Potassium μ-(*trans*-Hyponitrito-*N,N′*)-bis{pentacyanocobaltate(III)} and Potassium μ-(*Trans*-Hyponitrito-*O,O′*)-Bis-{Pentacyanocobaltate(III)}

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$K_6[Co_2(CN)_{10}(N_2O_2)]\cdot 2H_2O$ (orange salt) was prepared by reaction of $[Co(NO)(NH_3)_5]Cl_2$ with an aqueous solution of potassium cyanide. $K_6[Co_2(CN)_{10}(N_2O_2)]\cdot 4H_2O$ (yellow salt) was obtained by adding an aqueous solution of the orange salt to methanol. On the basis of IR and Raman spectra for their ^{14}NO- and ^{15}NO-salts, and of IR spectra for their gaseous decomposition products, the orange salt is considered to be a linkage isomer of the yellow salt with respect to the *trans*-hyponitrito bridge. It is presumed that the orange salt is potassium μ-(*trans*-hyponitrito-*N,N′*)-bis{pentacyanocobaltate(III)}, the yellow salt being potassium μ-(*trans*-hyponitrito-*O,O′*)-bis{pentacyanocobaltate(III)}.

Toyuki[1)] and Jezowska-Trzebiatowska *et al.*[2)] prepared $K_6[Co_2(CN)_{10}(N_2O_2)]\cdot 4H_2O$ with a *cis*- or *skew*-hyponitrito bridge by the method given by Nast and Rohmer.[3)] On the other hand, Raynor[4)] prepared $K_6[Co_2(CN)_{10}(N_2O_2)]\cdot 4H_2O$ with a *trans*-hyponitrito group, according to the method given by Nast, Mesche and Neubauer.[5)] While investigating the method of Nast and Rohmer,[3)] we prepared two new isomers with a *trans*-hyponitrito group, $K_6[Co_2(CN)_{10}(N_2O_2)]\cdot nH_2O$ ($n=2$ or 4 for orange and yellow salts, respectively).[6)]

This paper describes studies on the two isomers with respect to IR and Raman spectra, UV spectra, and thermal decomposion. The product prepared according to the method of Nast and Rohmer[3)] is also discussed by comparing its IR absorption bands with those of the two isomers.

Experimental

Preparation. Synthetic procedures and elementary analyses for the orange and the yellow salts were reported in detail.[6)] From 1 to 3 g of $[Co(NO)(NH_3)_5]Cl_2$ was used for preparing the orange salt. Powdered $[Co(NO)(NH_3)_5]Cl_2$ was added little by little to a 30% aqueous solution of potassium cyanide with stirring in order to keep the reaction vessel at constant temperature (−10 °C). The procedure differs from that reported by Nast and Rohmer.[3)] Yield, 0.6—2 g. χ_g (at 293K) $= -0.45\times 10^{-6}$ (c.g.s.). One gram of the orange salt was used for preparing the yellow salt. Yield, 0.8 g. χ_g (at 293K) $= -0.36\times 10^{-6}$ (c.g.s.).

Thermal Decomposition and Decomposition with 10% Potassium Cyanide Aqueous Solution. Decomposition was carried out in a vacuum line. A reaction vessel containing the salt (*ca.* 0.5 g) was heated *in vacuo* in an electric furnace at a rate of *ca.* 1—2 °C min^{-1}. Both the orange and the yellow salts decomposed violently at *ca.* 155 and 116 °C, respectively, to give gray powders. About 0.5 g of the salt was added in a reaction vessel containing 5 ml of 10% KCN solution frozen with the aid of liquid nitrogen, and the reaction vessel was evacuated. When the frozen solution was melted, both the salts decomposed by contact with the aqueous solution. The gaseous products thus obtained were dehydrated with P_4O_{10} and transferred to a gas cell with windows of calcium difluoride.

Measurements. The magnetic susceptibility was measured by the Gouy method. The IR spectra of the salts were measured as Nujol and hexachlorobutadiene mulls in the region 200—4000 cm^{-1} on JASCO 402G and JASCO model IR-F spectrometers. The Raman spectra of the powdered samples were recorded in the region 100—1500 cm^{-1} on a JASCO R-300 spectrometer equipped with He–Ne laser. The gaseous products were identified by means of their IR spectra.[7)] The mole ratio of the liberated NO to N_2O was determined.[8)] The diffuse reflection spectra of the salts were measured with a Hitachi EPS-3T spectrometer. The UV spectra in aqueous solution were recorded with a Hitachi 124 spectrometer.

