Another band due to the COO^- group appears at 1365–1285 cm.$^{-1}$; the Ce(III) and Bi(III) chelates follow the previously noted trend[2] of the frequency decreasing as the stability constant increases. No apparent correlations exist between the absorption frequency and the character of the chelate for the rest of the complexes in Fig. 1, 2 and 3.

Four additional absorption bands which may be due to the COO^- groups are listed in Table I; at 1285–1160, 1055–995, 990–900 and 890–810 cm.$^{-1}$. No significant correlations can be made but the peaks are useful for identification purposes. The band at 1285–1160 cm.$^{-1}$ may be due to the C–N bond rather than to the COO^- group; spectra for ethylenediamine chelates frequently have an absorption band in this region.

The absorption band at 1145–1065 cm.$^{-1}$ has been assigned to the C–N bond in EDTA chelates[1,2,5] and is exhibited by all of the EDTA chelates collected in Table I. For the chelates in Fig. 1 only one peak is exhibited in this region. For the chelates whose spectra are shown in Fig. 2 and 3, several peaks are shown in this region, which appears to be characteristic of covalently bonded chelates. The frequency of the major peak for these covalently bonded chelates appears to decrease as the bonding becomes more covalent. If this conclusion is correct, then the Mo(V) chelate must be highly covalently bonded.

An additional absorption band appears in the 785–705 cm.$^{-1}$ region for all of the EDTA chelates. Although a specific assignment has not been made for this peak, it is useful for qualitative identification. The strong peak at 840 cm.$^{-1}$ for the Mo(VI) chelate has been established to be due to the Mo–O bond.

Conclusion

The general trends of decreasing frequency with increasing ionic radii, which were observed for the EDTA chelates of divalent ions, are confirmed in the spectra of the Ce(III) and Bi(III) chelates. The infrared data for the COO^- absorption peaks support the conclusion that the bonding for the Al(III), Ce(III) and Bi(III) chelates is primarily ionic. Similar data for the V(III), V(IV), Cr(III), Fe(III), Co(III), Ti(IV), Th(IV), Mo(V) and Mo(VI) EDTA chelates lead to the conclusion that for these complexes the bonding is primarily covalent. Thus, a peak for the antisymmetrical vibration of the COO^- group in the 1610–1550 cm.$^{-1}$ region is evidence for ionic bonding; when this peak is in the 1660–1630 region this is evidence for covalent bonding. As this peak increases in frequency it approaches the frequency of the C=O stretching bond (1700 cm.$^{-1}$), which would be expected for purely covalent bonding.

The data for the 1630–1660 cm.$^{-1}$ band indicate (but do not prove) that the EDTA molecule is serving as a sexadentate ligand in the case of the Fe(III), Co(III) and Mo(V) chelates. A like conclusion is possible in the case of the Cr(III), V(III) and V(IV) chelates but the broader maxima suggest that other interpretations are possible. The shoulders in the 1600 cm.$^{-1}$ region for the Bi(III), Th(IV) and Mo(VI) chelates indicate either that one or more of the COO^- groups are not bonded to the metal ion or that these groups are bonded differently. For the Ti(IV) chelate two of the COO^- groups have protons; thus the chelate has the formula $TiOH_2EDTA \cdot H_2O$.

The difference in frequency between the major peak for the symmetrical vibration (1450–1350 cm.$^{-1}$) and the peak for the antisymmetrical vibration (1660–1570 cm.$^{-1}$) of the COO^- group indicates the degree of covalent bonding for the EDTA chelates. The frequency difference increases as the bonding becomes more covalent; for chelates for which the difference is 225 cm.$^{-1}$ or greater the bonding is concluded to be primarily covalent. If the difference is less than 225 cm.$^{-1}$ the bonding is primarily ionic.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY, NASHVILLE 5, TENNESSEE]

The Effect of Coördination on the Reactivity of Aromatic Ligands. I. Some Reactions of Trichlorotrianilinechromium(III) and Trichlorotripyridinechromium(III)

BY JAMES C. TAFT[1] AND MARK M. JONES[2]

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An improved method for preparing trichlorotripyridinechromium(III) and a method of preparing trichlorotrianilinechromium(III) were developed. The reactivity of the coördinated pyridine toward typical electrophilic reagents was examined and, for the experimental conditions used, was found to be identical with that of free pyridine. The reactivity of the coördinated aniline toward bromine was also found to be quantitatively the same as that of free aniline. These observations can be explained readily on the basis of Pauling's principle of electroneutrality. Both of the complexes prepared reacted rapidly with methanol to give conducting species.

