Academician of the Academy of Sciences of the Moldavian SSR A. V. ABLOV, I. D. SAMUS

1962

SovietRxiv

Abstract

Full Text

CHEMISTRY

Academician of the Academy of Sciences of the Moldavian SSR A. V. ABLOV,
I. D. SAMUS

ON THE BONDING OF THIOCYANATO AND SELENOCYANATO GROUPS WITH THE CENTRAL ATOM IN COBALT(III) AMMINES AND DIOXIMINES

The question of by which atom the NCS group is attached to cobalt in cobaltiammines was raised by A. Werner. At first he believed that this group could be attached both through the nitrogen side in isorhodanato compounds and through the sulfur side in rhodanato compounds (^{1}). Later, however, Werner came to the conclusion that in cobaltiammines the NCS group is always attached through nitrogen, and thus all cobaltiammines containing this group in the inner sphere are isothiocyanato compounds (^{2}).

An X-ray structural study of $[Co(NH_3)_5(NCS)](NO_3)_2$, carried out by T. I. Malinovskii, I. D. Samus, and N. V. Belov (^{3}), confirmed this proposal of Werner.

Proceeding from the regularity of trans influence of I. I. Chernyaev, one of us (^{4}) proposed that in dinitro-bis-dimethylglyoximatocobaltic acid $H[Co(DH)_2(NO_2)_2]^*$ the most probable arrangement is that of the two nitro groups in the trans position. Further study of acids of the type $H[Co(DH)_2XY]$, where X and Y are various monovalent acid radicals, for example Cl, Br, J, SCN, confirmed that their behavior is explained only if it is assumed that the groups X and Y are in the trans position relative to one another (^{5,6}).

In the study of rhodanonitro-bis-dimethylglyoximatocobaltic acid $H[Co(DH)_2(NO_2)(SCN)]\cdot H_2O$ (^{7}), it was shown that its behavior can be explained on the basis of the regularity of trans influence and by assuming that the thiocyanato group in cobalt dioximes has a stronger trans influence than the nitro group. Somewhat later (^{8}), new facts were presented indicating that the thiocyanato group in cobalt dioximes indeed has a stronger trans influence than the nitro group.

These facts required explanation, since I. I. Chernyaev and A. Ganiev (^{9}) showed that in $[Co(NH_3)_3(NO_2)_2(NCS)]$ the nitro group has a stronger trans influence than the thiocyanato group. The synthesis and study of cobalt dioximes containing in the inner coordination sphere one and two molecules of thiourea (^{10}) made it possible to put forward certain assumptions explaining such strange behavior of the thiocyanato group in cobalt dioximes. It was found that thiourea

Fig. 1. Projection of 1/4 of the unit cell of interatomic vectors onto the XY plane

Figure 1: Fig. 1. Projection of 1/4 of the unit cell of interatomic vectors onto the XY plane

in cobalt dioximes has a stronger trans influence than the acid residues Cl, Br, and NO_2. In trans activity, thiourea is close to the thiocyanato group.

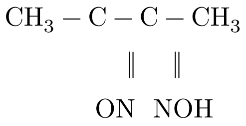
X-ray structural studies of addition products of thiourea and ethylenethiourea with nickel salts ([11]), cadmium ([12,13]), and others showed that these ligands are bound to the metal atom through sulfur. There is no doubt that also in cobalt(III) dioximes containing thiourea, the bond of the latter with cobalt is likewise effected through sulfur. In view of the considerable simil—···properties in the behavior of cobalt dioximes containing thiourea in the inner sphere with dioximes containing the thiocyanato group, the idea suggested itself that in cobalt(III) dioximes the thiocyanato group is bonded to the central metal atom not through nitrogen, but through sulfur. This supposition received substantial confirmation as a result of the synthesis and study of the properties of cobalt(III) dioximes containing in the inner sphere the selenocyanato group and selenourea [(14)]. The ion $[Co(DH)_2(SeCN)_2]^-$ is very similar in its properties and chemical behavior to the dithiocyanato-bis-dimethylglyoximatocobaltiate ion. It was found that in cobalt dioximes the selenocyanato group, just like the thiocyanato group, has a greater trans influence than the nitro group. Particularly noteworthy is the exceptional stability of the diselenocyanato-bis-dimethylglyoximatocobaltiate ion toward acids. Taking into account, on the other hand, the extreme instability of the free selenocyanate ion toward hydrogen ions, this circumstance may serve as a very serious indication that the SeCN group, and consequently also the thiocyanato group, in cobalt dioximes is bonded to the metal atom through selenium and, respectively, through sulfur.

