

$$\text{Rate} = k_1[\text{MBrO}_3^+] + k_2[\text{MBrO}_3\text{Br}] + k_3[\text{MBrO}_3\text{Br}_2^-] \quad (7)$$

The total concentration of divalent metal will then be divided among uncomplexed and complexed species. In the previous study of zinc bromate decomposition at 250°, values of $K_1 = 1.3 \text{ mole}^{-1}$ and $k_1 = 0.46 \text{ min.}^{-1}$ were obtained. In the experiments reported in the present article, the bromide concentration was kept high and $[\text{Zn}^{++}]$ also high, with bromate concentration lower than either. However, due to the formation of the zinc-bromide complexes, it turned out that the free zinc ion was much lower than the bromate; therefore, the mixed zinc-bromate-bromide complexes were assumed to be insignificant in their contribution to the material balance of the zinc species

$$([\text{Zn}^{++}]_T = [\text{Zn}^{++}] + [\text{ZnBr}^+] + [\text{ZnBr}_2] + [\text{ZnBr}_3^-] + [\text{ZnBrO}_3^+] \quad (8)$$

Combining eq. 8 with the various equilibrium constant equations and solving for the three Zn species in the rate equation in terms of $[\text{Zn}^{++}]_T$,

one obtains the rate expression

$$\text{Rate} = \frac{[\text{Zn}^{++}]_T [\text{BrO}_3^-] \{k_1 K_1 + k_2 K_1 K_2 [\text{Br}^-] + k_3 K_1 K_2 K_3 [\text{Br}^-]^2\}}{1 + K_1 [\text{BrO}_3^-] + K_{01} [\text{Br}^-] + K_{01} K_{12} [\text{Br}^-]^2 + K_{01} K_{12} K_{23} [\text{Br}^-]^3} \quad (9)$$

In this expression, the $[\text{Zn}^{++}]_T$ is the total zinc ion concentration in all forms, but the $[\text{BrO}_3^-]$ and $[\text{Br}^-]$ are actual concentrations and as the equilibrium constants are evaluated from the data, successive approximations must be made to correct the $[\text{Br}^-]$ particularly. The data in Table I were programmed for the IBM Magnetic Drum calculator and the equilibrium constants evaluated. The constants, K_2 and K_3 are not separable from the rate constants; K_{01} , K_{12} and K_{13} were found to be 250, 40 and 10 mole^{-1} , respectively. The products of the constants $k_2 K_1 K_2$ and $k_3 K_1 K_2 K_3$ were, respectively, 1500 $\text{min.}^{-1} \text{ mole}^{-2}$ and 500–1300 $\text{min.}^{-1} \text{ mole}^{-3}$. The precision is reasonably good for K_{01} but K_{12} and K_{23} are approximate values.

Acknowledgment.—We are greatly indebted to Mr. Wayne Dunning of this Laboratory for programming the data and evaluating the constants on the IBM Magnetic Drum Calculator.

[CONTRIBUTION FROM JEPSON LABORATORY OF CHEMISTRY, CLARK UNIVERSITY, WORCESTER, MASSACHUSETTS]

Infrared Spectra of Metal Chelate Compounds. III. Infrared Spectra of Acetylacetonates of Divalent Metals¹

BY KAZUO NAKAMOTO, PAUL J. MCCARTHY AND ARTHUR E. MARTELL

RECEIVED JULY 29, 1960

The infrared spectra of acetylacetonates of six divalent metals have been measured in the range between 4000 and 400 cm.^{-1} . The vibrational frequencies have been calculated for each metal by the perturbation method. The calculated frequencies and assignments were used to (1) elucidate the complex spectra in the 1600 ~ 1400 cm.^{-1} region; (2) correlate the electronic structures of strong and weak chelates with the calculated force constants and (3) show the relationship between the force constant and thermodynamic data based on formation constants from solution equilibria. Also, three chelate compounds of beryllium were studied to locate the characteristic infrared absorption bands of the Be-O bonds.