Although coördination compounds have been used as catalysts for organic reactions for almost a century, there is very little specific information on how the coördination process, *per se*, compares with typical substituent groups in varying the reactivity of a ligand species. The present work was undertaken to provide information of this sort on pyri-

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dine and aniline. Unfortunately, many of the catalytically useful complexes are materials of either unknown composition or unknown structure. For this reason we decided to study this phenomenon in complexes of known composition and structure and selected such complexes from those classed as "inert" by H. Taube.[3] These possess the considerable advantage of undergoing ligand replacement reactions at a rather slow rate. The central ion chosen was Cr^{+3} because of the availability of anhydrous chromium(III) chloride[4] and because it presented the possibility of readily making complexes with easily oxidized ligands, a feature missing from the chemistry of the inert complexes of Co(III). The ligands, pyridine and aniline, were selected as representing extremes in reactivity toward electrophilic substitution. Pyridine undergoes such reactions only under extreme conditions while aniline undergoes bromination, etc., at rates which are so fast that they have not been measured with any precision. Furthermore, for these two ligands, there is an enormous background of information on the effect of various substitutions on reactivity.

Another reason for selecting inert complexes for this study is that they possess the additional advantage of allowing a comparison to be made of the reactivities of free and bound ligand without introducing the possibility of catalytic actions such as are found in many analogous labile systems.

Experimental

Preparation of Trichlorotripyridinechromium(III).—Pfeiffer[5] prepared trichlorotripyridinechromium(III) by the reaction of pyridine and anhydrous chromium(III) chloride[5a] as well as by the reaction of pyridine with dichlorotetraquochromium(III) chloride 2-hydrate,[5b] but neither details of the preparations nor yields were reported. Both reactions were examined in detail, but the one using anhydrous chromium(III) chloride was found to be by far the most satisfactory from the viewpoints of both yield and purity of product.

Anhydrous chromium(III) chloride (26.4 g.), anhydrous pyridine (79 g.) and a stirring magnet were placed in a one-liter round bottomed flask with a standard taper opening. A water cooled condenser was connected to this and a Vigreux column was inserted in the top of the condenser. A heating mantle was placed under the flask and a magnetic stirrer under the heating mantle. The slurry was stirred magnetically and heated slowly until the pyridine boiled gently. In about fifteen minutes a vigorous reaction occurred and most of the chromium(III) chloride reacted; the violet color of the chromium(III) chloride vanished and the solution turned a deep green. A considerable amount of heat was evolved at this point and the Vigreux column served to prevent the loss of pyridine at this point. The solution was heated and stirred for an additional 5 hr. It then was cooled and 500 ml. of ice-cold water was poured into the reaction flask. The dark green crystals which separated were collected on a Buchner funnel and washed with cold water until the filtrate was clear. The crystals were air-dried and then extracted with chloroform in a Soxhlet extractor. The chloroform extract was evaporated under vacuum to obtain the final purified product. The yield was 60 g. (90% of theoretical based on $CrCl_3$).

Anal. Calcd. for $[Cr(C_5H_5N)_3Cl_3]$: Cr, 13.14; C, 45.54; H, 3.82. Found: Cr, 13.15; C, 44.96; H, 3.77.

