platinum anode disappeared after the electrode had become oxidized.

If the platinum anode is only partially oxidized an anodic chronopotentiometric wave is still observed but the transition time is smaller than for an unoxidized anode. This is demonstrated by the chronopotentiograms of iodide ion in Fig. 4 obtained with different degrees of prior oxidation of the anode.

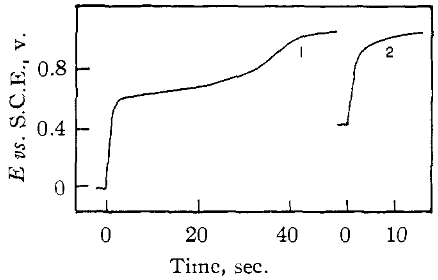


Fig. 3.—Anodic chronopotentiograms for 0.094 milliformal potassium iodide in phosphate buffer at *p*H 6.5 at a current density of 0.3 milliamp./cm.^{2}: (1) with a previously reduced electrode; (2) resulted when the trial was repeated.

Acknowledgment.—Appreciation is expressed to Merck and Co. for sponsoring the Merck Graduate Fellowship in Analytical Chemistry held by one of us (F.C.A.).

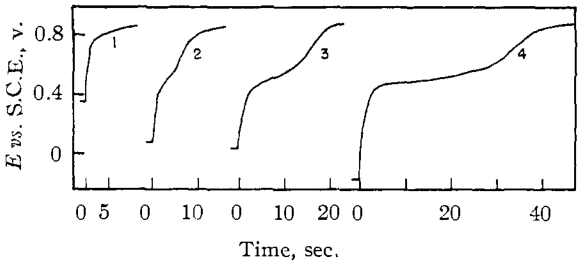


Fig. 4.—Anodic chronopotentiograms for 0.094 milliformal potassium iodide in borax buffer at *p*H 8.5 at a current density of 0.3 milliamp./cm.^{2}: (1) previously oxidized electrode; (2) oxidized electrode cathodized for 6 sec. at 0.3 milliamp./cm.^{2}; (3) oxidized electrode cathodized for 10 sec. at 0.3 milliamp./cm.^{2}; (4) oxidized electrode totally reduced by cathodizing for *ca.* 20 sec. at 0.3 milliamp./cm.^{2}.

Cambridge, Mass.

[Contribution from the Department of Chemistry, Osaka University]

Infrared Spectra of Metallic Complexes. IV. Comparison of the Infrared Spectra of Unidentate and Bidentate Metallic Complexes

By Kazuo Nakamoto, Junnosuke Fujita, Shizuo Tanaka and Masahisa Kobayashi

Received April 4, 1957

The infrared spectra of sulfato, carbonato, oxalato and acetato metallic complexes in which those ligands coördinate to the metal as an unidentate and as a bidentate have been measured in the range between 5000 and 400 cm.$^{-1}$. From the comparison of the spectra of bidentate with that of unidentate complexes of the same ligands, it has been found that lowering of symmetry of the ligand or frequency shifts of the fundamentals due to coördination is, in general, more remarkable in the former than in the latter.

Introduction

Studies of the effect of coördination on the infrared spectra of metallic complexes afford valuable information on the nature of the metal–ligand bond and the stability of the complex. Coördination usually causes (1) appearance of new bands and splitting of the degenerate modes due to lowering of symmetry, (2) frequency shifts of the bands, and (3) intensification of the spectra. In the previous works,[1] our attention was focussed to the frequency shifts of the ligand fundamentals caused by complex formation. However, a study of the effect of coördination on the symmetry of the ligand is also important. It is well known that the ligands such as CO_3^{--} and $C_2O_4^{--}$ coördinate to the metal as an unidentate and as a bidentate. Therefore, comparison of the infrared spectra of unidentate and bidentate metallic complexes of those ligands will be of considerable interest. The present paper deals with the infrared spectra of sulfato, carbonato, oxalato and acetato complexes.

