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TWO ISOMERS OF POTASSIUM μ-(TRANS-HYPONITRITO)-BIS{PENTACYANOCOBALTATE(III)}

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Orange and yellow complex salts were prepared by a reaction of black-$[Co(NO)(NH_3)_5]Cl_2$ with an aqueous solution of potassium cyanide. On the basis of IR and Raman spectra of the complexes and of their decomposition products, they are considered to be dimeric, bridged with a trans-hyponitrito group, and formulated as $K_6[Co_2(CN)_{10}(N_2O_2)]\cdot nH_2O$(n = 2 and 4 for the orange and yellow salts, respectively).

It has been reported by Nast[1] and Griffith[2] that $K_3[Co(CN)_5(NO)]\cdot 2H_2O$ was prepared by the use of a reaction of black-$[Co(NO)(NH_3)_5]Cl_2$ with a potassium cyanide aqueous solution. On the other hand, Jeżowska-Trzebiatowska et al.[3] have recently prepared a dimer complex bridged with a cis- or skew-hyponitrito group, $K_6[Co_2(CN)_{10}(N_2O_2)]\cdot 4H_2O$, according to Nast's method. While investigating Nast's method, we obtained two new isomers of potassium μ-(trans-hyponitrito)-bis{pentacyanocobaltate(III)}. Their structures were investigated by the use of their ^{15}NO-substituted complexes.

Experimental Preparation of the Orange Salt: Powdered black-$[Co(NO)(NH_3)_5]Cl_2$ was added little by little to a 30 % aqueous solution of potassium cyanide kept at -10°C by a thermostat while being stirred. (The $[Co(NO)(NH_3)_5]Cl_2$ was finally mixed with the KCN in a mole of 1 : 5.) Orange precipitates were formed in the solution with liberation of NH_3 gas. The products obtained were filtered out and washed with methanol and ether successively, then dried in vacuo. Found: K, 33.7; Co, 16.8; N, 23.86; C, 17.19; H, 0.58 %. Calcd for $K_6[Co_2(CN)_{10}(N_2O_2)]\cdot 2H_2O$: K, 33.10; Co, 16.63; N, 23.72; C, 16.95; H, 0.54 %.

Preparation of the Yellow Salt: The orange salt was dissolved in a minimum amount of cold water. The solution was filtered and immediately the filtrate was added dropwise to cold methanol with constant stirring. A yellow precipitate formed, which was collected by filtration, washed with methanol and ether successively, and dried in vacuo. Found: K, 31.9; Co, 15.9; N, 22.70; C, 17.09; H, 1.29 %. Calcd for $K_6[Co_2(CN)_{10}(N_2O_2)]\cdot 4H_2O$; K, 31.50; Co, 15.83; N, 22.57; C, 16.13; H, 1.08 %.

Both orange and yellow salts were diamagnetic.

Their ^{15}NO-substituted complexes with ^{15}N atom % = 50 and 95 were prepared from ^{15}NO-black $[Co(NO)(NH_3)_5]Cl_2$ with the corresponding ^{15}N atom % by the same methods as described above. ^{15}NO-complexes of black-$[Co(NO)(NH_3)_5]Cl_2$ were

prepared by the method of Miki.[4)]

Physical Measurements: The IR spectra of the complex salts as Nujol or hexachlorobutadiene mulls in sodium chloride or in polyethylene plates were recorded from 200 - 4000 cm^{-1} on JASCO 402G and JASCO model IR-F spectrophotometers. The Raman spectra of solid state samples were measured from 100 - 2000 cm^{-1} on a JASCO R-300 spectrometer with Helium-Neon Laser as a light source. The complexes were decomposed in a vacuum line by heating them and also by dissolving them in 10 % KCN aqueous solution to obtain their gaseous products. The products were identified and determined by means of their IR spectra.

Results and Discussion The Raman spectra for the orange and yellow salts are shown in Fig. 1. The bands at 1257 and 1165 cm^{-1} for the orange salt and the bands at 1412 and 1070 cm^{-1} for the yellow salt shifted upon ^{15}NO-substitution (^{15}N atom % = 95); other bands showed no isotopic shifts. The 1257 cm^{-1} band for the orange salt shifted and split into three bands at 1253, 1242, and 1226 cm^{-1} (intensity ratio 1 : 2 : 1) upon ^{15}NO-substitution(^{15}N atom % = 50). For the yellow salt, the same phenomenon was observed: the 1412 cm^{-1} band split into three bands, 1414, 1392 and 1369 cm^{-1}(intensity ratio 1 : 2 : 1). This is considered to indicate that N-N bond is present in both the orange and yellow salts. The 1257 cm^{-1} band for the orange salt and the 1412 cm^{-1} band for the yellow salt can be assigned to N-N stretching vibrations. The 1165 cm^{-1} band for the orange salt and the 1070 cm^{-1} band for the yellow salt are assigned to N-O stretching vibrations.