Nitration of Trichlorotripyridinechromium(III).—Pfeiffer[5] showed that this complex could be recrystallized, unchanged, from concentrated nitric acid. It is thus a material of considerable stability. It does decompose in concentrated sulfuric acid, however, and this ruled out the use of the customary mixed acid in studying its nitration. The method used was that of Thomas, Anzilotti and Hennion[6] who demonstrated that mixtures of 92% nitric acid and boron trifluoride could be used to nitrate phthalic anhydride and other deactivated aromatic compounds. The only modification introduced in the present work was the use of 100% nitric acid.

The nitration studies were carried out in a 500-ml. three-necked flask equipped with a stirrer, a condenser and a gas delivery tube which allowed the boron trifluoride to be introduced under the surface of the nitric acid. One mole of HNO_3 and 0.0806 mole of $[Cr(C_5H_5N)_3Cl_3]$ were placed in the flask which was then put into an ice bath and cooled. Boron trifluoride (0.55 mole) was then passed in rapidly. The resulting solution was heated at reflux (93°) for 17 hr. The reaction mixture was allowed to cool, was neutralized and then extracted with ether. Evaporation of the ether and pyridine left less than 0.1 g. of tar. The experiment was repeated with 0.25 mole of pyridine and 0.1 g. of iron metal as catalyst. Only pyridine and a very small amount of tar were recovered.

Chlorination of Trichlorotripyridinechromium(III).—In a one-liter flask, equipped as in the previous experiment, were placed 500 ml. of chloroform and 0.0447 mole of $[Cr(C_5H_5N)_3Cl_3]$. The solution was heated at reflux for 24 hr., during which time chlorine gas was passed slowly into the solution. The solution became colorless and a violet precipitate of chromium(III) chloride was found at the bottom of the flask. The liquid was filtered, dried over KOH and distilled. Less than 0.1 g. failed to distill below 115°. All the reported monochloropyridines boil above 140°.

Subsequently a nitrobenzene solution was used in order to raise the reaction temperature. Chlorine was passed into a solution of 25 g. (0.063 mole) of $[Cr(C_5H_5N)_3Cl_3]$ in 100 ml. of nitrobenzene for 18 hr. at a temperature of 150°. The reaction mixture then was cooled and extracted with hot 5% hydrochloric acid. This aqueous extract was neutralized and extracted with ether. The ether solution on evaporation left 10 g. of liquid of b.p. 113–114°, none of which was chloropyridine.

Preparation of Trichlorotrianilinechromium(III).—The apparent inertness of coördinated pyridine to substitution reactions suggested the use of a more reactive aromatic ligand, and aniline was selected. A literature search revealed only one compound of aniline and chromium(III): anilinium bis-(oxalato)-dianilinechromium(III).[7] This compound was not considered suitable because of the difficulty of preparing it and because the presence of the oxalato groups would lead to the decomposition of the complex in the presence of electrophilic reagents (oxidizing agents).

The preparation of a compound analogous to trichlorotripyridinechromium(III) then was attempted with the substitution of aniline for pyridine in a procedure based on that given above. This was found to be successful after minor modifications.

A round bottom flask, fitted with a Vigreux column and heating mantle, all mounted on a magnetic stirrer, served as the reaction vessel. Into this were placed a stirring magnet, 13.2 g. of $CrCl_3$ (0.084 mole) and 46.5 g. of freshly distilled aniline (0.50 mole). This was then heated, without stirring, to the reflux temperature of aniline. The color of the reaction mixture changed to a dark brownish-black and then a sudden exothermic reaction occurred, and the solution turned green. After the appearance of the green color, heating at reflux and stirring were continued for two minutes. The hot solution was filtered quickly through a sintered glass filter. Three hundred ml. of ether was added to the filtrate, and the sticky semi-solid which resulted was broken up with a stirring rod. The ether was decanted and another 300 ml. of dry ether was poured on the solid. After partially breaking up the product with a stirring rod, the slurry was stirred rapidly with a magnetic stirrer for 1 hr. The result was a fine powder which was easily collected on a filter. After filtration the solid was dried for

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(3) H. Taube, *Chem. Revs.*, **50**, 69 (1952).

(4) Kindly furnished for our work by the Diamond Alkali Company, Cleveland, Ohio.

