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Abstract

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ADDITION PRODUCTS OF IODINE WITH COBALT(III) DIOXIMINES

A. V. Ablov and N. M. Samus' (1) described the compound $H[CoJ_2(DH)_2]J_2$*, which is formally the product of addition of one molecule of iodine to trans-diiodo-bis-dimethylglyoximatocobaltic acid. With regard to the structure of this compound, it could be assumed that the iodine molecule is attached to the iodide ion with formation of a triiodide ion coordinated by cobalt, or that the iodine molecules fill voids in the crystal lattice of the dioxime. The present investigation was undertaken in order to elucidate the structure of this compound. Addition products of iodine to an iodide ion and to neutral molecules are distinguished.

Recently, polyiodides and other polyhalides have found successful application for the determination of cesium in river water (2), as well as for obtaining salts of this metal of very high purity (3).

The structure of polyiodide ions has been well studied. In crystals of $[NH_4]J_3$, the triiodide ion is a group of three iodine atoms arranged almost linearly, with unequal distances between neighboring iodine atoms: 2.82 and 3.10 Å (4). This same anion in crystals of $[(C_6H_5)_4As]J_3$ proves to be symmetrical, with distances J—J = 2.90 Å (5). The ion J_5^- is planar and has the shape of the letter V, with distances between iodine atoms along the sides of the angle of 2.81 and 3.17 Å (6,7). It is interesting to note that the structure of this ion differs completely from the structure of the ion JCl_4^-, which forms a square with an iodine atom in the center (8). The structure of Cs_2J_8 consists of Cs^+ and J_3^- ions and J_2 molecules (9). Pairs of J_3^- ions form, with one J_2 molecule, a centrosymmetric, almost planar group J_8^{2-} in the shape of the letter z, with a weak bond between its constituent groups. The anion J_7^- is a loose complex of the J_3^- ion with two J_2 molecules (10,11).

It is known that polyhalide ions are the more stable with respect to elimination of halogen molecules, the smaller the charge of the cation and the larger its radius. Therefore the most stable polyhalides are those of organic or complex cations having large volumes. It is further known that among polyhalides the polyiodides are the most stable. The formation of polyhalide ions has been explained (12,13) by electrostatic interaction between a monohalide ion and polarizable molecules. However, the existence of centrosymmetric trihalide ions is incompatible with such an explanation. Comparatively recently, Havinga and Wiebenga (14), assuming delocalization of π-electrons, were able to interpret the structures of polyhalide ions within the framework of the molecular-orbital method. The observed configurations of the ions could be explained and the bond lengths calculated.

Addition products of iodine molecules to neutral molecules have been described, and the structures of some of them are known. Thus, for example, in the compound $(CH_3)_3NJ_2$, the nitrogen and iodine atoms lie on one straight line; the distance N—J = 2.27 Å, and J—J = 2.83 Å (15).

In the addition products of iodine molecules with 1,4-dithiane $C_4H_8S_2 \cdot 2J_2$ (16), and, respectively, diselenane $C_4H_8Se_2 \cdot 2J_2$ (17), iodine molecules are attached to sulfur atoms and, respectively, selenium atoms.

It is interesting to note that the distance between iodine atoms which in in the isolated molecule J_2 is 2.67 Å, and in J_3^- and in other polyiodide ions it increases to 2.81-2.90 Å. The distance between the iodine atoms in the iodine molecule attached to nitrogen, sulfur, or selenium in the above-mentioned molecular addition products increases in approximately the same way.

Trans-iodo-bis-dimethylglyoximatoaquocobalt was dissolved by heating in dilute hydroiodic acid, to which molecular iodine had previously been added. On cooling the solution, even when iodine was taken in large excess, only the previously described substance of composition $H[\mathrm{Co}J_2(\mathrm{DH})_2] \cdot J_2$ separated.