Fig. 1. Projection of 1/4 of the unit cell of interatomic vectors onto the *XY* plane

To confirm the correctness of the conclusions obtained by chemical means concerning the mode of bonding of the thiocyanato group in cobalt(III) dioximes, an X-ray structural study was undertaken of cobalt dioximes containing thiocyanato and selenocyanato groups in the inner sphere.

---

* DH —dimethylglyoximate ion,



$$\begin{array}{c} CH_3 - \underset{\underset{\displaystyle ON}{\|}}{C} - \underset{\underset{\displaystyle NOH}{\|}}{C} - CH_3 \end{array}$$

A goniometric and X-ray photographic study of the crystals $NH_4[Co(DH)_2(SCN)_2] \cdot 3H_2O$ and $NH_4[Co(DH)_2(SeCN)_2] \cdot 3H_2O$ (15) showed that they are isomorphous and have the following structural characteristics:

$$NH_4[Co(DH)_2(SCN)_2] \cdot 3H_2O:$$

$$a = 9.98 \pm 0.05\,\text{Å}, \quad b = 12.07 \pm 0.05\,\text{Å}, \quad c = 8.48 \pm 0.04\,\text{Å}, \quad \beta = 95°20', \quad \sigma_{\text{pycn}} = 1.53,$$

$$\sigma_{\text{roentg}} = 1.56, \quad Z = 2$$

$$NH_4[Co(DH)_2(SeCN)_2] \cdot 3H_2O:$$

$$a = 10.02 \pm 0.05\,\text{Å}, \quad b = 12.18 \pm 0.05\,\text{Å}, \quad c = 8.37 \pm 0.04\,\text{Å}, \quad \beta = 95°, \quad \sigma_{\text{pycn}} = 1.75,$$

$$\sigma_{\text{roentg}} = 1.86, \quad Z = 2$$

In accordance with the extinctions of reflections found on the zero-layer photographs of both compounds, taken with unfiltered molybdenum radiation upon rotation of the crystal about the Z axis and, respectively, about the Y axis, the space group was determined unambiguously as $C_{2h}^5 = P2_1/n$.

The smallest multiplicity of positions in this space group is two (at centers of inversion). Since the cell contains two formula units, the cobalt atom and the ammonium ion may occupy two of these special positions. The atoms of the thiocyanato groups and, respectively, of the selenocyanato groups must be in general positions.

The intensity data were collected using the method of multiple exposures in a back-reflection photographic camera with Mo radiation. The intensities of the $h0l$ and $hk0$ reflections were determined visually by means of a blackening-mark scale in relative units and were corrected for the polarization and kinematic factors. The temperature factor and absorption factor were not taken into account.

The values of $|F|^2$ obtained were used to construct Patterson projections $P_0(xy)$ and $P_0(xz)$. Figures 1 and 2 show projections of 1/4 of the cell of the interatomic-vector space for $NH_4[Co(DH)_2(SeCN)_2] \cdot 3H_2O$.

The independent region of the projection onto the plane (001) contains strong maxima, which should correspond to the vectors Co–Se and Se–Se. As a result

Fig. 2. Projection of 1/4 of the cell of the interatomic-vector space onto the XZ plane

Figure 2: Fig. 2. Projection of 1/4 of the cell of the interatomic-vector space onto the XZ plane

of analysis of the pattern of interatomic vectors, the maximum with coordinates $x = 0.148$ and $y = 0.135$ was identified as corresponding to the vector Co—Se. In the independent region of the projection onto the plane (010) (1/4 of the cell projection) there is a strong maximum at the point with coordinates $x = 0.146$, $z = 0.129$, which should correspond to the vector Co—Se.