(5) P. Pfeiffer (a) *Z. anorg. Chem.*, **24**, 283 (1900); (b) *ibid.*, **55**, 99 (1907).

(6) R. J. Thomas, W. F. Anzilotti and G. F. Hennion, *Ind. Eng. Chem.*, **32**, 408 (1940).

(7) J. Meisenheimer, *Ann.*, **438**, 233 (1924).

1 hr. at 65° and 1 mm. in a vacuum drying pistol. The yield was 29 g. (79% of theoretical based on $CrCl_3$).

Anal. Calcd. for $[Cr(C_6H_7N)_3Cl_3]$: Cr, 11.88; C, 49.4; H, 4.84; N, 9.60. Found, Cr, 11.87; C, 49.64; H, 5.45; N, 9.78.

Bromination of Trichlorotrianilinechromium(III).—Trichlorotrianilinechromium (III) was found to be soluble in acetone, methanol, chloroform and acetic acid. Acetic acid was chosen as the solvent for the bromination study because it does not react with bromine under the conditions used. The experiments were carried out in such a manner that the bromination of free and coördinated aniline occurred under strictly comparable conditions and were run in paired samples.

Samples of aniline (0.5015 g.) and $[Cr(C_6H_7N)_3Cl_3]$ (0.7854 g. which contains 0.5015 g. of aniline) were subjected separately to the following treatment. The respective samples were transferred to 200 ml. volumetric flasks and diluted up to volume with glacial acetic acid (99.7% min.). The flasks were swirled to insure complete mixing and the solutions were transferred to 500 ml. Erlenmeyer flasks with ground glass stoppers. To each flask was added 10 ml. of a solution of bromine in glacial acetic acid. After mixing, a 5 ml. aliquot was removed, placed in 110 ml. of 3% potassium iodide solution and titrated with 0.0515 *N* $Na_2S_2O_3$. The bromine solution was standardized by a similar procedure. No change in the concentration of bromine in the pure glacial acetic acid could be detected in less than 24 hr. and the normal laboratory light was found to have no effect on the concentration of the bromine solutions exposed to it. A typical pair of runs is summarized in Table I.

TABLE I

COMPARISON OF THE BROMINATION OF ANILINE AND TRICHLOROTRIANILINECHROMIUM(III)

$T = 24°$; 0.0626 equivalent of Br_2 added to each sample

Time	Aniline (0.00538 mole)		$[Cr(C_6H_7N)_3Cl_3]$ (0.00180 mole)	
	Br_2 consumed	% reaction[a]	Br_2 consumed	% reaction[a]
0	0	0	0	0
1 min.	0.0214	66.2	0.0214	66.3
1 hr.	.0276[b]	85.6	.0389[b]	89.7
2 hr.	.0292	90.3	.0302	93.7
3 hr.	.0296	91.7	.0309	95.8
5 hr.	.0300	93.0	.0313	97.1

[a] Reaction to give 2,4,6 tribromoaniline. These results could be duplicated to ±4% of the values reported here. This probably represents the magnitude of the experimental error. [b] A precipitate appeared at this point.

After 5 hr. the solutions were diluted with water and the solids isolated. Each solid was recrystallized first with benzene. The solid isolated from the aniline solution melted at 119–120° and that from the trichlorotrianilinechromium (III) solution melted at 118°–119°. The reported melting point of 2,4,6-tribromoaniline is 120°.

Stabilities of the Complexes in Solution.—Several experiments were carried out to determine the stability of trichlorotrianilinechromium(III) in acetic acid and other solvents.

Although aniline is a weak base in water, in acetic acid it is a sufficiently strong base to be titrated with standard perchloric acid.[8] When the complex was dissolved in glacial acetic acid, less than 5% of the contained aniline could be titrated with standard perchloric acid in glacial acetic acid. Samples were titrated immediately after dissolving the compound in acetic acid and after standing for 24 hr. with no change in the amount of aniline which could be titrated.

