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A. S. Antsyshkina and M. A. Porai-Koshits

Dimeric Complexes in Paramagnetic Nickel Compounds

The Structure of Crystals of $Nien_2Cl_2$ and $Nien_2Br_2$

(Presented by Academician I. I. Chernyaev, 12 X 1961)

Numerous structural studies of recent years ([1–9]) have shown that paramagnetic nickel compounds of composition NiA_4X_2 are built of molecular octahedral complexes $[NiA_4X_2]^0$ with a trans arrangement of the acid residues X. In particular, this applies to $Nien_2(NCS)_2$, a partial structural investigation of which was carried out by T. S. Khodasheva in 1952 ([8]). According to the data obtained by her, crystals of this compound belong to the monoclinic system; lattice parameters: $a = 10.03$, $b = 8.08$, $c = 9.36$ Å, $\beta = 126^\circ$; space group $P2_1/a$; the cell contains two formula units of composition $Nien_2(NCS)_2$. The Ni atoms are located at centers of inversion, and the complexes have an octahedral trans structure. Lingafelter ([9]) came to an analogous result; he also gives the interatomic distances Ni—N(en) and Ni—N(NCS) (2.10 and 2.15 Å, respectively).

Recently A. V. Babaeva and Chzhan Shou-gan ([10]) obtained a series of new nickel compounds of the type $Nien_2XY$ and investigated their physicochemical properties. For interpretation of the results obtained it was essential to obtain confirmation that not only $Nien_2(NCS)_2$, but also other initial compounds, in particular $Nien_2Cl_2$ and $Nien_2Br_2$, have a trans-octahedral structure. At the request of the authors ([10]), we carried out a structural investigation of these compounds, which led to a somewhat unexpected result. Contrary to expectation, in these compounds there was found a type of complex previously not observed for compounds of composition MA_4X_2.

Crystals of $Nien_2Cl_2$ and $Nien_2Br_2$ are isomorphous and belong to the monoclinic system. Space group $P2_1/n$. Lattice parameters: $a = 13.9$, $b = 11.3$, $c = 6.3$ Å, $\beta = 92.5^\circ$ and $a = 14.2$, $b = 11.3$, $c = 6.6$ Å, $\beta = 94^\circ$, respectively. The unit cell contains 4 formula units of monomeric composition.

The structure analysis was carried out from ordinary and weighted projections of the interatomic function and from projections of the electron density onto three coordinate planes for both compounds. X-ray photographs were taken in a KFOR diffractometer (De Jong–Bouman type camera) using λ_{Cu} and λ_{Mo} radiation. For oscillation about the Z axis, crystals of needle habit with a square

cross section were chosen; layer lines perpendicular to the Y axis were obtained from a spherical specimen.

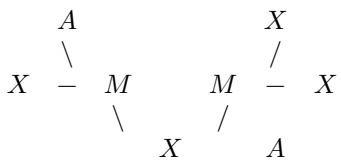
Figures 1 and 2 show projections of the first-approximation electron density onto the planes (001) and (010) for the $Nien_2Cl_2$ crystal. In both cases the signs of the amplitudes were determined only from the coordinates of the Ni and Cl atoms. The positions of the maxima corresponding to Ni and Cl atoms, and the presence of weaker maxima in the trans position to Cl along the coordinate Cl—Ni—A on these and other projections obtained, show that the complexes have a dimeric structure: the Ni atoms are linked pairwise by bridging Cl (Br) atoms; the coordination of Ni is completed to a cis-octahedral one by cyclic en groups;

the remaining ions Cl^- (Br^-) are in the outer sphere. The distances are Ni—Cl = 2.5 Å, Ni—Br = 2.7 Å, Ni—N = 2.0 Å. At present the crystal structure is being refined. The results will be published separately.

Complexes of the type found may be regarded as intermediate between monomeric octahedral complexes MA_4X_2 and polymeric chain formations MA_2X_2, built of octahedral units. Limitation of the chain to two units in the case of $[MA_4X_2]^{2+}$ leads to yet another feature—the cis arrangement of the acid residues X, which is not characteristic of other Ni compounds. This type of dimeric complex is, to a certain extent, analogous to the complexes of dimeric compounds of Pt and Pd of the type

Fig. 1

Fig. 1



($A = PR_3,\ AsR_3,\ X = Cl,\ Br,\ NCS$ etc.), where the bond between metal atoms is also effected through two acid residues. The difference consists only in the replacement of square-planar coordination by octahedral coordination and in the presence of an overall positive charge.