In discussing the symmetry of the ligand from the spectra obtained in the crystalline state, site group or factor group analysis based on the knowledge of crystal structure is desirable. Unfortunately, for most of the compounds discussed here, crystal structural data are lacking. It is anticipated, however, that the effect of coördination upon the ligand absorption is much stronger than the effect of the over-all crystal field. Hence, ignorance of rigorous site group analysis may be justified.

By coördination, all the fundamentals are more or less shifted according to their modes of vibration. As the metal–ligand bond becomes stronger, their shifts to lower or higher frequencies increase. Furthermore, when coördination lowers the symmetry of the ligand, forbidden vibrations of the free ion are permitted, and degenerate vibrations are split. The stronger the metal–ligand bond, the larger the splitting of the degenerate mode. Therefore, frequency shifts, the magnitude of the splitting, and the intensity of newly permitted bands are useful as a measure of the effect of coördination.

As to the change of relative intensity caused by complex formation, it is generally expected that newly developed fundamentals have weak or medium intensity, and other fundamentals active in

---

(1) J. Fujita, K. Nakamoto and M. Kobayashi, This Journal, **78**, 3295, 3963 (1956); *J. Phys. Chem.*, **61**, 1014 (1957).

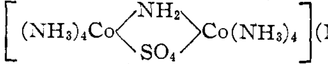
the free ion increase their intensity. As is shown later, this anticipation is correct in the present series of the compounds.

Since most of the compounds examined here are Co(III) acido ammine complexes, they exhibit the bands characteristic of the acido group in question together with that of ammonia ligands. Therefore, care was taken not to confuse the former with the latter bands which are easily identified in the spectra.

Experimental

Preparation.—The compounds used in this work were prepared according to the literature which is given in Table I, III, V and VI. Since most of the compounds studied here are typical metallic complexes, their purity was checked by comparing the ultraviolet spectra with the published data.[2] However, the following two sulfato complexes which are comparatively difficult to prepare, were analyzed to examine their chemical composition.

Anal. Calcd. for $[Co(NH_3)_5SO_4]Br$: Co, 18.41; N, 21.88; Br, 24.97. Found: Co, 18.20; N, 21.95; Br, 25.01. For



$\left[(NH_3)_4Co\left\langle\begin{matrix}NH_2\\SO_4\end{matrix}\right\rangle Co(NH_3)_4\right](NO_3)_3$: Co, 21.35; N, 30.44. Found Co, 21.20; N, 30.23.

Absorption Measurements.—The infrared spectra were obtained by a Perkin-Elmer Model 21 double beam infrared spectrophotometer using NaCl and KBr prisms. The KBr disk method and Nujol mull technique were employed for the spectra of the NaCl and KBr regions, respectively.

Results and Discussion

(1) **Sulfato Complexes.**—Free sulfate ion has high symmetry of T_d. Of the four fundamentals, only ν_3 and ν_4 are infrared active. If the ion is coordinated to the metal, the spectra will undergo marked change. Figure 1 and Table I indicate the spectra of 1200 ~ 900 cm.$^{-1}$ region and the location of those four fundamentals in the free ion, unidentate complex, and binuclear complex joined by a sulfate bridge. In $[Co(NH_3)_6]_2(SO_4)_3\cdot 5H_2O$, ν_3 and ν_4 are strong, but ν_1 is very faint and ν_2 is not observed. Therefore, it is concluded that T_d symmetry of the ion still holds although ν_1 is weakly allowed by the perturbation of $[Co(NH_3)_6]^{3+}$ ion.

