Infrared Spectroscopic Studies of Acido-pentammine Cobalt(III) Complexes. Sulfato, Nitrito, Nitrato and Carbonato Complexes

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Several infrared spectroscopic studies of cobalt(III) complexes co-ordinated with oxy-anions, such as sulfate, nitrate, carbonate and nitrite, have been reported.[1-4] The spectra of these co-ordinated oxyanions have been found to differ from those of the free anions, because the co-ordination usually causes a change in the symmetry and structure of the ligands. For the nitrato, carbonato and nitrito complexes, empirical assignments of the observed absorption bands have been carried out, but not for the sulfato complexes.

In this investigation, the assignment of the observed frequencies of sulfato and other acido pentammine complexes has been made on the basis of a normal co-ordinate treatment. The effect of co-ordination on the structure of these oxyanions and the applicability of the Urey-Bradley type potential field have been discussed.

Experimental

Preparation.—The $[Co(SO_4)(NH_3)_5]^+$, $[Co(NO_3)(NH_3)_5]^{2+}$ and $[(NH_3)_4Co\langle{}^{NH_2}_{SO_4}\rangle Co(NH_3)_4]^{3+}$ complexes were prepared according to the methods of Jörgensen,[5] Benrath[6] and Werner[7] respectively, and they were recrystallized more than three times. Since all the compounds studied were typical metallic complexes, their purity was checked by comparing the visible and ultraviolet spectra with the published data.[8,9]

Measurements.—The infrared spectra in the NaCl and the KBr prism region (5000∼400 cm^{-1}) were obtained by using a Hitachi EPI-2G infrared spectrophotometer, while those in the CsBr prism region (400∼250 cm^{-1}) were obtained by using a Nihonbunko 402-G infrared spectrophotometer. The wavelength calibration was made with the polystyrene, water vapor and carbon dioxide in the air. Spectra were measured by the KBr disk and the Nujol mull methods.

Calculation and Discussion

The vibrations of metal complexes can be divided into two types, one the vibration of ligands, and the other, that of metal-ligand bonding. The former generally appears in the rock salt region, while the latter appears in the longer wavelength region. The infrared absorption spectra of sulfato and nitrato complexes and their deuterated complexes show only two bands, near 330 and 270 cm^{-1}, in the range from 400 to 250 cm^{-1}.

In the calculation, the ligand vibrations were treated separately, without considering the coupling between the ligand vibrations and the metal-ligand vibrations, which has been found to be fairly small in carbonato-pentamminecobalt(III) complexes.[10] The secular equations were set up according to Wilson's procedure,[11] and the Urey-Bradley potential field[12] was used. Internal co-ordinates and symmetry co-ordinates for the

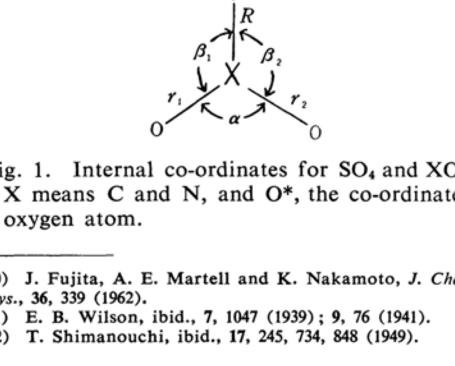

Fig. 1. Internal co-ordinates for SO_4 and XO_3. X means C and N, and O*, the co-ordinated oxygen atom.

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9) R. Tsuchida, ibid., **13**, 388, 436 (1938).

10) J. Fujita, A. E. Martell and K. Nakamoto, *J. Chem. Phys.*, **36**, 339 (1962).

