

this case the d electrons of the metal will be held more strongly and so will be less available for dative π -bonding.

The fact that in the NiDBH complexes the phosphines appear to be less constrained than the amines can be attributed to a decrease in F- and B-strain. In fact, the atomic radius of phosphorus (1.10 Å.) is about 0.40 Å. larger than that of nitrogen (0.70 Å.). As a consequence, with the phosphine adducts, the alkyl chains will be 0.8 Å. further away from the NiDBH plane than with the amine adducts. It is therefore expected that the F-strain will be much weaker, or lacking, in phosphine complexes. Moreover, B-strain is to be considered as absent in trialkylphosphines¹⁷ because of the larger size of P as compared with N, and because the C-P-C angles (100° in trimethylphosphine) are less than tetrahedral and are smaller than the C-N-C angles in trialkylamines (108–109° for trimethylamine).¹⁸ In this case, as suggested by Spitzer and Pitzer, B-strain may be more base-strengthening than base-weakening.¹⁹

In conclusion the higher stability of phosphine adducts in comparison with that of amines appears ascribable to the lower steric strain between phosphines and NiDBH.

Equilibria between Triphenyl-amine, -Phosphine, -Arsine and -Stibine and NiDBH.—The coordinating ability of these substances toward transition metal atoms is well established. Many stable metal complexes of triphenyl-amine, -phos-

(17) H. C. Brown, *THIS JOURNAL*, **67**, 503 (1945); H. C. Brown, D. H. McDaniel and O. Häffiger, in E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., Publ., New York, N. Y., 1955, p. 642.

(18) L. O. Brockway and H. O. Jenkins, *THIS JOURNAL*, **58**, 2036 (1936); H. D. Springall and L. O. Brockway, *ibid.*, **60**, 996 (1938).

(19) R. Spitzer and K. S. Pitzer, *ibid.*, **70**, 1261 (1948).

phine, etc., have been described.²⁰ These ligands, however, show no coordinating tendency toward NiDBH: solutions of the complex do not turn brown on addition of these bases. This fact can be accounted for in terms of steric and electronic effects.

As is well known, the phenyl group, on account of the resonance effect, is an electron-withdrawing substituent and so decreases the σ -bonding tendency of the ligands and increases their π -bonding ability. Since the nickel-phosphorus bonding in the NiDBH adducts appears to be essentially σ in character, the Ni-P bonding will be much too weak and so the adducts with triphenylphosphine will not form. This reason holds also for triphenylarsine, etc. For triphenylamine one can also invoke the influence of steric factors. In fact, in this triphenyl derivative the three phenyl groups lie preferably in planes at 120° passing through the axis of the pyramid having the nitrogen as vertex. For this reason the phenyl groups will protrude beyond the N atom. This does not give rise to steric hindrance when the triphenylamine is bound to a tetraordinated metal atom at one of the four vertices of the square or tetrahedron. However, in the case of NiDBH, it is to be expected that the phenyl groups which coordinate to the nickel atom above and below the equatorial plane of NiDBH will interfere with the atoms in such plane. On the other hand, the three phenyl groups cannot avoid this strain by rotation without clashing.

(20) W. Reppe and W. J. Schweckendieck, *Ann.*, **560**, 104 (1948); K. Yamamoto, *Bull. Chem. Soc. Japan*, **27**, 501 (1954); L. M. Venanzi, *J. Chem. Soc.*, 719 (1958); L. Vallarino, *J. Inorg. & Nuclear Chem.*, **8**, 288 (1958); J. Chatt and G. A. Rowe, International Conference on Coordination Chemistry, London, April, 1959, Abstract No. 8.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LAWRENCE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA]

Ruthenium(III) Chloride Complexes: RuCl_2^+

BY ROBERT E. CONNICK AND DWIGHT A. FINE

RECEIVED JANUARY 8, 1960

Ruthenium in the +3 oxidation state in aqueous solution is known to form a number of complexes with chloride ion which equilibrate only slowly. Because of the complexity of this system, only one of these, RuCl^{+2} , previously has been isolated in solution and identified unambiguously. In the present study two more of the complexes have been obtained in pure form and characterized. The formulas of these complexes, which are cationic species, have been determined by use of properties of ion-exchange resins. The total charge per species was determined by equilibrating the unknown species and hydrogen ion with ion-exchange resin in a pair of experiments. The charge per metal atom on one species was determined by a modification of a previously reported method involving the pushing of the species from an ion-exchange column with an ion of known charge. The salt of a weak acid had to be used to produce a concentrated band. The charge per metal atom of the other species was established by determination of the amount of a known ion displaced from an ion-exchange column by a solution of the species. The number of chloride ions bound to the metal atom was determined by direct analysis. The species were both found to have the formula RuCl_2^+ and are presumed to be *cis* and *trans* isomers. The species were separable by elution from an ion-exchange column.

