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The Preparation of Nitro-Carbonato and -Acetylacetonato Complexes of Cobalt(III) and Their IR and UV Spectra

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Two new nitro complexes of cobalt(III), $K_2[Co(NO_2)_2CO_3acac]\cdot H_2O$ and $K_3[Co(NO_2)_4CO_3]\cdot H_2O$, have been prepared by the reaction of tricarbonatocobaltate(III) and the desired ligand. The 700—200 cm^{-1} region IR spectra for these complexes and the other related dinitro complexes have been measured, and the geometrical structures of these dinitro complexes have been determined as of the *cis*-form on the basis of the IR data. Furthermore, the absorption spectra of these nitro complexes have also been measured, and the stability of these complexes has been related to the spectral data.

We reported, in a previous paper, the preparation of a series of *cis*-dinitro complexes of cobalt(III), namely, $[Co(NO_2)_2(CO_3)_2]^{3-}$, $[Co(NO_2)_2CO_3ox]^{3-}$, and $[Co(NO_2)_2(ox)_2]^{3-}$.[1] In the present paper we will report the preparation of a new dinitro and a new tetranitro complex, namely, $K_2[Co(NO_2)_2CO_3acac]\cdot H_2O$ (acac=acetylacetonato ligand) and $K_3[Co(NO_2)_4CO_3]\cdot H_2O$. It has been found that the above carbonatoacetylacetonato complex is the most unstable of the five nitro complexes, including the previous three complexes. We will also report the 700—200 cm^{-1} region IR spectra for these complexes. On the basis of the data and some elemental knowledge of the group theory, the geometrical structures of the dinitro complexes are determined to be of the *cis*-form.

Furthermore, the frequency values of the nitro specific band of the complexes have been compared in terms of their stability in an aqueous solution.

Experimental

Preparation. 1) *Potassium Dinitrocarbonatoacetylacetonatocobaltate(III) Monohydrate,* $K_2[Co(NO_2)_2CO_3acac]\cdot H_2O$. Into a green solution of tricarbonatocobaltate(III) ($CoCl_2\cdot 6H_2O$ 10 g scale; 0.048 mol) prepared by the usual method,[2] 10 m*l* (0.10 mol) of acetylacetone were added, drop by drop. The mixture was then stirred under an iced condition for half an hour. After filtering the *tris*(acetylacetonato) complex and a residue out, 34 g (0.40 mol) of potassium nitrite were stirred into the filtrate under an iced condition. After a while, red needle-shaped crystals of the desired complex began to appear. The crystals were then washed thoroughly with benzene to remove the *tris*-(acetylacetonato) complex. The yield was about 6 g.

Found: C, 17.79; N, 6.68; H, 2.30%. Calcd for

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[1] H. Ichikawa and M. Shibata, This Bulletin, **42**, 2873 (1969).

[2] M. Shibata, *Nippon Kagaku Zasshi*, **87**, 771 (1966).

$K_2[Co(NO_2)_2CO_3acac]\cdot H_2O$: C, 17.74; N, 6.90; H, 2.24%.

The complex decomposed very rapidly in an aqueous solution, giving a brown residue, but it kept stable in an aqueous solution in which potassium nitrite had been dissolved.

2) *Potassium Tetranitrocarbonatocobaltate(III) Monohydrate*, $K_3[Co(NO_2)_4CO_3]\cdot H_2O$. To a green solution of tricarbonatocobaltate(III) prepared on the same scale as 1), 26 g (0.30 mol) of potassium nitrite were added under cooling. The mixture was then stirred under an iced condition for an hour, after which 30 m*l* of 6N acetic acid were added, drop by drop. The mixed solution was further stirred for 3—4 hr to complete the reaction. Then, the resulting red solution was allowed to stand in a refrigerator overnight. After a small quantity of a precipitated material, $K_3[Co(NO_2)_6]$, had been filtered off, 50 m*l* of ethanol were added to the filtrate; the whole was then kept in a refrigerator for a day to precipitate orange, needleshaped crystals. The yield was about 7 g.

Found: C, 3.04; N, 12.46; H, 0.59%. Calcd for $K_3[Co(NO_2)_4CO_3]\cdot H_2O$: C, 2.74; N, 12.79; H, 0.46%.

When 100 m*l* of ethanol were added to the mother liquor and the mixture was allowed to stand in the cold, a mixture of tetranitrocarbonato- and dinitrodicarbonatocobaltate(III) was obtained.