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TABLE I. SYMMETRY CO-ORDINATES FOR THE C_{3v} AND THE C_{2v} CO-ORDINATED SULFATE

The C_{3v} co-ordinated sulfate	
A_1	$S_1=\Delta/\sqrt{3}\ (r_1+r_2+r_3)$
	$S_2=\Delta R$
	$S_3=\Delta/\sqrt{6}\ (\beta_1+\beta_2+\beta_3-\alpha_1-\alpha_2-\alpha_3)$
E	$S_4=\Delta/\sqrt{6}\ (2r_1-r_2-r_3)$
	$S_5=\Delta/\sqrt{6}\ (2\alpha_3-\alpha_1-\alpha_2)$
	$S_6=\Delta/\sqrt{6}\ (2\beta_1-\beta_2-\beta_3)$
The C_{2v} co-ordinated sulfate	
A_1	$S_1=\Delta/\sqrt{2}\ (r_1+r_2)$
	$S_2=\Delta/\sqrt{2}\ (R_1+R_2)$
	$S_3=\Delta/\sqrt{12}\ (2\gamma-\beta_1-\beta_2-\beta_3-\beta_4+2\alpha)$
	$S_4=\Delta/\sqrt{2}\ (\gamma-\alpha)$
B_1	$S_5=\Delta/\sqrt{2}\ (R_1-R_2)$
	$S_6=\Delta/2\ (\beta_1+\beta_2-\beta_3-\beta_4)$
B_2	$S_7=\Delta/\sqrt{2}\ (r_1-r_2)$
	$S_8=\Delta/2\ (\beta_1-\beta_2+\beta_3-\beta_4)$

TABLE II. SYMMETRY CO-ORDINATES FOR THE C_{2v} CO-ORDINATED NITRATE AND CARBONATE

A_1	$S_1=\Delta/\sqrt{2}\ (r_1+r_2)$
	$S_2=\Delta R$
	$S_3=\Delta/\sqrt{6}\ (2\alpha-\beta_1-\beta_2)$
B_2	$S_4=\Delta/\sqrt{2}\ (r_1-r_2)$
	$S_5=\Delta/\sqrt{2}\ (\beta_1-\beta_2)$

oxyanions investigated are given in Fig. 1 and in Tables I and II respectively.

(1) **Sulfato Complexes.**—The symmetry of a free SO_4^{2-} ion belongs to the point group T_d, and only two triply-degenerate vibrations of the four fundamentals are infrared active. When this ion is co-ordinated to a metal as a unidentate ligand, its symmetry is lowered to the point group C_{3v} and the triply-degenerate vibration splits into a doubly-degenerate vibratoin (E) and a totally symmetric vibration

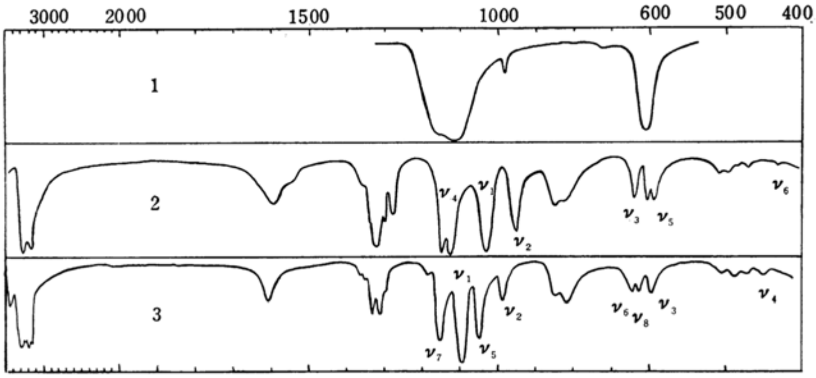

Fig. 2. Observed spectra of K_2SO_4 (1) ; $[Co(SO_4)(NH_3)_5]I$ (2) ; $[(NH_3)_4Co\langle{}^{NH_2}_{SO_4}\rangle Co(NH_3)_4]Br_3$ (3).