Introduction

In a previous paper, a method for the determination of the formulas of aqueous ruthenium(III) species which equilibrate only slowly was described.¹ This method involves the use of ion-exchange resins to determine the charge per metal atom and the

charge per species. The formula may be inferred from these two data if only one type of complexing anion is involved. The method was used to identify the species Ru^{+3} and RuCl^{+2} . A third species was identified tentatively as RuCl_2^+ . A more definite identification of the latter species was desired, as well as the identification of other ruthenium(III) species present in hydrochloric acid solution.

(1) H. H. Cady and R. E. Connick, *THIS JOURNAL*, **80**, 2646 (1958).

In the previous experiments, the method for determination of the charge per metal atom had been to load the top of a cation exchange column in the hydrogen ion form with the ruthenium species and elute the column with a cerous perchlorate solution containing a small amount of perchloric acid. This elution served to separate the ruthenium species and push them from the column in compact bands of relatively high concentration. Ruthenium and hydrogen ion analyses of the eluted bands permitted calculation of the charge per ruthenium atom. The method proved unfeasible for the species designated $\text{RuCl}_2^+(?)$ in the previous paper. This species was held so loosely by the resin that it was eluted gradually from the column, along with the perchloric acid, rather than being pushed in a compact band in front of the cerous ions.

It was thought that a difficulty of this nature could be overcome if elution was done with a solution buffered in such a way that the hydrogen ion concentration in the aqueous phase of the column was kept below a concentration sufficient to readily elute the species. The use of a calcium chloroacetate-chloroacetic acid solution for this purpose was found convenient. The calcium is held strongly enough by the resin so as to displace nearly completely hydrogen ion and the ruthenium species. Hydrogen ions displaced from the resin are removed from solution by the chloroacetate ions to such an extent that the ruthenium species is not eluted appreciably by the displaced hydrogen ion. The ruthenium species is then pushed out of the column in a compact band by the calcium. Ruthenium and hydrogen ion analyses on samples from the band permit the calculation of the charge per ruthenium atom. The charge per atom α is given by the expression

$$\alpha = \frac{2(\text{Ca}^{++})_i + (\text{HClOAc})_i + (\text{H}^+)_i - (\text{H}^+)_f - (\text{HClOAc})_f}{(\text{Ru})_f} \quad (1)$$

where parentheses indicate concentrations in moles per liter, i and f designate elutriant and eluate, respectively, HClOAc designates chloroacetic acid, and $(\text{Ru})_f$ is in gram-atoms per liter. All quantities in the expression except $(\text{HClOAc})_f$ are known either beforehand or from measurements during the experiment. The value of $(\text{HClOAc})_f$ may be calculated from known quantities

$$(\text{HClOAc})_f = (\text{ClOAc}^-)_i + (\text{HClOAc})_i - (\text{ClOAc}^-)_f \\ = 2(\text{Ca}^{++})_i + (\text{HClOAc})_i + (\text{H}^+)_i - (\text{ClOAc}^-)_f \quad (2)$$

Now

$$(\text{ClOAc}^-)_f = \frac{Q_a(\text{HClOAc})_f}{(\text{H}^+)_f} \quad (3)$$

where Q_a is the ionization quotient of chloroacetic acid expressed in moles per liter. Substituting the expression for $(\text{ClOAc}^-)_f$ into equation 2 and solving for $(\text{HClOAc})_f$, one obtains

$$(\text{HClOAc})_f = \frac{(\text{H}^+)_f[2(\text{Ca}^{++})_i + (\text{HClOAc})_i + (\text{H}^+)_i]}{(\text{H}^+)_f + Q_a} \quad (4)$$

Substitution of this expression into equation 1 yields for the charge per ruthenium atom

$$\alpha = \frac{Q_a[2(\text{Ca}^{++})_i + (\text{HClOAc})_i + (\text{H}^+)_i] - (\text{H}^+)_f}{(\text{Ru})_f[(\text{H}^+)_f + Q_a]} \quad (5)$$

A second cationic species was encountered which was held even more loosely by the resin than the species discussed above. A pushing experiment was not feasible with this species. The $p\text{H}$ of the calcium chloroacetate-chloroacetic acid solution used to push the first species was sufficiently low that the second species was eluted. Buffer solutions of higher $p\text{H}$ caused a chemical reaction of the species, as indicated by its absorption spectrum.