Introduction

Relationships between infrared spectra and the stability of the metallic complexes have been a subject of considerable interest. For example, Bellamy and Branch² have found a linear relation between the carbonyl stretching frequency and the stability constant in a series of metallic salicylaldehydes. They concluded, however, that no such simple relation exists in a series of metallic acetylacetonates. Holtzclaw and Collman³ and West and Riley,⁴ on the other hand, claim that the order of the carbonyl stretching frequency is the same as the stability order of the divalent acetylacetonates if the highest frequency band near 1600 cm.^{-1} is selected as the carbonyl stretching band. Harkins, *et al.*,⁵ have

also found for a series of divalent metal chelates of imidazole derivatives that the order of frequencies of the band near 1250 cm.^{-1} is shifted regularly according to the stability order of Mellor-Maley.⁶

In view of the conflicting nature of previous work, it is of considerable importance to determine whether a relationship between stability and infrared frequency really exists in a series of divalent metal acetylacetonates and, more generally, whether such a simple correlation can be justified on theoretical grounds.

In the previous paper of this series,^{7,8} vibrational frequencies and force constants have been calculated for trivalent metal acetylacetonates through the use of perturbation theory. The metal-oxygen force constants thus obtained seem to be more suited to the examination of the relationship between stability and spectra than are the frequencies of the infrared bands, since the latter involve the

(1) This work was supported by the Office of Ordnance Research under contract no. DA-19-020-ORD-5119.

(2) L. J. Bellamy and R. F. Branch, *J. Chem. Soc.*, 4487, 4491 (1954).

(3) H. F. Holtzclaw and J. P. Collman, *J. Am. Chem. Soc.*, **79**, 3318 (1957).

(4) R. West and R. Riley, *J. Nuclear Inorg. Chem.*, **5**, 295 (1958).

(5) T. R. Harkins, J. L. Walter, O. R. Harris and H. Freiser, *J. Am. Chem. Soc.*, **78**, 260 (1956).

(6) D. P. Mellor and L. E. Maley, *Nature*, **169**, 379 (1947); **161**, 436 (1948).

(7) K. Nakamoto and A. E. Martell, *J. Chem. Phys.*, **32**, 588 (1960).

(8) K. Nakamoto, H. J. McCarthy, A. Ruby and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1066 (1961).

effects of the mass and bond distance. Whether or not a true correlation exists, or may even be expected, between the relatively complex functions such as infrared frequencies and solution stabilities and the relatively simpler function, bond order, it is believed that the latter is a more fundamental quantity and the better measure of the degree of covalent binding. This paper will deal, therefore, with perturbation calculation of the vibrational frequencies and associated force constants of the divalent metal acetylacetonates for which sufficient thermodynamic data are available. The results of these calculations will be used to examine the possible relationships between spectroscopic and thermodynamic data.

Experimental

Spectral Measurements.—A Perkin-Elmer Model 21 infrared spectrophotometer equipped with NaCl and KBr optics was used to obtain the spectra in the range between 4000 and 400 cm^{-1} . The KBr disk method was employed for the preparation of samples. Calibration of the frequency reading was made with polystyrene film (NaCl region), 1,2,4-trichlorobenzene (KBr region) and water vapor for both regions.

Preparation of Compounds.—All the compounds were prepared according to the methods described in the literature.⁹ The purity of each compound was checked by comparisons of melting points and the ultraviolet spectra with literature values.

Results and Discussion

I. Infrared Spectra and Force Constants.—Although the infrared spectra of divalent metal acetylacetonates have been measured by several workers, the reported frequencies differ somewhat from each other. For this reason, and since no data are available on the spectra in the KBr region where the metal-oxygen stretching and other metal-sensitive bands are expected to occur, self-consistent measurements have been made in a wide frequency range between 4000 and 400 cm^{-1} , and Fig. 1 illustrates the infrared spectra thus measured for the acetylacetonates of six divalent metals.

TABLE I

SYMMETRY OF THE METAL CHELATE AND NUMBER OF INFRARED ACTIVE STRETCHING VIBRATIONS

Note: This relation holds for most of the vibrational modes except the bending modes including the angles in the ring.

Type of metal chelate	Symmetry whole molecule	Distribution of stret. vibrat.	No. infrared active vibrations
1:1	C_{2v}	$1a_1 + 1b_2$	2
1:2 (square planar)	V_h	$1a_g + 1b_{1g} + 1b_{2u} + 1b_{3u}$	2
1:2 (tetrahedral)	C_{2v}	$2a_1 + 1b_1 + 1b_2$	4
1:3 (octahedral)	D_3	$1a_1 + 1a_2 + 2e$	3

It is interesting to note that the infrared spectra of acetylacetonates are essentially alike regardless of the combining ratio between the metal and the ligand. This can be seen immediately from a comparison of the infrared spectra of divalent metals with those of monovalent and trivalent metals previously reported. From a theoretical viewpoint, however, the number of infrared active vibrations is

(9) See, for example, N. V. Sidgwick, "Chemical Elements and Their Compounds," Oxford University Press, London, 1950.