Measurements. The infrared absorption spectra in the 700—200 cm^{-1} region were measured by the Nujol mull technique using a Hitachi EPI-L grating infrared spectrometer. The IR spectra in the 4000—700 cm^{-1} region and the visible and near-ultraviolet absorption spectra were measured with the same instruments as were used in a previous investigation.[1] In addition, an automatic recording spectrophotometer (JASCO Model UV-5) was used for the rapid measurement of the absorption spectrum of the carbonatoacetylacetonato complex.

Results and Discussion

Preparation and Measurement. As another reaction, we attempted partial replacement of the carbonato ligand in $[Co(NO_2)_2CO_3)_2]^{3-}$ with acetylacetonate, but the reaction gave a mixture of *trans*-$[Co(NO_2)_2(acac)_2]^-$ [3,4] and a brown, unknown material.

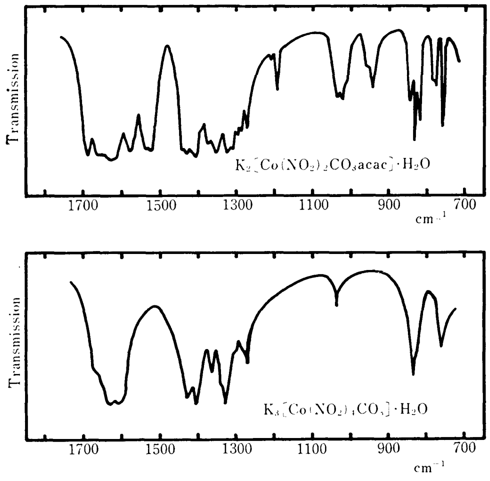

Fig. 1. Infrared absorption spectra of the *cis*-$K_2[Co(NO_2)_2CO_3acac]\cdot H_2O$ and $K_3[Co(NO_2)_4CO_3]\cdot H_2O$.

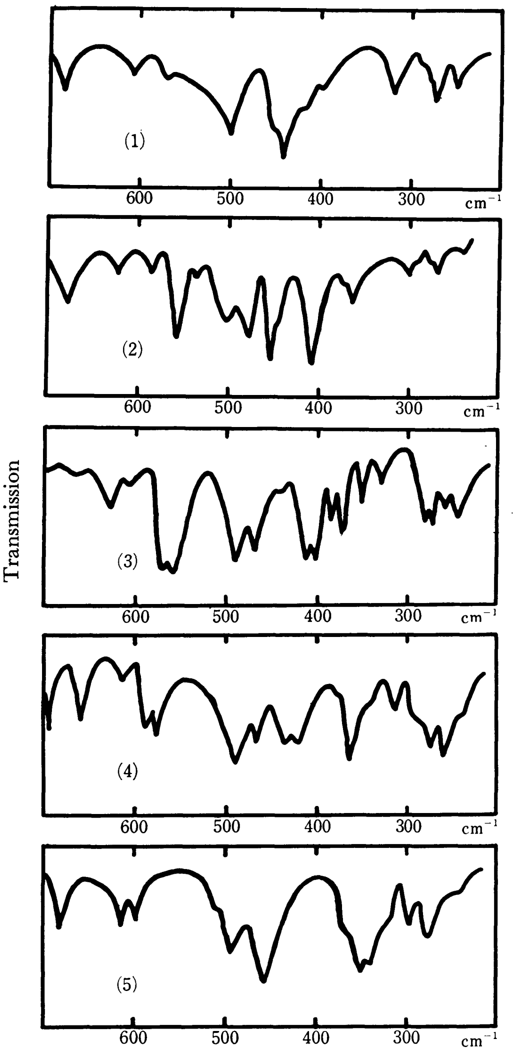

Fig. 2. Far-infrared absorption spectra of the nitro complexes of cobalt(III).

(1) $K_3[Co(NO_2)_2(CO_3)_2]\cdot H_2O$
(2) $K_3[Co(NO_2)_2CO_3ox]$
(3) $K_3[Co(NO_2)_2(ox)_2]\cdot H_2O$
(4) $K_2[Co(NO_2)_2CO_3acac]\cdot H_2O$
(5) $K_3[Co(NO_2)_4CO_3]\cdot H_2O$

The complexes were unstable in an aqueous solution. The measurement, therefore, of the absorption spectrum of the tetranitrocarbonato complex was carried out in a 0.10M potassium bicarbonate aqueous solution. The carbonatoacetylacetonato

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[3] L. J. Boucher and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **27**, 1093 (1965).