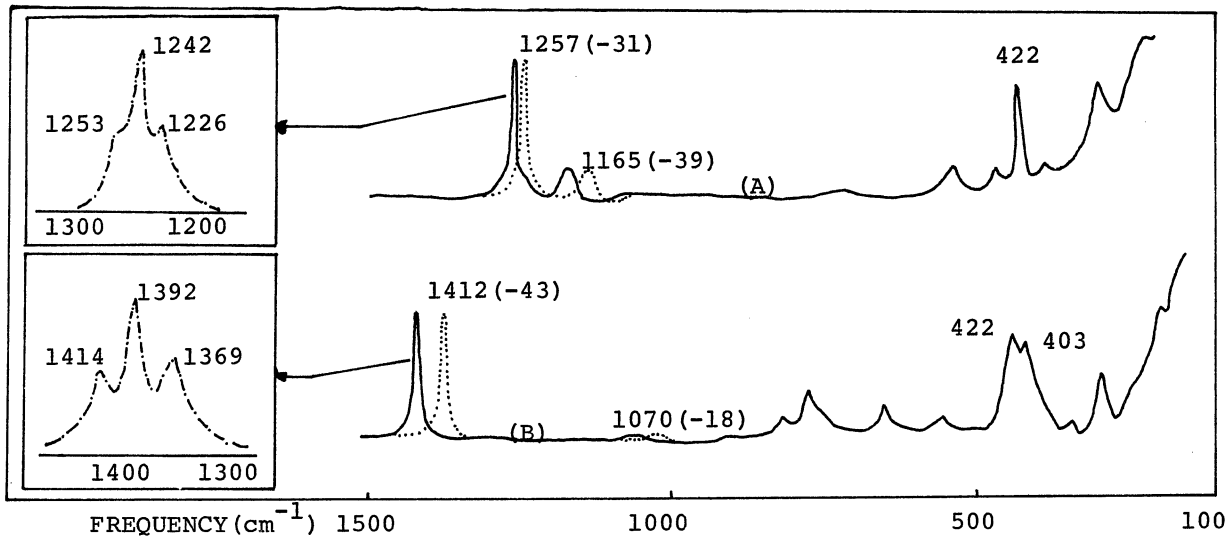


Fig. 1. Raman spectra of the orange(A) and yellow(B) salts.
———, ^{14}NO-complexes ; ·····, ^{15}NO-complexes(^{15}N atom% = 95)
-·-·-·-, ^{15}NO-complexes(^{15}N atom % = 50).

The IR spectra for the orange and yellow salts are shown in Fig. 2. Upon ^{15}NO-substitution(^{15}N atom % = 95), the bands at 1157, 609, and 299 cm^{-1} for the orange salt shifted downwards by 21, 14, and 2 cm^{-1}, 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 1157 cm^{-1} band for the orange salt and the 987 cm^{-1} band for the yellow salt can be assigned to N-O stretching vibrations. The 299 and 609 cm^{-1}

bands for the orange salt, and the 329 and 630 cm^{-1} bands for the yellow salt are considered to be due to the bridged hyponitrito group. The bands at 1630 and 3580 cm^{-1} for the orange salt, and the bands at 1643 and 3620 cm^{-1} for the yellow salt are due to water of crystallization. The sharp bands at 2127 cm^{-1} for both the orange and yellow salts are assigned to C-N stretching vibrations. Many absorption bands in the region 200 -600 cm^{-1} could not be assigned, although some of them are considered to be due to the skeletal vibrations between the cobalt atom and CN^- group.

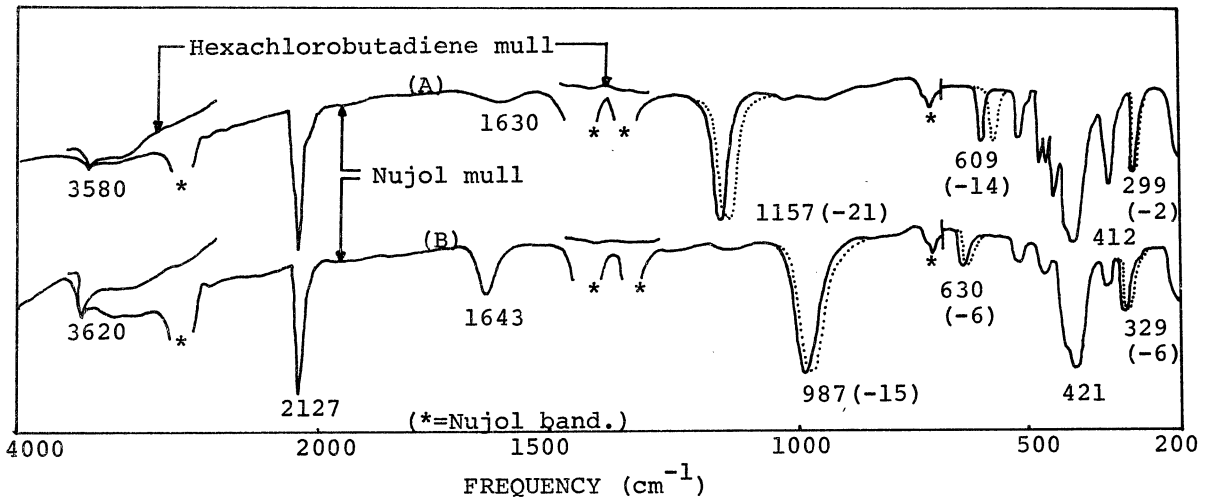


Fig. 2. IR spectra of the orange(A) and yellow(B) salts.
——, ^{14}NO-complexes ; ·····, ^{15}NO-complexes(^{15}N atom % = 95).

