CHEMISTRY

1958

SovietRxiv

Abstract

Full Text

CHEMISTRY

A. V. ABLOV and T. I. MALINOVSKII

STRUCTURE OF THE ADDITION PRODUCTS OF AROMATIC AMINES TO ZINC HALIDES

(Presented by Academician I. I. Chernyaev on 26 VI 1958)

There are two closely related theories that attempt to explain the influence exerted by ligands on the behavior of the *d*-electrons of the central atoms of elements occupying the middle of the first long period of D. I. Mendeleev' s system.

The first, also called the crystal-field theory, proceeds from the premise that in complexes the bond between the central atom and the ligands (ions and polar molecules) is electrostatic. From the course of the reasoning it follows that the potential energy of electrons in degenerate *d*-states changes in the electric field of the ligands. Recently this theory has been applied to explain the absorption spectra and stability of many complex ions.

Williams (1) believes that this theory in its modern form makes assumptions, not corresponding to reality, concerning the strength of the electrostatic field formed by different ligands. A. V. Ablov and M. P. Filippov (2,3) showed that the first absorption band of trivalent cobalt complexes of the type $[\mathrm{Co\ en_2(Amine)\ Hal}]X_2$ does not depend on the dipole moment of the aromatic amine, which is in contradiction with the electrostatic theory of the absorption spectra of complex compounds developed by Hartmann (4,5) on the basis of the crystal-field theory.

The second theory assumes that the bond in complexes has a partially covalent character. To apply this theory one may use the method of superposition of valence schemes or the method of molecular orbitals. Van Vleck (6) considered bonding and antibonding states between combinations of the σ-orbitals of ligands and the d_γ-orbitals of the cation. Griffith and Owen (7) additionally take into account π-orbitals for the case when the cation is an acceptor. A detailed consideration of this question shows that, with an increase in the number of unsaturated ligands in the complex, its stability should increase. Williams (1) believes that bonding πd_ε states may have decisive importance for the shape of molecules even in elements with filled *d*-shells. For this reason, complex compounds of zinc with aromatic amines should have an octahedral structure.

These conclusions were not confirmed for compounds of divalent cobalt. Indeed, whereas cobalt chloride dihydrate $CoCl_2 \cdot 2H_2O$ (^{8}) and the violet form of cobalt chloride dipyridinate $CoCl_2 \cdot 2Py$ (^{9}) form chain structures with coordination numbers for cobalt equal to 6, the addition product of *p*-toluidine to cobalt chloride $CoCl_2 \cdot 2n = H_2N \cdot C_6H_4 \cdot CH_3$ has a molecular lattice. In the molecule, two chlorine atoms and two nitrogen atoms are arranged around the cobalt atom (^{10,11}).

It is known that zinc chloride diamminate and, correspondingly, zinc bromide diamminate form a molecular crystal lattice, where each

the zinc atom is surrounded by two halogen atoms and two ammonia molecules, located at the vertices of a distorted tetrahedron (^{12}). In the dichlorodiamminezinc molecule the Zn—Cl and Zn—N bonds are covalent; their lengths are respectively equal to 2.30 ± 0.06 and 2.0 ± 0.1 Å.

It was of particular interest to determine the structure of the addition products of aromatic amines with zinc salts. For this purpose the structure of the product of addition of *p*-toluidine to zinc chloride, $ZnCl_2 \cdot 2n = H_2N \cdot C_6H_4 \cdot CH_3$, was studied. This compound was obtained by mixing slightly heated solutions of anhydrous zinc chloride and *p*-toluidine in absolute ethyl alcohol. On cooling, colorless needle-like plates separated; these were washed with alcohol and dried to constant weight in a desiccator over calcium chloride.

Fig. 1. Projection of the interatomic-vector function of $ZnCl_2 \cdot 2H_2N \cdot C_6H_4 \cdot CH_3$ onto the plane (010). No. 1—peak corresponding to the vector Zn—Cl, No. 2—peak corresponding to the vector Cl—Cl

Found, %: Zn 18.63; Cl 20.18
$ZnCl_2 \cdot 2C_6H_9N$. Calculated, %: Zn 18.65; Cl 20.23

The X-ray structural investigation of the crystals obtained was carried out by the usual method. The parameters of the monoclinic cell, determined on an oscillation camera, are: $a = 12.44 \pm 0.05$ Å, $b = 4.78 \pm 0.02$ Å, $c = 26.2 \pm 0.1$ Å, $\beta = 93°30' \pm 30'$. The density, determined pycnometrically, is 1.52, which gives, for the number of formula units in the unit cell, $n = 4.06 \simeq 4$. The density determined X-rayographically is 1.49. As a result of indexing the X-ray goniometric photographs, the following extinction rule was established:

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

This regularity corresponds to the space groups J^2, $a = C^6_{2h}$, and $J_a = C^4_s$.