Determination of the charge per metal atom for such a species is possible, however, by the simple procedure of placing a solution of the pure species on a cation exchange column in the hydrogen ion form, washing the column with water and determining the total hydrogen ion in the eluate plus wash. The hydrogen ion and ruthenium content of the original solution being known, the number of hydrogen ions displaced from the column per atom of ruthenium placed on the column can be calculated. This quantity is the charge per ruthenium atom.

Experimental

Experimental Apparatus.—Absorption spectra were measured on a Cary Recording Spectrophotometer Model 11, Serial 4. Measurements of $p\text{H}$ were made with a Beckman Model G $p\text{H}$ meter. The $\log^{-1}(-p\text{H})$ was divided by the mean activity coefficient of hydrochloric acid at the same ionic strength to yield an approximate value of the hydrogen ion concentration.

Solutions.—The water used in all experiments was normal distilled water which gave a negative test for chloride ion.

Solutions of ruthenium(III) chloride species were prepared by refluxing a solution of Chemical Commerce ruthenium chloride in 0.3 M HCl over mercury for 24 hours. A typical preparation contained 10 g. of ruthenium chloride in 50 cc. of 0.3 M HCl . Solutions so obtained were either red-brown or dark green in color; the green color changed to red-brown in a few days at room temperature, though it persisted for several weeks if a solution was kept in a refrigerator. The green color is thought to be due to lower oxidation states of ruthenium. Experimental work with a solution was not begun until the green color was gone. The solutions were kept over mercury; solutions not kept over mercury showed gradual oxidation to Ru(IV) .

Calcium chloroacetate-chloroacetic acid buffer solutions were prepared by dissolving J. T. Baker Analyzed C.P. calcium carbonate in chloroacetic acid solutions which had been analyzed by titration with standard sodium hydroxide. The solutions were heated to expel carbon dioxide.

Analysis.—The ruthenium concentration in solution was determined by making the solution alkaline with sodium hydroxide, oxidizing the ruthenium to a mixture of RuO_4^+ and RuO_4^- with excess hypochlorite, reducing the RuO_4^- to RuO_4^+ and the ClO^- to Cl^- with excess sodium iodide and determining the RuO_4^+ spectrophotometrically. This method proved more convenient than the previously employed method involving oxidation to RuO_4^2 ; the latter method entails danger of oxidation of chloride to chlorine and removal of chloride before oxidation is difficult. To make an analysis an aliquot of ruthenium solution was added to a 5 ml. volumetric flask containing 1 cc. of about 1 M NaOH . The mouth of the flask was held in a stream of chlorine generated by pouring hydrochloric acid on calcium hypochlorite. It was not necessary to bubble the chlorine into the solution. Oxidation of ruthenium was indicated by change in color of the solution from yellow to brown to orange to yellow-green. Sodium iodide solution was then added with a micropipet until the deep orange color of RuO_4^+ appeared and remained permanently. The solution then was diluted to the mark and the visible absorption spectrum was measured. Absorbance of the blank solution was not appreciable at this wavelength. The molar extinction coefficient used for analysis was $\epsilon_{4600 \text{ \AA.}} = 1820$.³

(2) P. Wehner and J. C. Hindman, *THIS JOURNAL*, **72**, 3911 (1950); J. L. Swanson and A. S. Wilson, Hanford Atomic Works Quarterly Report of the Chemistry Unit, HW-29619, November 16, 1953.

(3) R. E. Connick and C. R. Hurley, *THIS JOURNAL*, **74**, 5012 (1952).

