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Preparation and Properties of the Mixed Dinitro Complexes of Cobalt(III) with the Carbonato or Oxalato Ligand[*1]

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Three new tervalent dinitro complexes of cobalt(III) have been prepared by the use of a tricarbonatocobaltate(III) solution or a similar solution as the starting material. These complexes, $[Co(NO_2)_2(CO_3)_3]^{3-}$, $[Co(NO_2)_2(OX)_2]^{3-}$ and $[Co(NO_2)_2CO_3OX]^{3-}$ are characterized by their absorption spectra in solution. The geometrical structures of these complexes have been determined as of the *cis*-form on the basis of their IR spectra. The compounds were not stable against decomposition in aqueous solutions: the bis(oxalato) compound was most unstable against the decomposition to the Co(II) state. The stability has been discussed in connection with the specific absorption band of the coordinated NO_2^- ligand.

A number of mixed dinitro complexes of cobalt(III) have already been prepared. The tetraammine-type and bis(ethylenediamine)-type1) complexes are quite familiar and are typical univalent cationic complexes. For these complexes, *cis* and *trans* isomers are known. On the other hand, as the univalent anionic complexes the bis(acetylacetonato)2–4) and the bis(glycinato)5) complexes are known in only the *trans*-form and in only the *cis*-form respectively. Furthermore, the oxalato (or carbonato)diammine(or ethylenediamine)-type complexes6,7) have also been reported, and a none-electrolyte complex *cis*-dinitroglycinatoethylenediaminecobalt(III)5) has been prepared.

In the present work, the preparation of tervalent anionic dinitrocomplexes containing carbonato or oxalato ligands, or both, was undertaken. The complex $[Co(NO_2)_2(CO_3)_2]^{3-}$ was obtained from a reaction mixture of potassium tricarbonato cobaltate(III)8) and potassium nitrite. The complexes $[Co(NO_2)_2(OX)_2]^{3-}$ and $[Co(NO_2)_2CO_3\text{-}OX]^{3-}$ were obtained by the reaction of potassium nitrite with a green solution produced by oxidizing the Co^{2+} ion with hydrogen peroxide in the presence of potassium oxalate and bicarbonate. The geometrical structures of these complexes were determined as of the *cis*-form on the basis of the IR spectra.

Experimental

Preparation. *1) Potassium Dinitrodicarbonatocobaltate(III) Monohydrate,* $K_3[Co(NO_2)_2(CO_3)_2]\cdot H_2O$. To a green solution of tricarbonatocobaltate(III) ($CoCl_2\cdot 6H_2O$ 10 g scale, 0.048 mol), which had been prepared by the usual method,8) 13 g (0.15 mol) of potassium nitrite was added. The reaction mixture was then stirred under an iced condition for 3—4 hr. A large amount (100 m*l*) of ethanol was added to the resulting red solution, and the whole was kept in a refrigerator for a day to precipitate the crude product. The precipitates was recrystallized by dissolving them in a minimum amount of cold water and by then adding

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8) M. Shibata, *ibid.*, **87**, 771 (1966).

ethanol. The complex was violet-red needle-shaped crystals. The yield was about 3 g.

Found: C, 6.21; N, 6.95; H, 0.55%. Calcd for $K_3[Co(NO_2)_2(CO_3)_2]\cdot H_2O$: C, 5.91; N, 6.90; H, 0.50%.

2) Potassium Dinitrobis(oxalato)cobaltate(III) Monohydrate, $K_3[Co(NO_2)_2(OX)_2]\cdot H_2O$. Twenty-seven grams (0.15 mol) of potassium oxalate monohydrate and 5 g (0.05 mol) of potassium bicarbonate were dissolved in a minimum amount of hot water (50°C). Separately, 10 g (0.042 mol) of cobalt chloride hexahydrate were dissolved in a minimum amount of hot water. After cooling, 15 m*l* of hydrogen peroxide (30%) were added. This latter solution was added, drop by drop to the 40—50°C warmed oxalate-bicarbonate solution. To the resulting green solution there were added 9 g (0.10 mol) of potassium nitrite; the mixture was stirred at 40—50°C for 2—3 hr, whereupon the solution turned red. On the ice cooling of the solution, the desired complex was precipitated. This was filtered, washed with methanol, and then dried in air. On the other hand, the filtrate was used for another complex of 3). The product was needle-shaped crystals; the yield was about 7 g. Found: C, 10.45; N, 6.27; H, 0.55%. Calcd for $K_3[Co(NO_2)_2(OX)_2]\cdot H_2O$: C, 10.39; N, 6.08; H, 0.44%. The complex was not recrystallized from water because of its rapid decomposition to cobalt(II) oxalate.