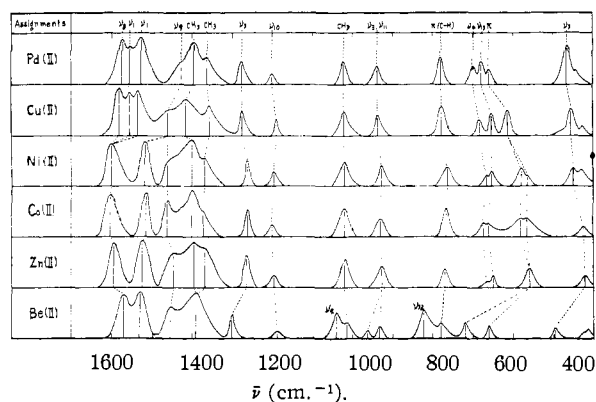


Fig. 1.—Infrared spectra of acetylacetonates of divalent metals.

different in each type of the complex as is seen in Table I. Since the observed spectra are essentially similar for all these types, it can be said that the interactions between two or more ligands attached to the same metal ion are fairly small. Thus the simplified 1:1 complex model used in the following perturbation calculation is considered satisfactory for all of these compounds.

In Table II the observed frequencies are compared with the values calculated by the perturbation method. In Table III the force constants and other variables used in the calculations are listed. It is seen that the M-O stretching force constant increases in the order of $Zn \approx Co < Ni < Cu < Pd$, and the corresponding C=O force constant decreases in the same order. It is noted that this order is in accord with the stability order of these complexes published by other investigators. More detailed examination of the relationship between the spectra and thermodynamic data will be given below.

Table II indicates that the agreement between the calculated and observed frequencies is quite satisfactory for the ν_5 vibration. This is due to the fact that ν_5 is almost a pure M-O stretching vibration and adjustment of the M-O stretching force constant can be done quite independently of other vibrational modes. In this respect, the value of the metal-oxygen stretching force constant can be used as a reliable measure for comparing the strengths of the metal-oxygen bonds.

Agreements between the observed and calculated frequencies are less satisfactory for ν_4 and ν_{12} since, in the present calculations, only the C=O and M-O stretching force constants were taken as the variables whereas ν_4 and ν_{12} are the coupled vibrations involving M-O stretching and vibrational modes other than C=O stretching. It is seen, however, that relative shifts of these two bands are in good agreement with the theoretical assignments.

It should be mentioned, however, that the assignments for the bands between 1600 and 1400 cm^{-1} on the basis of the present calculations are still somewhat obscure. According to the results, the highest frequency bands at $1580 \sim 1570 \text{ cm}^{-1}$ in the Pd(II) and Cu(II) complexes are assigned to ν_8 (ca. 75% C=C stretching, 25% C=O stretching). The lower frequency bands at $1465 \sim 1430 \text{ cm}^{-1}$ are assigned to ν_9 (ca. 50% C=O stretching,

TABLE II
 COMPARISON OF OBSERVED AND CALCULATED FREQUENCIES IN METALLIC ACETYLACETONATES (CM.⁻¹)