TABLE III. OBSERVED AND CALCULATED FREQUENCIES AND FORCE CONSTANTS OF $[Co(SO_4)(NH_3)_5]^+$

		ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
Calculated frequencies, cm^{-1}	(a)	1072	961	618	1126	613	445
	(b)	1043	963	621	1142	617	452
Assignment		ν(S-O) + ν(S-O*)	ν(S-O*) + ν(S-O)	$\delta(SO_4)$	ν(S-O)	$\delta(SO_3)+\rho(SO_3)$	$\rho(SO_3)+\delta(SO_3)$
Observed frequencies, cm^{-1}	$[Co(SO_4)(NH_3)_5]Cl$	1044	974	646	1135	614 603	446
	$[Co(SO_4)(ND_3)_5]Cl$	1047	973	645	1136	608	445
	$[Co(SO_4)(NH_3)_5]Br$	1050 1037	974	647	1148 1126	612 600	438
	$[Co(SO_4)(NH_3)_5]I$	1033	958	645	1152 1127	610 595	440
	$[Co(SO_4)(ND_3)_5]I$	1036	959	640	1130	617 596	440
	$[Co(SO_4)(NH_3)_5]NO_3$	1054 1036	974	647	1147 1126	613 598	440

		K_{SO^*}	K_{SO}	F_{OO^*}	F_{OO}	H_{OSO^*}	H_{OSO}	ρ_{SOSO^*}	ρ_{SOSO}
Force constant, mdyn./Å	(a)	5.1	6.3	0.7	0.8	0.40	0.45	0	0
	(b)	5.1	6.3	0.7	0.8	0.45	0.45	0.1	−0.2
		$\kappa=0.6$ mdyn.Å							

TABLE IV. OBSERVED AND CALCULATED FREQUENCIES AND FORCE CONSTANTS OF $\left[(NH_3)_4Co\begin{smallmatrix}NH_2\\SO_4\end{smallmatrix}Co(NH_3)_4\right]^{3+}$

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8
Calculated frequencies, cm^{-1}	1109	958	590	472	1068	630	1146	620
Assignment	ν(S-O)	ν(S-O*)	$\delta(SO_4)$	$\delta(SO_4)$	ν(S-O*)	$\delta(SO_4)$	ν(S-O)	$\delta(SO_4)$
Observed frequencies, cm^{-1}	$\left[(NH_3)_4Co\begin{smallmatrix}NH_2\\SO_4\end{smallmatrix}Co(NH_3)_4\right](NO_3)_3$							
	1109	997	613	454	1064	653	1171	641
	$\left[(NH_3)_4Co\begin{smallmatrix}NH_2\\SO_4\end{smallmatrix}Co(NH_3)_4\right]Br_3$							
	1101	991	605	455	1056	649	1155	637
	The deuterated complex							
	1096	988	602		1054	668	1166 1140	658
Force constant, mdyn./Å	K_{SO^*}	K_{SO}	$F_{O^*O^*}$	F_{OO^*}	F_{OO}	$H_{O^*SO^*}$	H_{OSO^*}	H_{OSO}
	5.7	6.8	0.65	0.70	0.80	0.40	0.50	0.45
	κ=0.6 mdyn.Å							

(A_1), and all vibrations become infrared-active. On the other hand, in the case of the binuclear complex, in which the SO_4^{2-} ion is co-ordinated as a bidentate, its symmetry becomes C_{2v} and all degeneracies split.[1] This correlation is apparent from the observed spectra shown in Fig. 2 and from the results of the normal coordinate calculation.

The vibrational frequencies were calculated with the force constant values listed in Tables III and IV ((a) in Table III) using the Urey-Bradley potential field. Those force constants were determined on the basis of the values of the free ions.[13] The bond angles were regarded as tetrahedral, while the bond lengths, $r_{SO^*}=1.53$ and $r_{SO}=1.47$ Å, were assumed from the value of the free SO_4^{2-} ion ($r_{SO}=1.50$ Å[14]). The asterisk indicates the co-ordinated oxygen atom. The values of F', the linear terms of the interaction between non-bonded atoms, were determined from the relation, $F'=-1/10\,F$.[15] The results are given in Tables III and IV ((a) in Table III).

