New Red-pentamminenitrosylcobalt(III) Complexes

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The black and red series of the compounds with the composition of $Co(NH_3)_5(NO)X_2$ have been extensively studied ever since they were originally prepared by Sand and Genssler.[1] The red series (Red salt I) are binuclear, and the two cobalt atoms are bridged through a hyponitrite ion.[2]

Recently, the present authors prepared the new "red-pentamminenitrosylcobalt(III) chloride and nitrate" (Red salt II) by the use of a procedure similar to that for the red series reported by Odell *et al.*[3] To a cobalt(II) chloride or nitrate solution (5 g of $CoCl_2 \cdot 6H_2O$ or $Co(NO_3)_2 \cdot 6H_2O$/20 m*l* H_2O), enough ammonia water was added to give about 5 mol/*l*; the solution was then exposed to air for more than 20 hr at room temperature. The solution was placed in a reaction apparatus which had been outgassed with nitrogen gas. When nitric oxide gas was passed into the solution cooled with an ice-water bath, the red precipitate was yielded. Red salt II (nitrate) obtained could be recrystallized only from dimethylsulfoxide, but not from an aqueous solution.

Found: Co, 21.5; N, 30.84; H, 5.42; NH_3, 32.0; Cl, 25.2%. Calcd for $[Co_2(NH_3)_{10}(NO)_2]Cl_4 \cdot 4H_2O$: Co, 20.97; N, 29.90; H, 6.81; NH_3, 30.30; Cl, 25.23%. Found: Co, 18.9; N, 33.63; H, 4.62; NH_3, 27.2%. Calcd for $[Co_2(NH_3)_{10}(NO_2)](NO_3)_4 \cdot 2H_2O$: Co, 18.64; N, 35.44; H, 5.42; NH_3, 26.94%.

The molar conductivities of Red salt II in aqueous and dimethylsulfoxide solutions were examined by the method of Feltham and Hayter[4]; the relations between the conductivities and the square root of the concentrations for these salts coincided with those for Red salt I. It was suggested that Red salt II was a 4 : 1-type electrolyte.

The infrared spectra of Red salt II were similar to those of Red salt I. For Red salt I, the shifts of three absorption bands on the ^{15}NO-substitution were observed (from 1137, 1048, and 930 cm^{-1} to 1112, 1027, and 916 cm^{-1}). These shifts coincide with those reported by Mercer *et al.*[5] On the other hand, for the chloride of Red salt II the absorptions at 1481, 1278, 1020 and 804 cm^{-1} shifted to 1450, 1259, 1019 and 783 cm^{-1} respectively.

The gaseous products obtained by the decomposition of Red salt I and II were detected by the use of an infrared spectrophotometer. The ^{15}NO-complex of Red salt II (chloride) was decomposed by the addition of 6 M H_2SO_4 to give $^{15}NOCl$ and a small amount of $^{15}N^{15}NO$, while only $^{15}N^{15}NO$ was derived from the ^{15}NO-complex of Red salt I (nitrate). In the thermal decomposition *in vacuo*, for Red salt II (chloride and nitrate) $^{14}N^{14}NO$ and $^{14}N^{15}NO$ were derived from both the ^{15}NO-complex and the mixture of the ^{14}NO- and ^{15}NO-complex (1 : 1), while for Red salt I (nitrate) $^{14}N^{14}NO$ and $^{15}N^{15}NO$ were derived from both the ^{15}NO-complex and the mixture of the ^{14}NO- and ^{15}NO-complex (1 : 1). A part of the N_2O was formed as a by-product in the thermal decomposition; it contained two nitrogen atoms which came from the nitrogen of ammines in the complex. The ^{15}NO-Red salt II yielded $^{15}N^{15}NO$ upon mild decomposition by an acid, and $^{14}N^{15}NO$ upon thermal decomposition *in vacuo*.

Thus, the chloride and nitrate of Red salt II may be represented as $[Co_2(NH_3)_{10}(NO)_2]Cl_4 \cdot 4H_2O$ and $[Co_2(NH_3)_{10}(NO)_2](NO_3)_4 \cdot 2H_2O$ respectively. Furthermore, it is considered that the two cobalt atoms are bridged through a hyponitrite ion in Red salt II and that the N–N bond strength in the hyponitrite bridge may be weaker than that for Red salt I. Crystal X-ray study has determined that, in Red salt I, one cobalt atom is bound to an oxygen atom and the other to a nitrogen atom.[2] Red salt II may be considered to be the linkage isomer of Red salt I with respect to the hyponitrite bridge.

The details of this study will be published later.

1) J. Sand and O. Genssler, *Ber.*, **36**, 2083 (1903).

2) B. F. Hoskins, F. D. Whillans, D. H. Dale and Dorothy Crowfoot Hodgkin, O. M., *Chem. Commun.*, **1969**, 69.

3) A. L. Odell, R. W. Olliff and A. A. Taggart, *J. Chem. Soc.*, **1965**, 6024.

4) R. D. Feltham and R. G. Hayter, *ibid.*, **1964**, 4587.

5) E. E. Mercer, W. A. McAllister and J. R. Durig, *Inorg. Chem.*, **6**, 1816 (1967).