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Abstract

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CRYSTAL STRUCTURE OF THE COMPLEX OF ZINC CHLORIDE WITH ACETONITRILE

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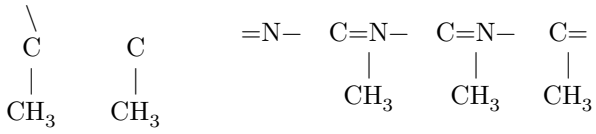
Complex compounds of metal halides are formed with ligands containing electron-donor atoms. In the formation of the crystalline structure of a complex, the spatial arrangement of the monomer molecules becomes ordered, facilitating their connection into polymer chains [(1)]. From the melt of the complex of zinc chloride with acetonitrile
$Cl_2Zn \cdot 2N \equiv C - CH_3$, polyacetonitrile is obtained,



which has semiconducting properties.

In order to establish the spatial structure of the complex and to obtain crystal-chemical data on the nature of the donor–acceptor bond, the crystal structure of $Cl_2Zn \cdot 2N \equiv C - CH_3$ was determined. Single crystals were grown from a solution of the complex in acetonitrile in a chamber filled with nitrogen. The single crystals were placed in thin-walled capillaries made of Pyrex glass. X-ray photographs were taken using Cu K_α radiation. X-ray data: orthorhombic system; $a = 12.83$ Å, $b = 10.04$ Å, $c = 6.65$ Å; space group D_{2h}^{16}—$Pnma$; number of molecules in the cell 4; density—X-ray 1.664, pycnometric 1.669 g/cm^3.

The structure determination was carried out by calculating three two-dimensional interatomic-vector functions and two projections of the electron density of the crystal.

The zinc and chlorine atoms occupy the special fourfold position 4c of the group $Pnma$ and are located in mirror symmetry planes m. The nitrogen and carbon atoms occupy the general eightfold position 8d.

The atomic coordinates are given below.

Fig. 1

Figure 1: Fig. 1

	x	y	z
Zn	0.997	0.250	0.250
Cl_1	0.924	0.250	0.547
Cl_2	0.161	0.250	0.164
N	0.925	0.100	0.125
C	0.889	0.035	0.243
CH_3	0.825	0.955	0.391

The coordinates x and y of all atoms were determined from the electron-density projection $\rho(xy)$. To determine the z coordinates of the zinc, chlorine, and nitrogen atoms, two interatomic-vector functions $p(xz)$ and $p(yz)$ and electron-density projections $\rho(xz)$ and $\rho(yz)$ were calculated. The z coordinates of the carbon atoms were calculated from geometrical analysis. The reliability factor R is equal to 0.19 for the structural amplitudes $F(hk0)$. For the synthesis of $\rho(xy)$, the magnitudes of 52 structural amplitudes $F(hk0)$ were measured. The atoms form a tetrahedral configuration of bonds: 2Zn—Cl and 2Zn ... N. The interatomic distances are Zn—Cl 2.17 Å and Zn ... N 2.0 Å. The valence angle Cl—Zn—Cl is equal to

131°. The projection of the structure along the [001] axis is given in Fig. 1. Fig. 2 shows the projection of the electron density $\rho(xy)$, with the relative heights of the peak maxima indicated. The number of isoelectron-density curves depicting the heavy zinc and chlorine atoms is reduced by half in comparison with the light nitrogen and carbon atoms. Judging from the magnitude of the maxima, the atomic peaks considerably exceed the false peaks arising from series-termination waves. The acetonitrile molecule has a linear configuration. The atomic coordinates will subsequently be refined from three-dimensional sections of the electron density.

Fig. 1

Polymerization of acetonitrile must be accompanied by the formation, in place of each triple bond $C \equiv N$, of one double bond $C = N$ and one single bond $C - N$. In Fig. 1, the thin dotted lines show the distances between the atoms N ... C of the nearest $C \equiv N$ bonds, approximately corresponding to the sum of the intermolecular radii of nitrogen and carbon.

In the crystal structure of the zinc chloride complex with acetonitrile, the shortest N ... C distances occur both between neighboring complexes and within complexes. In the initial zinc chloride molecule $ZnCl_2$, the interatomic distance $Zn - Cl$ is 2.05 Å and the valence angle

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

Fig. 2

$Cl-Zn-Cl$ is 180° ([2]). Comparison of the structure of the complex $Cl_2Zn \cdot 2N \equiv C-CH_3$ and of the $ZnCl_2$ molecule shows that, upon formation of the complex, the $Zn-Cl$ bonds lengthen by 0.12 Å and the valence angle $Cl-Zn-Cl$ decreases by 49°.

In the structurally similar complex of zinc chloride with thiourea, $Cl_2Zn \cdot 2S=C(NH_2)_2$ (Fig. 3), according to E. Yu. Koiranskaya, the interatomic distances $Zn-Cl$ are increased to 2.26 Å (i.e., by 0.21 Å in comparison with the $ZnCl_2$ molecule) and correspond to the $Zn-Cl$ distance, equal to 2.25 Å, in the tetrahedral ion $ZnCl_4^{2-}$ ([3]). In contrast to the structure of zinc chloride with acetonitrile, in the structure of zinc chloride with thiourea the shortest distances between the atoms S ... C of the $C-S$ bonds occur between neighboring complexes. An analogous result was obtained for the structure of chlo-

of cadmium chloride with thiourea, where, according to N. S. Ivanova, the interatomic distance Cd—Cl is considerably increased to 2.54 Å in comparison with the distance of 2.21 Å in the original molecule $CdCl_2$ ([4]).

As is seen from a comparison of the values of the interatomic distances Zn—Cl and the valence angles Cl—Zn—Cl in different complexes, the donor-acceptor bond of zinc chloride with acetonitrile is considerably weaker than the bond of zinc chloride with thiourea. This agrees with the conclusion of work ([5]), in which it was indicated that in complexes of boron fluoride with ligands containing nitrogen atoms, the strongest donor-acceptor bond B ···N is formed with pyridine and the weakest bond with acetonitrile.

Fig. 3

To establish the mechanism of polymerization, it is necessary to determine the influence of various structural factors on the polymerization process: 1) the mutual arrangement of monomer molecules in the crystal structures of the complexes; 2) the preservation of short-range order in the melt; 3) the strength of the donor-acceptor bond of metal halides with monomers and polymers. For this purpose, systematic structural investigations must be carried out.

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