In $[Co(NH_3)_5SO_4]Br$, however, both ν_1 and ν_2 appear with medium intensity, and moreover, ν_3 and ν_4 split into two bands, respectively. The correlation diagram of Table II suggests that this result can be interpreted reasonably only when we assume that T_d symmetry of the ion is lowered to C_{3v} by complex formation. Thus we conclude that one of the oxygens of the ion is different from

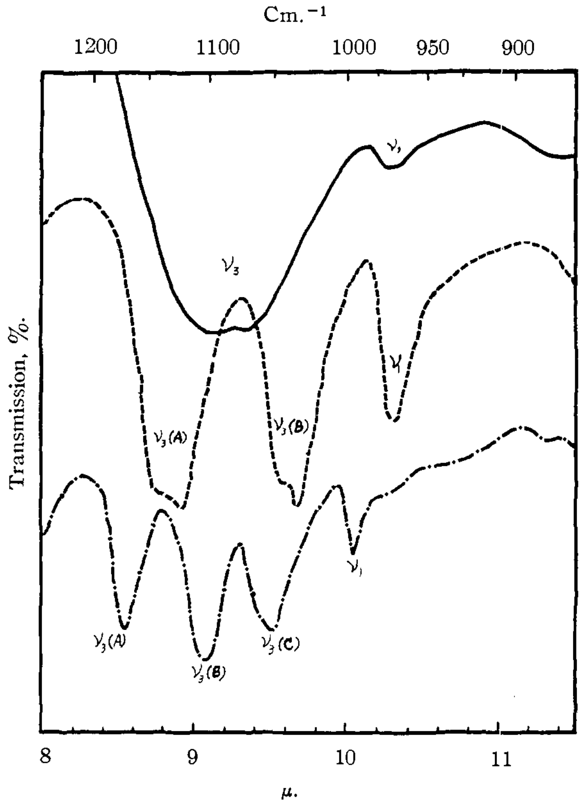
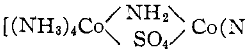


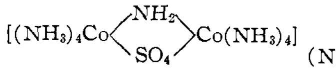
Fig. 1.—Infrared absorption spectra of: ———, $[Co(NH_3)_6]_2(SO_4)_3\cdot 5H_2O$; --------, $[Co(NH_3)_5SO_4]Br$; —·—·—,



$[(NH_3)_4Co\left\langle\begin{matrix}NH_2\\SO_4\end{matrix}\right\rangle Co(NH_3)_4](NO_3)_3$; (KBr disk method).

TABLE I

THE INFRARED SPECTRA OF SULFATO COMPLEXES (CM.$^{-1}$)

Compound	Symmetry	ν_1	ν_2	ν_3	ν_4
Free SO_4^{--} *ion*[a]	T_d	....[e,g]	...[f,g]	1104(VS)	613(S)
$[Co(NH_3)_6]_2(SO_4)_3\cdot 5H_2O$[b]	T_d	973(VW)	...	1130 ~ 1140(VS)	617(S)
$[Co(NH_3)_5SO_4]Br$[c]	C_{3v}	970(M)	438(M)	1032 ~ 1044(S) 1117 ~ 1143(S)	645(S) 604(S)
 $[(NH_3)_4Co\left\langle\begin{matrix}NH_2\\SO_4\end{matrix}\right\rangle Co(NH_3)_4](NO_2)_3$[d]	C_{2v}	995(M)	462(M)	1050 ~ 1060(S) 1170(S) 1105(S)	641(S) 610(S) 571(M)

[a] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 167. [b] S. M. Jörgensen, *Z. anorg. Chem.*, **17**, 457 (1898). [c] S. M. Jörgensen, *J. prakt. Chem.*, **31**, 270 (1885). [d] A. Werner, *Ber.*, **40**, 4610 (1907). [e] Raman, 981 cm.$^{-1}$. [f] 451 cm.$^{-1}$. [g] VS, very strong; S, strong; M, medium; w, weak; VW, very weak.

TABLE II

CORRELATION TABLE[a] BETWEEN T_d, C_{3v} and C_{2v}

	ν_1	ν_2	ν_3	ν_4
T_d	$A_1(R)$	$E(R)$	$F_2(I,R)$	$F_2(I,R)$
C_{3v}	$A_1(I,R)$	$E(I,R)$	$A_1(I,R) + E(I,R)$	$A_1(I,R) + E(I,R)$
C_{2v}	$A_1(I,R)$	$A_1(I,R) + A_2(R)$	$A_1(I,R) + B_1(I,R) + B_2(I,R)$	$A_1(I,R) + B_1(I,R) + B_2(I,R)$

[a] I, infrared active; R, Raman active.