Zn(II)		Co(II)		Ni(II)		Cu(II)		Pd(II)		Be(II)		Predominant modes
Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	
1592	1594	1601	1600	1598	1599	1580	1580	1570	1572	1571	1580	C=C str. (ν_8)
	1593		1603		1602	1554	1544					1547
1523	1513	1513	1517	1514	1518	1464	1489	1430	1484	1455	1480	C=O str. + CH bend. (ν_9)
1394	..	1398	..	1398	..	1415	..	1395	..	1387	..	CH ₃ deg. def.
1361	..	1366	..	1367	..	1356	..	1358	..	1387	..	CH ₃ sym. def.
1264	1266	1261	1267	1261	1268	1274	1264	1273	1262	1298	1261	CC str. + C-CH ₃ str. (ν_2)
1197	1232	1199	1234	1198	1234	1190	1226	1199	1226	1185	1224	C-H in-plane bend. (ν_{10})
1019	..	1020	..	1020	..	1020	..	1022	..	1015	..	CH ₃ rock
927	937	931	938	929	944	937	936	936	940	930	928	CCH ₃ str. + CO str. (ν_3)
	900		901		904		901					
769	..	767	..	764	..	781	..	781	..	780	..	CH out-of-plane bend.
666	634	672	639	666	657	684	659	697	648	1040	1054	Ring def. + M-O str. (ν_4)
651	590	659	592	..	622	654	628	676	644	824	747	CCH ₃ bend. + M-O str. (ν_{12})
559	..	580	..	579	..	614	..	659	..	720	..	Out-of-plane (?)
		566		563						659		
422	424	422	424	452	452	455	457	464	472	500	464	M-O str. (ν_5)
..	427	..	427	..	442	..	423	..	Out-of-plane (?)
..	415	..	
..	373	..	373	..	373	..	373	..	373	..	358	Ring def. (ν_{13})
..	258	..	258	..	290	..	302	..	317	..	362	M-O str. (ν_{14})
..	248	..	249	..	255	..	272	..	268	..	525	C-CH ₃ bend. (ν_6)
..	176	..	180	..	183	..	197	..	186	..	278	Ring def. (ν_7)

 TABLE III
 MASS, BOND DISTANCE AND FORCE CONSTANT OF DIVALENT METAL ACETYLACETONATES

Metal	Atomic wt.	Metal-oxygen distance (Å.)	Force constant (10 ⁹ dyne/cm.) ^a	
			K(M-O)	K(C=O)
Pd(II)	106.7	1.95	2.65	6.75
Cu(II)	63.54	1.95	2.20	6.90
Ni(II)	58.69	2.05	2.05	7.65
Co(II)	58.94	2.05	1.50	7.70
Zn(II)	65.38	2.05	1.50	7.55
Be(II)	10.82	1.72	2.25	6.70

^a $K(\text{C}=\text{C})$, 5.35 and $K(\text{C}-\text{CH}_3)$, 3.60 were used.⁸ Other force constants are the same as in the previous publication.⁷

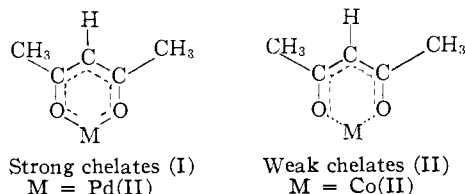
50% C-H in-plane bending). Two closely located bands between ν_8 and ν_9 are assigned to ν_1 (75% C=O, 25% C=C). The splitting of the predicted band into the two observed bands in this case is not immediately obvious, however.

In Table II and III it is seen that the M-O stretching frequency (ν_5) and the corresponding force constant are much lower in Co(II) and Zn(II) chelates than in the Pd(II) and Cu(II) compounds. Thus it is theoretically reasonable to expect that the bond order of the C=O bond next to the M-O bond is much larger in the weaker Co(II) and Zn(II) chelates than in the latter compounds. The Jacobian matrix obtained from the normal coordinate treatment of the Cu(II) complex⁷ indicate that ν_1 is shifted to higher frequency much more rapidly than ν_8 since the predominant mode in ν_1 is a C=O stretching vibration. Since ν_1 cannot be shifted to lower frequency by increasing the C=O stretching

force constant, a probable explanation for the highest frequency band in weak chelates is to assume that ν_8 and ν_1 overlap in these weak chelates. The second band near 1520 cm.⁻¹ then is attributed to the ν_9 -vibration. This leaves the band near 1460 cm.⁻¹ unassigned. It should be pointed out that this band may be due to another C=O stretching vibration which was not calculated in the 1:1 complex model. As is seen in Table I, tetrahedral 1:2 complexes are expected to show more bands than the square planar and octahedral ones. And it is conceivable that the Ni(II), Co(II) and Zn(II) complexes are tetrahedral or nearly square planar, the metal being off from the plane (C_{2v} symmetry).

It should be noted that further detailed study of these infrared carbonyl and M-O stretching vibrations is warranted as a possible approach to the stereochemistry of metal complex compounds.

