Holtzclaw.

Apparatus and Procedure.—All ultraviolet spectra were determined with a Beckman quartz spectrophotometer model DU. Density readings were never further apart than 5 mμ intervals, and in regions of special interest readings were made at 1 mμ intervals. The silica absorption cells had a 1-cm. light path. The concentrations of the complexes employed varied with the degree of absorption, but were in the range of 0.00005 to 0.02 mole per liter. Measurements were made at room temperature and complete spectra were obtained from 220 to 625 mμ.

Distilled water and reagent grade methanol were used as solvents. In every case the reference blanks were obtained by using a volume of water equal to that used in the preparation of the concentrated aqueous solution and diluting with methanol and absolute ethanol.

Measurements in the solid state employed the potassium bromide disk method.[9] The potassium bromide used in the preparation of the disks for both the ultraviolet and infrared studies was recrystallized reagent grade potassium bromide, ground to 200 mesh or finer and dried at 110° for several days. Samples of the coördination compounds were mixed and ground with the potassium bromide powders in an agate mortar with successive mixing and grinding. A disk of pure potassium bromide of the same weight as that in the sample disk was used as the comparison plate.

Absorption Spectra.—Extinction coefficients for the ultraviolet spectra obtained by the disk method were calculated using the equation $E = 1/cd \log_{10}(I_0/I)$, in which c is reported in moles per liter of potassium bromide, and d is the length of the light path, 0.1 cm.

A Perkin–Elmer model 21 double beam recording infrared spectrophotometer was employed with a NaCl prism to study the 2 to 15 μ range.

Results and Discussion

The ultraviolet absorption spectra of *cis*- and *trans*-dinitrotetramminecobalt(III) chloride using the solid disk method compare favorably with those obtained using solutions of these compounds and also compare favorably with the values reported by Basolo.[13] Table I summarizes the absorption spectra of the *cis* and *trans* isomers.

TABLE I

ULTRAVIOLET ABSORPTION DATA OF COMPLEXES

$[Co(NH_3)_4(NO_2)_2]Cl$	3rd Band		2nd Band		1st Band	
	mμ	log	mμ	log	mμ	log
(Soln.) *cis*-	239	4.12	328	3.7	448	2.18
(Disk) *cis*-	Plateau	3.83	330	3.53	445[a]	2.82
(Soln.) *trans*-	255	4.08	348	3.73	439[a]	2.38
(Disk) *trans*-	255	3.69	355	3.3	440[a]	2.73

[a] Peak not well defined.

A comparison of the spectra reveals that the maxima obtained with the solid disk technique are not

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[5] I. I. Chernyaev, *Ann. inst. platine (U.S.S.R.)*, **4**, 261 (1926).

[6] Y. Shibata, *J. Chem. Soc. Japan*, **36**, 1243 (1915); *J. College Sci. Imp. Univ. Tokyo*, **37**, Art. 2 (1915).

[7] R. Tsuchida, *Bull. Chem. Soc. Japan*, **11**, 721 (1936); **13**, 388, 436 (1938); see also Y. Shimura, THIS JOURNAL, **73**, 5079 (1951).

[8] T. J. Lane, D. N. Sen and J. V. Quagliano, unpublished data.

[9] M. M. Stimson and M. J. O'Donnell, THIS JOURNAL, **74**, 1805 (1952).

[10] H. Biltz and W. Biltz, "Laboratory Methods of Inorganic Chemistry," 2nd Edition, adapted by W. T. Hall and A. A. Blanchard, John Wiley and Sons, Inc., New York, N. Y., 1928, pp. 179–180.

[11] J. Bjerrum and J. P. McReynolds, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 216.

[12] Reference 10, p. 149.

[13] F. Basolo, THIS JOURNAL, **72**, 4393 (1950).

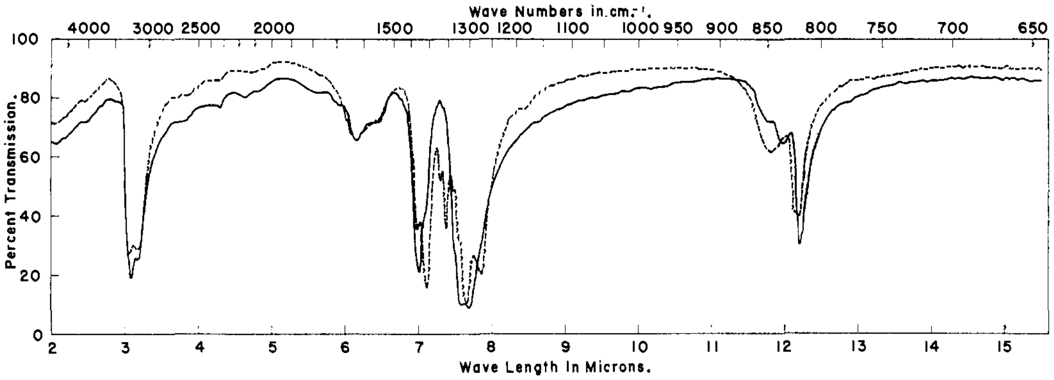

Fig. 1.—Infrared absorption spectra of isomers in KBr disks: ———, *trans*-dinitrotetramminecobalt(III) chloride; - - - -, *cis*-dinitrotetramminecobalt(III) chloride.