Analysis for total chloride in ruthenium solutions was accomplished by adding excess silver nitrate to the solution, oxidizing the ruthenium to RuO_4 by the dropwise addition of ceric perchlorate solution, volatilizing the RuO_4 out of solution by gentle heating and then filtering, washing, drying and weighing the silver chloride precipitate. Determination of chloride by direct titration with silver nitrate was not feasible due to uncertainty as to the speed with which silver ion attacks chloride bound to ruthenium and the fact that silver, ruthenium and chloride form a complex precipitate of unknown composition.⁴ The method employed removes the ruthenium from the solution and from the precipitate. No evidence of oxidation of chloride to chlorine was obtained.

The calcium content of the calcium chloroacetate-chloroacetic acid solutions was checked by precipitating the calcium as the oxalate, dissolving the oxalate in sulfuric acid and titrating the oxalic acid with standard potassium permanganate. The calcium concentration was found to agree with the concentration corresponding to the weight of calcium carbonate used in the preparation of the solution.

Qualitative tests for Ru(IV) were made by addition of sodium iodide and starch to the ruthenium solution. Appearance of the starch-iodine color was considered to indicate the presence of Ru(IV).⁵

Ion-Exchange Resins.—The ion-exchange resins were analytical grade resins obtained from Bio-Rad Laboratories. Specific resins used were Dowex 50W \times 8, hydrogen form and Dowex 1 \times 10, chloride form. Particle size was 200–400 mesh. Capacity of the cation resin was determined by titration of air-dried resin with standard sodium hydroxide.

Results

Separation of Species.—Solutions of the species identified in this work were obtainable by charging a cation exchange column with the stock solution of Ru(III) species, washing the column with water to remove anionic and neutral species and then eluting the column with 0.1 M HCl. Absorption spectra of samples eluted from the column indicated that only two species were eluted by this dilute acid. The efficiency of 0.1 M acid for elution indicated that these species were loosely held by Dowex 50 resin in comparison with hydrogen ion. Clean-cut separation of the species by elution was not achieved. Samples from the beginning and the end of the elution were considered to be pure species, absorption spectrum being used as a criterion of purity. The more tightly held of the two species had a spectrum similar to that of the species identified tentatively in the previous paper as RuCl_2^+ .¹ Solutions of the species gave negative reactions to the starch-iodide test for Ru(IV).

Determination of Charge per Atom.—A cation exchange column in the hydrogen ion form was charged with the stock solution of Ru(III) species. The column was washed with water to remove neutral and anionic species and then was eluted with a solution of calcium chloroacetate in chloroacetic acid of pH ca. 2.75. Although one of the cationic species was eluted along with hydrogen ion even at this low acidity, a second species (the $\text{RuCl}_2^+(?)$ of the previous paper) was pushed out in a compact band. Spectra were taken of samples from the band and hydrogen ion and ruthenium analyses were made. The spectra showed no evidence of complexing by chloroacetate. The charge per atom was calculated from equation 5. Q_a was determined empirically: the hydrogen ion concentration in the elutriant solution was calculated from pH measurement, and the concentrations of chloro-

acetic acid and chloroacetate ion in the solution were known. The data and results are shown in Table I.

TABLE I

CHARGE PER ATOM DETERMINATIONS, SPECIES RuCl_2^+ (C)

No. ^a	Ca(Cl-OAc) ₂ in elutriant, mole/l.	HClOAc in elutriant, mole/l.	Q_a	Ru in eluate, mole/l.	H ⁺ in eluate, mole/l.	Charge per Ru atom
13	0.252	0.333	3.3×10^{-3}	0.077	0.026	0.9 ± 0.1^b
14				.119	.016	1.1
15				.158	.012	1.1
16				.196	.0083	1.2
17				.246	.0087	0.9
7	0.245	0.298	3.7×10^{-3}	.027	.042	0.9
8				.046	.033	1.0
9				.076	.026	1.0
10				.094	.024	0.9
11				.121	.020	0.9

^a Samples were taken consecutively in two separate experiments. ^b Uncertainty calculated by assuming an uncertainty of ± 0.03 unit in the pH measurement.