The Co—Se distance is approximately 2.4 Å, which agrees with the sum of the covalent radii 1.25 Å (Co) + 1.25 Å (Se) (16). Thus it has been proved that, in the compound $NH_4[Co(DH)_2(SeCN)_2] \cdot 3H_2O$, the selenocyanato group is bonded to cobalt through selenium. Work on determining the coordinates of the light atoms is continuing.

Fig. 2. Projection of 1/4 of the cell of the interatomic-vector space onto the XZ plane.

Since ammonium diselenocyanato- and dithiocyanato-bis-dimethylglyoximatocobaltates are isomorphous, and the corresponding anions are similar in chemical behavior, there can be no doubt that, in the latter compound, the thiocyanato group is bonded to the cobalt atom through sulfur, and not through nitrogen.

In the literature there are contradictory statements concerning the degree of trans influence of the thiocyanato group as compared with the nitro group in complex compounds of cobalt(III) (9,17). This is due to the fact that not all complex cobalt compounds containing thiocyanato groups in the inner sphere can be generalized. In those compounds in which the NCS group is bonded to cobalt through nitrogen, i.e., in cobaltammines, the nitro group has the stronger trans influence. In those compounds, however, in which this group is bonded to cobalt through sulfur, as for example in cobalt dioximes, the thiocyanato group has the stronger trans influence.

The fact that the bond of cobalt with the thiocyanato group in cobalt(III) dioximes occurs through sulfur seems, of course, unusual; however, it is not the only exception. Crystallographic studies by D. Hodgkin (17) showed that, in vitamin B_{12}, the cobalt atom can add selenocyanato and thiocyanato groups, forming Co—Se and, respectively, Co—S bonds.

In conclusion, the authors consider it their pleasant duty to express their deep gratitude to Academician N. V. Belov for reading the manuscript and for his attentive discussion of the results.

Institute of Chemistry
Academy of Sciences of the Moldavian SSR

Kishinev Agricultural
Institute named after M. V. Frunze

Received
1 VI 1962

References Cited

1. A. Werner, F. Bräunlich, *Z. anorg. Chem.*, **22**, 95, 123 (1900).
2. A. Werner, *Lieb. Ann.*, **386**, 38 (1912).
3. T. I. Malinovskii, I. D. Samus' , N. V. Belov, *DAN*, **131**, 1327 (1960).
4. A. V. Ablov, *DAN*, **97**, 1019 (1954).
5. A. V. Ablov, G. N. Syrtsova, *ZhOKh*, **25**, 1304 (1955).
6. A. V. Ablov, N. M. Samus' , *ZhNKh*, **5**, 852 (1960).
7. A. V. Ablov, N. M. Samus' , M. S. Popov, *DAN*, **106**, 665 (1956).
8. A. V. Ablov, N. M. Samus' , *ZhNKh*, **4**, 1753 (1959).
9. I. I. Chernyaev, A. Ganiev, *ZhNKh*, **2**, 765 (1957).
10. A. V. Ablov, N. M. Samus' , *DAN*, **123**, 457 (1958).
11. L. Cavalca, M. Nardelli, A. Braibanti, *Gazz. chim. ital.*, **86**, 942 (1956).
12. M. Nardelli, L. Cavalca, A. Braibanti, *Gazz. chim. ital.*, **87**, 137 (1957).
13. L. Cavalca, M. Nardelli, G. Fava, *Acta crystallogr.*, **13**, 127 (1960).
14. A. V. Ablov, N. M. Samus' , *DAN*, **133**, 1327 (1960).
15. I. D. Samus' , *Izv. AN MSSR*, No. 10 (88), 85 (1961).
16. G. Lipson, V. Kokren, *Determination of the Structure of Crystals*, IL, 1956.
17. A. V. Babaeva, I. B. Baranovskii, *ZhNKh*, **6**, 1786 (1961).
18. *Annual Rep. Progress of Chemistry for 1959*, Chemical Society, London, 1959, p. 102.

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