3) Potassium Dinitrocarbonatooxalatocobaltate(III), $K_3[Co(NO_2)_2CO_3OX]$. To the filtrate of 2), ethanol (*ca.* 20 m*l*), was added, and the whole was kept in a refrigerator for a few hours in order to precipitate some of the bis(oxalato) complex and potassium oxalate. After the removal of these precipitated salts, an additional 50 m*l* portion of ethanol was added to the filtrate and the whole was kept in a refrigerator for a day. The red crystals thus precipitated were purified twice by dissolving them in a minimum amount of cold water and by adding ethanol. The final product was red stick-form crystals. The yield was about 4 g.

Found: C, 8.62; N, 6.80%. Calcd for $K_3[Co(NO_2)_2CO_3C_2O_4]$: C, 8.65; N, 6.73%.

Measurements. The infrared absorption spectra in the 4000—650 cm^{-1} region were measured as KBr disks using a Japan Spectroscopic Co., DS-301 infrared spectrometer. The visible and near-ultraviolet absorption spectra were measured with a Hitachi Perkin-Elmer 139 UV-VIS spectrophotometer, using a 0.10 M potassium bicarbonate aqueous solution as the solvent for the dicarbonato complex, a 0.10 M potassium oxalate aqueous solution for the bis(oxalato) complex, and a 0.05 M bicarbonate - 0.05 M oxalate mixed aqueous solution for the carbonatooxalato complex.

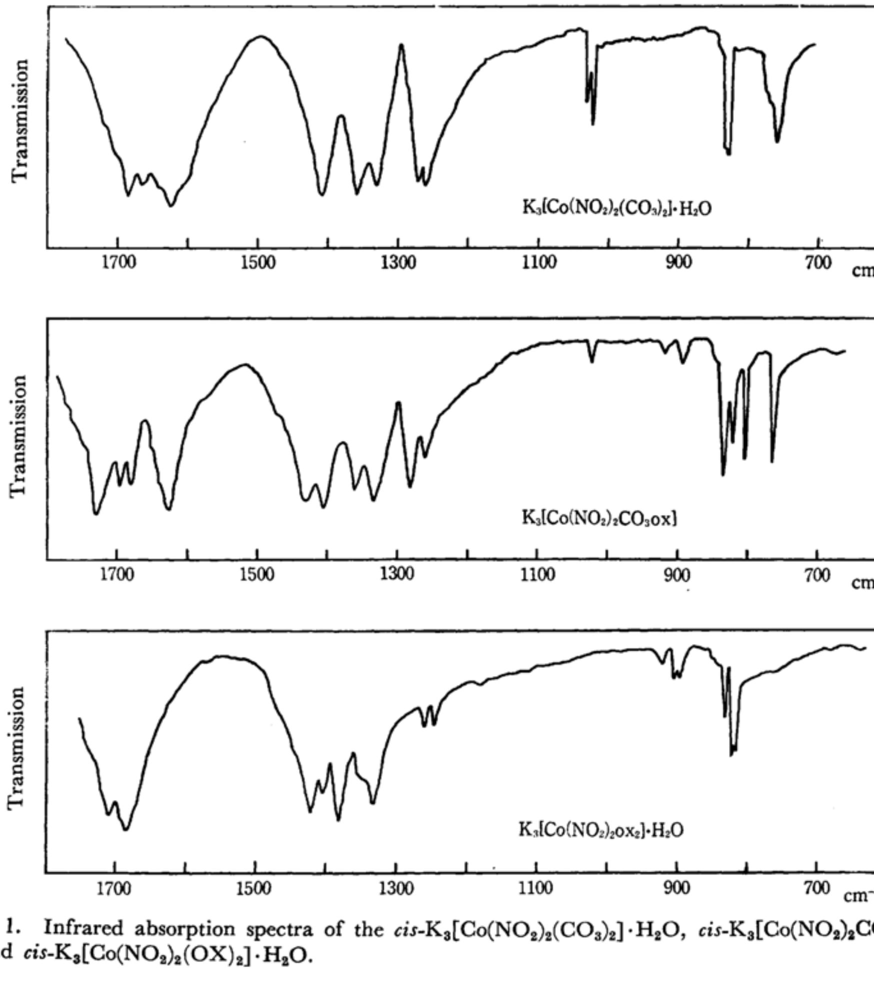

Fig. 1. Infrared absorption spectra of the *cis*-$K_3[Co(NO_2)_2(CO_3)_2]\cdot H_2O$, *cis*-$K_3[Co(NO_2)_2CO_3OX]$, and *cis*-$K_3[Co(NO_2)_2(OX)_2]\cdot H_2O$.