---

(2) Y. Shimura, *Bull. Chem. Soc. Japan*, **29**, 311 (1956).

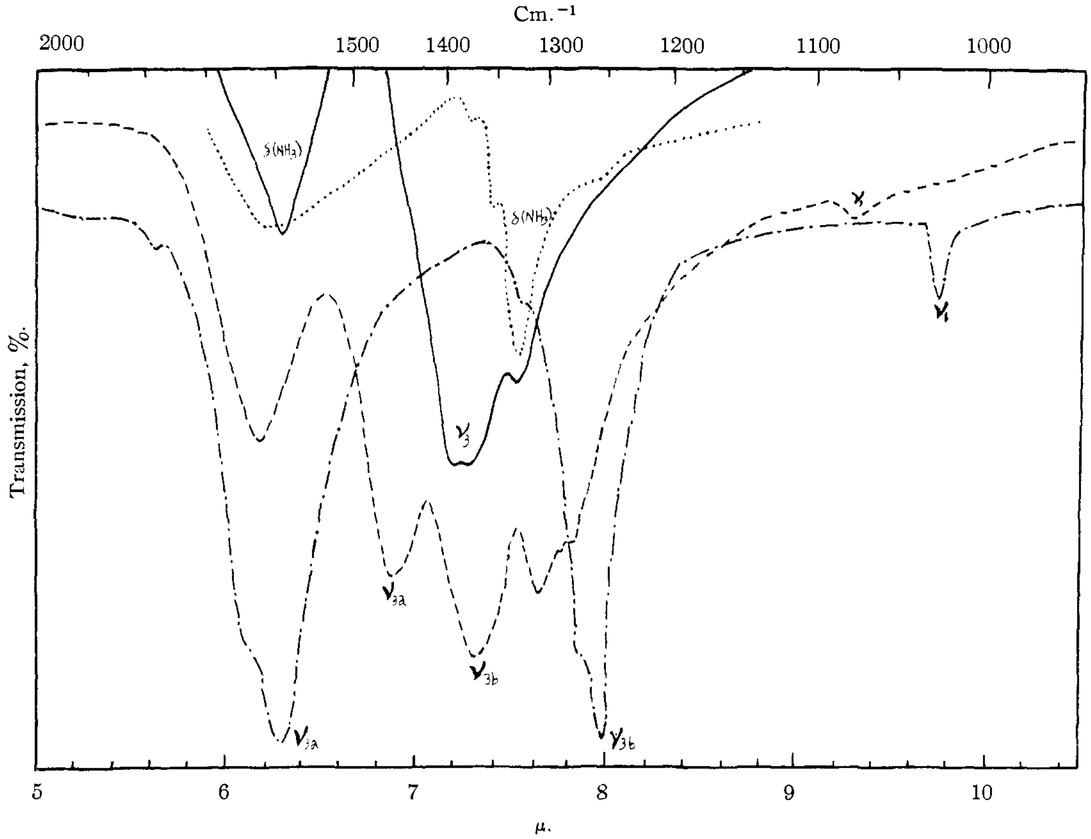
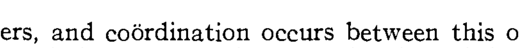
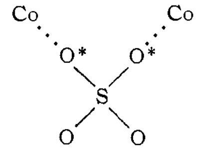


Fig. 2.—Infrared absorption spectra (KBr disk method) of: ......, $[Co(NH_3)_6]Br_3$; ———, $[Co(NH_3)_6]Cl{\cdot}CO_3$; --------, $[Co(NH_3)_5CO_3]Br$; –·–·–, $[Co(NH_3)_4CO_3]Cl$.

others, and coördination occurs between this oxygen and the metal. The anomaly of the infrared spectrum of the sulfate ion at 1100 cm.$^{-1}$ in $[Co(NH_3)_5SO_4]Cl$ was reported previously by Mizushima and Quagliano,[3] who, however, gave no detailed discussion.