[4] R. O. Archer and B. P. Cotsoradis, *Inorg. Chem.*, **4**, 1584 (1965).

Table 1. IR data of the nitro complexes of cobalt(III) (cm^{-1})

Complex	NO_2^-			CO_3^{2-}				
	asym. ν(NO)	sym. ν(NO)	sym. δ(ONO)	sym. $\nu(C\text{-}O_{II})$	asym. $\nu(CO_I)$	sym. $\nu(CO_I)$	out-of-plane $\pi(O_ICO_{II})$	sym. $\delta(O_ICO_I)$
$K_2[Co(NO_2)_2CO_3acac]\cdot H_2O$	1401	1355 1323 1310	840 833 823	1683 1664 1614	1291 1276	1025	833	759
$K_3[Co(NO_2)_4CO_3]\cdot H_2O$	1436 1407	1366 1331sh 1321	833 830	1677sh 1641 1601	1274sh 1267	1031	833	758

sh: shoulder

Table 2. IR data of the nitro and related complexes (cm^{-1})

Complex	NO_2^-			CO_3^{2-}			$C_2O_4^{2-}$			
	wagging δ(ONO)	sym. ν(M-N)	rocking δ(ONO)	asym. $\delta(O_ICO_{II})$	asym. $\nu(MO_I)$	sym. $\nu(M\text{-}O_I)$	asym. δ(CCO)	asym. ν(MO)	sym. δ(CCO)	
$K_3[Co(NO_2)_6]$	637	418	293							a)
$K_3[Co(NO_2)_2(CO_3)_2]\cdot H_2O$	606 576	443 425	295sh 284	685	503					b)
$K_3[Co(NO_2)_2CO_3ox]$	623 585	443 407	272	680	502		558	478		b)
$K_3[Co(NO_2)_2(ox)_2]\cdot H_2O$	627	415 405	280 274				570 562	471 490	444	b)
$K_2[Co(NO_2)_2CO_3acac]\cdot H_2O$	590 574	435 423	274	658	492					b)
$K_3[Co(NO_2)_4CO_3]\cdot H_2O$	613 598	456		683	493	349 341sh				b)
$K[Co(NH_3)_2(CO_3)_2]$				673	444 411	366				c)
$K_3[Co\ (ox)_3]\cdot 3H_2O$							559	476	446	d)

a) I. Nakagawa, I. Shimanouchi and K. Yamasaki, *Inorg. Chem.*, **3**, 772 (1964).
b) Present work.
c) J. Fujita, A. Martell and K. Nakamoto, *J. Chem. Phys.*, **36**, 339 (1962).
d) J. Fujita, K. Nakamoto and M. Kobayashi, *J. Phys. Chem.*, **61**, 1014 (1957).

Table 3. IR data of the $K_2[Co(NO_2)_2CO_3acac]\cdot H_2O$ complex (cm^{-1})

Location	Tentative assignment
1577	sym. ν(CO)
1520	asym. ν(CC)
1440	CH_3 deg. def.
1401	asym. ν(CO)
1374	CH_3 sym. def.
1291 1276	sym. ν(CC)
1196	CH in-plane bend.
1038sh 1033 1025	CH_3 rock.
950sh 942	$\nu(C\text{-}CH_3)$
788 785	CH out-of-plane bend.
695	ring def.$+\nu$(M-O)
668sh 658	$C\text{-}CH_3$ bend.$+\nu$(M-O)
467	asym. ν(M-O)
365	ring deformation

complex rapidly changed from red to green in a potassium bicarbonate aqueous solution, but the green solution thus produced rapidly returned to the original red state on the addition of potassium nitrite, and the recovered solution was stable for a few hours at room temperature. This phenomenon seems to arise from the rapid substitution between CO_3^{2-} and NO_2^- ions. Therefore, a potassium nitrite aqueous solution in a high concentration was used as the solvent of the carbonatoacetylacetonato complex. However, because of the absorption of the nitrite ion itself, the absorption spectrum of the complex was measured only in the 700—400 mμ region, with a 0.50M potassium nitrite aqueous solution (Fig. 3, ------). The measurement in the 700—250 mμ region was carried out with a 0.10M aqueous solution (Fig. 3, ——).