Figure 1: Amount of J_2 transferred into carbon tetrachloride from iodine addition products to cobalt dioximes: 1 $-KJ$; 2 $-NH_4[\mathrm{Co}(J_3)_2(\mathrm{DH})_2]$; 3 $-K[\mathrm{Co}J(J_3)(\mathrm{DH})_2]$; 4 $-K[\mathrm{Co}(\mathrm{NO}_2)_2(\mathrm{DH})_2] \cdot KJ_3$

On adding iodo-bis-dimethylglyoximatoaquocobalt to an aqueous solution of potassium iodide, into which molecular iodine had previously been introduced, two products were obtained, $K[\mathrm{Co}J_2(\mathrm{DH})_2] \cdot J_2$ and $K[\mathrm{Co}J_2(\mathrm{DH})_2] \cdot 2J_2$. If ammonium iodide or sodium iodide was taken instead of potassium iodide, then $NH_4[\mathrm{Co}J_2(\mathrm{DH})_2] \cdot 2J_2$ and, respectively, $Na[\mathrm{Co}J_2(\mathrm{DH})_2] \cdot 2J_2$ were formed.

From an alcoholic solution of potassium iodonitro-bis-dimethylglyoximatocobaltate, on addition of iodine, crystals of the addition product $K[\mathrm{Co}J(\mathrm{NO}_2)\mathrm{DH})_2] \cdot J_2$ separated. Products richer in iodine could not be obtained. Undoubtedly,

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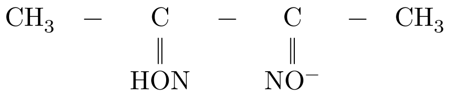
* DH denotes the dimethylglyoximate ion



$$\begin{array}{ccccccc} \mathrm{CH_3} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{CH_3} \\ & & \| & & \| & & \\ & & \mathrm{HON} & & \mathrm{NO^-} & & \end{array}$$

in all these dioximes the iodine molecules are bound to the iodide ion coordinated at cobalt, so that they should be regarded as complex compounds containing triiodide ions in the inner coordination sphere: $H[\mathrm{Co}J(J_3)(\mathrm{DH})_2]$; $K[\mathrm{Co}J(J_3)(\mathrm{DH})_2]$; $K[\mathrm{Co}(J_3)_2(\mathrm{DH})_2]$; $K[\mathrm{Co}(J_3)(\mathrm{NO}_2)(\mathrm{DH})_2]$. Confirmation of this point of view is the fact that potassium and ammonium dinitro-bis-dimethylglyoximatocobaltates do not form addition products with iodine. However, crystals of composition $K[\mathrm{Co}(\mathrm{NO}_2)_2(\mathrm{DH})_2] \cdot KJ_5$ and $NH_4[\mathrm{Co}(\mathrm{NO}_2)_2(\mathrm{DH})_2] \cdot NH_4J_5$ were obtained; these are double salts with the anions J_5^- and $[\mathrm{Co}(\mathrm{NO}_2)_2(\mathrm{DH})_2]^-$.

With respect to organic solvents, the polyiodides of cobalt dioximes behave similarly to potassium triiodide. From $K[\mathrm{Co}(J_3)J(\mathrm{DH})_2]$ and $NH_4[\mathrm{Co}(J_3)_2(\mathrm{DH})_2]$, carbon tetrachloride gradually extracts iodine. The double salt $K[\mathrm{Co}(\mathrm{NO}_2)_2(\mathrm{DH})_2] \cdot KJ_5$ in the crystalline state loses iodine only with great difficulty; however, on heating with water, iodine can be removed without difficulty.

Experimental Part

Trans-iodo-bis-dimethylglyoximatoaquocobalt was heated with hydroiodic acid, to which various amounts of molecular iodine were added (from 1 to 4 moles). The concentration of hydroiodic acid was also varied over wide limits. Under all conditions, however, from the hot solution there precipitated only the previously (1) described iodine addition product $H[\mathrm{Co}(J_3)J(\mathrm{DH})_2]$. Increasing the concentration of both molecular iodine and hydroiodic acid led only to an increase in the yield of the iodine addition product to the cobalt dioxime. The same compound was also obtained when dichloro- or dibromo-bis-dimethylglyoximatocobaltic acid was dissolved by heating in the minimum amount of water and then a solution of iodine in hydroiodic acid was added.

