# *X*-Ray Structures of $[Zn(S_2CNMe_2)_3]^-$ and $[Zn(C_7H_4NS_2)_3(OH_2)]^-$, Possible Intermediates in Zinc-assisted Rubber Vulcanisation

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*Summary* Reaction of $[Zn(S_2CNMe_2)_2]$ or $[Zn(C_7H_4NS_2)_2]$ ($C_7H_5NS_2$ = 2-mercaptobenzothiazole) with stearic acid in the presence of $R_4NOH$ (R = Et or $Bu^n$) afforded $[Et_4N][Zn(S_2CNMe_2)_3]$(I), and $[Bu^n{}_4N][Zn(C_7H_4NS_2)_3]\cdot H_2O$ (II), respectively, and the structures of (I) and (II) have been determined crystallographically.

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It has been proposed[1] that, in the zinc dithiocarbamate-assisted† acceleration of the vulcanisation of natural rubber, $[Zn(S_2CNR_2)_2]$ forms 1:2 adducts with naturally occurring fatty acids, *e.g.* stearic acid. The suggestion has been made that these adducts are the source of nucleophilic dithiocarbamate ion which could attack sulphur, present in the vulcanising ingredients, thereby forming perthiocarbamates. These polysulphidic anions could then react with the rubber hydrocarbon polymer forming intermediates

structure was solved by conventional Patterson and Fourier methods and refined by block-diagonal least-squares to $R = 0{\cdot}043$, allowing anisotropic thermal motions for all non-hydrogen atoms. The contributions of all hydrogen atoms (located from difference Fourier syntheses) were included in the final cycles of structure factor calculations but parameters were not allowed to vary.

A crystal of tetra-n-butylammonium aquatris(benzothiazolethiolato)zincate (II), was obtained from aqueous acetone, and gave the following crystal data: $C_{37}H_{49}N_4OS_6Zn$, $M = 823{\cdot}58$; monoclinic, $a = 9{\cdot}854(5)$, $b = 16{\cdot}027(13)$, $c = 27{\cdot}008(22)$ Å, $\beta = 94{\cdot}325(6)^\circ$, $U = 4253(5)$ Å$^3$, $D_c = 1{\cdot}286$, $D_m = 1{\cdot}28$ g cm$^{-3}$, $Z = 4$; space group $P2_1/c$ ($C^5_{2h}$, No. 14) from systematic absences. The data were collected and the structure solved and refined as described for (I) using 3407 independent reflections, converging to $R = 0{\cdot}040$

atom is at a distance of 3·12 Å. The co-ordination geometry of the zinc atom is close to tetrahedral (distorted trigonal bipyramidal if all three exocyclic S atoms are considered to be bonded to Zn). The zinc is displaced from the main planes of each of the bts ligands by 0·43, 0·78, and 0·06 Å, the first value referring to the uniquely co-ordinated ligand, which is further asymmetrically co-ordinated in that the zinc atom is significantly displaced from the external bisector of the C–N–C bond angle. The Zn–N–C angles of 113 and 133° are such as to give rise to a shorter-than-necessary Zn–S contact which is very similar in length to those found in (I). In neither (I) nor (II) is a Zn–S contact of this magnitude (van der Waals distance is 3·27 Å) a necessary consequence of intramolecular or intermolecular constraints, there being available intramolecular rotational pathways which would ease undesirable interaction at negligible cost to the potential energy of the system. It may therefore be concluded that a weak bonding interaction between zinc and sulphur occurs in these two species. It may be noted that in (II), the unique ligand, in its interaction with zinc, may be formally represented as the anion derived from (**1a**) while the other two ligands may be represented as derived from (**1b**). In each molecule, the geometry of the tetraalkylammonium cation is unexceptional.

The structures of both (I) and (II) reveal, unexpectedly, that at least two of the potentially chelating ligands are only weakly bidentate with respect to zinc. This mode of bonding may facilitate attack by dithiocarbamate or bts$^-$ ion at elemental sulphur giving perthiocarbamate or $[(\text{bts})\text{–}S_x]^-$. In connection with this point, we have observed that (I) reacts with $S_8$ in boiling toluene to give a deep red solution, while $[\text{Zn}(S_2\text{CNMe}_2)_2]$ is inert. The nature of the red solution is being investigated.

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[1] P. W. Allen, D. Barnard, and B. Saville, *Chem. in Britain*, 1970, **6**, 382.

[2] J. A. McCleverty and N. J. Morrison, *J.C.S. Chem. Comm.*, 1974, 1048; *J.C.S. Dalton*, in the press.

[3] C. L. Raston and A. H. White, *J.C.S. Dalton*, 1976, 36, 791, and references therein; J. H. Noordik, *Crystal Structure Comm.*, 1973, **2**, 81.

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