In  $\left[(NH_3)_4Co\langle{}^{NH_2}_{SO_4}\rangle Co(NH_3)_4\right](NO_3)_3$, both ν_1 and ν_2 appear with medium intensity, and ν_3 and ν_4 split into three bands, respectively. This result together with Table II suggests that the symmetry of the sulfate ion is once again lowered and probably reduced to C_{2v}. Hitherto, the following structure has been assumed for the sulfate bridge.



Our infrared study will present an evidence for the above structure in which C_{2v} symmetry is given.

(2) **Carbonato Complexes.**—Using the idea of site symmetry, Halford[4] explained the difference of the spectra between calcite and aragonite which have the same chemical composition. According to the site analysis, D_{3h} symmetry of the free ion is lowered to D_3 in calcite and to C_s in aragonite. Thus, ν_4 vibration which appears in calcite at 710 cm.$^{-1}$ splits into two bands in aragonite. Moreover, totally symmetric vibration, ν_1, appears weakly at 1080 cm.$^{-1}$ in the latter. As is shown in Table III and IV, these results are in complete harmony with the prediction of site analysis.

Since the effect of coördination is much stronger than the effect of interaction between the ions, more remarkable change of the spectra is expected when the ion is coördinated to the metal. In carbonato complexes, Raman active vibrations of the free ion will appear more strongly and the degenerate vibrations will split more markedly.

Figure 2 and Table III show the spectra between 2000 and 1000 cm.$^{-1}$ and location of the four fundamentals of the carbonate ion, respectively. In $[Co(NH_3)_6]Cl{\cdot}CO_3$, ν_1 does not appear, and ν_3 and ν_4 do not split. Since the feature of the spectrum is very similar to that of calcite, we conclude that the symmetry of the ion may be D_3. In $[Co(NH_3)_5CO_3]Br$, ν_1 appears very weakly and ν_3 splits into two bands. The correlation diagram of Table IV suggests that the symmetry of the carbonate ion in this complex is C_{2v} at the highest. This result is consistent with the expectation that the ion is linked to the metal with one of its oxygens.

Similar trend is seen in the bidentate complexes of $[Co(NH_3)_4CO_3]Cl$ and $[Co\ en_2\ CO_3]Br$. However, ν_1 appears more strongly, and ν_3 splits more markedly than in the case of the unidentate com-

---

(3) S. Mizushima and J. V. Quagliano, THIS JOURNAL, **75**, 4870 (1953).

(4) R. S. Halford, *J. Chem. Phys.*, **14**, 8 (1946).

TABLE III

THE INFRARED SPECTRA OF CARBONATO COMPLEXES (CM.$^{-1}$)

Compound	Symmetry	ν_1	ν_2	ν_3	ν_4
Free CO_3^{--} ion[a]	D_{3h}	......[h]	879(S)	1415(VS)	680(S)
Calcite[b]	D_3	......[i]	874(S)	1430(VS)	710(M)
Aragonite[c]	C_s	1080(W)	855(S)	1470(VS)	710(M), 696(W)
$[Co(NH_3)_6]Cl\cdot CO_3$[d]	D_3	......	868(S)	1390 ~ 1370(VS)	688(M)
$[Co(NH_3)_5CO_3]Br$[e]	C_{2v}	1070(VW)	848(S)	1450(S), 1370(S)	750(W)
$[Co(NH_3)_4CO_3]Cl$[f]	C_{2v}	1025(M)	837(S)	1592(S), 1255(S)	752(M)
$[Coen_2CO_3]Br$[g]	C_{2v}	1015(M)	825(S)	1575(S), 1278(S)	757(M)

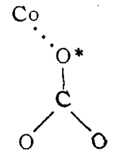
[a] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 178. [b] Natural mineral, examined by X-ray powder photograph. [c] Synthesized, examined by X-ray powder photograph. [d] L. Jacobsen, *Overs. Danske Selsk. Forh.*, 595 (1899). [e] A. Werner and N. Goslings, *Ber.*, **36**, 2381 (1903). [f] S. N. Jörgensen, *Z. anorg. Chem.*, **2**, 283 (1892). [g] A. Werner and J. Rapiport, *Ann.*, **386**, 73 (1912). [h] Raman, 1063 cm.$^{-1}$; [i] 1087 cm.$^{-1}$.