Since the calculated frequencies were not in satisfactory agreement with the observed ones, especially for the stretching vibrations, the calculation was also made, in the case of the sulfatopentamminecobalt(III) complex, using a modified Urey-Bradley potential function[16] expressed as:

TABLE V. POTENTIAL ENERGY DISTRIBUTION OF THE C_{3v} AND THE C_{2v} CO-ORDINATED SULFATE

The C_{3v} co-ordinated sulfate

	ν_1	ν_2	ν_3
Calculated frequencies, cm^{-1}	1072	961	618
S_1	1.00	0.57	0.01
S_2	0.62	1.00	0.06
S_3	0.19	0.06	1.00
	ν_4	ν_5	ν_6
Calculated frequencies, cm^{-1}	1126	613	446
S_4	1.00	0.08	0.00
S_5	0.09	1.00	0.72
S_6	0.07	0.60	1.00

The C_{2v} co-ordinated sulfate

	ν_1	ν_2	ν_3	ν_4
Calculated frequencies, cm^{-1}	1109	958	590	472
S_1	1.00	0.28	0.00	0.01
S_2	0.37	1.00	0.00	0.02
S_3	0.00	0.00	1.00	0.06
S_4	0.12	0.02	0.04	1.00
	ν_5	ν_6		
Calculated frequencies, cm^{-1}	1068	630		
S_5	1.00	0.08		
S_6	0.18	1.00		
	ν_7	ν_8		
Calculated frequencies, cm^{-1}	1146	620		
S_7	1.00	0.15		
S_8	0.14	1.00		

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[13] S. Mizushima and T. Shimanouchi, "Infrared Absorption Spectra and Raman Effect," Kyoritsu, Tokyo (1958).

[14] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y. (1960).

[15] T. Shimanouchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **74**, 266 (1953).

[16] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **18**, 101 (1962).

$$V=(1/2)\sum_{i}K_i(\Delta r_i)^2+(1/2)\sum_{i<j}H_{ij}(r_{ij}\Delta\alpha_{ij})^2 + (1/2)\sum_{i<j}F_{ij}(\Delta q_{ij})^2+(\text{linear terms}) + \sum_{i<j}\rho_{ij}(\Delta r_i)(\Delta r_j) \tag{1}$$

where ρ represents the bond-bond interaction constant. The calculated frequencies which were obtained with Eq. 1 using the force constants of (b) in Table III are given in Table III(b).

The potential energy distribution was calculated, and the band assignments were made. These are given in Table V and Fig. 2 respectively.

The use of the Urey-Bradley potential field failed to give a satisfactory agreement between the calculated and the observed frequencies in the C_{2v} calculation (Table II) also. This, however, seems partly due to the neglect of the effect of the ring vibration, which should have been taken into account for the metal chelate complexes.[10]

Nevertheless, it may be concluded, from the force constants obtained, that a SO_4^{2-} ion combines with cobalt(III) more strongly as a unidentate than as a bidentate.

(2) Nitrito Complex.—In the nitrito complex, ONO* belongs to the point group C_s, and the three A_1 vibrations are all infrared-active. Table VI shows the calculated and the observed frequencies of the nitritopentamminecobalt(III) complex. The molecular dimensions given in Table VI were assumed from the structures of $NaNO_2$[17] and CH_3ONO.[18] Table VI shows that the effect of the bond angle on the calculated values is not significant. The force constants in Table VI indicate a marked difference in bond orders between the NO and NO* bonds. This suggests that the co-ordination effect is fairly large.

