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1963

SovietRxiv

schematic structures I, II, and III showing loss of NH_3 from the cobalt complex

Figure 1: schematic structures I, II, and III showing loss of NH_3 from the cobalt complex

Abstract

Full Text

CHEMISTRY

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SUBSTITUTION OF AMMONIA BY NITRITE IONS ON HEATING IN THE CRYSTALLINE STATE OF OPTICALLY ACTIVE cis-$[Co(NH_3)_2en_2](NO_2)_3$

It was shown earlier (^{1}) that, on heating cis-diammine-bis-ethylenediaminecobalt nitrite in the crystalline state, the complex cation loses ammonia from the inner sphere and is converted into cis-dinitro-bis-ethylenediaminecobalt nitrite. Since the initial and final salts can exist in the form of optical antipodes, it was of interest to study the heating of an optically active isomer. It could be hoped that such a study would make it possible to gain insight into the mechanism of the substitution reaction.

Nitrite d-cis-$[Co(NH_3)_2en_2](NO_2)_3 \cdot H_2O$ was heated, as in the previous experiments (^{1}), for 12 h at 105—110° and was converted completely into inactive cis-dinitro-bis-ethylenediaminecobalt nitrite. Heating, under the same conditions, of the active chloride, d-cis-$[Co(NH_3)_2en_2]Cl_3$, did not decrease its optical activity. Thus, racemization of the complex is a consequence of the reaction in which ammonia is replaced by nitro groups. It is most natural to suppose that, in the crystal lattice, the reaction of substitution of ammonia by nitrite ions proceeds in two stages:

$$\text{cis-}[Co(NH_3)_2en_2](NO_2)_3 \rightarrow [Co(NH_3)en_2\{(NO_2)\}](NO_2)_2 \rightarrow \text{cis-}[Co\,en_2(NO_2)_2]NO_2$$

by the S_N1 dissociation mechanism. The intermediate reaction products with coordination number 5 at both stages may have the form of a tetragonal pyramid I or of one of two trigonal bipyramids II and III (^{2}).

Formation of the trigonal bipyramid (III) is impossible at either stage, since the final reaction product has the "cis" configuration without admixture of "trans." The reaction cannot proceed through the formation, at both stages, of intermediate tetragonal pyramids (I), since this would necessarily lead to retention of optical activity, which is not actually observed. Since racemization takes place, at least one of the intermediate products must have the form of trigonal bipyramid (II). Thus, substitution of two molecules

of ammonia by nitrite ions may proceed from the initial to the final product through II and III, or II and I, or I and II.

It is difficult to imagine that the reaction in the solid state proceeds by an S_N2 mechanism. But such a mechanism is also impossible because it cannot lead to complete racemization of the initial optically active substance (2).

The proposed S_N1 dissociation mechanism should not be understood literally in the sense that ammonia first actually splits off from the complex $[Co(NH_3)_2en_2]^{3+}$, and only then is its place occupied by the nitrite ion. If the reaction followed such a path, then the detachment of ammonia would occur just as readily from other salts of this cation, which is not in fact observed. Thus, in particular, heating the chloride of *d*-cis-diamminobis(ethylenediamine)cobalt at the same temperature as the corresponding nitrite causes no change.

Further examples can be cited which show that the nitrite ion enters the inner sphere of cobaltammines much more readily than other anions. For example, hexamminecobalt(III) chloride begins to lose ammonia only at 173° (3), whereas hexamminecobalt nitrite, heated in air, loses ammonia already at 130–135° (4). We have already noted that, for the quantitative occurrence of the reaction of replacement of ammonia by nitrite ions, slow heating of the salts is essential. In addition, an ordering of the cations and nitrite ions is required. Insertion reactions proceed only when crystalline nitrites are used. On heating mechanical mixtures obtained by grinding, for example, hexamminecobalt nitrate and sodium nitrite, decomposition occurs. When nitrites are heated in the crystalline state, the nitrite ions, owing to vibrations, approach the cation and weaken the Co–NH_3 bond. Thus, in this case the S_N1 mechanism is to some extent associated with the formation of an intermediate state characteristic of the S_N2 mechanism.

For a more detailed elucidation of the reaction mechanism it would have been necessary to study the thermal decomposition of optically active cis-nitroamminebis(ethylenediamine)cobalt nitrite. However, by none of the methods used have we so far been able to obtain it.

Experimental Part

The starting product for obtaining optically active cis-diamminobis(ethylenediamine)cobalt(III) nitrite was trans-dibromobis(ethylenediamine)cobalt(III) nitrate. Since we never succeeded, by Werner' s method (5), in obtaining dibromobis(ethylenediamine)cobalt bromide in pure form without an admixture of tris(ethylenediamine)cobalt bromide, we dissolved the crude product obtained in cold water and added nitric acid. The sparingly soluble nitrate $[CoBr_2en]NO_3$ separated in pure form as dark-green lustrous crystals. On treating these crystals with dilute ammonia $^{(6)}$, a violet product was obtained, which, for purification, was triturated with concentrated hydrobromic acid with vigorous stirring and then recrystallized from water.