Figure 2. Comparison plot of the intensities (I) of reflections of $ZnCl_2 \cdot$ 2n-toluidine (1) and $CoCl_2 \cdot$ 2n-toluidine (2)

Figure 1: Figure 2. Comparison plot of the intensities (I) of reflections of $ZnCl_2 \cdot$ 2n-toluidine (1) and $CoCl_2 \cdot$ 2n-toluidine (2)

The further investigation was carried out from X-ray goniometric photographs obtained in a back-reflection camera with Mo—Kα radiation. The total number of reflections used from the layer-line scans $h0l$, $h1l$, and $h2l$ was 421. The intensity was estimated visually, by blackening standards. The values of F^2 were found with allowance for the kinematic and polarization factors. On the basis of these data, two-dimensional F^2_{hkl}-series were constructed for the zero, first, and second layer lines

$$P_K(x,z) = \sum_{\substack{h \\ k=K}} \sum_{l} F^2_{(hkl)} \cdot \cos 2\pi(hx/a + lz/c)$$

$(K = 0, 1, 2)$. On the projection, maxima 1 and 2 (Fig. 1) were clearly revealed; these were identified with the vectors Zn—Cl and Cl—Cl. From analysis of the weighted two-dimensional F^2_{hkl}-series along the first and second layer lines, $P_1(xz)$ and $P_2(xz)$, it was possible to establish that the vector Cl—Cl is parallel to the plane XOZ, whence it follows that the chlorine atoms are connected by a twofold axis passing through the zinc atom. From comparison of the peak heights on the projections of the first—

of the first and second layer lines ($P_1(xz)$ and $P_2(xz)$), it was found that the chlorine atom is located at a height $y/b = 0.3$ relative to the plane in which the zinc atom is located. The Zn—Cl distance is 2.35 ± 0.05 Å. This value, in view of the weighted-projection method used for interatomic vectors, cannot claim high accuracy.

Fig. 2. Comparison plot of the intensities (I) of reflections of $ZnCl_2 \cdot$ 2n-toluidine **(1)** and $CoCl_2 \cdot$ 2n-toluidine **(2)**

The distance found indicates a predominantly covalent bond between the central atom and the halogen, as also in the structure of $CoCl_2 \cdot$ 2n-toluidine ([11]). The closeness of the lattice parameters, the coincidence of the space symmetry groups, and also the similarity of the projection diagrams of interatomic vectors led us to suppose that the addition products of para-toluidine with zinc chloride and cobalt chloride are isostructural. Comparison plots were constructed for the intensities of di-para-toluidine dicobalt chloride and di-para-toluidine dichlorozinc. As can be seen from Fig. 2, the intensities of both compounds have the same character of variation from reflection to reflection, which confirmed the isostructural nature of these compounds.

It follows from this that the structure of $ZnCl_2 \cdot$ 2n-toluidine is molecular. The zinc atom is located at the center of an almost regular tetrahedron, two vertices of which are occupied by Cl atoms and two by N atoms.

Thus, replacement of ammonia by aromatic amines does not change the coordination number of zinc in compounds of the type $ZnCl_2 \cdot 2A$, as was also found for the corresponding compounds of divalent cobalt.

The authors consider it their pleasant duty to express their gratitude to Corresponding Member of the Academy of Sciences of the USSR Ya. K. Syrkin for discussion of the results.

Moldavian Branch
of the Academy of Sciences of the USSR

Received
23 VI 1958

CITED LITERATURE

1. R. J. P. Williams, *J. Chem. Soc.*, **1956**, 8.
2. A. V. Ablov, M. P. Filippov, *Zhurn. neorg. khim.*, **2**, 42 (1957).
3. A. V. Ablov, M. P. Filippov, *Zhurn. neorg. khim.*, **2**, 2390 (1957).
4. F. E. Ilse, H. Hartmann, *Zs. Naturforsch.*, **6a**, 751 (1951).
5. H. Hartmann, H. Schläfer, *Angew. Chem.*, **66**, 768 (1954).
6. J. H. Van Vleck, *J. Chem. Phys.*, **3**, 807 (1955).
7. J. H. Griffiths, J. Owen, *Proc. Roy. Soc.*, A, **226**, 96 (1954).
8. B. K. Vainshtein, *DAN*, **68**, 301 (1949).
9. J. D. Dunitz, *Acta Cryst.*, **10**, 307 (1957).
10. G. B. Bokii, T. I. Malinovskii, A. V. Ablov, *Kristallografiya*, **1**, 49 (1956).
11. T. I. Malinovskii, *Kristallografiya*, **2**, 734 (1957).
12. G. H. McGillavry, J. M. Bijvoet, *Zs. Kristallogr.*, (A) **94**, 249 (1936).

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