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Synthesis and Crystal Structure of Potassium *cis*-Diamminetetranitrocobaltate(III). Completion of the Nitroammine Series

Takashi FUJIHARA,* Akira FUYUHIRO, Kazuaki YAMANARI, and Sumio KAIZAKI
Department of Chemistry, Faculty of Science, Osaka University,
Toyonaka, Osaka 560

cis-$K[Co(NO_2)_4(NH_3)_2]$ was first synthesized from hexanitrocobaltate(III) in liquid ammonia and characterized by the elemental analysis and electronic and infrared spectra. The *cis* structure was confirmed by the X-ray analysis. The anomalous congested contact among three oxygens of three nitro ligands was found in the crystal.

trans-$NH_4[Co(NO_2)_4(NH_3)_2]$ has been known as so-called Erdmann's salt[1)] before the age of Werner. The corresponding *cis* isomer has been a long-standing missing link in a series of nitroammine cobalt(III) complexes of $[Co(NO_2)_x(NH_3)_{6-x}]^{3-x}$ (x = 1-5) type; one of the simplest inorganic complexes.[2)] This complex is interesting and valuable not only from electronic, vibrational, and NMR spectroscopic aspects, but also from a stereochemical view of the rotational conformers of coordinated nitro ligands. Although there have been a few attempts to seek this isomer, no successful study has been reported so far.[2,3)] Since the corresponding ethylenediamine complex $[Co(NO_2)_4(en)]^-$ could be prepared,[3a)] there seems to be no reason that the *cis* diammine complex is too labile to isolate.

The formation of the *cis* isomer was recognized by a QAE-Sephadex column chromatography of an aqueous reaction solution for Erdmann's salt, but the yield was too low to be isolated. Hence, we have developed a new preparative method, which is based on the substitution of nitro ligands in hexanitrocobaltate(III) into ammine ligands in liquid ammonia. It was found that this new preparative method for nitroammine complexes possesses advantage of one step formation of a series of nitroammine complexes in better yield without by-products over the method in aqueous solution.

$Na_3[Co(NO_2)_6]$(4 g, 0.01 mol) was added to 70 cm^3 of liquid ammonia in a pressure glass tube at -70 °C. After the tube was sealed, the complex was dissolved with shaking. The resultant red-brown solution was allowed to stand for 30 min in an ice bath. After ammonia was removed to dryness, yellow-brown solid was collected. The aqueous solution of this product was poured onto a 4.5 cm x 35 cm column of QAE-Sephadex A-25 (Cl^- form). The column chromatography was carried out at 4 °C in the dark. When the column was slowly swept with water, five yellow bands of neutral and cation complexes were separated, leaving a reddish yellow band of anion complexes on the top of the column. The five yellow water-eluted bands were found to be $[Co(NO_2)(NH_3)_5]^{2+}$, *trans*- and *cis*-$[Co(NO_2)_2(NH_3)_4]^+$, and *mer*- and *fac*-$[Co(NO_2)_3(NH_3)_3]$ in the elution order by their UV-vis absorption measurements. The adsorbed reddish yellow band gave two bands (E-I and E-II in the elution order) by eluting with a 0.15 mol dm^{-3} KCl aqueous solution. The UV-vis absorption spectra confirmed that the E-II band was *trans*-$[Co(NO_2)_4(NH_3)_2]^-$. The E-I eluate was concentrated by a rotary evaporator under reduced pressure at 20 °C. Potassium chloride was precipitated and this was filtered off. After the repeated removal of KCl for a few times in the same manner, about 20 cm^3 of methanol was added to about 2 cm^3 of the condensed solution of the E-I eluate. This solution was allowed to stand in a freezer overnight. Red-brown needles were crystallized. Yield 9.8%. Found: N, 25.90; H, 1.92%. Calcd for $K[Co(NO_2)_4(NH_3)_2]$: N, 26.59; H, 1.91%.

