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The Structure of a New Addition Complex of Zinc Iodide with a Schiff Base

N. BRESCIANI PAHOR*, L. RANDACCIO
Istituto di Chimica, Università di Trieste, 34127 Trieste, Italy

and E. LIBERTINI
Istituto Dipartimentale di Chimica e Chimica Industriale, Università di Catania, 95125 Catania, Italy

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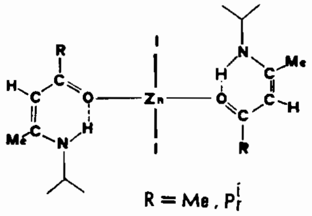
Schiff bases in their anionic form act as polydentate ligands of metal atoms. The structural features of many such complexes with different kinds of metal ions have been extensively studied [1] To our knowledge, however, only in one case has it been shown by means of structure analysis, that a Schiff base, bis(salicylaldehyde)ethylenediamine (salenH$_2$), acts as a neutral ligand coordinating tin(IV) atom through its oxygen atoms [2].

Recently, addition complexes of zinc iodide with Schiff bases derived from β diketones and i-propylamine of formula I$_2$ZnA$_2$ (A = Schiff base) have been reported [3]. On the basis of mass spectrometry and infrared data these adducts have been suggested to adopt a tetrahedral *trans*-structure (Scheme)



R = Me, Pr^i

The benzene solution of the derivative with R = Me gave white crystals which were suitable for structural study. The crystals are orthorhombic with unit-cell parameters a = 15.798(8), b = 10.374(4), c = 44.26(1) Å, V = 7254 Å^3, D_{exp} = 1.67 g cm^{-3}, D_{calc} = 1.65 g cm^{-3}, with Z = 12 I$_2$Zn(C$_{16}$H$_{30}$O$_2$N$_2$)$_2$ units, space group *Pna2*$_1$. X-ray intensity data were collected on a SIEMENS AED automatic diffractometer using MoK$_\alpha$ radiation. A total of 2761 independent reflexions, having $I_0 > 3\sigma(I_0)$ and $\theta \leqslant 28°$, were collected and corrected for Lorentz-polarization and absorption effects (μ = 48.6 cm^{-1}, $0.02\langle r_{crystal}\rangle 0.03$ cm). Vector distribution on the Patterson map unequivocably suggested the non centrosymmetric space group. Direct methods with the program MULTAN were used to locate the six I and three Zn independent atoms, while Fourier syntheses yielded the rest of the structure. Least-squares refinement gave a present value of R = 0.058.

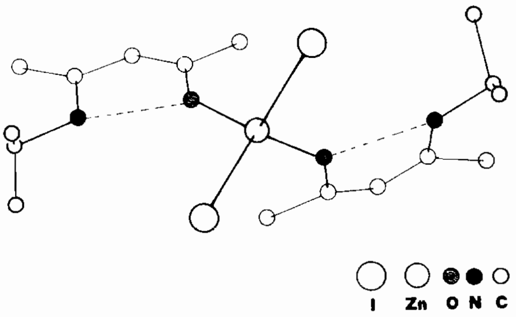


Fig. 1. A view of one of the three independent molecules along the pseudo C_2 axis.

The unique portion of the structure consists of three independent, but very similar I$_2$ZnA$_2$ units, one of which is shown in Fig. 1. The molecules in the solid state have a distorted tetrahedral stereochemistry of rough C_2 symmetry with a nearly *trans*-arrangement of the two Schiff bases coordinated through their oxygen atoms as previously suggested [3]. The mean $\widehat{I{-}Zn{-}I}$ angle of 120.8(2)° largely deviates from ideality in order to minimize the I···I non-bonded interactions. The mean $\widehat{O{-}Zn{-}O}$ angle of 104(1)° reflects the larger $\widehat{I{-}Zn{-}I}$ angle. As a probable consequence, the Zn–I bond lengths, ranging from 2.557(5) to 2.573(6) Å with a mean value of2.564 Å, are slightly but significantly shorter than the mean value of 2.605(1) Å found in the nearly tetrahedral ZnI$_4^=$ anion [4]. A similar trend in bond lengths and angles has been found in Cl$_2$ZnB$_2$ complexes (B = Lewis base) [5].

The atoms of the Schiff base are approximately coplanar with exception of the two isopropilic methyl groups. The N···O distances, which vary from 2.53(4) to 2.66(4) Å, indicate that the intramolecular hydrogen bond in the free ligand [6] is retained after coordination as found in SalenH$_2$-SnCl$_2$Me$_3$ [2] and in agreement with I.R. evidences [3]. Unfortunately, because of the low accuracy of the positional parameters of the light atoms it is difficult to state if the coordinated Schiff base exists in the enoliminic or in the ketoaminic form. However since this base is chemically more similar to bis(acetylacetone)ethylenediamine (acacenH$_2$) than to salenH$_2$, an enoamineketone structure is the most probable. In fact it has been shown that acacenH$_2$ exhibits in the solid state [6b] and in solution [7] the latter structure, while salenH$_2$ prefers the enoliminic one [6a].

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*Author to whom correspondence should be addressed.

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