The ultraviolet and visible absorption spectra of trichlorotrianilinechromium(III) in solution were obtained using a Cary Model 14 recording spectrophotometer. In methanol, ultraviolet absorption bands were found at 2850 and 2350 Å. These correspond to the reported absorption maxima of aniline. In acetic acid the compound absorbs at 5800, 4375 and 2500 Å. In aniline, the compound absorbs at 6200, 4575 and 3300 Å. The strong absorption which was found at 3300 Å. for aniline solutions but not for acetic acid solutions was unexpected. Since amines are capable of occupying more than three coördination positions of the chromium(III), it was suspected that further displacement of halide ion by aniline occurred under these conditions. To verify this suspicion, a solution of the complex in aniline was sealed in a heavy walled Pyrex tube and heated to 220° for 1 hr. The resulting solution was found to absorb at 3300 Å. with a 30% increase in absorbance over the unheated solution. This indicates that this absorption is due to a complex which contains four or more anilines coördinated to the central chromium ion. The similar appearance of the other portions of the spectra indicate that the species in the two solvents are quite similar.

To further test the assumption that the aniline was still coördinated to the chromium in glacial acetic acid, it was decided to isolate and analyze the chromium species in such a solution. For this purpose 2 g. of the aniline complex was dissolved in 50 ml. of glacial acetic acid and stirred for 15 minutes. The solution then was filtered and diluted with 150 ml. of *n* hexane. The solid which precipitated was filtered and washed with ether. After drying for 1 hr. at 65° in a 1 mm. vacuum, the compound was analyzed for chromium and nitrogen. The Cr/N weight ratio was found to be 1.31 for the precipitate obtained in this manner as compared with 1.24 in the original compound. The precipitate was a different shade of green than the starting material and apparently had been formed in a substitution reaction that did not result in any appreciable loss of aniline from the complex.

In order to determine the type of species which might form when these complexes were dissolved, conductivity values were obtained on some methanol and acetic acid solutions. These were measured using a bridge of moderate precision at a frequency of 1000 c.p.s. and a temperature of 25.0 ± 0.1°. The results are summarized in Table II.

TABLE II

CONDUCTANCE DATA

Solvent	Compound	Concn. (m./l.)	(Ohm^{-1} cm.$^{-1}$)	No. ions
CH_3OH	$[(C_6H_5)_4As]Cl$	0.001	200.0	2
	$[Cr(C_6H_7N)_3Cl_3]$	.001	184.2	2
	$[Cr(C_5H_5N)_3Cl_3]$	.001	183.4	2
CH_3COOH	$[(C_6H_5)_4As]Cl$	.001	4.23	2
	$[Cr(C_6H_7N)_3Cl_3]$	.001	1.95	2

It is obvious from the data that these compounds interact with the solvents. Since no titratable aniline is formed as the aniline complex stands in acetic acid, the probable reaction is one in which a chloro group is replaced by an acetato group. All of the experimental evidence is consistent with the retention of the coördinated aniline by the central Cr(III) species.

Reaction of *p*-Bromoaniline and Anhydrous Chromium (III) Chloride.—Although the bromination of trichlorotrianilinechromium(III) results in its ultimate disruption, it was found possible to prepare a stable solid by the reaction of *p*-bromoaniline and anhydrous chromium(III) chloride. The composition of this product was found to be consistent with the assumption that it is a mixture of tri-, tetra- and penta-ammine. When *p*-bromoaniline and anhydrous chromium(III) chloride were mixed in a 3:1 ratio and heated to 240° (the boiling point of the amine), a blue-violet solid was formed. This was dissolved in chloroform, filtered and the solvent evaporated. On analysis it was found to contain 5.36% Cr. $[Cr(C_6H_6NBr)_3Cl_3]$ requires 7.71% Cr and $[Cr(C_6H_6NBr)_4Cl_2]Cl$ requires 6.14%. When the preparation was repeated with a *p*-bromoaniline to chromium(III) chloride ratio of 4:1, an exothermic reaction was found to occur after five minutes at reflux. Analysis of this solid gave 4.26% Cr. The blue-violet color is probably not characteristic of the complex as *p*-bromoaniline is oxidized to blue-violet products on heating in air to 240°. These experiments did show that a complex ammine was formed as anhydrous chromium(III) chloride is insoluble in all of the solvents used to carry the complex.