Results and Discussion

Raman and IR Spectra for the Orange and Yellow Salts. Wave numbers of the IR and Raman bands and their assignments are summarized in Table 1.

Raman Spectra: Upon ^{15}NO-substitution (^{15}N atom% $=95$), the bands at 1257 and 1165 cm^{-1} for the orange salt shifted downwards by 31 and 39 cm^{-1}, respectively and, the bands at 1412 and 1070 cm^{-1} for the yellow salt shifted downwards by 43 and 18 cm^{-1}, respectively. Upon ^{15}NO-substitution (^{15}N atom % $=50$), the 1257 cm^{-1} band for the orange salt shifted and split into three peaks at 1253, 1242, and 1226 cm^{-1} (their intensity ratio 1:2:1). The same phenomenon was observed with the yellow salt; the 1412 cm^{-1} band shifted and split into three peaks, 1414, 1392, and 1369 cm^{-1} (their intensity ratio 1:2:1). This indicates that N–N bond is present in both the orange and yellow salts. For other bands, no isotopic shifts upon ^{15}NO-substitution could be observed. The bands in the region *ca.* 400—550 cm^{-1} are considered to be due to the $Co(CN)_5$ group.[9)]

IR Spectra: The bands at 1157, 609, and 299 cm^{-1} for the orange salt shifted downwards by 21, 14, and 2 cm^{-1} upon ^{15}NO-substitution (^{15}N atom % $=95$), respectively, while the bands at 987, 630, and 329 cm^{-1} for the yellow salt shifted downwards by 15, 6, and 6 cm^{-1}, respectively.

The 1630 and 3580 cm^{-1} bands for the orange salt

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TABLE 1. WAVE NUMBERS AND ASSIGNMENTS OF RAMAN AND IR BANDS FOR THE ORANGE AND YELLOW SALTS

Orange salt		Yellow salt		Assignments
IR	Raman	IR	Raman	
3580 m		3620 s		O–H str
2140 sh		2147 sh		C–N str
2127 vs		2127 vs		
2090 sh		2092 sh		
1630 w		1643 s		H–O–H def
	1257 (31)[a]		1412 (43)	N–N sym str
1157 (21) vs		987 (15) vs		N–O asym str
	1165 (39)		1070 (18)	N–O sym str
			830	
	704		760	in-plane NNO sym def
			650	
609 (14) s		630 (6) s		out-of-plane ONNO distortion
	550		550	Co–C–N bend
544 s				
536 s		538 s		
			500	
474 s	473		480	
466 s		462 s	468	
453 s				
440 vs				
423 sh	422	421 vs	422	Co–CN str
412 vs				
404 sh			403	
	370	373 s		
365 s				
353 sh				
338 sh				
299 (2) s		329 (6) s		in-plane NNO asym def
	286		288	
200 s		200 s	203	
	182		166	

a) The value in parentheses indicates observed isotopic shift. Abbreviations; str=stretching, bend=bending, asym=antisymmetric, sym=symmetric, def=deformation, vs=very strong, s=strong, m=medium, w=weak, sh=shoulder.

and the 1643 and 3620 cm^{-1} bands for the yellow salt are considered to be due to the water of crystallization. The sharp bands at 2127 cm^{-1} with two shoulders for the orange and yellow salts are assigned to the C–N stretching vibrations. Many absorption bands were observed in the region 200—600 cm^{-1}. Some of them in the region *ca.* 400—550 cm^{-1} are considered to be due to the skeletal vibrations between the cobalt atom and the CN group.[9)]

Assignments of the Bands due to the Bridged Hyponitrito Group: The Raman and IR bands for the orange and yellow salts can be explained on the basis of the bands due to the hyponitrito group. Raman and IR studies on $M_2N_2O_2$ (M=Na and K) containing a *cis*- or *trans*-hyponitrite ion show that one band at 1380—1420 cm^{-1} is assigned to the N–N stretching and two bands at 830—1120 cm^{-1} to the N–O stretching vibrations.[10—14)]