II. Structural Considerations.—From the force constants listed in Table II, the electronic structures of the strong and weak chelates may be approximated by



In strong chelates, π -electrons as well as d-electrons of the metal tend to be more or less delocalized in the whole chelate ring, whereas in weak chelates,

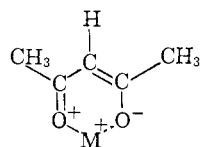
TABLE IV

THERMODYNAMIC QUANTITIES ASSOCIATED WITH THE FORMATION OF METALLIC ACETYLACETONES IN AQUEOUS SOLUTIONS

	Mn(II)	Zn(II)	Co(II)	Ni(II)	Cu(II)	Pd(II)
$-\log k_1 k_2^2$	7.25	8.81	9.51	10.38	14.93	27.1
$-\Delta F$ (kcal./mole)	10.0	12.2	13.14	14.3	20.6	37.5
ΔF (kcal./mole) relative to Mn(II)	...	2.2	3.14	4.3	10.6	27.5
$T\Delta S$ (kcal./mole) relative to Mn(II)	...	0.9	0.6	-2.4	6.9	..
ΔH_c (kcal./mole) relative to Mn(II)	...	1.3	2.5	6.7	3.7	..
ΔH_h (kcal./mole) ^b relative to Mn(II)	...	47	43	62	63	...
ΔH_{ML} (kcal./mole) relative to Mn(II)	...	48.3	45.5	68.7	66.7	..

^a Obtained at 30° at ionic strength zero. Izatt, Haas, Block and Fernelius, *J. Phys. Chem.*, **58**, 1133 (1954). ^b P. George and D. S. McClure, "Progress in Inorganic Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1959.

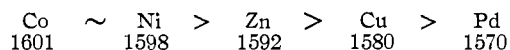
π -electrons are more localized in the ligand skeleton of the chelate ring. It should be mentioned, however, that an asymmetric structure of the chelate ring such as (III) would also account for the spectra



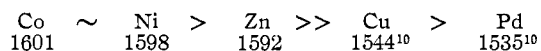
Weak chelates (III)

of weak chelates, since an increase of the separation between two C=O stretching frequencies (ν_1 and ν_2) is expected as a consequence of the inequality of the two coordinate bonds. Furthermore, the similarity between the spectra of the enolate ion of acetylacetonate and that of the weak chelates seems to support structure III, since the chelate ring of the enolate ion probably is not symmetric. It is not possible, however, to distinguish between II and III from the present study because the perturbation calculations are based on C_{2v} symmetry of the chelate ring. It is hoped that even more detailed structural studies will be made in the future on the weak chelates.

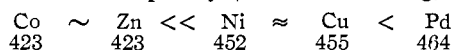
III. Relationship between Spectra and Thermodynamic Data.—Since previous investigators²⁻⁴ discussed the relationship between the C=O stretching frequencies and the stability constants, it is interesting to examine such a relation based on the new infrared band assignments made as a result of the present work described above. According to the results of calculations, the order of ν_3 -frequency (C=C stretching) is



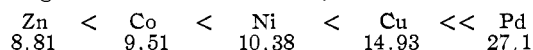
The order of ν_1 -frequency (C=O stretching) is



The order of ν_2 -frequency (M—O stretching) is



On the other hand, the order of stability constants (as log of formation constants) is

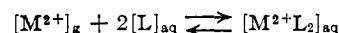


Thus it is seen that with the exception of Zn, the frequency order of the metal-sensitive bands is the same as the stability order. On the other hand the magnitudes of the frequency shifts do not match

(10) Average of two bands.

the stability differences, so that there is no apparent quantitative agreement.

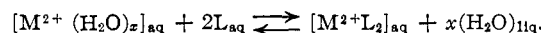
A quantitative relation between the spectra and thermodynamic data might be expected if the M—O force constant is compared to the enthalpy ΔH_{ML} of the reaction



The quantity ΔH_{ML} can be obtained from the relationship

$$\Delta H_{ML} = \Delta H_h + \Delta H_c$$

where ΔH_h is the heat of hydration of the metal and ΔH_c is the enthalpy of the reaction



The M—O stretching force constant is considered an unique spectroscopic quantity for correlation since it does not involve the influence of the mass and the bond distance as does the frequency. ΔH_{ML} is the best quantity to compare with the M—O force constant since it is the heat of reaction for the formation of the metal oxygen bond from the free metal ion and the free ligand anion.