IR Spectra. The IR spectra in the 4000—700 cm^{-1} region for the present complexes are shown in Fig. 1, while the numerical data are given in Tables 1 and 3. The 700—200 cm^{-1} region spectra of the present complexes and of related complexes are shown in Fig. 2, and the numerical data are given in Tables 2 and 3.

It is clear that the NO_2^- in the present complexes coordinates to a central atom through the N-atom, because of the absence of a nitrito characteristic band (sym. ν(NO)) at 1050 cm^{-1} 5,6) and a characteristic bridged nitrito band (asym. ν(NO)) near 1520 cm^{-1}.7)

When we assume that the C_{2v} symmetry of a free nitrite ion is maintained in the complex, the number of infrared active modes becomes 6 for the M-NO_2. These 6 fundamentals were observed for all the complexes except the tetranitro complex in the range of 1450—400 cm^{-1} (Tables 1 and 2). For the tetranitro complex, 5 bands were observed.

In the previous paper,1) we determined the geometrical structures of the dinitro complexes on the basis of the number of NO_2^- symmetrical stretching and bending vibrations. In this work, we expected that the IR spectra of these complexes in the far-infrared region (below 700 cm^{-1}) would afford more information about the structure, since the Co–NO_2 stretching and the wagging of the nitro group appear in this region. For example, *cis*-$[Co(NO_2)_2(NH_3)_4]^+$ has two bands, at 605 and 587 cm^{-1}, attributable to the NO_2^- wagging vibration, whereas *trans*-$[Co(NO_2)_2(NH_3)_4]^+$ has only one band, at 623 cm^{-1}.7) In the case of the present complexes, one or two bands attributable to the NO_2^- wagging vibration were observed (Table 2).

From a group theoretical consideration, the *trans* dinitro complex was expected to have one IR active M-NO_2 stretching mode in a D_{4h} or D_{2h} symmetry, and the corresponding *cis* complex, to have two modes in a C_{2v} or C_2. For the present dinitro complexes, two bands attributable to the Co–NO_2 stretching vibration were observed. The assignment was tentatively achieved by the method of Nakagawa *et al.*8) (Table 2). From this result, it may be concluded that these dinitro complexes belong to the *cis*-form.

The symmetry, D_{3h}, of the free carbonate ion is lowered to C_{2v} by chelation, and the complexed carbonate ion has 9 fundamentals. Among the 9 fundamentals, 7 in-plane modes belong to the A_1 and B_2 representations, and 2 out-of-plane modes belong to B_1. We observed at least 7 bands for the four nitro complexes in the 1700—340 cm^{-1} region. Their locations are shown in Tables 1 and 2.

In our previous paper,1) we identified a broad and strong band in the 1700—1600 cm^{-1} region as asym. ν(C–O_I) (where O_I represents the oxygen atom coordinated to a central atom), according to the method of Gatehouse.9) Fujita *et al*,10) however, have identified the same band as ν(C–O_{II}) (where O_{II} represents the free oxygen atom). Judging from the fact that the C–O_{II} bond has a double-bond character in $[Co(NH_3)_4CO_3]^+$,11) we will now regard the absorption band (1700—1600 cm^{-1}) as ν(C–O_{II}).

The band near 500 cm^{-1} may be assigned to the M–CO_3 asymmetrical stretching vibration (Table 2). In fact, the corresponding Co–CO_3 mode in the double complex $[Co(NH_3)_6]\cdot[Co(CO_3)_3]$ has been observed at 488 and 465 cm^{-1}.10) In the case of *trans*-$[Co(NO_2)_2(acac)_2]^-$, no absorption band was observed near 500 cm^{-1}.

When C_{2v} symmetry is assumed for a chelated structure of an oxalate ion, there are 15 fundamentals.12,13) The number of infrared active modes of M–C_2O_4 is 13 in C_{2v}. Of these fundamentals, 8 bands were observed in the 1750—450 cm^{-1} range. Their locations in the 1750—700 cm^{-1} range were shown previously,1) while those in the 700—450 cm^{-1} range are shown in Table 2.