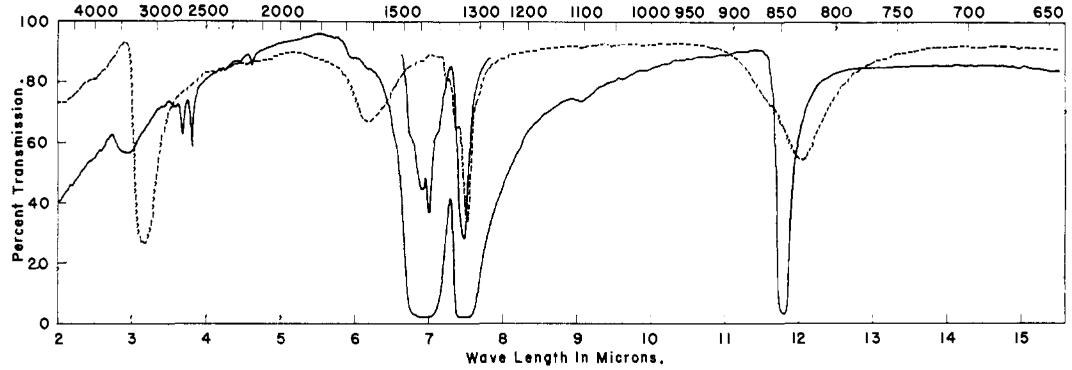

Fig. 2.—Infrared absorption spectra of complexes in KBr disks: - - - -, hexamminecobalt(III) chloride, $[Co(NH_3)_6]Cl_3$; ———, sodium hexanitrocobaltate(III), $Na_3[Co(NO_2)_6]$.

as pronounced as those obtained in solutions in the region of the first band. In the region of the third band, however, the absorption maximum of the *trans* compound in the solid disk is well defined. The principal difference in the absorption maxima obtained for *cis*-dinitrotetramminecobalt(III) complex in solution and in the solid disk appears in this region; the sharp peak at 239 mμ observed in solution is replaced in the disk by a flat plateau extending from 220 to 265 mμ. On the other hand, *trans*-dinitrotetramminecobalt(III) ion shows a strong absorption maxima at 255 mμ both in solution and in the solid state.

From the above results it can be seen that the data are in agreement with the theory of Shibata and Tsuchida, in that the third band appears in inorganic octahedral complexes if a pair of negative groups are coördinated in *trans* positions to one another. The appearance of the third band in the solution of the *cis* compound as reported by Basolo[13] and confirmed by this investigation is probably due to solvent effects, as no third band was observed in the spectrum of the *cis* complex in the solid state. This investigation dealing with the ultraviolet absorption spectra of solid inorganic coördination compounds supports the validity of the *trans* anions hypothesis concerning the absorption spectra of geometrical isomers.[6,7]

The infrared spectra of *cis*- and *trans*-dinitrotetramminecobalt(III) chloride and of hexamminecobalt(III) chloride and sodium hexanitrocobaltate(III) have been obtained. The infrared spectra of these complexes in potassium bromide disks, given in Figs. 1 and 2, show the vibrational frequencies due to the motions of the NH_3 Ligand which are in some way related to the motions of the NH_3 molecule. It is well established that the infrared and Raman spectra of NH_3 can be accounted for on the basis of a symmetrical pyramidal structure (C_{3V}) which has four fundamental vibrations, two totally symmetric and two doubly degenerate.[14] The formation of the N→Co bond should bring about an appreciable change in some of the frequencies.

The band in the 3 μ region can be assigned undoubtedly to the NH stretching vibrations. The small difference of the wave lengths from those of NH_3 is due to the formation of the N→metal bonds and to the coupling of vibrations of the ligands among themselves. The strongest peak appears at 3.1 μ for *cis*- and *trans*-$[Co(NO_2)_2(NH_3)_4]Cl$ and at 3.2 μ for the hexammine complex, whereas for the free NH_3 molecule the strongest peak is observed at 3.0 μ. The band at 6.1 ∼ 6.2 μ is also observed for the free ammonia molecule and this corresponds to one of the deformation vibrations of the NH_3 ligand. This band as well as a band at 3 μ has also been observed in the Raman spectrum of ammonia.

In addition to the bands described above, we have observed for the hexamminecobalt(III) complex two strong absorption bands at 7.5 and at 12.0 μ, neither of which is related to any of the infrared

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(14) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 111.

or Raman frequencies of the free NH_3. One might assign these bands to the N→metal stretching frequencies but this assignment is not probable; particularly the band at 7.5 μ cannot be so explained. These are probably associated with deformation vibrations of the NH_3 ligand, due to the formation of N→metal bonds.