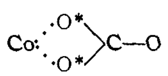
TABLE IV

CORRELATION TABLE BETWEEN D_{3h}, D_3, C_{2v} AND C_s

	ν_1	ν_2	ν_3	ν_4
D_{3h}	A'_1(R)	A''_2(I)	E'(I,R)	E'(I,R)
D_3	A_1(R)	A_2(I)	E(I,R)	E(I,R)
C_{2v}	A_1(I,R)	B_1(I,R)	A_1(I,R) + B_2(I,R)	A_1(I,R) + B_2(I,R)
C_s	A'(I,R)	A''(I,R)	A'(I,R) + A'(I,R)	A'(I,R) + A'(I,R)

plex. Therefore, we conclude that the symmetry of the ion does not differ whether it is an unidentate or a bidentate. This is in good accord with the chemical formula hitherto assumed.



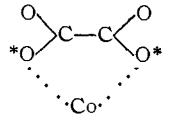


However, the effect of coördination undoubtedly is stronger in the bidentate than in the unidentate complex as is shown by the magnitude of the splitting of the degenerate mode and the intensities of the Raman active vibrations.

(3) **Oxalato Complexes.**—Free oxalate ion has high symmetry of V_h and exhibits 12 fundamentals. Among those, 9 are in-plane and 3 are out-of-plane vibrations. The number of infrared active in-plane modes is only 4 in V_h. If the symmetry is reduced to C_{2v} by coördination, all the 9 modes become infrared active.

Three Co(III) oxalato ammine complexes examined here show more than 9 bands in the region between 1600 and 400 cm.$^{-1}$. Therefore, it is obvious that V_h symmetry is destroyed by complex formation. In $[Co(NH_3)_5C_2O_4]Br\cdot{}^3/_2H_2O$, however, 4 or 5 bands which originate in g-type vibrations of V_h symmetry are very weak or almost vanished. Therefore, we suspect that the symmetry of the ion in the unidentate complex may be approximated by V_h because of weak interaction.

In $[Co(NH_3)_4C_2O_4]Cl$, all the 9 bands appear strongly. This result is expected from the following structure of the bidentate in which C_{2v} symmetry is assumed.



Since complete assignment is difficult, not all the observed bands will be discussed. Therefore, we discuss only the CO stretching bands which can be identified unambiguously. The CO stretching frequencies of the oxalato complexes are listed in Table V. It should be noted that the separation of the four bands is more remarkable in $[Co(NH_3)_5HC_2O_4]Br_2$ than in $[Co(NH_3)_4C_2O_4]Cl$. At first glance, this result seems contradictory to the general rule that the effect of coördination is stronger in the bidentate than in the unidentate complex. However, the oxalate ion in the former can be regarded as a bidentate coördinated by hydrogen and the metal. Furthermore, since the effect of O–H bonding on the spectrum of the oxalate ion is stronger than that of Co–O bonding, the CO stretching frequencies of $[Co(NH_3)_5HC_2O_4]Br_2$ would undergo larger shifts than those of the bidentate complex.

TABLE V

THE CO STRETCHING FREQUENCIES OF OXALATE COMPLEXES (CM.$^{-1}$)

Irred. rep. in V_h	b_{1g}	b_{2u}	a_g	b_{3u}
Free $C_2O_4^{--}$ ion	....[c]	1630(s)	.....[d]	1335, 1316
$[Co(NH_3)_5C_2O_4]Br\cdot\frac{3}{2}H_2O$[a]	....	1567(s)	1362(w)	1280(s)
$[Co(NH_3)_4C_2O_4]Cl$[b]	1705(s)	1663(s)	1395(s)	1260(s)
$[Co(NH_3)_5HC_2O_4]Br_2$[a]	1757(s)	1672(s)	1396(s)	1250(s)
Irred. rep. in C_{2v}	b_1	a_1	a_1	b_1

[a] S. M. Jörgensen, *Z. anorg. Chem.*, 11, 425 (1896). [b] W. Schramm, *ibid.*, **180**, 167 (1929). [c] Raman, 1664 cm.$^{-1}$. [d] 1485 and 1450 cm.$^{-1}$.