The tentative assignment of the complexed acetyl-

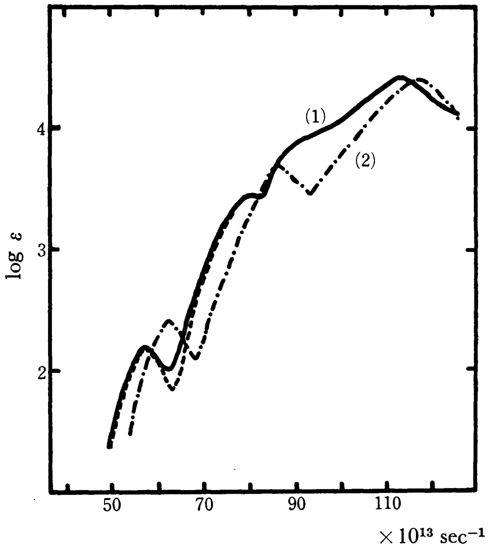

Fig. 3. Absorption spectra of the nitro complexes of cobalt(III).

(1) $K_2[Co(NO_2)_2CO_3acac]\cdot H_2O$ —— in 0.10M KNO_2 and ------ in 0.50M KNO_2

(2) $K_3[Co(NO_2)_4CO_3]\cdot H_2O$ -·-·- in 0.10M $KHCO_3$

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5) K. Nakamoto, J. Fujita and H. Murata, *J. Chem. Soc.*, **1959**, 4073.

6) R. B. Perland, T. J. Lane and J. V. Quagliano, *J. Amer. Chem. Soc.*, **78**, 883 (1956).

7) K. Nakamoto, J. Fujita and H. Murata, *ibid.*, **80**, 4817 (1958).

8) I. Nakagawa, I. Shimanouchi and K. Yamasaki, *Inorg. Chem.*, **3**, 772 (1964); *ibid.*, **7**, 1332 (1968).

9) B. M. Gatehouse, S. E. Livingstone and R. S. Nyholm, *J. Chem. Soc.*, **1958**, 3137.

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

11) G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, **1962**, 586.

12) K. Nakamoto, J. Fujita, S. Tanaka and M. Kobayashi, *J. Amer. Chem. Soc.*, **79**, 4904 (1957).

13) J. Fujita, A. E. Martell and K. Nakamoto, *J. Chem. Phys.*, **36**, 324 (1962).

Table 4. Absorption data for the new nitro complexes ($\times 10^{13}$sec^{-1})

Complex	ν_1	ν_{sp}	ν_3	$\nu_{sp}-\nu_1$
$K_2[Co(NO_2)_2CO_3acac]\cdot H_2O$	56.10 (2.18)	*ca.* 80.8 (3.39) *ca.* 90.1 (3.75)sh	*ca.* 113.3 (4.36)	*ca.* 24.7
$K_3[Co(NO_2)_4CO_3]\cdot H_2O$	61.56 (2.39)	85.65 (3.69)	114.20 (4.27)	24.09

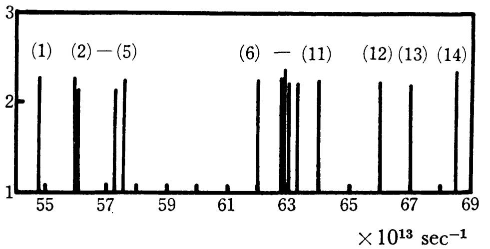

Fig. 4. The position of first absorption band of *cis*-dinitro complexes of cobalt(III).

(1) $[Co(NO_2)_2(CO_3)_2]^{3-}$
(2) $[Co(NO_2)_2CO_3ox]^{3-}$
(3) $[Co(NO_2)_2CO_3acac]^{2-}$
(4) $[Co(NO_2)_2(ox)_2]^{3-}$ (5) $[Co(NO_2)_2(acac)_2]^-$
(6) α-$[Co(NO_2)_2CO_3(NH_3)_2]^-$
(7) $[Co(NO_2)_2CO_3en]^-$ (8) $[Co(NO_2)_6]^{3-}$
(9) α-$[Co(NO_2)_2ox(NH_3)_2]^-$
(10) $[Co(NO_2)_2ox\ en]^-$ (11) $[Co(NO_2)_2(gly)_2]^-$
(12) $[Co(NO_2)_2gly\ en]$
(13) $[Co(NO_2)_2(NH_3)_4]^+$ (14) $[Co(NO_2)_2(en)_2]^+$

acetonate was attempted according to the references.[14–16] The data are given in Table 3.