Of three bands in the region 990 - 1400 cm^{-1} two bands (N-N and N-O stretching vibrations) are Raman active, and a band assigned to N-O stretching vibration is IR active: the mutual exclusion rule holds for the sets of the three bands as well as observed on trans-$Na_2[N_2O_2]$[5] (see Table 1). Thus, it can be considered that both the orange and yellow salts contain a trans-hyponitrito group.

The IR spectra for the orange and yellow salts were different from those reported in Ref. (3), indicating that two complexes obtained here may be thought to be new ones.

Table 1. IR and Raman spectra of $Na_2[N_2O_2]$ and of the orange and yellow salts in the region 900 - 1500 cm^{-1}

Compounds	Raman		IR
	ν(NN)s	ν(NO)s	ν(NO)as
Trans-$Na_2[N_2O_2]$	1383	1115	1020
Orange salt	1257	1165	1157
Yellow salt	1412	1070	987

ν(NN)s, N-N symmetric stretching ; ν(NO)s, N-O symmetric stretching ; ν(NO)as, N-O antisymmetric stretching

Table 2 shows the gaseous products obtained by the thermal decomposition and the decomposition with 10 % potassium cyanide aqueous solution. The thermal

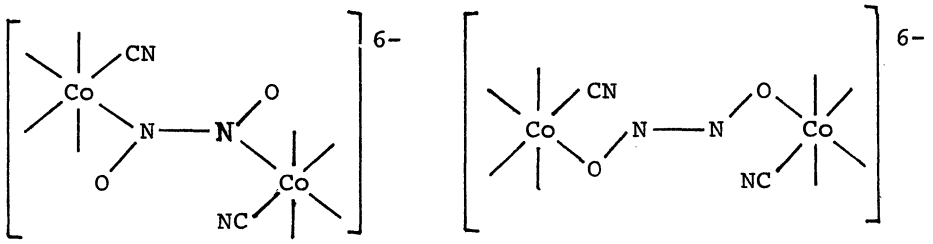
decomposition gave NO and N_2O as major products, while a mild decomposition with a potassium cyanide aqueous solution gave N_2O only.

Table 2. Gaseous products from thermal decomposition and decomposition with 10 % KCN aqueous solution of the orange and yellow salts

Complexes	Method	Gaseous Products
Orange salt ^{14}NO-complex	thermal	^{14}NO(40%), $^{14}N^{14}NO$(60%)
^{15}NO-complex	thermal	^{15}NO(40%), $^{15}N^{15}NO$(60%)
Mixture of ^{14}NO- and ^{15}NO-complexes (^{15}N atom%=95)	thermal	^{14}NO(20%), ^{15}NO(20%), $^{14}N^{14}NO$(30%), $^{15}N^{14}NO$(4%), $^{14}N^{15}NO$(6%), $^{15}N^{15}NO$(20%)
^{14}NO-complex	10% KCN aq.soln.	$^{14}N^{14}NO$(ca. 100%)
Yellow salt ^{14}NO-complex	thermal	^{14}NO(30%), $^{14}N^{14}NO$(70%)
^{15}NO-complex (^{15}N atom%=95)	thermal	^{15}NO(30%), $^{15}N^{15}NO$(70%)
^{14}NO-complex	10% KCN aq.soln.	$^{14}N^{14}NO$(ca. 100%)

The results obtained from identification of the gaseous products and isotopic analyses of N_2O suggest that a hyponitrito group is present in both the orange and yellow salts, and that N_2O is yielded without a cleavage of N-N bond in the hyponitrito group on the decompositions.

Thus, the orange and yellow complexes may be considered to be linkage isomers with respect to the bonding of the trans-hyponitrito group. On the basis of the difference in wave numbers of the N-N and N-O stretching vibrations observed for the orange and yellow salts and also on the basis of the difference in the mole ratio of NO to N_2O formed in their thermal decompositions, it is predicted that the orange complex has a symmetrical structure(A), and the yellow complex has a structure(B) as shown in Fig. 3.



(A) (B)

Fig. 3. Probable structures of the orange(A) and yellow(B) salts.

REFERENCES

1) R. Nast and M. Rohmer, Z. anorg. allgem. Chem., 285, 271 (1956).
2) W. P. Griffith, J. Lewis, and G. Wilkinson, J. Inorg. Nucl. Chem., 7, 38 (1958).
3) B. Jeżowska-Trzebiatowska, J. Hanuza, M. Ostern, and J. Ziołkowski, Inorg. Chim. Acta, 6, 141 (1972).
4) E. Miki, Bull. Chem. Soc. Japan, 41, 1835 (1968).
5) D. J. Millen, C. N. Polydoropoulos, and D. Watson, J. Chem. Soc., 1960, 687.

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