THE CRYSTAL STRUCTURE OF THE ISOMORPHOUS DIHALOGENO-DI PYRIDINEATES OF COBALT AND ZINC

(THE PROBLEM OF THE NATURE OF THE ISOMERIC COBALT COMPOUNDS WITH COMPOSITION CoA₂X₂)

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A partial structural investigation of ZnPy₂Cl₂ and the isostructural CoPy₂Br₂ has been carried out. The angle Cl₁-Zn-Cl₁I is 126°. The angles N-Zn-Cl₁ and N-Zn-Cl₁I are 100-110°. The compound is molecular (monomeric); the complexes have a tetrahedral structure.

The violet α and blue β forms of the compounds CoA₂X₂ are polycoordination isomers; the α forms are polymers with octahedral coordination about Co; the β forms are monomers with tetrahedral coordination.

The transition metals of the fourth period form a large group of compounds with the composition M II A₂X₂, where M II = Mn, Fe, Co, Ni, Cu, Zn; X = monovalent acid residue; A = H₂O, NH₃, Py and other organic ligands.

It is particularly interesting that the cobalt compounds with this composition occur in two isomeric series which differ both in the color of the crystals and in the chemical properties; the α series have reddish violet crystals and the β series blue ones. The most characteristic members of these series are the violet and blue crystals of CoPy₂Cl₂. The problem of the structures of these isomers has several times attracted the attention of investigators.

Use of Werner's coordination theory led Blitz and Fektenheuer[1] and Hantzsch[2] to the conclusion that the α and β forms were geometric isomers, i.e., trans- and cis-isomers. Cox and his co-workers[3] supported this idea. They carried out the first crystallographic and x-ray measurements of both CoPy₂Cl₂ modifications. From the small value of the period c in α-CoPy₂Cl₂ crystals they attributed a trans square planar structure to this complex. Correspondingly a cis-structure was attributed to the blue form. In this work it was also shown that β-CoPy₂Cl₂ is isomorphous with CoPy₂Br₂ and CoPy₂I₂. Cox's suggestion of a square structure for CoPy₂Cl₂ was refuted by Mellor and Coryell[4] on the basis of the magnetic moments of these compounds. Mellor and Coryell were led to the conclusion that α-CoPy₂Cl₂ has a chain structure with octahedral coordination around Co, and that the blue β-form has a tetrahedral structure.

The stereochemical conclusions of Mellor and Coryell concerning the isomeric dichlorodipyrindinocobalts were further directly supported by the structural investigations of Vainshtein[5] [Co(H₂O)₂Cl₂ with octahedral coordination], Malinovskii [6] [Co(p-CH₃C₆H₄NH₂)₂Cl₂ and Co(p-CH₃C₆H₄NH₂)₂I₂ with tetrahedral coordination] and finally by structural investigations of the crystals of α-CoPy₂Cl₂ itself in papers by Porai-Koshits and
Tishchenko [7], Dunitz [8] and Ferroni and Bondi [9] who independently showed that $\alpha$-CoPy$_2$Cl$_2$ has a chain structure with octahedral coordination around Co. However, the final solution of the problem of the nature of the $\alpha$ and $\beta$ isomers of CoPy$_2$Cl$_2$ undoubtedly requires that structural data on the second, $\beta$ form of this compound be obtained. It is true that the instability of $\beta'$-CoPy$_2$Cl$_2$ prevents one from obtaining experimental x-ray data directly from samples of this compound. But it has been established convincingly that this compound is isostructural with CoPy$_2$Br$_2$ and the latter (as the result of our investigations) with ZnPy$_2$Cl$_2$. This makes it possible to use these compounds as models for determining the structure of $\beta$-dichlorodipyridinocobalt.

![Image of crystal habits](image)

**Fig. 1. Crystal habit of CoPy$_2$Br$_2$ and ZnPy$_2$Cl$_2$.**

The discovery by Cox that $\beta$-CoPy$_2$Cl$_2$ and CoPy$_2$Br$_2$ are isostructural was confirmed by comparing Debye photographs of these compounds. The isostructural nature of CoPy$_2$Br$_2$ and ZnPy$_2$Cl$_2$ followed directly from the equality of their crystallographic characteristics and lattice parameters. The crystals of CoPy$_2$Br$_2$ and ZnPy$_2$Cl$_2$ have almost identical habits (Fig. 1). Goniometric measurements showed that the crystals belonged to the monoclinic-prismatic symmetry form. The lattice parameters were determined from three oscillating x-ray photographs:

**Table 1**

<table>
<thead>
<tr>
<th></th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$\beta$</th>
<th>Space group</th>
<th>$d_{\text{meas}}$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoPy$_2$Br$_2$</td>
<td>8,40</td>
<td>18,0</td>
<td>8,52</td>
<td>101°15'</td>
<td>P2$_1$/c</td>
<td>1,87</td>
<td>4</td>
</tr>
<tr>
<td>ZnPy$_2$Cl$_2$</td>
<td>8,44</td>
<td>17,5</td>
<td>8,25</td>
<td>102°</td>
<td>P2$_1$/c</td>
<td>1,64</td>
<td>4</td>
</tr>
</tbody>
</table>

* Our Debye photographs showed that $\alpha$-CoPy$_2$Cl$_2$ and NiPy$_2$Cl$_2$ are isostructural.