Absorption Spectra. The absorption spectra in the solution are shown in Fig. 3, while the numerical data are listed in Table 4. The frequency values of the first absorption band for a number of dinitro complexes including the hexanitro complex are diagrammatically represented in Fig. 4. From this figure, it may be seen that the positions of the first absorption band shift according to the spectrochemical series.[17] We therefore calculated the position of the first absorption band of hexanitrocobaltate(III) by the following equation, based on "the rule of average environment"[18];

$$2/3(A) + 1/3(X) = (B)$$
$$(X) = 3(B) - 2(A)$$

where (A) and (B) are the positions of the first band for a $[CoA_6]$-type and a $[Co(NO_2)_2A_4]$-type complex respectively, and where (X) is the frequency value to be estimated. In the case of a $[Co(NO_2)_2(aa)(bb)]$-type complex, (A) was taken as the mean value of a $[Co(aa)_3]$-type complex and a $[Co(bb)_3]$-type complex. The results are represented in Fig. 5. The positions, estimated from the mixed dinitro complexes with carbonato, oxalato, and acetylacetonato ligands, are at 70—73 × 10^{13} sec^{-1}. On the other hand, the positions estimated from the other dinitro-ammine-type complexes are at 75—78 × 10^{13} sec^{-1}. From these results, it may be said that the nitro-ligand field of the mixed dinitro complex with the *bis*(bidentate O–O)-type ligand is less weak than that of the mixed-dinitro complex with the ammine-type ligand. In fact, the aqueous solutions of the mixed dinitro complexes with the O–O type ligands are unstable, while the solutions of the dinitro-ammine type complexes are stable.

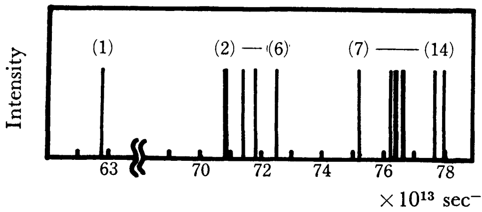

Fig. 5. The estimated position of first absorption band of hexanitrocobaltate(III).

(1) $[Co(NO_2)_6]^{3-}$
(2) $[Co(NO_2)_2(acac)_2]^-$
(3) $[Co(NO_2)_2CO_3acac]^{2-}$
(4) $[Co(NO_2)_2(CO_3)_2]^{3-}$
(5) $[Co(NO_2)_2CO_3ox]^{3-}$
(6) $[Co(NO_2)_2(ox)_2]^{3-}$
(7) $[Co(NO_2)_2(NH_3)_4]^+$
(8) $[Co(NO_2)_2ox\ en]^-$
(9) $[Co(NO_2)_2gly\ en]$
(10) α-$[Co(NO_2)_2ox(NH_3)_2]^-$
(11) $[Co(NO_2)_2(gly)_2]^-$
(12) α-$[Co(NO_2)_2CO_3(NH_3)_2]^-$
(13) $[Co(NO_2)_2en_2]^+$
(14) $[Co(NO_2)_2CO_3en]^-$

The maximum frequency of the nitro specific absorption band was found at *ca.* 80.8 × 10^{13} sec^{-1} for the carbonatoacetylacetonato complex and at 85.65 × 10^{13} sec^{-1} for the tetranitrocarbonato complex. The position for the former complex lies in the longest-wavelength side among the dinitro complexes (81.02 for $[Co(NO_2)_2(ox)_2]^{3-}$; 85.85 for $[Co(NO_2)_2CO_3ox]^{3-}$; 87.15 for $[Co(NO_2)_2(CO_3)_2]^{3-}$). It should be noted that the positions for the $[Co(NO_2)_2CO_3acac]^{2-}$, $[Co(NO_2)_2(ox)_2]^{3-}$, and $[Co(NO_2)_6]^{3-}$ complexes, which are unstable in an aqueous solution, are at lower frequencies than that (84.93 × 10^{13} sec^{-1}) for the free nitrite ion.

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

[15] K. Nakamoto, P. J. McCarthy, A. Ruby and A. E. Martell, *J. Amer. Chem. Soc.*, **83**, 1066 (1961).

[16] G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 433 (1956).

[17] Y. Shimura and R. Tsuchida, This Bulletin, **29**, 311 (1956).

[18] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, New York and London (1961).