In the case of the more loosely held species, the hydrogen ion concentration in a solution of the pure species, obtained by elution of a cation column with 0.1 M HCl, was reduced by stirring the solution with anion exchange resin in the hydroxide form until the hydrogen ion concentration, as determined by pH measurement, was about the same as the ruthenium concentration. The resin was centrifuged out, the solution was analyzed for ruthenium, and a measured volume of the solution was placed on a short column of cation exchange resin, hydrogen form. The column was washed with water. The hydrogen ion in the effluent was determined by titration with standard sodium hydroxide. The lowering of the HCl/Ru ratio as a result of the stirring with hydroxide-form resin appeared to lead to decomposition of the species. This decomposition was preventable by keeping the solutions of the species at around 0° as much as possible during the experiment. The hydrogen ion displaced by the ruthenium was calculated by subtracting the measured hydrogen ion content of the ruthenium solution from the total hydrogen titrated in the column effluent. The data and results are shown in Table II.

TABLE II

CHARGE PER ATOM DETERMINATIONS, SPECIES RuCl_2^+ (T)

Experiment	Ru in solution, mg. atoms	H ⁺ in solution, meq.	H ⁺ + Ru	H ⁺ titrated in effluent, meq.
1	0.033	0.057	0.090	0.095
2	.049	.155	.204	.205
3	.019	.017	.036	.040
4	.044	.044	.088	.089

Determination of Charge per Species.—The method presented in the previous paper¹ was employed. A solution of the pure species was diluted with hydrochloric acid of known concentration and equilibrated with cation exchange resin, hydrogen form, by stirring in a beaker. Time studies showed that equilibrium was attained within 30 minutes. A spectrum of the solution was taken, water was added to lower the acidity and the equilibration was repeated.

(4) L. Brizard, *Ann. Chim. Phys.*, [7] **21**, 342 (1900).

(5) W. R. Crowell and D. M. Yost, *THIS JOURNAL*, **50**, 374 (1928); O. Ruff and E. Vidic, *Z. anorg. allgem. Chem.*, **136**, 49 (1924).

TABLE III
 CHARGE PER SPECIES DETERMINATIONS

Experiment	Total Ru (111), mg. atoms	Initial (H ⁺), M	Volume, ml.	Weight of resin, g.	Resin capacity, meq.	Ru (111), g.-atoms/l.	Calculated charge per species
Species RuCl ₂ ⁺ (C)							
1	0.0214	0.100	10	1.32	5.07	1.41 × 10 ⁻³	1.2
2	.0214	.050	20	1.32	5.07	6.6 × 10 ⁻⁴	
1	.0145	.145	10	2.20	8.15	1.12 × 10 ⁻³	1.1
2	.0145	.0725	20	2.20	8.15	5.5 × 10 ⁻⁴	
Species RuCl ₂ ⁺ (T)							
1	0.00905	8.9 × 10 ⁻³	5	0.0440	0.171	1.40 × 10 ⁻³	1.0
2	.00905	4.6 × 10 ⁻³	10	.0440	.171	7.0 × 10 ⁻⁴	
1	.0104	8.7 × 10 ⁻³	5	.0778	.300	1.28 × 10 ⁻³	1.0
2	.0104	4.7 × 10 ⁻³	10	.0778	.300	6.4 × 10 ⁻⁴	

Analysis was made of the gram atoms of ruthenium per liter in the solution. The ruthenium concentration in the solutions from the equilibrations was determined from the absorbance at selected wave lengths relative to that of the initial solution. A check was obtained by direct analysis of the solution from the second equilibration. The ruthenium concentration in the resin was calculated by difference, the weight of the resin being known. The hydrogen ion concentration in the solution also was calculated by difference. The hydrogen ion concentration in the resin was approximately constant and equal to the capacity of the resin; the correction for the hydrogen ion displaced by the ruthenium was negligible under the conditions employed. The use of only a small amount of resin in the case of the more loosely held species was found to be essential as the use of amounts in excess of 0.1 g. produced changes in the spectrum of the species, possibly due to impurities in the resin. A correspondingly lower hydrogen ion concentration was needed, and the species used in the experiments was obtained by elution of a cation column with 0.01 M rather than 0.1 M HCl. The data and results are given in Table III.

