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Abstract

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STRUCTURE OF THE ADDITION PRODUCTS OF AROMATIC AMINES WITH CADMIUM HALIDES

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The absorption of light, stereochemistry, stability, and other properties of complex compounds of elements occupying the middle of the large periods of D. I. Mendeleev' s system depend on chemical bonds involving *d*-orbitals. In the formation of complexes, ions and molecules coordinated around the central atom create an electric field around it. The superposition of the latter leads to splitting of the degenerate *d*-level, for example, with an octahedral arrangement of ligands, into a triplet d_ε and a doublet d_γ. At present it is believed that the bond between the central atom and the ligands is, at least in part, covalent. Applying the molecular-orbital method, Van Vleck (1) considered the bonding and antibonding bonds that result from the combination of the ligand σ-orbitals and the d_γ-orbitals of the cation. Other authors additionally take into account the contribution of π-orbitals—Kimball (2) for the case when the ligand is an electron acceptor, and Griffith and Orgel (3) for the case when the cation is the acceptor. Williams (4) believes that unsaturated ligands accept electrons from the d_ε-orbitals. Since molecular orbitals extend over the entire complex, its stability should increase as the number of attached ligands increases. Irving and Williams (5) see in this an explanation of the fact that the difference between stepwise stability constants is smaller for chelating aromatic ligands than for analogous aliphatic compounds. Williams expressed the opinion that πd_ε-bonds may be of decisive importance for the spatial structure of complexes and that, therefore, aliphatic amines of zinc are generally tetrahedral, whereas aromatic amines show no tendency to remain with coordination 4, and in these cases the cation gives octahedral complexes.

In our work (6) it was shown that the addition product of an aromatic amine (*n*-toluidine) with zinc chloride has a molecular lattice in which zinc is surrounded by 2 chlorine atoms and 2 nitrogen atoms, i.e., the same structure as zinc chloride diammine $ZnCl_2 \cdot 2NH_3$ (7). Thus it turned out that the conclusion reached by Williams does not agree with reality, and the replacement of ammonia by aromatic amines does not change the coordination number of zinc in compounds of the type $ZnX_2 \cdot 2A$.

As MacGillavry and Bijvoet (^{8}) showed, the addition product of ammonia with cadmium chloride has a chain structure with the coordination number of the metal equal to 6. It was of particular interest to compare the structures of the addition products of aliphatic and aromatic amines with cadmium.

The addition products of aniline or n-toluidine with cadmium halides have the composition $\mathrm{Cd\,Hal_2 \cdot 2\,Amine}$.

For the X-ray structural investigation, the addition product of aniline with cadmium iodide was taken. This product was obtained by mixing hot-

methanolic solutions of cadmium iodide and aniline in a molar ratio of 1 : 4. The crystals had the form of white rods.

Found, %:	Cd 20.21; J 45.93
$CdJ_2 \cdot 2C_6H_7N$. Calculated, %:	Cd 20.34; J 45.94

The X-ray structural study of the crystals obtained was carried out by the usual method. The parameters of the monoclinic cell, determined in an oscillation camera and refined on a KFOR X-ray goniometer, are: $a = 13.76 \pm 0.05$ Å; $b = 5.23 \pm 0.01$ Å; $c = 23.10 \pm 0.10$ Å; $\beta = 96^\circ \pm 20'$. The density, determined pycnometrically, is 2.32, which gives 4 formula units in the unit cell. The density determined roentgenographically is 2.23. As a result of indexing the X-ray goniometric photographs, the following extinction rule was established:

Reflection type	hkl	$h0l$	$0k0$
Condition under which this type of reflection is present	$h + k + l = 2n$	$h = 2n,\ l = 2n$	$k = 2n$

This regularity corresponds to the space groups $J2/a = C_{2h}^6$ and $Ja = C_s^4$.