The chemical analysis of the E-I complex agrees with $K[Co(NO_2)_4(NH_3)_2]$. The chromatographic behavior indicated that the E-I is a univalent anion. The UV-vis absorption spectrum of the E-I is similar to that of the corresponding ethylenediamine complex $[Co(NO_2)_4(en)]^-$ more than that of the *trans* isomer as shown in Fig. 1. The infrared bands for the $\delta_w(NO_2)$ near 830 cm^{-1} are also similar to those of the ethylenediamine complex, but more complicated than those of the *trans* isomer. These facts support the assignment of the E-I complex to

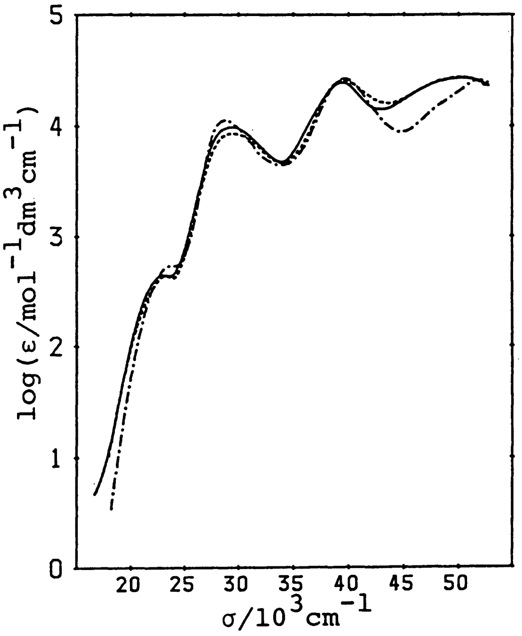

Fig. 1. UV-vis absorption spectra of *cis*-$K[Co(NO_2)_4(NH_3)_2]$(——), *trans*-$K[Co(NO_2)_4(NH_3)_2]$(–·–), and $K[Co(NO_2)_4(en)]$(---) in H_2O.

the *cis* isomer of $[Co(NO_2)_4(NH_3)_2]^-$, though there is an exceptional chromatographic behavior that the elution order of the E-I and E-II complexes is reverse to the generally recognized one.[4)]

The *cis* geometrical structure of potassium salt of the E-I isomer was confirmed by the X-ray single crystal structure analysis.[5)] A perspective view of this Co(III) complex is shown in Fig. 2. Two crystallographically independent complexes are contained in an asymmetric unit. The coordination geometry of each complex anion is nearly octahedral with two ammine ligands at the *cis* position. The bond lengths and angles around the cobalt atoms are approximately equal to those found in ammonium and potassium salts of *trans*-$[Co(NO_2)_4(NH_3)_2]^-$,[6)] and *cis*-$[Co(NO_2)_2(en)_2]$-$[Co(NO_2)_4(en)]$,[7)] *fac*-[8)] and *mer*-$[Co(NO_2)_3(NH_3)_3]$.[9)] The bond lengths of Co(1)-N(2) and Co(1)-N(5) at the *trans* position of the ammine ligands are a little shorter than other Co-NO_2 bonds as found for the corresponding ethylenediamine complex.[7)] In Co(2), however, four Co-NO_2 bonds show almost the same lengths with each other. There are anomalous mutual orientations of three nitro ligands in such a way that three oxygens come into van der Waals contact with each other in the Co(2) complex anion; O(11)-O(16) 2.92 Å, O(16)-O(17) 3.08 Å, and O(17)-O(11) 2.77 Å.