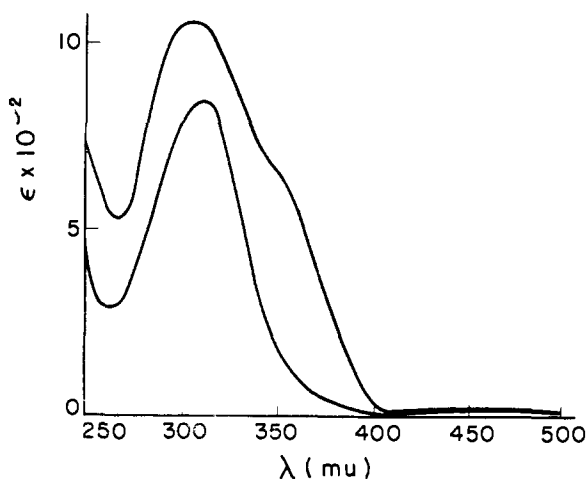


Fig. 1.—Spectra of RuCl₂⁺ isomers: upper curve, RuCl₂⁺ (C); lower curve, RuCl₂⁺ (T).

Determination of Chlorides per Ruthenium.—The total chloride content of solutions of the pure species was determined as described under Analysis. The chloride bound to ruthenium was calculated

as the difference between the total chloride and the free chloride content of the solution. The free chloride concentration was taken to be the same as that of the hydrochloric acid solution used to elute

 TABLE IV
 CHLORIDE PER RUTHENIUM DETERMINATIONS

Weight AgCl, g.	Total chloride, meq.	Free chloride, meq.	Ru, mg.-atoms	Chlorides per Ru
Species RuCl ₂ ⁺ (C)				
0.0615	0.430	0.300	0.0594	2.19
.0610	.426	.300	.0594	2.12
.0603	.421	.300	.0594	2.04
Species RuCl ₂ ⁺ (T)				
0.0478	0.334	0.250	0.0422	2.0
.0483	.338	.250	.0422	2.1
.0286	.200	.150	.0253	2.0

the species from a column. This HCl solution had been prepared from standard HCl and the free chloride ion content should not be altered by passage through a cation exchange column. The results are given in Table IV.

Discussion

The species labeled RuCl₂⁺ (C) in the tables is the species held more tightly by the cation resin. The results in Tables I and II indicate a charge per ruthenium atom of +1 for both RuCl₂⁺ (C) and RuCl₂⁺ (T). The results of Table III indicate a charge of +1 for each of these species. This is supported by the charge per atom experiments, since the charge per species must be an integral multiple of the charge per atom.

Since for both species the charge per atom and the charge per species are +1, the formula of each species must be RuCl₂⁺, taking cognizance of the fact that chloride is the only complexing anion present. The chloride per ruthenium analyses confirm this formula. Since both species have the formula RuCl₂⁺, they are presumed to be the *cis* and *trans* isomers of the ion [Ru(H₂O)₄Cl₂]⁺. Evidence will be presented in a later paper that RuCl₂⁺ (C) is probably the *cis* isomer and RuCl₂⁺ (T) the *trans* isomer.

Spectra.—The molar extinction coefficients of the two species are plotted in Fig. 1 as a function of wave length. Solutions of both species are bright yellow in color. The spectrum given by Rehn and

Wilson⁶ as that of RuCl_2^+ is somewhat similar to our curve for $\text{RuCl}_2^+(\text{C})$. Their molar extinction coefficient at the maximum is very nearly the same but at 270 and 370 $\text{m}\mu$ their molar extinction coefficient is *ca.* 40% higher and *ca.* 25% lower, respectively, than found here. A mixture of $\text{RuCl}_2^+(\text{C})$ and $\text{RuCl}_2^+(\text{T})$ would not explain the discrepan-

(6) I. M. Rehn and A. S. Wilson, "Ruthenium (III) Chloride Complexes in Trifluoroacetic Acid Solution," Hanford Atomic Works, Richland, Washington.

cies. The previous paper¹ gives two spectra for RuCl_2^+ ; both of these spectra resemble that of $\text{RuCl}_2^+(\text{C})$ above 300 $\text{m}\mu$. Below 300 $\text{m}\mu$ the spectrum obtained in 0.2 *M* HClO_4 corresponds more closely to that of $\text{RuCl}_2^+(\text{C})$. Again a mixture of the two isomers would not explain the spectra and it is concluded that additional species were present in the earlier work.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIFORNIA]

Properties and Infrared Spectra of Ethylenediaminetetraacetic Acid Complexes. III. Chelates of Higher Valent Ions

BY DONALD T. SAWYER AND JEAN M. MCKINNIE

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Infrared spectra have been recorded for the EDTA chelates of Al(III), Ce(III), Bi(III), V(III), V(IV), Cr(III), Fe(III), Co(III), Ti(IV), Th(IV), Mo(V) and Mo(VI). The spectra, when related to previous studies, indicate that the bonding between ligand and metal ion is primarily ionic for the Al(III), Ce(III) and Bi(III) chelates, and primarily covalent for the remainder of the chelates. Correlations are made between the various functional groups and their resulting absorption peaks. The EDTA chelates for this group of metal ions have been synthesized and isolated.