TABLE VI. OBSERVED AND CALCULATED FREQUENCIES AND OBTAINED FORCE CONSTANTS OF $[Co(ONO)(NH_3)_5]Cl_2$

Calculated frequencies,*1 cm^{-1}	(a)*2	1463	1063	824
	(b)*2	1466	1064	835
Observed frequencies, cm^{-1} [4]		1468	1065	825
Assignment		ν(N-O)	ν(N-O*)	δ(ONO*)
Force constant, mdyn./Å	K_{NO^*}	K_{NO}	F_{OO^*}	H_{ONO^*}
	4.2	8.7	2.0	0.90

1 R(N-O) = 1.30 Å r(N-O) = 1.20 Å,
*2 (a) ∠ONO = 120°, (b) ∠ONO = 115°

(3) Nitrato and Carbonato Complexes.—Both NO_3^- and CO_3^{2-} in the state of free ions belong to the point group D_{3h}, and two degenerate and one out-of-plane vibrations of the four fundamentals are infrared-active. When these anions are co-ordinated as unidentate ligands, the symmetry lowers to C_{2v} and the irreducible representation, E, splits into A_1 and B_2. Tables VII and VIII present the observed and the calculated frequencies. The latter was obtained with the force constants given in these tables. The bond angles of the nitrato and the carbonato complexes are assumed to be 120° ((a) and (b) in Tables VII and VIII), but in the case of the nitrato complex the calculation was made also with the bond angles, $\alpha=130°$ and $\beta=115°$ ((c) in Table VII). The bond lengths of these complexes are considered to be $r_{XO^*}=1.30$ and $r_{XO}=1.25$ Å. The potential energy distributions of the co-ordinated nitrate and carbonate as unidentate ligands are given in Table IX.

The results of the calculation show that the usual Urey-Bradley force field does not apply well in these molecules. The following four points, therefore, will be discussed:

(i) The effects of the coupling with oxygen-cobalt bond vibrations;

(ii) The effect of hydrogen-bond formation;

(iii) The effect of the molecular dimension and

(iv) The applicability of the Urey-Bradley type force field to the molecules that have unlocalized π-electrons.

In order to investigate the effects of the coupling with oxygen-cobalt bond vibrations, the spectra in the CsBr prism region were obtained. The observed frequencies are given in Table X. The bands of some 330 cm^{-1} shift to lower frequencies by 30 cm^{-1} upon deuteration, while those of some 27 cm^{-1} do not. Although the assignments of these bands are not clear at present, the calculation was made with the value, $K_{Co-O^*}=2$ mdyn./Å[10] and the C_{2v} point symmetry. The results suggested that the effect of the coupling with oxygen-cobalt bond vibrations is insignificant.

As to the molecular dimensions, the effects of the bond length and the bond angle were taken into consideration. It was found that the former is negligibly small, as Table XI shows, whereas the latter is considerably large, as may be seen from the calculated frequencies given in Table VII.

According to the electron diffraction studies of nitric acid in the solid state,[19] the bond angle of ONO is 134° and that of HO-NO, 113°, indicating that the HO-N bond is a

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[17] G. B. Carpenter, *Acta Cryst.*, **8**, 852 (1955).
[18] F. Rogowski, *Ber.*, **75**, 244 (1942).

[19] V. Luzzati, *Acta Cryst.*, **4**, 120 (1951).

TABLE VII. OBSERVED AND CALCULATED FREQUENCIES AND FORCE CONSTANTS OF $[Co(NO_3)(NH_3)_5]^{2+}$

		ν_1	ν_2	ν_3	ν_4	ν_5
Calculated frequencies, cm^{-1}	(a)	1341	1018	735	1467	696
	(b)	1290	1026	736	1484	711
	(c)	1305	1019	730	1481	699
Assignment		ν(N-O) + ν(N-O*)	ν(N-O*) + ν(N-O)	$\delta(NO_3)$	ν(N-O)	$\rho(NO_2)$
Observed frequencies, cm^{-1}	$[Co(NO_3)(NH_3)_5]Cl_2$	1280	1017	754	1481	724
	$[Co(NO_3)(NH_3)_5](NO_3)_2$	1266	1016	745	1481	716
	$[Co(NO_3)(ND_3)_5](NO_3)_2$	1287	1018		1484	