(4) **Acetato Complexes.**—Free acetate ion has 15 infrared active fundamentals. Among those, the vibrations due to COO^- group are asym. CO stretching (1578 cm.$^{-1}$), sym. CO stretching (1425 cm.$^{-1}$), CO_2 bending, CO_2 out-of-plane bending and CO_2 rocking modes.

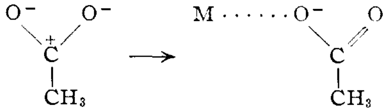
If the ion coördinates to the metal, the selection rule does not differ since all the modes are already infrared active in the free ion. Therefore, we will discuss the effect of coördination from the frequency shifts caused by complex formation. The X-ray studies[5] indicate that CH_3COO^- ion in $Ni(CH_3COO)_2\cdot 4H_2O$ is an unidentate whereas it is a bidentate in $Cu_2(CH_3COO)_4\cdot 2H_2O$ in which the ion is linked to two copper atoms.

Table VI gives the frequencies of the two CO stretching modes which can be assigned with certainty. It is seen that the separation of the two stretching frequencies is two times larger in the unidentate Co^{3+} complex than in the Ni^{2+} complex. It is expected that, as the metal–oxygen bond be-

---

(5) J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, 6, 609, 227 (1953).

comes stronger, two C–O bonds of the acetate ion become uneven, and the separation of the two CO stretching frequencies may increase.



Thus we conclude that the effect of coördination is stronger in the Co^{3+} complex than in the Ni^{2+} complex. This result suggests the importance of the formal charge of the central metal in discussing the effect of coördination from the infrared spectra.

Table VI also indicates that the asymmetric CO stretching frequency is higher in the bidentate Cu^{2+} complex than in the unidentate Ni^{2+} complex. This fact may suggest that two Cu–O bondings in the former are responsible for higher frequency shift of the asymmetric CO stretching mode.

TABLE VI

THE CO STRETCHING FREQUENCIES OF ACETATO COMPLEXES (CM.$^{-1}$)

	Asym.	Sym.	Separation
Free CH_3COO^- ion	1578(s)	1425(s)	153
$Ni(CH_3COO)_2 \cdot 4H_2O$	1530(s)	1418(s)	112
$Cu_2(CH_3COO)_4 \cdot 2H_2O$	1603(s)	1418(s)	185
$[Co(NH_3)_5CH_3COO](ClO_4)_2$[a]	1603(s)	1380(s)	223

[a] M. Linhard and B. Rau, *Z. anorg. Chem.*, **271**, 121 (1953).

NAKANOSHIMA, KITA, OSAKA, JAPAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Iodides of Thorium(III), (II) and (I)[1]

BY GEORGE W. WATT, D. M. SOWARDS AND S. C. MALHOTRA

RECEIVED MAY 20, 1957

The formation of iodides of thorium(III), (II) and (I) by the reduction of thorium(IV) iodide with excess elemental thorium at 550° is described. Procedures for the separation of the five components of the resulting reaction mixture have been devised; the resulting data confirm the existence of ThI_3 and provide evidence also for the existence of ThI_2 and ThI.

Earlier efforts to provide evidence for the existence of $Th^{<4+}$ as the fluoride,[2] chloride,[3] bromide[3] and iodide[3-6] lead to the conclusions that (a) thorium(IV) fluoride is not reduced by thorium between 1175 and 1600°, (b) thorium(III) chloride, bromide and iodide are formed by direct union, and (c) the iodide of thorium(III) also results from the reduction of thorium(IV) iodide with either thorium or aluminum and probably from the thermal decomposition of thorium(IV) iodide. Most of the evidence for halides of $Th^{<3+}$ arises from the study of disproportionation of thorium(III) halides or reactions involving direct union at low halogen–thorium ratios and consists of marginal analytical data on unresolved mixtures of products that have not been characterized on the basis of either physical properties or selectivity of chemical reactions.