In work ([10]) the preparation of a series of ethylenediamine nickel compounds of composition $Nien_2XY$, where $X, Y = Cl, Br, I, NO_2, NCS$, by cocrystallization of the compounds $Nien_2X_2$ and $Nien_2Y_2$ was described. In light of the structural data obtained, the interpretation of the chemical reactions and of the properties of the compounds obtained requires certain changes, since the authors quite naturally proceeded from the assumption of a monomeric structure of the complexes and a trans arrangement of the addends X and Y in all starting and resulting compounds. In particular, the first stage of the cocrystallization

reaction of $[Nien_4Cl_2]Cl_2$ and $[Nien_4Br_2]Br_2$ should probably be regarded as a simple exchange of outer-sphere anions X^- and Y^-, as a result of which two isomers could be formed: $[Nien_4Br_2]Cl_2$ and $[Nien_4Cl_2]Br_2$. Since, however, the data

according to electrical conductivity; the color and other properties of the solutions, given in (10), show that the nickel complexes under consideration readily dissociate into ions; the most probable result is the precipitation of crystals with a statistical distribution of some residues, i.e., $[Ni_2en_4ClBr]ClBr$, or of that one of the possible isomeric forms which has the lowest solubility. In the cocrystallization reaction of monomeric $Nien_2(NCS)_2$ and dimeric $(Nien_4Cl_2)Cl_2$, substitution of one of the rhodanide groups along the coordinate SCN—Ni—NCS by the outer-sphere

Fig. 2

Fig. 2

ion Cl^- must primarily take place. Therefore it is not excluded that a compound of gross composition $Nien_2NCSCl$ can in principle exist in two isomeric forms: as monomeric $[Nien_2NCSCl]$ with a trans arrangement of the acid residues, and as dimeric $[Ni_2en_4Cl_2](NCS)_2$ with a cis arrangement of the Cl atoms.

The authors of (10) note that all cocrystallization reactions of the compounds under consideration proceed in the direction of those compounds that have the poorest solubility. The exception is the reactions involving $Nien_2(NCS)_2$. This circumstance may presumably be connected with a difference in the structure of the initial compounds: upon exchange of outer-sphere anions or upon complete decomposition of the complexes into ions, the direction of the reaction should naturally be determined by the relative solubility of the compounds participating in the reaction; upon substitution of the inner-sphere group NCS by the ion X^-, the determining role should be played by the comparative strength of the Ni—NCS and Ni—Cl bonds. If this is indeed so and no rearrangement of the dimeric complexes occurs in the course of the reaction, then it may be assumed that compounds of composition $Nien_2X_2$, where X = J and NO_2, also have a dimeric structure. All these assumptions undoubtedly require structural verification. We intend subsequently to carry out a structural study of $Nien_2(NO_2)_2$ crystals, as well as of some compounds of the $Nien_2XY$ type, in order to elucidate the structure of the complexes and to detect ionization isomers.

We take this opportunity to express our gratitude to A. V. Babaeva for proposing that a structural study of compounds of this class be carried out and for providing crystals of the bromine salt.

Thus, determination of the crystal structure of the compounds $Nien_2Cl_2$ and $Nien_2Br_2$ showed that in the crystalline state both compounds are built of dimeric complex cations $[Nien_4X_2]^{2+}$ and anions X^-. The nickel atoms are octahedrally coordinated by two bidentate en groups and by two inner-sphere acid residues X, which are in the cis position. The latter serve as bridges be-

tween two Ni atoms of the dimeric cation. On the basis of the data obtained, a number of assumptions can be made about the course of exchange reactions in the formation of compounds of the type $Nien_2XY$, and a hypothesis can be advanced concerning the possibility that isomeric forms of the monomer–dimer type and of the ionization-isomerism type exist for these compounds.

Institute of General and Inorganic Chemistry
named after N. S. Kurnakov
Academy of Sciences of the USSR

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