Force constant, mdyn./Å		K_{NO^*}	K_{NO}	F_{OO^*}	F_{OO}	H_{ONO^*}	H_{ONO}	ρ_{NONO^*}	ρ_{NONO}
	(a)	3.9	6.5	1.5	1.7	0.50	0.60	0	0
	(b)	4.0	6.1	1.5	1.7	0.55	0.60	0.2	−0.5
	(c)	4.1	6.25	1.5	1.7	0.50	0.60	0	0

TABLE VIII. OBSERVED AND CALCULATED FREQUENCIES AND FORCE CONSTANTS OF $[Co(CO_3)(NH_3)_5]^+$

		ν_1	ν_2	ν_3	ν_4	ν_5
Calculated frequencies, cm^{-1}	(a)	1414	1051	729	1468	668
	(b)	1366	1054	728	1468	668
Assignment		ν(C-O) + ν(C-O*)	ν(C-O)* + ν(C-O)	$\delta(CO_3)$	ν(C-O)	$\rho(CO_2)$
Observed frequencies, cm^{-1} 10)	$[Co(CO_3)(NH_3)_5]Br$	1373	1070	756	1453	678
	$[Co(CO_3)(ND_3)_5]Br$	1369	1072	751	1471	687
	$[Co(CO_3)(NH_3)_5]I$	1366	1065	776	1449	679
	$[Co(CO_3)(ND_3)_5]I$	1360	1063	742	1467	687

Force constant, mdyn./Å		K_{CO^*}	K_{CO}	F_{OO^*}	F_{OO}	H_{OCO^*}	H_{OCO}	ρ_{COCO^*}	ρ_{COCO}
	(a)	4.7	5.9	1.5	2.0	0.40	0.50	0	0
	(b)	4.7	5.7	1.5	2.0	0.40	0.50	0.2	−0.2

TABLE IX. POTENTIAL ENERGY DISTRIBUTION OF THE C_{2v} CO-ORDINATED NITRATE AND CARBONATE

The C_{2v} co-ordinated nitrate

	ν_1	ν_2	ν_3
Calculated frequencies, cm^{-1}	1341	1018	735
S_1	1.00	0.55	0.04
S_2	0.56	1.00	0.23
S_3	0.38	0.17	1.00

	ν_4	ν_5
Calculated frequencies, cm^{-1}	1467	690
S_4	1.00	0.07
S_5	0.21	1.00

The C_{2v} co-ordinated carbonate

	ν_1	ν_2	ν_3
Calculated frequencies, cm^{-1}	1414	1051	729
S_1	1.00	1.25	0.01
S_2	0.99	1.00	0.14
S_3	0.47	0.08	1.00

	ν_4	ν_5
Calculated frequencies, cm^{-1}	1468	668
S_4	1.00	0.07
S_5	0.21	1.00

TABLE X. OBSERVED FREQUENCIES IN cm^{-1} OBTAINED IN THE KBr AND THE CsBr PRISM REGION

$[Co(SO_4)(NH_3)_5]I$	511	501	(486)	469		326	259
$[Co(SO_4)(ND_3)_5]I$		489				296	257
$[Co(SO_4)(NH_3)_5]Br$	515	499				332	264
$\left[(NH_3)_4Co\langle\genfrac{}{}{0pt}{}{NH_2}{SO_4}\rangle Co(NH_3)_4\right]Br_3$	510	499	476			323	290
The deuterated complex		493				291	259
$\left[(NH_3)_4Co\langle\genfrac{}{}{0pt}{}{NH_2}{SO_4}\rangle Co(NH_3)_4\right](NO_3)_3$	507			460		323	277
$[Co(NO_3)(NH_3)_5](NO_3)_2$		510	498	475		335	278
$[Co(NO_3)(ND_3)_5](NO_3)_2$						307	271
$[Co(NO_3)(NH_3)_5]Cl_2$		507		460	345	330	284
$[Co(CO_3)(NH_3)_5]NO_3$		505		468	358	333	310
$[Co(CO_3)(NH_3)_5]Cl$	510	495		470	358	330	290

