*Brown Nitrosylpentamminechromium(III) Salts and Green Nitrosylpentamminechromium(III) Perchlorate**

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An ammoniacal solution of chromium(II) salt is readily oxidized; the oxidation products vary widely, depending upon the kind of oxidizing agent employed. Thus, when it is allowed to evolve hydrogen at a temperature near 0°C, especially in the presence of iron(II) salt as a catalyst, the main product is hexamminechromium(III) salt[1,2], while a rapid stream of oxygen produces μ-hydroxobis{pentamminechromium(III)} salt as an oxidation product[3]. The present authors have found that the same binuclear complex is also formed by oxidation with ammonium nitrate and that, in this case, brown crystals, however small in quantity, are often found admixed in the red μ-hydroxo salt. Further research has shown that the brown crystals are nitrosylpentamminechromium(III) dichloride, a new type of acidopentamminechromium salt, and that the perchlorate prepared by metathesis is green in contrast to chloride, bromide and nitrate, all of which have been found to be brown; that is to say, the color of crystals is completely changed by a mere substitution of an anion which is not coordinated in the ordinary sense. Such an example seems to be quite rare, though analogous cobalt compounds might be regarded as another example. There are, however, points of considerable difference between these two cases, as will be discussed below. In this paper the method of preparation of and an investigation of infrared absorption spectra pertaining to the new chromium ammines will be described.

Experimental

Preparation.—Although nitrosylpentamminechromium(III) salts were first obtained as described above, the best way of preparing them is by oxidizing an ammoniacal chromium(II) solution with sodium nitrite. The reaction may be represented by the equation:

$$2[Cr(NH_3)_6]Cl_2+NaNO_2+NH_4Cl \rightarrow [CrNO(NH_3)_5]Cl_2+[CrOH(NH_3)_5]Cl_2 +NaCl+3NH_3$$

Nitrosylpentamminechromium(III) Chloride. — Fifteen grams of potassium dichromate are mixed in a 1 l. beaker with 20 ml. of ethanol and 40 ml. of 12 N hydrochloric acid. When the violent reaction has ceased somewhat, the mixture is heated on a hot plate until no orange crystals of potassium dichromate are left at the bottom of the beaker.

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[1] S. M. Jörgensen, *J. prakt. Chem.*, **30**, 1 (1884).

[2] M. Mori, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **74**, 253 (1953).

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TABLE I. INFRARED ABSORPTION PEAKS OF NITROSYLPENTAMMINECHROMIUM(III) SALTS AND THEIR ASSIGNMENTS (wave number, cm^{-1})

$[CrNO(NH_3)_5]Cl_2$ (brown)	$[CrNO(NH_3)_5](ClO_4)_2$ (green)	Assignments
3300 vs (broad)	3410 vs (sharp)	NH_3 stretch.
	3340 vs (sharp)	
2960 vs (sharp)	2960 vs (sharp)	NH_3 stretch.
2900 vs (sharp)	2900 vs (sharp)	
2030 vw	2030 vw	?
1690 vs	1730 vs	NO stretch.
1610 s	1625 s	NH_3 deg. def.
1465 m (sharp)	1465 m (sharp)	?
1380 m (sharp)	1380 m (sharp)	?
1275 vs (sharp)	1300 vs (sharp)	NH_3 sym. def.
1240 w (sharp)	——	
——	1120 (shoulder)	ClO_4 deg. stretch.
	1080 vvs (broad)	
770 s (broad)	760 (shoulder)	NH_3 rock.
730 (shoulder)	730 s	

Abbreviations: v, very; s, strong; w, weak; stretch., stretching; deg., degenerate; def, deformation; sym., symmetric; rock., rocking.

The green solution is then transferred into a smaller beaker and covered with a 3 cm. layer of ligroin or liquid paraffine. It is then kept at 80～90°C, together with 30 g. of pure zinc grains, until the green chromium(III) solution has been completely reduced to the bivalent state with a pure blue color. If the solution has become turbid before the complete reduction, 1～2 ml. of hydrochloric acid may be added and heating continued.

The pure azure-colored solution is cooled in running water to room temperature and quickly poured, together with the mineral oil, into an Erlenmeyer flask containing a mixture of 40 g. of ammonium chloride and 100 ml. of 15 M aqueous ammonia; the whole mixture is then carefully stirred and cooled in an ice bath. To this is then added 15 g. of sodium nitrite dissolved in 25 ml. of 15 M aqueous ammonia; the mixture is stirred vigorously and allowed to stand for several minutes, and the precipitate of crude chloride is separated by filtration. Not only the chloride, but also various other salts may be prepared from this crude product.

In order to prepare pure chloride, the crude product is dissolved in the smallest possible quantity (ca. 1000 ml.) of cold water, and after filtration pure nitrosylpentamminechromium(III) chloride is recrystallized by the slow addition of 200 g. of ammonium chloride and 10 ml. of 12 N hydrochloric acid. The brown crystals are washed with ethanol, air-dried, and kept in a desiccator protected from light. Yield, 9 g.

Found: Cr, 22.69; N (total), 34.85; NH_3, 35.70; Cl, 30.02. Calcd. for $[CrNO(NH_3)_5]Cl_2$: Cr, 22.32; N (total), 36.06; NH_3, 36.53; Cl, 30.42%.

Nitrosylpentamminechromium(III) Nitrate. — The crude precipitate of nitrosylpentamminechromium(III) chloride is dissolved in ca. 1000 ml. of cold water, and the solution is filtered. The nitrate may be crystallized by slowly adding 300 g. of ammonium nitrate and 10 ml. of 14 N nitric acid. Yield, 3.6 g. The precipitate may be further purified by dissolution in water and recrystallization with ammonium nitrate.