The experiments described below are concerned with the formation of at least four different iodides of thorium and with procedures for their separation.

Experimental

Materials.—Unless otherwise indicated, all materials employed in this work were reagent grade chemicals.

Elemental reagent grade thorium metal powder gave an X-ray pattern that was characteristic of the pure metal and did not include any lines attributable to oxide and/or other impurities. Furthermore, oxide contamination was not detectable in thorium residues from reactions in which thorium(IV) oxide does not participate (*e.g.*, with iodine) and therefore would be expected to concentrate if present. Iodine was resublimed, dried and stored over calcium chloride. Ammonia was dried and stored over sodium amide; that the gas was oxygen-free was ensured by passing it through a solution of potassium in ammonia prior to condensation in reaction vessels. Commercial N,N-dimethylformamide was successively dried over P_2O_5, KOH and CaO, and finally distilled; only the fraction boiling at 150–151° at 750 mm. was used.

Methods.—X-Ray diffraction patterns were obtained with a Hayes unit, Cu Kα radiation, a Ni filter, a tube voltage of 35 kv., and a filament current of 15 ma. Samples were diluted with starch, and the exposure time was 6 hr. Relative intensities were estimated visually.

Magnetic susceptibility measurements were made with a modified Curie-Cheneveau balance[7,8]; Mohr salt was used for calibration. For samples of iodides that contained elemental thorium, susceptibilities were assumed to be additive and the susceptibility of the iodide(s) was obtained by subtracting the contribution of known thorium content from the total measured susceptibility.

Reactions between thorium or thorium iodides and iodine were carried out in Vycor tubes of 20 mm. i.d. that were degassed at 600°. After introduction of the reactants, the pressure was reduced to 10^{-3} mm. and the tubes were sealed.

Reactions in liquid ammonia were carried out in appropriate modifications of the equipment described elsewhere.[9]

Thorium was determined gravimetrically as ThO_2 (after complete removal of iodine), and iodine as AgI. Nitrogen was determined by the semimicro-Kjeldahl method.

Formation of Thorium Iodides.—Known weights of iodine and thorium corresponding to different reaction ratios were intimately mixed and heated at 100° for *ca.* 50 min. (*i.e.*, until the color of iodine vapor was no longer evident). The resulting mixtures (ThI_4 and Th) were then heated at 550° for 3 days. Over this period, ThI_4 that sublimed into the cool end of the tubes was returned to the main body of the reaction mixtures at regular intervals. Finally, the small quantities of ThI_4 that remained were separated from the non-volatile fraction by sublimation. The tubes were cooled, transferred to a dry-box and opened in an oxygen-free helium atmosphere.

The ends of the tubes containing ThI_4 were removed

---

[1] This work was supported in part by The U. S. Atomic Energy Commission, Contract AT-(40-1)-1639.

[2] J. C. Warf, THIS JOURNAL, **74**, 1864 (1952).

[3] E. Hayek, T. Rehner and A. Frank. *Monatsh.*, **82**, 575 (1951).

[4] J. S. Anderson and R. W. M. D'Eye, *J. Chem. Soc.*, S244 (1949).

[5] E. Hayek and T. Rehner, *Experientia*, **5**, 114 (1949).

[6] G. Jantsch, T. Homayr and F. Zemek. *Monatsh.*, **85**, 526 (1954).

[7] F. W. Gray and J. Farquharson, *J. Sci. Instr.*, **9**, 1 (1932).

[8] W. K. Witherspoon, Thesis, Tulane University, New Orleans, La., 1949.

[9] G. W. Watt and C. W. Keenan, THIS JOURNAL, **71**, 3833 (1949).