From the known values of ΔH_h and ΔH_c , values of ΔH_{ML} have been calculated for a series of acetylacetonates as is shown in Table IV. It is seen that the order of ΔH_{ML} is quantitatively in good agreement with the order of the M—O force constant.¹¹

Relative ΔH_{ML} (kcal./mole)	Co	Zn	Cu	Ni
	45.5	48.3	66.7	68.7

M—O force Const. (10^6 dyne/cm.)	Co	Zn	Ni	Cu	Pd
	1.50	1.50	2.05	2.20	2.65

If, on the basis of this comparison, it is assumed that good correlation exists between force constants and coordinate bond strengths, it becomes apparent that correlation with frequency would occur only if metals of similar covalent radii and similar mass are compared.

IV. Be—O Bonds.—Fig. 1 indicates that the spectrum of the Be(II) complex is markedly different from those of the acetylacetonates of other metals. This evidently is due to the light mass of beryllium atom and the very short Be—O distance. Therefore, it is to be expected that the perturbation method used for other metals may not be applicable in this case. In spite of this fact, we have calculated the vibrational frequencies using the same method, and the results are shown in Table II. It is seen that agreements are poor in the lower frequency region. Thus no definite conclusion can be

(11) Because of scarcity of data, however, it is better at present not to attempt a more quantitative relation between ΔH_{ML} and force constant.

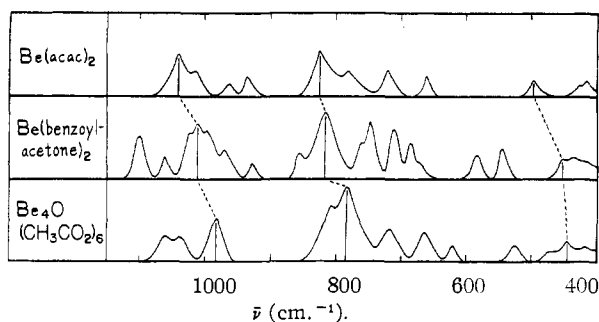


Fig. 2.—Infrared spectra of Be(II) chelates with various β -diketones.

drawn with respect to the Be-O bands from the present calculations.

Fig. 1 indicates, however, that the strong bands at 1040, 824 and 500 cm.^{-1} are characteristic of the Be-O compounds. As is shown in Fig. 2, bis-(benzoylacetato)-Be(II) and basic beryllium acetate also show three analogous strong bands at similar frequencies. This fact may suggest that

they are characteristic of the chelate ring involving the Be-O bond.¹² Table I indicates that the band at 1040 cm.^{-1} corresponds to ν_4 , involving the coupling of ring deformation and Be-O stretching.

West and Riley⁴ previously suggested that the strong band at 824 cm.^{-1} in bis-(acetylacetonato)-Be(II) may be a Be-O stretching mode. Since this band may correspond to a ν_{12} vibration in the present calculation, it may be a coupled vibration between the Be-O stretching and C-CH₃ bending modes. The band at 500 cm.^{-1} may be a purer Be-O stretching vibration, although a calculation of the L-matrix is necessary to determine the character of these bands.

Acknowledgment.—The authors are indebted to the Massachusetts Institute of Technology Computation Center for the use of its I.B.M. 704 computer for their calculations.

(12) The structure of basic beryllium acetate is different from the other two compounds, although it has a chelate ring containing the Be-O bond; see Bragg and Morgan, *Proc. Roy. Soc. (London)*, **104**, 437 (1923).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES, CALIFORNIA]

Kinetics of Hydrolysis of *cis*-Difluoro-bis-(ethylenediamine)-chromium(III) Cation¹