Found: Cr, 18.12; NH_3, 28.76. Calcd. for $[CrNO(NH_3)_5](NO_3)_2$: Cr, 17.86; NH_3, 29.25%.

Nitrosylpentamminechromium(III) Bromide. — The bromide can be obtained by a procedure analogous to that used for preparing the nitrate. The bromide is much less soluble and a better yield is obtained by the use of a somewhat smaller quantity of ammonium bromide. However, special care should be taken to prevent the precipitate from becoming too fine. Thus, ammonium bromide is added little by little while the solution is continuously agitated.

Found: Cr, 15.91; NH_3, 25.62; Br, 49.72. Calcd. for $[CrNO(NH_3)_5]Br_2$: Cr, 15.91; NH_3, 26.04; Br, 48.86%.

Nitrosylpentamminechromium(III) Perchlorate.—The precipitate of crude chloride is dissolved in a mixture of 180 ml. of 6 N sulfuric acid and 220 ml. of water, and the solution is filtered. To the filtrate is added 200 ml. of 60% perchloric acid. The mixture is cooled in an ice bath, and the green precipitate of the perchlorate is collected on a glass filter under suction and washed with ethanol. Yield, 6 g. It may be purified by dissolution in the smallest possible quantity of water and by recrystallization with perchloric acid in an ice bath.

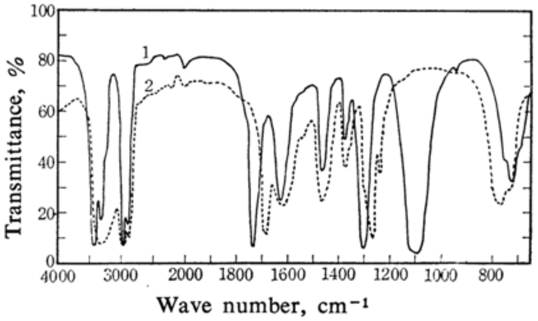

Fig. 1. Infrared absorption spectra of nitrosylpentamminechromium(III) salts.
1: Perchlorate 2: Chloride

Found: Cr, 14.58; NH_3, 22.73; Cl, 19.79. Calcd. for $[CrNO(NH_3)_5](ClO_4)_2$: Cr, 14.21; NH_3, 23.26; Cl, 19.37.

Infrared Absorption Spectra.—The infrared absorption spectra of powder samples of the chloride and the perchlorate were obtained by the Nujol mull technique in the rock salt region with a Hitachi EPI-2 spectrometer. The spectra are given in Fig. 1.

Results and Discussion

The wave numbers of the main infrared absorption peaks and their possible assignments are given in Table I. The assignments were made on analogy with the nitrosylpentamminecobalt(III) salts studied by Bertin, Mizushima, Lane and Quagliano[4]. All the features of the spectra are analogous to those of cobalt compounds, but the rocking frequency of the ligating NH_3 is somewhat lower in chromium ammines and especially so in green perchlorate (chloride: 770; perchlorate: 730; cobaltammines: 800 cm^{-1}). This seems to show indirectly that the coordinate linkage is weaker[5], especially in green nitrosylpentamminechromium(III) perchlorate. The spectra also show that the vibrational frequency of NO is higher in the green perchlorate (1730) than in the brown chloride (1690)*. This would seem to be evidence that in the green form the ligating NO is influenced less by the central ion than in the brown chloride. (Gaseous NO: 1876 cm^{-1})

There is evidence to show that nitrosylpentamminechromium(III) compounds are not simple analogues of similar cobalt compounds[6]. For example, the black series of nitrosylpentamminecobalt(III) salts can be prepared only in the absence of air, the pink series, in the presence of air[7], and the two series are not interchangeable[8]. Moreover, they are reported to behave differently toward acids: the salts of the black series are readily decomposed to give cobalt(II) salts, whereas those of the pink series form acidopentamminecobalt(III) salts[8]. Thus, in cobalt compounds the difference in anions is probably not the only factor causing color change.

On the other hand, both green nitrosylpentamminechromium(III) perchlorate and brown nitrosylpentamminechromium(III) chloride are stable when dissolved in cold water, both solutions presenting exactly the same absorption spectra; from any such solutions, either the perchlorate or the chloride may be crystallized by a mere choice of the precipitant (i. e., perchloric acid or hydrochloric acid). Thus, the environment in the ionic lattices seems to have an effect sufficient to cause a difference in the state of the complex cation, as is evidenced by the difference in color and vibrational frequencies.

A spectroscopic investigation of these chromium compounds is now under way and will shortly be reported. Let us say here, however, that the color of the chloride changes to orange when cooled to the temperature of liquid nitrogen, but that the color of the green perchlorate does not change appreciably down to this temperature.

Summary

A new series of chromium ammines, i. e., nitrosylpentamminechromium(III) salts, were obtained by the reaction of an ammoniacal chromium(II) solution with sodium nitrite. The derivatives are usually reddish brown, but only the perchlorate is bright green. The infrared absorption spectra indicate that in the green perchlorate the rocking frequency of ligating ammonia is lower, while the stretching frequency of the nitrosyl group is higher than in the brown chloride. These results seem to show indirectly that the coordinate linkage is weaker in the green perchlorate.

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* In the case of the cobalt compounds, such a frequency overlaps that of the degenerate deformation vibration of NH_3 (1630 cm^{-1}, Ref. 4).

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[7] T. Moeller and G. L. King, "Inorganic Syntheses", Vol. 4 (1953), p. 168.

[8] T. Moeller and G. L. King, ibid., Vol. 5 (1957), p. 186.