In the spectrum of sodium hexanitrocobaltate-(III) strong absorption bands associated with the nitro group are observed at 6.8 $\sim$ 7.1, 7.5 and 11.8 μ and a weak band at 12.0 μ. The observed spectrum of the sodium hexanitrocobaltate(III) resembles that of a nitro alkane much more closely than an alkyl nitrite spectrum, indicating that coordination takes place between nitrogen and the central metal of the complex.

In the spectra of the *cis*- and *trans*-dinitrotetramminecobalt(III) chloride the absorption peaks appearing between 7 and 8 μ and at 12 μ are undoubtedly due to the overlapping of the NO_2 ion and the NH_3 ligands, taking into account the fact that the NO_2 ion frequencies are changed to some extent in different salts. It is interesting to note that fewer absorption peaks are present in the spectrum of *trans*-$[Co(NO_2)_2(NH_3)_4]Cl$ than in the *cis* compound. For example, in the region 7 $\sim$ 8 μ, two adjacent peaks appear in the *cis* compound but only one peak appears for the *trans* isomer. This is the natural consequence of the selection rule, since the *trans* complex has a center of symmetry while the *cis* complex does not.

The configurations of the coördination compounds which are in accord with the observed spectra, are octahedral d^2sp^3 hybridization for the *cis* and *trans* isomers, angular d^2 hybridization, and a d^2sp irregular tetrahedron. The latter two structures, which yield weaker covalent bonds, are also in accord with the diamagnetism of the isomers and fulfill the conditions required for the resonance structures.

Acknowledgment.—The generous gift of a set of dies for preparation of the potassium bromide disks from Sister Miriam Michael Stimson, O.P. is greatly appreciated. We are thankful to Brother Columba Curran, C.S.C. and Professor San-ichiro Mizushima for their many helpful suggestions concerning these investigations.

NOTRE DAME, INDIANA

NOTES

The Temperature-Independent Paramagnetism of Ammonium Hexabromoösmate(IV)

BY ROLF B. JOHANNESEN AND ANDREW R. LINDBERG

RECEIVED JUNE 11, 1954

As a part of a program on the investigation of the magnetic properties of compounds of the palladium and platinum triads, we have measured the magnetic susceptibility of ammonium hexabromoosmate(IV), $(NH_4)_2OsBr_6$, over the range of temperatures from 25 to $-180°$. The Bohr magneton number, $\mu_{\text{eff.}}$, defined by the equation $\mu_{\text{eff.}} = 2.83\sqrt{\chi_A T}$, has been found to be 1.51 at 18°, compared with the reported value[1] of 1.49. Moreover, it has been found that χ_A, the susceptibility, is independent of temperature, so that $\mu_{\text{eff.}}$ varies as the square root of the absolute temperature. Although the temperature dependence of susceptibility has been measured for some binary halides and oxides of platinum group metals,[2,3] the interpretation of the results is complicated by strong exchange coupling between the paramagnetic centers. Measurements on magnetically dilute compounds are therefore desirable. We believe this to be the first report of the temperature dependence of susceptibility for a platinum group compound which may reasonably be expected to be magnetically dilute.

Kotani[4] has calculated the magnetic moments to be expected for 6-coördinate complex ions in which the central atom has an incomplete shell of d electrons. These calculations depend on the following assumptions: (1) a large intramolecular and crystalline electrostatic energy of cubic symmetry is present; (2) exchange coupling between paramagnetic ions is negligible. The results are presented in the form of equations expressing $\mu_{\text{eff.}}$ as a function of A, the spin-orbit coupling coefficient, and T, the absolute temperature. In the general case, $\mu_{\text{eff.}}$ is a function of temperature and Curie's law is not obeyed. When there are four d electrons, as in quadrivalent osmium, Kotani's equation leads to the expectation that at low temperatures (up to 800° for this osmium compound) $\mu_{\text{eff.}}$ will vary as the square root of the absolute temperature and χ_A will be temperature independent. The temperature independent susceptibility found for ammonium hexabromoösmate(IV) can thus be accounted for on the basis of Kotani's calculations. From our data it is possible to estimate a value of 6400 cm.$^{-1}$ for A, the spin-orbit coupling coefficient. From Kotani's equation it may be estimated that, within the present experimental error of 2%, ammonium hexabromoösmate(IV) will continue to show paramagnetic susceptibility independent of temperature to the limit of its range of stability (170°).

This verification of even a part of Kotani's calculations is interesting in view of the small number of data presently available It would be interesting to subject these calculations to further tests to

(1) D. P. Mellor, *J. Proc. Roy. Soc. N.S. Wales*, **77**, 145 (1943).

(2) A. N. Guthrie and L. T. Bourland, *Phys. Rev.*, **37**, 303 (1931).

(3) B. Cabrera and A. Duperier, *Proc. Phys. Soc.*, **51**, 845 (1939).

(4) M. Kotani, *J. Phys. Soc. Japan*, **4**, 293 (1949).