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

		NO_2^-			CO_3^{2-}					$C_2O_4^{2-}$						
		asym.	sym.	sym.	asym.	sym.	sym.	out of plane	sym.	asym.		sym.		sym.	asym.	Ref.
		ν(NO)	ν(NO)	δ(ONO)	ν(CO)	ν(CO)	ν(CO)	(OCC)	δ(OCO)	ν(CO)	ν(CO)	ν(CO)	ν(CO)	ν(CC)	δ(OCO)	
$K_3[Co(NO_2)_2(CO_3)_2]\cdot H_2O$		1403	1360 1323	833[a] 830	1685 1623	1272 1260	1030 1024	833	759 772 sh							*
$K_3[Co(NO_2)_2CO_3OX]$		1405	1360 1332	833[b] 820	1680 1623	1282	1022	833	764	1730	1695	1430	1257	920 894	802	*
$K_3[Co(NO_2)_2(OX)_2]\cdot H_2O$		1402	1380 1346 sh 1337	838 824[c]						1707	1684	1420	1255 1248	902 892	824 818	*
$K_3[Co(CO_3)_3]\cdot 3H_2O$					1527	1330	1037	851	—							8
$K_3[Co(C_2O_4)_3]\cdot 3H_2O$										1710	1658	1389	1257	900	824 810	8
$K_3[Co(NO_2)_6]$		1386	1332	827												21
$[Co(NO_2)_2\,en_2]Cl$	*cis*	1422	1344 1312	837 819												17
	trans	1414	1325 1312 sh	819												
$[Co(NO_2)_2(NH_3)_4]Cl$	*cis*	1406	1374 1357	825 822												**
	trans	1407	1361	828 819												
$Na[Co(NO_2)_2(acac)_2]$		1425	1308	827												4

* Present work.

a) Overlap sym. δ(ONO) and out of plane (OCO) for $K_3[Co(NO_2)_2(CO_3)_2]\cdot H_2O$.

b) Overlap sym. δ(ONO) and out of plane (OCO) for $K_3[Co(NO_2)_2CO_3OX]$.

c) Overlap sym. δ(ONO) and sym. δ(OCO) for $K_3[Co(NO_2)_2(OX)_2]\cdot H_2O$.

** I. R. Beatlie and H. J. V. Tyrrell, *J. Chem. Soc.*, **1956**, 2849.

TABLE 2. ABSORPTION DATA FOR THE NEW DINITRO COMPLEXES

	ν_1	ν_{sp} 10^{13} sec^{-1} (log ε)	ν_3	$\nu_{sp}-\nu_1$
$K_3[Co(NO_2)_2OX_2]\cdot H_2O$	57.32(2.13)	81.02(3.60)	110.22(4.19)	23.70
$K_3[Co(NO_2)_2CO_3OX]$	56.00(2.26)	85.85(3.55)	113.80(4.38)	29.85
$K_3[Co(NO_2)_2(CO_3)_2]\cdot H_2O$	54.80(2.24)	87.15(3.47)	113.80(4.31)	32.35

Results and Discussion

Preparation. The green solution which is used for the preparation of the bis(oxalato) and carbonatooxalato complexes is prepared in the same way as the tricarbonatocobaltate(III) solution.[8] The attempt to isolate the complexes from the green solution failed because of the high solubility of the complex species, but the absorption spectrum of the solution suggested the formation of such mixed complexes as $[Co(CO_3)_n(OX)_{3-n}]^{3-}$ $(n=1, 2)$. When a cold solution of $CoCl_2$ containing H_2O_2 was added not to a warmed but to an ice-cold solution of potassium oxalate and bicarbonate, a large quantity of the Durrant's salt,[9,10] $K_4[(C_2O_4)_2Co\langle\begin{smallmatrix}OH\\OH\end{smallmatrix}\rangle Co(C_2O_4)_2]\cdot 4H_2O$, was precipitated. Furthermore, when H_2O_2 was added toan ice-cold oxalate-bicarbonate solution which had previously mixed with a $CoCl_2$ solution, the Durrant's salt was almost quantitatively precipitated. When the reaction was carried out at 40—50°C, tris(oxalato)cobaltate(III) was precominantly formed.