The complexes formed between the ions of divalent metal ions and ethylenediaminetetraacetic acid (hereafter referred to as EDTA) have been discussed relative to their infrared spectra in the previous two papers of this series.^{1,2} Additional infrared studies have been reported for the EDTA chelates of Co(III),^{3,4} Cu(II),⁵ Pd(II)⁶ and Pt(II).⁶ The present study is concerned with the infrared spectra of the EDTA chelates of Al(III), Ce(III), Bi(III), V(III), V(IV), Cr(III), Fe(III), Co(III), Ti(IV), Th(IV), Mo(V) and Mo(VI). Although the solution properties for this group of chelates have been studied extensively,⁷⁻⁹ little is known of their properties in the solid phase.

The previous investigations^{1,2} have shown that the bonding is primarily ionic for the EDTA chelates of the divalent metal ions. However, for many of the metal ions considered here the bonding would be expected to be primarily covalent,¹⁰ but with the exception of the Co(III)-EDTA chelate,³ data are not available to confirm this supposition. Determination of the kind of bonding in EDTA chelates by the use of infrared data has been reviewed previously.¹⁻³ As the bonding of the carboxylate groups becomes more covalent the absorption peak for the antisymmetrical vibration

(or free carbonyl bond, $\text{C}=\text{O}$) of the COO^- groups shifts to higher frequencies. Some limitation can be given from infrared data, for the maximum number of EDTA-donor groups involved in chelation but the actual number usually cannot be determined.

Experimental

Infrared Spectra.—The infrared spectra were recorded with a Perkin-Elmer model 21 recording spectrophotometer equipped with a sodium chloride prism. The solid chelates were pressed into disks¹¹ using KBr as the diluent. Approximately 1-3 mg. of the chelate were mixed with 500 mg. of KBr for each disk.

Reagents.—The inorganic salts, acids and bases used in preparing the complexes were reagent grade in all cases. The disodium salt of EDTA as well as the tetraacid of EDTA (both purchased from J. T. Baker Co.) were used in preparing the solid chelates. *pH* titrations indicated that these materials were essentially pure. The preparation and analysis of tetrasodium-EDTA has been discussed previously.¹

Preparation of the EDTA Complexes of Higher Valent Ions.—The following inorganic salts were used directly in preparing solid chelates: $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{BiCl}_3 \cdot \text{H}_2\text{O}$, VOCl_2 , $\text{CrCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$. To a solution of 0.062 mole of the inorganic salt in 50 ml. was added 0.062 mole of disodium dihydrogen ethylenediaminetetraacetic acid ($\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$) dissolved in 100 ml. of H_2O . The two hydrogen ions released from the ligand were neutralized by adding 0.124 mole of NaHCO_3 to the solution. The resulting solution was adjusted with HCl , NaHCO_3 or NaOH to *pH* 3 for the Bi(III) chelate; to *pH* 5 for the Fe(III) chelate; to *pH* 7 for the Ce(III), V(IV) and Cr(III) chelates; and to *pH* 9 for the Th(IV) chelate. The solutions for this group of chelates were evaporated at ambient temperature until the volume for each solution was reduced to about 25 ml. In the case of the Fe(III) chelate, crystals started to form and this solution was placed in an ice bath. For the solution of the V(IV) chelate NaCl crystallized out and was separated prior to placing the solution in an ice bath. Methanol was added to the concentrated solutions of the Ce(III), Bi(III) and Th(IV) chelates and ethanol to the concentrated solution of the Cr(III) chelate to help induce crystallization. These solutions were also placed in an ice bath. The resulting crystalline materials in these

(1) D. T. Sawyer and P. J. Paulsen, *THIS JOURNAL*, **80**, 1597 (1958).

(2) D. T. Sawyer and P. J. Paulsen, *ibid.*, **81**, 816 (1959).

(3) M. L. Morris and D. H. Busch, *ibid.*, **78**, 5178 (1956).

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