The further investigation was carried out from X-ray goniometric photographs obtained in a camera for photographing the reciprocal lattice with Mo $K\alpha$-radiation. The values of F_{h0l}^2, obtained from 141 nonidentical reflections, served as the material for constructing a projection of interatomic vectors according to the formula

$$P_0(xz) = \sum_{h=-\infty}^{+\infty} \sum_{l=-\infty}^{+\infty} F_{h0l}^2 \cos 2\pi(hx + lz).$$

On the projection (Fig. 1) maxima No. 1 and No. 2 were clearly revealed; these were identified with the vectors Cd—J and J—J. Analysis of the weighted projection of interatomic vectors $P(xz)$ makes it possible to conclude that the

Fig. 1. $CdJ_2 \cdot 2H_2NC_6H_5$. Projection of the function of interatomic vectors on the plane (010). No. 1 is the peak corresponding to the Cd—J vector; No. 2 is the peak corresponding to the J—J vector

Figure 1: Fig. 1. $CdJ_2 \cdot 2H_2NC_6H_5$. Projection of the function of interatomic vectors on the plane (010). No. 1 is the peak corresponding to the Cd—J vector; No. 2 is the peak corresponding to the J—J vector

Fig. 2. $CdJ_2 \cdot 2H_2NC_6H_5$. 1 —Fcalc; 2 —Fexp

Figure 2: Fig. 2. $CdJ_2 \cdot 2H_2NC_6H_5$. 1 —Fcalc; 2 —Fexp

iodine atoms are at one height and are connected by a second-order axis passing through the cadmium atom. The cadmium atom occupies a fourfold position of the space group C_{2h}^6: 1/4, y, 0; 3/4, $1/2+y$, 1/2; 3/4, y, 0; 1/4, $1/2-y$, 1/2, where $y = -0.175$. The iodine atom occupies an 8-fold position with coordinates $x = 0.368$, $y = 0.475$, $z = 0.058$.

Fig. 1. $CdJ_2 \cdot 2H_2NC_6H_5$. Projection of the function of interatomic vectors on the plane (010). No. 1 is the peak corresponding to the Cd—J vector; No. 2 is the peak corresponding to the J—J vector.

The graph comparing the experimental and calculated values of the structural amplitudes (calculated only with allowance for the atoms of cadmium and iodine) permits one to judge their satisfactory agreement and, consequently, the correctness of the coordinates found (Fig. 2). From the coordinates of cadmium and iodine, the interatomic distances were calculated: Cd—J, equal to 2.77 Å, and J—J, equal to 4.20 Å. The Cd—J distance corresponds, within the experimental error, to the sum of the covalent radii of iodine (1.33 Å) and cadmium (1.49 Å). The distance between two iodine atoms connected by a second-order axis, equal to 4.20 Å, corresponds, within the experimental error, to the sum of the intermolecular radii of iodine (4.40 Å).

It follows from the data obtained that the addition product of aniline to cadmium iodide has a molecular lattice with tetrahedral coordination around the cadmium atom. Two vertices of the nearly regular tetrahedron are occupied by iodine atoms, and two by nitrogen atoms belonging to aniline molecules.

Hence a very interesting consequence follows: in zinc complexes, replacement of ammonia by an aromatic amine did not increase the coordination number of the metal, whereas in cadmium complexes it was found that such replacement even lowered the coordination number of the metal, which directly contradicts the conclusions drawn by Williams.

Fig. 2. $CdJ_2 \cdot 2H_2NC_6H_5$. 1 —F_{calc}; 2 —F_{exp}

As has already been noted (^{6}), these conclusions were not confirmed for compounds of divalent cobalt either. Cobalt chloride dihydrate $CoCl_2 \cdot 2H_2O$ (^{9}) and the violet form of dipyridinate $CoCl_2 \cdot 2Py$ (^{10}) form chain structures with cobalt coordination numbers equal to 6, whereas the addition product of *n*-toluidine, $CoCl_2 \cdot 2n-H_2N \cdot C_6H_4 \cdot CH_3$, has a molecular lattice in which the coordination number of the metal is equal to 4 ([11,12]).

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