Thus a substance was obtained containing as cation only cis-$[CoBr(NH_3)en_2]^{2+}$, which was proved by recording the absorption spectrum. The substance was a mixture of bromide and nitrate, the composition of which may be represented conventionally by the formula $[CoBr(NH_3)en_2]Br_x(NO_3)_{2-x}$.

For resolution of the racemate into optical antipodes, to this mixture, dissolved in a small amount of water, calculated amounts of silver salt (for precipitation of bromide ion) and ammonium salt of α-bromo-*d*-camphor-π-sulfonic acid $^{(7)}$ were added. After some time, long lilac needles of *d*-bromocamphorsulfonate of *d*-cis-bromoamminebis(ethylenediamine)cobalt separated from the solution; after recrystallization from

hot water showed a rotation

	$[\alpha_C]$	M_C	l, dm	Conc., %
	+63.98°	385.9°	2	0.8
Literature data (^{6})	+65.7	396.3	2	0.8

The finely powdered bromocamphorsulfonate, *d*-cis-$[CoBr(NH_3)en_2] \cdot (d\text{-}C_{10}H_{14}SO_4Br)_2$, was treated with liquid ammonia until complete dissolution. After recrystallization from water, *d*-cis-$[Co(NH_3)_2en_2](d\text{-}C_{10}H_{14}SO_4Br)_3$ showed

	$[\alpha_D]$	M_D	l, dm	Conc., %
	80–82°	914.9–937.8°	2	0.5
Literature data (^{8})	81°	926.4	1	0.5

From 28.6 g of *d*-cis-$[CoBr(NH_3)en_2](d\text{-}C_{10}H_{14}SO_4Br)_2$, ∼ 15 g of *d*-cis-$[Co(NH_3)_2en_2](d\text{-}C_{10}H_{14}SO_4Br)_3$ was obtained.

To obtain the chloride, *d*-cis-$[Co(NH_3)_2en_2]Cl_3$, the bromocamphorsulfonate was moistened with water, concentrated hydrochloric acid was added until complete dissolution, and the chloride, very readily soluble in water, was precipitated from the solution with alcohol. After reprecipitation from aqueous solution with hydrochloric acid, it showed the rotation:

	$[\alpha_D]$	M_D	l, dm	Conc., %
	51°	162.94°	2	0.5
Literature data (^{8})	50	159.8	1	0.5

From 3 g of bromocamphorsulfonate, 0.63 g of chloride was obtained. By grinding the chloride with the calculated amount of silver nitrite and precipitating with alcohol, *d*-cis-diammin-bis-ethylenediaminecobalt nitrite, $[Co(NH_3)_2en_2](NO_2)_3 \cdot H_2O$, was obtained in 65% of the theoretical yield, in the form of light, large flakes of irregular shape.

$[\alpha_D]$	M_D	l, dm	Conc., %
49–50°	180.9–184.6°	2	0.5

The optically active nitrite of cis-diammin-bis-ethylenediaminecobalt was heated in the dry state for 12 hours at 105°. A loss in weight of 13.00% was found (calculated for loss of $2NH_3 + H_2O$, 14.09%). The amount of ammonia absorbed by the acid solution was 9.26% (calculated for $2NH_3$, 9.21%). The heating product, cis-$[Co(NO_2)_2en]NO_2$, as well as the nitrate prepared from it, showed absence of optical activity in the region of the *C*, *D*, and *E* lines.

A control experiment with heating the optically active chloride, *d*-cis-$[Co(NH_3)_2en_2]Cl_3$, at 105° for 10 hours showed that the specific rotation of the substance did not change.

Heating of Mixtures of Hexamminecobalt Salts and Sodium Nitrite

1. Hexamminecobalt nitrate was ground in an agate mortar with sodium nitrite. Both salts had been previously dried at 105°. 2. Hexamminecobalt nitrate and sodium nitrite were ground with a small amount of water; the mixture was then dried at 105°. Mixtures 1 and 2, and, for comparison, also $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_6](NO_3)_3$, were heated for 20-23 hours at 130–135°, i.e., under conditions in which hexamminecobalt nitrite, losing ammonia, is converted into trinitroamminecobalt (^{4}).

As a result of heating, the chloride and nitrite of hexamminecobalt remained unchanged and dissolved well in cold water; after recrystallization they gave yellow-orange crystals of the chloride and, respectively, of the nitrate.

In mixed samples 1 and 2, decomposition occurred to a very great extent. The samples turned black and did not dissolve completely in water. The portion that dissolved in cold water, after recrystallization, gave crystals similar to those of hexamminecobalt nitrate. Cobalt(III) hydroxide remained on the filter.

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Received
11 III 1963

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Note: Figure translations are in progress. See original paper for figures.