Iodine addition products to salts of trans-diiodo-bis-dimethylglyoximatocobaltic acid. K[Co(J)J(DH)]. 4.30 g (0.01 mole) of iodo-bis-dimethylglyoximatoaquocobalt, 5.00 g (0.03 mole) of potassium iodide, and 2.54 g (0.01 mole) of iodine were heated on a water bath with 100 ml of water. Gradually the iodoaquo compound passed into solution, from which, on cooling, beautiful triangular prisms of a dark-violet color separated. For analysis, as in all other cases, the air-dried substance was taken.

Found, %: Co 7.18; 7.19; K 4.58; 4.60; N 6.58; 6.76; J (titrated with thiosulfate) 30.50; 30.47; J (total) 60.67; 60.58
K[CoJ (C H N O)] • J . Calculated, %: Co 7.05; K 4.68; N 6.70; J (as added molecules J) 30.36; J (total) 60.73

K[Co(J) (DH)] was obtained analogously to the preceding compound, except that double the amount of iodine and potassium iodide was taken. The substance consists of large rhombs of a dark-cherry color.

Found, %: Co 5.46; 5.42; K 3.49; 3.45; J (titrated with thiosulfate) 46.49; 46.42; J (total) 69.81; 69.78
K[CoJ (C H N O)] · 2J . Calculated, %: Co 5.41; K 3.59; J (as added molecules J) 46.50; J (total) 69.90

If, in carrying out experiments, 3–4 and more moles of molecular iodine were taken per 1 mole of iodo-bis-dimethylglyoximatoaquocobalt, the product of addition of two iodine molecules to the salt K[CoJ (DH)] · 2J nevertheless precipitated; only the yield of the product increased.

Ammonium diiodo-bis-dimethylglyoximatocobaltate NH [CoJ (DH)]. Iodo-bis-dimethylglyoximatoaquocobalt and a large excess of ammonium iodide were dissolved in water on heating. After several days, small brown prisms separated from the solution.

Found, %: Co 10.37; 10.36; J 45.32; 45.40
NH [CoJ (C H N O)]. Calculated, %: Co 10.50; J 45.24

NH [Co(J) (DH)]. Obtained analogously to the corresponding iodine addition product to the potassium salt. The substance consists of large prisms of a dark-green color.

Found, %: Co 5.40; 5.45; N 6.60; 6.64; J (titrated with thiosulfate) 47.47; 47.51; J (total) 70.98; 70.70
NH [CoJ (C H N O)] · 2J . Calculated, %: Co 5.52; N 6.55; J (as added molecules) 47.52; J (total) 71.28

Na[Co(J) (DH)]. Working by an analogous procedure, but using sodium iodide, it was possible to isolate in pure form, in small yield, only one product, Na[Co(J) (DH)], which is a finely crystalline substance of a dark-violet color.

Found, %: Co 5.48; 5.60; J (titrated with thiosulfate) 47.18; 47.31; J (total) 70.83; 71.03
Na[CoJ (C H N O)] · 2J . Calculated, %: Co 5.49; J (as added molecules J) 47.28; J (total) 70.92

Iodine addition product to potassium iodonitro-bis-dimethylglyoximatocobaltate. K[Co(J)(NO)(DH)]. 3.53 g (0.01 mole) of nitro-bis-dimethylglyoximatoaquocobalt and 1.67 g (0.01 mole) of potassium iodide were dissolved with slight heating in 80 ml of ethyl alcohol. To the warm solution, colored dark brown, 2.54 g of molecular iodine dissolved in 30–40 ml of alcohol was added. Already on mixing the warm solutions, a precipitate began to separate as a finely crystalline substance of a gray-green color. Under the microscope, accumulations of small intergrown crystals are clearly distinguished.