Of the three bands in the region 990—1400 cm^{-1} observed on the IR and Raman Spectra for the orange and yellow salts, two bands are Raman active, and one band is IR active. The mutual exclusion rule holds for the set of the three bands as observed on the *trans*-hyponitrite ion.[11)] It can be considered that both the orange and yellow salts contain a *trans*-hyponitrite ion but not a *cis*-one. On the basis of the mutual exclusion rule and the ^{15}N-isotopic shifts, the 1257 cm^{-1} band for the orange salt and the 1412 cm^{-1} band for the yellow salt can be assigned to the N–N symmetric stretching vibrations, the 1165 cm^{-1} band for the orange salt and the 1070 cm^{-1} one for the yellow salt to the N–O symmetric stretching, and the 1157 cm^{-1} band for the orange salt and the 987 cm^{-1} band for the yellow salt to the N–O antisymmetric stretching vibrations.

For the bands in the region 200—800 cm^{-1} for *trans*-hyponitrite ion, Millen *et al.*[11)] and McGraw *et al.*[12)] assigned the Raman band at 485 or 698 cm^{-1} to the in-plane NNO symmetric deformation, the IR band at *ca.* 370 cm^{-1} to the in-plane NNO antisymmetric one, and the IR band at *ca.* 500 cm^{-1} to the out-of-plane ONNO distortion. McGraw *et al.*[12)] also reported that the bands due to both the in-plane NNO antisymmetric deformation and the out-of-plane ONNO distortion shifted downwards by *ca.* 10 cm^{-1}, but the band due to the in-plane NNO symmetric deformation hardly shifted upon ^{15}NO-substitution (^{15}N atom %=95).

As for complexes other than the cyano complexes with hyponitrito group, $[(C_6H_5)_3M]_2(N_2O_2)$ (M=Sn and Pb),[15] $\{[MoCl_2(NO)(das)]_2N_2O_2\}Cl_2$ (das=*o*-phenylene-bis(dimethylarsine)),[16] $[Co_2(N_2O_2)(NH_3)_{10}](NO_3)_4\cdot H_2O$,[17] and $Pt(N_2O_2)(PPh_3)_2$ (PPH_3=triphenylphosphine)[18] have been reported. IR study on μ-(*trans*-hyponitrito-*O,O′*)-bis{triphenyltin(II)} and its lead(II) analog has shown that the band at 580—620 cm^{-1} is due to the metal–O antisymmetric stretching, the band at 370—380 cm^{-1} to the out-of-plane ONNO distortion, and the band at 310—360 cm^{-1} to the in-plane NNO antisymmetric deformation.[15] IR study on μ-(*cis*-hyponitrito-*N,O*)-bis{pentaamminecobalt(III)} nitrate has shown that the band at 616 cm^{-1} is due to the NNO bending, the band at 577 cm^{-1} to the Co–NO stretching, the band at 536 cm^{-1} to the ONNO out-of-plane bending, the band at 374 cm^{-1} to another NNO bending, and the band at 247 cm^{-1} to the O_2N_2–Co–NH_3 bending vibrations.[17] On the other hand, IR study on $K_6[Co_2(CN)_{10}(N_2O_2)]\cdot 4H_2O$ with a *cis*- or *skew*-hyponitrito bridge has shown that the bands at 599, 537, 450, and 281 cm^{-1} are assigned to the Co–N stretching, the NNO bending, the Co–O stretching, and the N–Co–C or the Co–NO bending vibrations, respectively.[2] However, the bands other than the N–N and N–O stretching vibrations due to the hyponitrito bridge have not yet been definitely assigned.

From studies by means of IR and nitrogen-15, the 299 cm^{-1} band for the orange salt and the 329 cm^{-1} band for the yellow salt can probably be assigned to the in-plane NNO antisymmetric deformation, and the 609 cm^{-1} band for the orange salt and the 630 cm^{-1} band for the yellow salt to the out-of-plane ONNO distortion. The bands are considered to be coupled with the skeletal vibrations between the cobalt atom and the hyponitrito group. The Raman bands at 704 cm^{-1} for the orange salt and at 760 or 650 cm^{-1} for the yellow salt can be assigned to the in-plane NNO symmetric deformation.