IR Spectra. The IR spectra of three new complexes are shown in Fig. 1, while the numerical data are given in Table 1 with the related complexes. In the spectra of the dicarbonato and carbonatooxalato complexes, the key bands indicating the existence of the coordinated carbonate ion are observed as one or two sharp bands attributable to the CO symmetrical stretching vibration in the 1050—1020 cm^{-1} region——at 1033 and 1024 cm^{-1} for the dicarbonato complex and at 1022 cm^{-1} for the monocarbonato complex. If the carbonate ion is acting as a monodentate ligand, the corresponding CO vibration will appear in a higher-wave-number region.[11] The key bands indicating the existence of the coordinated oxalate ion are the C–C symmetrical stretching vibrations appearing in the 900 cm^{-1} region; the monooxalato complex has two distinct bands at 920 and 894 cm^{-1}, and the bis(oxalato) complex, at 902 and 892 cm^{-1}. If the oxalate ion is acting as a monodentate ligand, the corresponding C–C stretching vibration will appear in a higher-wave-number region.[11,12] Although the nitrite anion can coordinate to a central atom through the N- or O-atom, the present three complexes are coordinated through the N-atom, because of the absence of a nitrito characteristic band at 1050 cm^{-1}.[13,14] The absorption peaks appearing at 833, at 833 and at 824 cm^{-1} for the dicarbonato, carbonatooxalato, and bis(oxalato) complexes respectively, are undoubtedly due to the overlapping of the absorptions due to the oxalato, carbonato, and nitro ligands.

Several methods have been employed to distinguish between *cis* and *trans* isomers of dinitro complexes of cobalt(III).[3,15–18] It is said that the *cis* isomer gives a more complicated spectrum than the corresponding *trans* isomer because of the lower symmetry of the former.[15–18] For example, the IR spectrum of *trans*-$[Co(NO_2)_2(NH_3)_4]^+$ shows one band attributable to the NO_2^- symmetrical stretching vibration, whereas the spectrum of the *cis* isomer shows two bands.[15,18] The spectrum of *trans*-$[Co(NO_2)_2en_2]^+$ also shows one band attributable to the NO_2^- bending mode, whereas the *cis* isomer shows two bands.[16] Furthermore, *trans*-$[Co(NO_2)_2(acac)_2]^-$ exhibits one band each attributable to the NO_2^- symmetrical stretching and bending vibrations.[3] Each of the present complexes has two clear bands attributable to the NO_2^- symmetrical stretching vibration; the dicarbonato complex has them at 1360 and 1323 cm^{-1}; the carbonatooxalato one, at 1360 and 1332 cm^{-1}, and the bis(oxalato) one, at 1386 and 1327 cm^{-1} (with a 1346 cm^{-1} shoulder). From this evidence, it may be concluded that the present new complexes have *cis* structures.

UV Spectra. The absorption spectra in solution are shown in Fig. 2, while the numerical data are listed in Table 2. The maximum values of the first absorption bands (ν_1) for the present

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complexes are regularly shifted to a higher frequency in order of the dicarbonato, carbonatooxalato, and bis(oxalato) complexes, with 1.2—1.3 × 10^{13} sec^{-1} intervals. Those of *cis*-dicarbonato, carbonatooxalato, and bis(oxalato)diamminecobalt(III) complexes are also shifted to a higher frequency in the same order with regular intervals (0.9 × 10^{13} sec^{-1}).8) These regularities can be expected from "the spectrochemical series."19) However, the maximum values for these complexes themselves differ considerably from those calculated on the basis of "the rule of average environment";20) calcd maxima, 53.8 for $[Co(NO_2)_2(OX)_2]^{3-}$; 52.8 for $[Co(NO_2)_2CO_3OX]^{3-}$; 51.7 for $[Co(NO_2)_2(CO_3)_2]^{3-}$. Perhaps the reason for this poor agreement is the value (62.0 × 10^{13} sec^{-1})21) for the hexanitro complex, which is much lower than the expected value from "the spectrochemical series." On the other hand, the maximum frequencies (ν_{sp}) of the specific band of coordinated NO_2^- are shifted lower from the dicarbonato complex to the bis(oxalato) complex. In other words, the maximum positions of the first and specific bands move in an opposite direction from the dicarbonato to bis(oxalato) complexes. Accordingly, the values of $\nu_{sp}-\nu_1$ are calculated as a measure of the shifts; they are given in Table 2. The value for the dicarbonato complex is the largest one (32.35 × 10^{13} sec^{-1}) in the reported dinitro complexes. This fact seems to be interesting.

