The Structure of Basic Zinc *OO*-Dialkyl Phosphorodithioates

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WHILST preparing zinc *OO*-di-n-butyl phosphorodithioate (I, R = Bu^n) from zinc chloride and sodium *OO*-di-n-butyl phosphorodithioate in aqueous solution, Wystrach, Hook, and Christopher[1] isolated, as a by-product, the first of a new class of basic zinc salts. On the basis of elemental analyses and neutralisation equivalents from non-aqueous acid–base titrations, they suggested a basic double-salt formula (II; R = Bu^n) for this product. The formation of the basic salt was found to depend on the presence of hydroxyl ions and it was claimed that either the normal salt (I) or the basic salt (II) could be exclusively formed according to the stoicheiometry of the following equations:

$$2(RO)_2PS_2^- + Zn^{2+} \rightarrow Zn[S_2P(OR)_2]_2 \quad (I)$$

$$3(RO)_2PS_2^- + OH^- + 2Zn^{2+} \rightarrow Zn_2[S_2P(OR)_2]_3OH \quad (II)$$

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[1] V. P. Wystrach, E. O. Hook, and C. L. M. Christopher, *J. Org. Chem.*, 1956, **21**, 705.

The isopropyl derivative of the basic salt was similarly prepared and characterised as (II; R = Pr^i). Finally, the authors mentioned, without comment, that the infrared spectra of these basic salts did not contain an absorption due to the O–H stretching frequency.

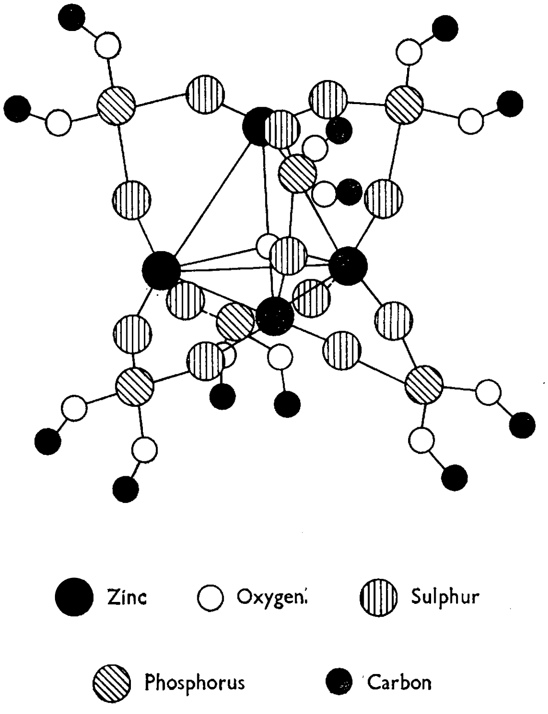
Later, Bacon and Bork[2] isolated further examples of this type of basic salt as by-products from the preparation of the normal salts (I) using zinc oxide and *OO*-dialkyl hydrogen phosphorodithioates. They confirmed, by titration, the previously suggested structure (II).

We have prepared, by the former method, the basic isopropyl salt, m.p. 214—215°, and the basic n-butyl salt, m.p. 154—155°, and have confirmed, by infrared and nuclear magnetic resonance spectroscopy, that these compounds do not contain a hydroxyl group. This leads us to suggest that a more acceptable formula for the basic salt is $Zn_4[S_2P(OR)_2]_6O$ (III) which requires, for R = Pr^i and for (III, R = Bu^n) figures virtually the same as those required by (II). Further, (III) would have the same neutralisation equivalents as the suggested double salt (II). The molecular structure of (III), by analogy with that established for basic beryllium acetate[3–5] and basic zinc acetate[6,7] would be as shown in the Figure, consisting of a central oxygen atom surrounded tetrahedrally by four zinc atoms and the six *OO*-dialkyl phosphorodithioate groups attached symmetrically to the six edges of this tetrahedron.

Molecular weights of both the isopropyl and n-butyl basic salts were determined ebullioscopically, cyclohexane being used as solvent, and by vapour-pressure osmometer, with benzene as solvent. The results were different according to solvent and method but were generally about half way between the values calculated from formulae (II) and (III), which provided supporting but not convincing evidence for formula (III).

Single-crystal *X*-ray crystallographic studies were made and provided more conclusive evidence. Crystals of the isopropyl basic salt are monoclinic with $a = 24{\cdot}93 \pm 0{\cdot}08$ Å, $b = 22{\cdot}76 \pm 0{\cdot}05$ Å, $c = 13{\cdot}67 \pm 0{\cdot}02$ Å, $\beta = 113° 28' \pm 15'$, $d = 1{\cdot}47$ g./c.c. (±1%). The space group is $P2_1/a$, and four molecules per unit cell being assumed, $M_{\text{calc.}}$ is 1575 ± 30; (III; R = Pr^i; *M*, 1557). By contrast, crystals of the n-butyl basic salt are trigonal with hexagonal axes $a_{\text{hex}} = 23{\cdot}9 \pm 0{\cdot}2$ Å, and $c_{\text{hex}} = 12{\cdot}84 \pm 0{\cdot}08$ Å, *d* 1·34 g./c.c. (±1%); the true cell being rhombohedral with $a_r = 14{\cdot}45$ Å and $\alpha = 111° 36'$. Three molecules being assumed per hexagonal cell, $M_{\text{calc.}}$ is 1710 ± 50 (III; R = Bu^n requires *M*, 1725). There are no space group extinctions (other than $-h + k + l = 3n$) and only three-fold diffraction symmetry is present so that the space group is $R3$ or $R\bar{3}$. In the space group $R\bar{3}$ the presence of one molecule in the rhombohedral cell demands that the molecule should have $\bar{3}$ symmetry which is impossible with four zinc atoms. The correct space group is therefore $R3$ which, in further agreement with our proposed structure of (III), makes the demand that the zinc atoms have a tetrahedral form with one zinc atom, and the central oxygen atom, lying on the three-fold axis.

We cannot at present account for the molecular weights obtained by the standard methods



Full alkyl group not shown

(Not to scale)

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[2] W. E. Bacon and J. F. Bork, *J. Org. Chem.*, 1962, **27**, 1484.

[3] W. H. Bragg and C. T. Morgan, *Proc. Roy. Soc.*, 1923, **104**, 437.

[4] G. T. Morgan and W. T. Astbury, *Proc. Roy. Soc.*, 1926, **112**, 441.

[5] L. Pauling and J. Sherman, *Proc. Nat. Acad. Sci. U.S.A.*, 1934, **20**, 340.

[6] J. W. Wyart, *Bull. Soc. franç. Min.*, 1926, **49**, 148.

[7] H. Koyama and Y. Saito, *Bull. Chem. Soc. Japan*, 1954, **27**, 112.

described above; however, the infrared and nuclear magnetic resonance spectra exclude the double-salt formula (II), and the *X*-ray results obtained give strong support to our proposed structure shown in the figure.

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