N_2O and NO Liberated by the Decompositions of the Orange and Yellow Salts. The results are shown in Table 2. The IR spectra of the gaseous products show that NO and N_2O were liberated as major products by the thermal decomposition, while the decomposition, with 10% KCN aqueous solution, milder than the thermal decomposition, gave N_2O only. The amount of the N_2O formed in the thermal decomposition was greater than that of the NO for both the orange and the yellow salts. The mole ratio of the NO to N_2O from the orange salt was greater than that from the yellow one. The results obtained by isotopic analyses of the N_2O suggest that the hyponitrito group is present in both the orange and yellow salts, and that the N_2O is formed without a cleavage of the N–N bond in the hyponitrite group.

UV Spectra for the Orange and Yellow Salts. The diffuse reflection spectrum for the yellow salt was the same as the spectrum for its fresh aqueous solution (Fig. 1). On the other hand, the diffuse reflection spectrum for the orange salt was different from that

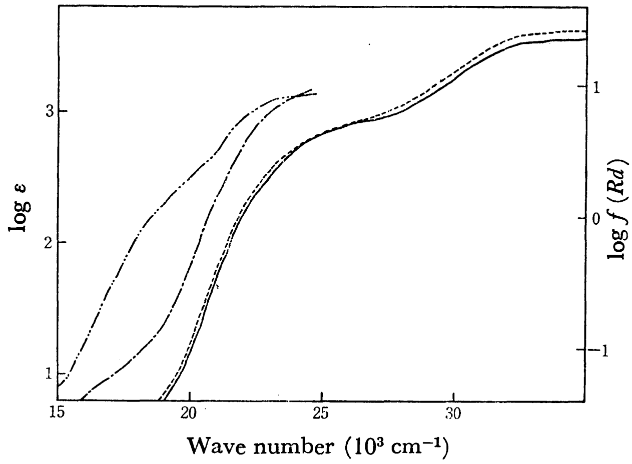

Fig. 1. Diffuse reflection spectra and spectra in an aqueous solution for the orange and yellow salts. —, the orange salt in an aqueous solution freshly prepared; ---, the yellow salt in an aqueous solution freshly prepared; -···-, the orange salt in solid state; -·-, the yellow salt in solid state.

TABLE 2. NO AND N_2O FROM THERMAL DECOMPOSITION AND DECOMPOSITION WITH 10% KCN AQUEOUS SOLUTION OF THE ORANGE AND YELLOW SALTS

Compounds		Method	Gaseous products
Orange salt	^{14}NO-complex	Thermal	^{14}NO(0.67)[a] ^{14}N^{14}NO(1)
	^{15}NO-complex (^{15}N atom%=95)	Thermal	^{15}NO(0.67) ^{15}N^{15}NO(1)
	Mixture of ^{14}NO- and ^{15}NO-complexes (^{15}N atom%=95)	Thermal	^{14}NO(0.67) ^{15}NO(0.67) ^{14}N^{14}NO(1) ^{15}N^{14}NO(0.13) ^{14}N^{15}NO(0.2) ^{15}N^{15}NO(0.67)
	^{14}NO-complex	10% KCN aq. soln.	^{14}N^{14}NO
Yellow salt	^{14}NO-complex	Thermal	^{14}NO(0.43) ^{14}N^{14}NO(1)
	^{15}NO-complex (^{15}N atom%=95)	Thermal	^{15}NO(0.43) ^{15}N^{15}NO(1)
	^{14}NO-complex	10% KCN aq. soln.	^{14}N^{14}NO

a) The values in parentheses indicate the relative mole ratio.

for the yellow one. The spectrum for the fresh aqueous solution of the orange salt was almost equal to that for the yellow one. The orange species is considered to change rapidly to the yellow one on dissolution as expected from the synthetic method of the yellow salt.6) The aqueous solution of the yellow salt was unstable; intensity of a shoulder at *ca.* 24 Kcm^{-1} due to the yellow species decreased to give a peak at 26 Kcm^{-1} after the solution had been allowed to stand for 2 weeks at room temperature. UV study on $K_3[Co(CN)_5(OH)]$ in an aqueous solution has shown that the $[Co(CN)_5(OH)]^{3-}$ decomposes to give $[Co(CN)_4(OH)_2]^{3-}$ and $[Co(CN)_6]^{3-}$ upon standing.19) The spectrum obtained for the yellow salt solution which had been allowed to stand was the same as that for the solution of the mixture of $[Co(CN)_4(OH)_2]^{3-}$ and $[Co(CN)_6]^{3-}$. It is suggested that the complex anion of the yellow salt decomposes in water to give $[Co(CN)_4(OH)_2]^{3-}$ and $[Co(CN)_6]^{3-}$ through $[Co(CN)_5(OH)]^{3-}$:

$$[Co_2(CN)_{10}(N_2O_2)]^{6-} + H_2O \longrightarrow 2[Co(CN)_5(OH)]^{3-} + N_2O$$

$$2[Co(CN)_5(OH)]^{3-} \longrightarrow [Co(CN)_4(OH)_2]^{3-} + [Co(CN)_6]^{3-}.$$

Comparison of Compounds Prepared by the Method of Nast and Rohmer with the Orange and the Yellow Salts. For the compound with a *cis*- or *skew*-hyponitrito bridge reported by Jezowska-Trzebiatowska *et al.*, IR bands at 1340—1400 (the N–N stretching vibration), 1043 (the N–O one), and 831 cm^{-1} (the N–O one) have been observed.2) IR spectra in the region 800—1400 cm^{-1} for the "yellow product," prepared by the authors according to the method of Nast and Rohmer3) on *ca.* 1/10 scale, gave broad bands at 1393(s), 1373(s), 1155(m), 1054 (m), 982(m), and 910(s) cm^{-1}, which shifted downwards by 31, 31, 25, 32, 13, and 17 cm^{-1}, respectively, upon ^{15}NO-substitution (^{15}N atom %=95). On the other hand, the IR spectra for the compound reported by Toyuki gave the bands at 1389(sh), 1333(w), 1158(w), 1058(w), and 984(w) cm^{-1}.1) The bands at *ca.* 1160 and 980 cm^{-1} for the "yellow product" might correspond to the N–O antisymmetric stretching vibrations due to the orange and yellow salts, respectively. The residual three components at 1393—1373, 1054, and 910 cm^{-1} for the "yellow product" might be due to a new linkage isomer of the compounds with a *cis*-hyponitrito group since wave numbers of these residual bands observed on the "yellow product" are different from those of the bands observed on the compounds with the *cis*-hyponitrito group reported by Toyuki1) and Jezowska-Trzebiatowska *et al.*,2) and also since all the N–N and the N–O stretching vibrations due to the *cis*-hyponitrito bridge are IR active. The IR study by Raynor on the compound prepared according to the method of Nast, Mesche and Neubauer5) has shown that the N–O stretching vibration is observed at 1120 cm^{-1}.4) However, it seems that this compound has not yet been well characterized.

The "yellow product" might be a mixture of the yellow salt, the orange salt, and an unknown compound with a *cis*-hyponitrito group. New linkage isomers with a *cis*-hyponitrito group can be expected to be isolated by subtle changes in the preparative conditions.

The yellow salt can be considered to be a linkage isomer of the orange salt. The N–N bond strength for the orange salt might be weaker than that for the yellow one. On the other hand, the N–O bond strength for the orange salt might be stronger than that for the yellow one. The mole ratio of NO to N_2O formed in the thermal decomposition for the orange salt is greater than that for the yellow one. This suggests that the N–N bond strength for the orange salt is weaker than for the yellow one as expected from the Raman spectra. Thus, it is presumed that the anion of the orange salt is μ-(*trans*-hyponitrito-*N*,*N*′)-bis{pentacyanocobaltate(III)} (A), that of the yellow salt being μ-(*trans*-hyponitrito-*O*,*O*′)-bis{pentacyanocobaltate(III)} (B) as shown in Fig. 2.

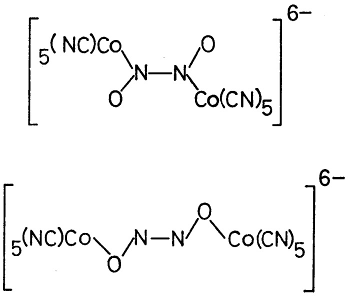

Fig. 2. Probable structures of the orange (A) and yellow (B) salts.

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