A similar experiment with anhydrous chromium(III) chloride and 2,4,6-tribromoaniline did not produce any detectable complex formation.

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[8] J. S. Fritz, "Acid-Base Titrations in Nonaqueous Solvents," G. F. Smith Chem. Co., Columbus, Ohio, 1952, p. 13 ff.

Related Halogenations.—Oda and Tamura[9] reported that pyridine was brominated slowly when dissolved in a glacial acetic acid solution of bromine. This experiment was repeated using pure acetic acid. It was found that *no* bromine is consumed under these conditions. This is expected as pyridine is generally reported to undergo bromination only at temperatures much above room temperature. Iodination of the aniline complex also was examined, but the conditions required for the usual iodination procedure were found to result in undesired side reactions.

Discussion

The experimental results indicate that no great changes in the reactivity of simple monodentate aromatic ligands occur on coördination. In the case of the pyridine–chromium (III) complex the reactivity was considerably less than might have been predicted on the basis of the known enhanced reactivity of the pyridine N-oxides. Whereas pyridine may be nitrated in 20% yield at 300–350°,[10] pyridine N-oxide hydrochloride can be nitrated to 4-nitropyridine N-oxide at 90°.[11] The coördinate bond in the N-oxide produces a much greater change in reactivity than the presumably similar bond in the ammine. Coördination may also be contrasted with the effect of typical substituents on the reactivity of pyridine. Amino-, hydroxy-, alkoxy- and aliphatic groups produce an activating effect on the pyridine nucleus which is easily measured.[12] It safely may be said that insofar as electrophilic substitutions, such as chlorination, are concerned the substitution of an amino group for a hydrogen on the pyridine nucleus produces a much more profound change than does the coördination of the nitrogen to a species such as Cr(III). This rather unusual result is predicted by one of the theories of charge distribution in complexes. The same theory is capable of explaining the rather different behavior observed with aniline.

In contrast to pyridine, aniline undergoes electrophilic substitution reactions with great ease. Thus, aniline reacts very rapidly with bromine to produce 2,4,6-tribromoaniline. When the aniline is converted to acetanilide, however, the reactivity is greatly reduced and it is possible to obtain *p*-bromoacetanilide on treatment with bromine without producing any considerable amounts of more highly brominated derivatives. Protonation is a process which might be expected to have a similar effect on the reactivity as coördination. When aniline is dissolved in concentrated sulfuric acid the nitrogen is protonated to give the anilinium ion. This species is considerably less reactive than aniline. In comparison with the amino group, the $-NH_3^+$ group is deactivating and meta directing with respect to electrophilic reagents. Formally, the formation of a coördinate bond between the nitrogen of aniline and a species such as Cr(III) would be expected to be analogous to protonation insofar as its effect on the reactivity of the aromatic ring is concerned. Such is definitely *not* the case. In fact, coördination has even less effect than the presence of slightly electron withdrawing substituents on the nitrogen.