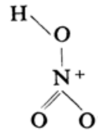
TABLE XI. EFFECT OF BOND LENGTH ON THE CALCULATED FREQUENCIES OF ONO_2 COMPOUND

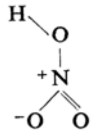
Bond length, Å						
R	r	ν_1	ν_2	ν_3	ν_4	ν_5
1.30	1.25	1341	1018	735	1467	696
1.30	1.20	1336	1017	732	1466	692
1.35	1.25	1336	1017	732	1466	692

TABLE XII. COMPARISON OF THE VALUE OF F_{OO} [20]

Ion	Atomic distance between non-bonded atoms, Å	F_{OO} (UBFF)	F_{OO} (Ne···Ne)
NO_3^-	2.11	1.59	1.41
CO_3^{2-}	2.27	1.74	0.53
SO_4^{2-}	2.47	0.76	0.15

single bond and that, as a result of the resonance of structures I and II, the N–O bonds come to have a more double-bond character.


(I)


(II)

From this fact and from the results of the calculation shown in Table VII, it may be concluded that the complex formation distorts the bond angles of a NO_3^- ion in a way similar to that it does nitric acid. The magnitude of this deformation, however, could not be estimated from these calculations.

The effect of hydrogen bond formation has not been considered in the present investigation, although there must be some influence, because in the case of these pentammine complexes, hydrogen atoms are located close around oxygen atoms.

Recently, several papers have reported on the potential field that can be applied to the compounds with unlocalized π-electrons. These compounds give larger repulsive force constants than the values that would be expected from the interatomic repulsive forces between the iso-electronic inert gas atoms. For example, the F constants for NO_3^-, CO_3^{2-} and SO_4^{2-} are much larger than those calculated from the Lennard-Jones equation[20] (Eq. 2), as Table XII shows.

$$F=(12\varepsilon^*/q^2)\ \ [13(r^*/q)^{12}-7(r^*/q)^6] \qquad (2)$$

were $\varepsilon^*=4.89\times10^{15}$ erg, $r^*=3.08$ Å

In the treatment of such compounds, the interaction terms are generally introduced as additional terms. In this study the bond-bond interaction terms were added to the usual Urey-Bradley function. The calculation of the potential energy distribution, however, requires no change in the assignment.

The negative sign of all the ρ_{XOXO} interaction terms could be interpreted by considering the localization of π-electrons in the X–O bonds.

It may be concluded from the normal coordinate treatment that the co-ordination effects in the sulfato-, nitrito-, nitrato- and carbonato-pentamminecobalt(III) complexes

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[20] T. Shimanouchi, "Force Constants of Small Molecules," Tokyo University, Tokyo (1962).

are fairly large. Upon co-ordination, the bond orders of X–O and X–O* become considerably different. Consequently, the bond length of X–O decreases and that of X–O* increases. At the same time, the bond angle of O–X–O increases and that of O–X–O* decreases. It may also be concluded from this investigation that the bond character between cobalt and oxygen is considerably covalent; if it is ionic, such a large difference would not appear among the X–O bonds of the co-ordinated oxyanions.

Summary

The infrared spectra of twelve acido-pentammine cobalt(III) complexes have been obtained in the range between 5000 and 250 cm^{-1}, and the vibrational frequencies of the co-ordinated oxyanions have been assigned from the normal co-ordinate treatment based on Wilson's method and on the Urey-Bradley potential field. The results of the calculation show that the co-ordination effects on these oxyanions are fairly large and that the bonds between cobalt and oxygen atoms have a considerably covalent character.

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