Found, %: Co 7.64; 7.72; N 9.20; 9.48; J (titrated with thiosulfate) 37.45; 37.44; J (total) 50.47; 50.57
K[CoJ(NO)(C H N O)] · J . Calculated, %: Co 7.80; N 9.28; J (as added molecules J) 33.62; J (total) 50.44

The elevated value of iodine titrated with thiosulfate is explained by the fact that, when the substance reacts with an aqueous solution of potassium iodide, the nitrite ion is liberated from the inner sphere of the dioxime (1).

Ammonium iodonitro-bis-dimethylglyoximatocobaltate. NH [CoJ(NO)(DH)]. Equivalent amounts of nit-

bis-dimethylglyoximatoaquocobalt and ammonium iodide dissolved on heating in ethyl alcohol. On cooling of the solution, small brown prisms separated.

Found, %: Co 12.15; 12.20; N 17.18; 17.44; J 26.42, 26.40
$NH_4[CoJ(NO_2)(C_4H_7N_2O_2)_2]$. Calculated, %: Co 12.28; N 17.51; J 26.44

The double salt $K[Co(NO_2)_2(DH)_2] \cdot KJ_5$. When aqueous solutions of potassium dinitro-bis-dimethylglyoximatocobaltate and potassium iodide, to which molecular iodine had previously been added, taken in different ratios, were mixed, a very sparingly soluble bulky crystalline precipitate separated in the form of long, thin needles, which under the microscope had a light golden color. On heating in a drying oven to 105–110° no change in weight was observed.

Found, %: Co 5.39; 5.41; K 7.10; 7.07; N 7.86; 7.91;
J (titrated with thiosulfate) 46.53; 46.41;
J (total) 57.90; 57.93

$K[Co(NO_2)_2(C_4H_7N_2O_2)_2] \cdot KJ_5$. Calculated, %: Co 5.39; K 7.15; N 7.68;
J (in the form of attached J_2 molecules) 46.53;
J (total) 58.05

The substance was heated with water until the evolution of iodine vapors ceased; then the solution was treated in a separatory funnel with carbon tetrachloride to remove traces of iodine. On addition to the hot solution of $[CoPy_2(DH)_2]NO_3$, dissolved in methyl alcohol, a finely crystalline yellow precipitate of $[CoPy_2(DH)_2][Co(NO_2)_2(DH)_2]$ formed. Analysis of the air-dry substance showed:

Found, %: Co 14.11; 14.19;
$Co_2C_{18}N_{12}H_{38}O_{12}$. Calculated, %: Co 14.22

The double salt $NH_4[Co(NO_2)_2(DH)_2] \cdot NH_4J_5$ was obtained by the interaction of ammonium dinitro-bis-dimethylglyoximatocobaltate and ammonium iodide containing dissolved iodine. The substance consists of plate-like crystals of light golden color.

Found, %: Co 5.57; 5.59; N 10.31; 10.35; J (titrated with thiosulfate) 48.33; J (total)
60.40; 60.38.

$NH_4[Co(NO_2)_2(C_4H_7N_2O_2)_2] \cdot NH_4J_5$. Calculated, %: Co 5.60; N 10.65; J (in the form
of attached J_2 molecules) 48.26; J (total)
60.31

Extraction of iodine with an organic solvent. A weighed portion of the substance, wrapped in filter paper, was placed in the thimble of a Soxhlet apparatus, and carbon tetrachloride was poured into the flask. As extraction proceeded, the solvent became increasingly intensely violet. After 1–2 hours, heating was stopped. In the cooled solution of iodine in carbon tetrachloride, the iodine was determined by titration. Fresh solvent was poured into the flask, and this was repeated several times. In Fig. 1 the points indicate the total amount of iodine J_2 extracted after 1, 2, etc., heatings over the time plotted on the abscissa.

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