The results obtained in this work, though quite unexpected if analogies are drawn with protonation or substitution processes, are completely in accord with Pauling's principle of electroneutrality.[13] Pauling states this principle as: "the *postulate of the essential electrical neutrality of atoms:* namely, that the electronic structure of substances is such as to cause each atom to have essentially zero resultant electrical charge, the amount of leeway being not greater than $\pm^1/_2$, and these resultant charges are possessed by the most electropositive and electronegative atoms, and are distributed in such a way as to correspond to electrostatic stability." For the complexes examined here, this principle would lead to the expectation that in the coördination of one neutral species to another (*i.e.*, C_5H_5N to $CrCl_3$) no new large partial charges will be generated on the atoms participating in the new bond. Some of the shortcomings of this theory as applied to quantitative calculations have been pointed out by Williams.[14] The present experiments, however, indicate that as a principle, it possesses a *qualitative* validity which may be obscured but certainly is not destroyed by arguments over the manner in which the principle is to be put on a *quantitative* basis. The charge distribution in trichlorotrianilinechromium(III) calculated in the usual manner leads to these charges for the species involved: Cr, −1.08; Cl, −0.32; N, +0.68, H, −10.15; $-C_6H_5$, 0.0. These values are too large because of the electronegativity value used for chromium (1.6) and because of the arbitrary method used in carrying out these calculations.[13,15] From the chemical behavior of this compound a charge of +0.68 on the nitrogen seems much too large. The principle of electroneutrality is qualitatively valid in these cases, though, and it seems reasonable to propose a probable corollary to it to cover complexes of the types studied here. This is: *the reactivity of a simple electrically neutral monodentate aromatic ligand toward electrophilic reagents is relatively slightly affected by coördination to a metal ion.*[16] It must be emphasized that in making comparisons of this sort the only difference between the species being compared is to be the presence of a coördinate linkage in one species. Thus for ligands which are bases, as aniline, the comparison is to be made with

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(9) R. Oda and K. Tamura, *Sci. Pap. Inst. Phys. Chem. Res. (Tokyo)*, **33**, 129 (1937).

(10) F. Friedl, *Ber.*, **45**, 428 (1912); H. J. den Hertog and J. Overhoff, *Rec. trav. chim.*, **49**, 552 (1930).

(11) H. J. den Hertog and J. Overhoff, *ibid.*, **69**, 471 (1950).

(12) H. S. Mosher in R. C. Elderfield's "Heterocyclic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, Ch. 8.

(13) L. Pauling, *J. Chem. Soc.*, 1461 (1948).

(14) R. J. P. Williams, *J. Phys. Chem.*, **58**, 121 (1954). Reference 2.

(15) Alternative methods of carrying out the calculation of the charge distribution can be used to reduce the charge on the central chromium. See, for example, K. Ito, *Naturwissenschaften*, **46**, 415 (1959), who, using a different method, obtained a charge of 0.2 on the central cobalt atom in $Co(NH_3)_6^{+3}$. Since cobalt and chromium have nearly the same electronegativity and nitrogen and chlorine also do, the charge on the central chromium would be close to 0.2 if calculated using Ito's method. Ito summarizes other evidence supporting the electroneutrality principle.

(16) The work of H. C. Brown and B. Kanner, THIS JOURNAL, **75**, 3865 (1953), suggests that an alternative explanation may be proposed to cover the reactions of pyridine and its complexes, namely, that *all* coördination processes deactivate the pyridine to roughly the same extent. We prefer the present explanation because it appears to cover both pyridine and aniline reactions satisfactorily and suggest instead that the limitations to *metal* atoms or ions mentioned above be taken to exclude coördination processes with species such as SO_3, H^+, etc. The reaction systems studied here are simpler than those previously studied in that no catalytic processes involving the coördinated metal are concurrently operative.

the free base and not with a protonated species such as the anilinium ion. A similar difference would probably be found for ligands which are anions, *i.e.*, benzoate ion. Here the comparison required would be that between the benzoate ion (not benzoic acid) and the coördinated benzoate.

A final point which emerged from this work was an indication of a considerable degree of variation of the inertness of the inert complexes used. Thus the pyridine complex was very stable, the aniline complex less so, and the bromoaniline complexes even less stable. Thus for inert complexes, the degree of inertness of the complex may sometimes depend on the base strength of the ligand. The reactivity of the trichlorotripyridinechromium(III) and the trichlorotrianilinechromium(III) toward methanol was also quite unexpected as methanol frequently is used as a solvent in studying the reactions of such complexes. The conductivity data indicate unambiguously that a rapid reaction occurs with methanol to produce conducting species. Measurements taken even a few minutes after the solutions were prepared indicated essentially complete reaction. The reaction which occurs is presumably one in which a chloride ion in the coördination sphere is replaced by a methyl alcohol molecule. In view of the great tendency of chromium(III) to coördinate to oxygen, this is the most reasonable explanation of the conductivity data. Herwig and Zeiss[17] found anhydrous chromium (III) chloride to react with tetrahydrofuran to give $[CrCl_3(C_4H_8O)_3]$, a compound which indicates the avidity with which Cr(III) coördinates even to ethereal oxygen. The tetrahydrofuran molecules are not lost when the compound is heated to 100° at 20 mm.