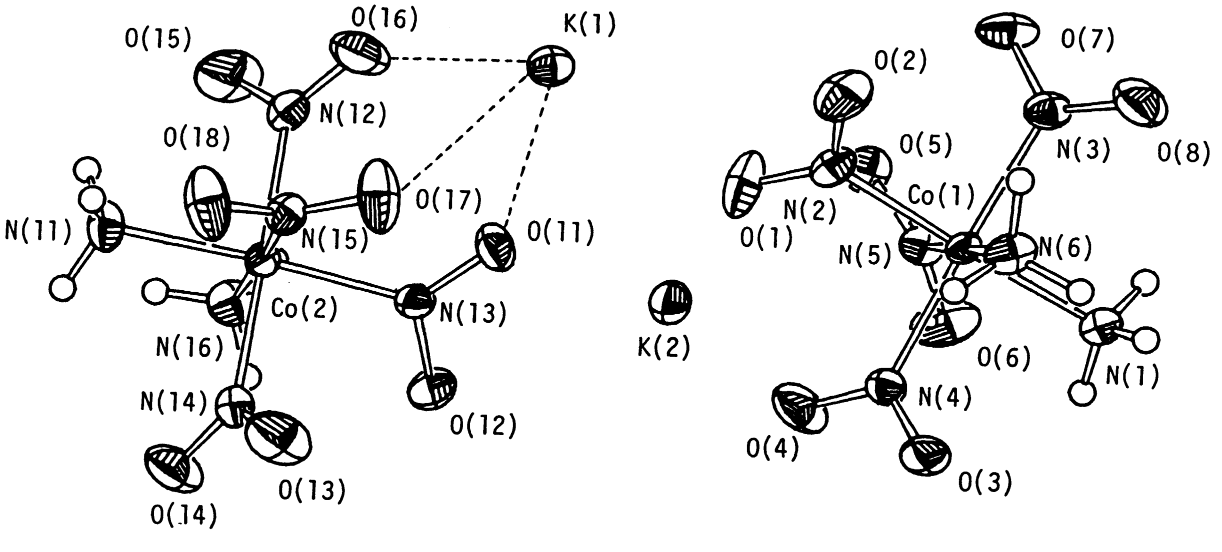

Fig. 2. An ORTEP drawing of *cis*-diamminetetranitrocobaltate(III) complexes in its potassium salt, *cis*-$K[Co(NO_2)_4(NH_3)_2]$.
Selected bond lengths(Å):
Co(1)-N(1) = 1.962(5); Co(1)-N(2) = 1.937(5); Co(1)-N(3) = 1.954(5);
Co(1)-N(4) = 1.951(5); Co(1)-N(5) = 1.928(5); Co(1)-N(6) = 1.963(5);
Co(2)-N(11)= 1.961(6); Co(2)-N(12)= 1.953(6); Co(2)-N(13)= 1.944(5);
Co(2)-N(14)= 1.952(6); Co(2)-N(15)= 1.954(6); Co(2)-N(16)= 1.967(5);
K(1)-O(11) = 2.636(5); K(1)-O(16) = 2.762(6); K(1)-O(17) = 2.807(6).

This anomaly arises from the coordination of the nitro oxygens (O(11), O(16), O(17)) to potassium ion (K(1)) which is located nearly on the pseudo-three fold axis perpendicular to the triangular facet consisting of three nitro ligands as shown by dotted lines in Fig. 2. Such a severely congested contact does not occur in another Co(1) complex anion, the corresponding ethylenediamine complex,[7] and *fac*-$[Co(NO_2)_3(NH_3)_3]$,[8] where the van der Waals contacts between two nitro oxygens were found.

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5) Crystal data: The X-ray crystal structure analysis was carried out at the X-ray Diffraction Service of the Department of Chemistry. The intensity data were collected by a RIGAKU AFC-5R diffractometer with use of Mo-Kα radiation (λ = 0.71069 Å). The program TEXSAN was used for the calculations. $CoN_6O_8H_6K$, M = 316.11, triclinic, $P\bar{1}$, a = 8.822(2) Å, b = 16.044(4) Å, c = 7.333(2) Å, α = 95.09(2) ° β = 107.76(2) °, γ = 92.22(2) °, V = 982.1(4) Å^3, Z = 4, D_{obsd} = 2.13 g cm^{-3}, D_{calcd} = 2.139 g cm^{-3}, R = 0.047 and R_w = 0.083 for 4547 independent reflections.

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