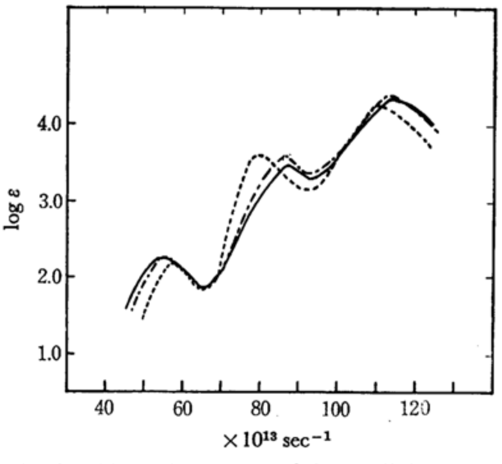

Fig. 2. Absorption spectra of the *cis* dinitro complexes.
(1) $K_3[Co(NO_2)_2(CO_3)_2]\cdot H_2O$ ——
(2) $K_3[Co(NO_2)_2CO_3OX]$ —·—
(3) $K_3[Co(NO_2)_2OX_2]\cdot H_2O$ ----

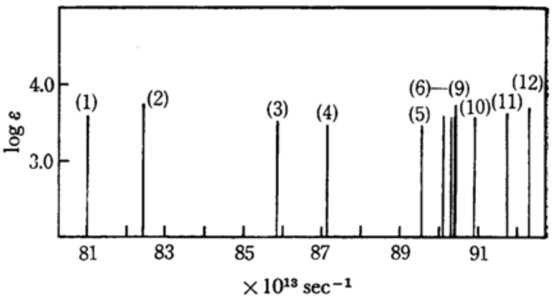

Fig. 3. The position of specific absorption band of *cis*-dinitro complexes of cobalt(III).
(1) $[Co(NO_2)_2OX_2]^{3-}$
(2) $[Co(NO_2)_6]^{3-}$
(3) $[Co(NO_2)_2CO_3OX]^{3-}$
(4) $[Co(NO_2)_2(CO_2)_2]^{3-}$
(5) γ-$[Co(NO_2)_2CO_3(NH_3)_2]^-$
(6) $[Co(NO_2)_2OX(NH_3)_2]^-$
(7) $[Co(NO_2)_2\,gly_2]^-$
(8) $[Co(NO_2)_2CO_3\,en]^-$
(9) $[Co(NO_2)_2\,edda]^-$
(10) $[Co(NO_2)_2OX\,en]^-$
(11) $[Co(NO_2)_2(NH_3)_4]^+$
(12) $[Co(NO_2)_2\,en_2]^+$

The frequency values of a number of dinitro complexes were inspected; they are diagrammatically represented in Fig. 3. From this inspection it was found that the maxima of the specific bands for the dinitro complexes shift to a lower frequency with the order of the ligands; en, NH_3 edda gly, CO_3^{2-}, NO_2^- and OX^{2-}. Since this order differs from that in the spectrochemical series, we can not discuss the stability of dinitro complexes in terms of the ligand-field theory.22) However, as far as the present three complexes are concerned, they are less stable than the tris(oxalato)cobaltate(III) complex in their aqueous solutions and rapidly decompose to the cobalt(II) state. Among the three complexes, the dicarbonato complex is the most stable and the bis(oxalato) complex is the least stable. It is well known that the hexanitrocobaltate(III) complex is not stable in solution. Considering these facts, the order of CO_3^{2-}, NO_2^-, and OX^{2-} ligands seems to represent the stability of the dinitro complexes against decomposition to the cobalt(II) state. Furthermore, if these decompositions depend upon the photochemical reaction, it can be said that these dinitro complexes will sensitively react to light in the 80.0—83.0 × 10^{13} sec^{-1} region.

In addition, it is interesting that in the dicarbonato or bis(oxalato) complex only the *cis* isomer is known in the case of present complexes as well as in the case of the diammine complexes.8)

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