Summary

1. Preparative methods which give good yields of trichlorotripyridinechromium(III) and trichlorotrianilinechromium(III) were developed.

2. The reactivities of pyridine or aniline coordinated to a metal do not differ greatly from those of the free ligands insofar as typical electrophilic reactions are considered.

3. Pauling's principle of electroneutrality provides a satisfactory qualitative theoretical explanation for the effect of coördination on the reactivity of simple neutral monodentate aromatic ligands.

4. Both of the chromium complexes examined reacted very readily with methanol to give conducting species.

This work was supported in part by a National Science Foundation Research Grant (No. 09919).

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(17) W. Herwig and H. H. Zeiss, *J. Org. Chem.*, **23**, 1404 (1958).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS]

Mechanism of Substitution Reactions of Complex Ions. XVII.[1] Rates of Reaction of Some Platinum(II) and Palladium(II) Complexes with Pyridine[2]

BY FRED BASOLO, HARRY B. GRAY[3] AND RALPH G. PEARSON

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The relative reactivities of replaceable ligands in planar complexes of platinum(II) follow the order: $NO_3^- > Cl^- > Br^- > I^- > SCN^- > NO_2^-$. This is the same order as for octahedral complexes of cobalt(III) except for an inversion in the reactivities of the halides. In both systems labilities parallel instabilities. Analogous palladium(II) complexes of the type $Pd(dien)X^+$ react 10^5 to 10^6 times faster than corresponding platinum(II) complexes.[4] Nickel complexes are again somewhat more reactive than palladium complexes.

Although there have been several kinetic studies[5] on substitution reactions of square complexes, there is as yet little quantitative comparison of the reactivities of analogous platinum(II) and palladium (II) complexes. There is also very little information on the relative rates of displacement of different ligands from similar complexes of the same metal.

This paper reports a kinetic study of the replacement of a ligand X in platinum(II) and palladium(II) complexes of the types $M(dien)X^+$ and $M(tripy)X^+$ by pyridine in aqueous solution.

Experimental and Results

Preparation of Compounds.—The known compounds were prepared by essentially the same methods as those described in the literature. This was the case for the halogen complexes of the types $[Pt(dien)X]X$,[6] $[Pt(tripy)X]X$[7] and $[Pd(tripy)X]X$.[8] The $Pd(dien)X]X$ compounds were prepared by almost the same procedure as that used for the corresponding platinum compounds. A reaction mixture containing 5 g. of $PdCl_2$, 6 g. of dien·3HCl, 5 g. of dien and 100 cc. of H_2O was allowed to reflux for 8 hr. During this time an orange solution is formed and some metallic palladium deposits. The solution was passed through a filter and the filtrate was concentrated to 30 cc. on a steam-bath. To a 10 cc. portion of this solution was added 2 g. of solid NH_4Cl and a yellow crystalline precipitate slowly separated. The yellow product was collected and washed with a small amount of cold water. It was recrystallized from a small amount of water, air dried at 50° and found to weigh 1.7 g. (65% yield). Addition of 1 g. of NaBr to a second portion of the original filtrate yielded $[Pd(dien)Br]Br$ and the addition of 1 g. of NaI to the third portion gave $[Pd(dien)I]I$.

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(1) Previous paper in this series, R. G. Pearson, H. B. Gray and F. Basolo, THIS JOURNAL, **82**, 787 (1960).

(2) This investigation was partly supported by a grant from the U. S. Atomic Energy Commission under contract AT(11-1)-89-project No. 2.

(3) Dow Chemical Company Fellow, 1958–1959.

(4) Symbols used: dien = diethylenetriamine, tripy = 2,2′,2″-tripyridyl, py = pyridine.

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