BY KLAUS R. A. FEHRMANN AND CLIFFORD S. GARNER

RECEIVED AUGUST 9, 1960

The rates of release of fluoride by acid and base hydrolysis of *cis*-[Cr(en)₂F₂]⁺ were determined over a range of pH 1-8. At 25° the pseudo first-order aquation rate constant for loss of the first fluoride in 0.1 *f* HClO₄ is 5.3×10^{-6} sec.⁻¹, much less than the corresponding rate constants of *cis*-[Co(en)₂F₂]⁺ and *cis*-[Cr(en)₂Cl₂]⁺ in 0.1 *f* HNO₃. The Arrhenius activation energy is 23 ± 1 kcal./mole. The aquation of *cis*-[Cr(en)₂F₂]⁺ is acid catalyzed like the cobalt analog but, unlike the dichloro cobalt and chromium analogs, presumably because the difluoro complexes aquate by a mechanism involving an intermediate reactive protonated complex. Cation-exchange and spectral evidence indicate that the aquation product is largely, if not entirely, *cis*-[Cr(en)₂(H₂O)F]⁺². Fluoride is taken up by one or more reaction products in later stages of the hydrolysis. The aquation appears not to be accelerated by visible light.

As part of a program of comparing the kinetics of substitution reactions of cobalt(III) and chromium(III) complexes an investigation was undertaken of the rates of loss of fluoride in acid and base hydrolysis of *cis*-[Cr(en)₂F₂]⁺. Evidence on the *cis-trans* configuration of the fluoroaquo aquation product was obtained from ion-exchange and spectral experiments.

Experimental

Preparation of Compounds.—The synthesis and characterization of *cis*-difluoro-bis-(ethylenediamine)-chromium(III) iodide has been described elsewhere.²

Anal. Calcd. for [Cr(en)₂F₂]I: Cr, 15.43; F, 11.27; I, 37.65; C, 14.25; H, 4.78. Found: Cr, 15.18; F, 11.46; I, 37.38; C, 14.34; H, 4.54.

All other chemicals were reagent-grade, except sodium azide, which was practical grade.

Rate Procedure.—Known weights of the complex were dissolved in 65- to 100-ml. portions of buffer solution in a thermostatically controlled bath, and aliquots removed at known times for fluoride analysis, and in some cases for spectral observation or ion-exchange experiments. The pH of the reaction mixture was assumed to be that of the buffer solution itself,³ which was measured at 25-30° with a Beckman Model G pH meter.

(1) This investigation was supported by the U. S. Atomic Energy Commission under Contract AT(11-1)-34, Project 12.

(2) K. R. A. Fehrmann and C. S. Garner, *THIS JOURNAL*, **82**, 6294 (1960).

Cation-exchange Resin Experiments.—Information on the nature of the hydrolysis products was obtained by absorbing several reaction mixtures (*ca.* 25% reaction) on Dowex 50W-X8 cation-resin columns (100- to 200-mesh, in H⁺ form) and subjecting them to fractional elution after washing iodide ion from each column with water. The reaction mixtures and resin columns were cooled to 0° to reduce hydrolysis during processing. Complexes adsorbed from 0.1 *f* HClO₄ reaction mixtures were successively subjected to elution with 100 ml. of 0.6 *f* HClO₄ and 80 ml. of 3 *f* HClO₄ or with 100 ml. of 1.2 *f* HCl. Investigations carried out in this Laboratory⁴ on *cis*- and *trans*-[Cr(en)₂Cl₂]⁺, and their aquation products, have shown that *cis*-[Cr(en)₂Cl₂]⁺, and hence *cis*-[Cr(en)₂F₂]⁺, is essentially completely eluted by the 0.6 *f* HClO₄ without loss of the haloaquo products and that *trans*- and *cis*-[Cr(en)₂(H₂O)Cl]⁺², and hence any of the *trans*- and *cis*-[Cr(en)₂(H₂O)F]⁺² remaining, are eluted by the 1.2 *f* HCl and 3 *f* HClO₄, respectively, in agreement with the general rule that the *cis* isomer, because of its greater dipole moment, is more difficult to elute. F/Cr atom ratios in the fractions eluted with HClO₄ were determined, fluorine as described earlier² for the analysis of *cis*-[Cr(en)₂F₂]I and chromium by decomposition and oxidation of the complex to Cr(VI) by boiling with alkaline peroxide solution, followed by spectrophotometric determination of the chromium concentration.

(3) The assumption was found valid at pH 2 in a check experiment. Borate and phthalate buffers were prepared according to Clark and Lubs (N. A. Lange, ed., "Handbook of Chemistry," 9th Ed., Handbook Publishers, Inc., Ohio, 1956, pp. 951-952); other buffers made had about the same buffer capacity.

(4) D. J. MacDonald and C. S. Garner, unpublished research.