# Aspects of the Inorganic Chemistry of Rubber Vulcanisation. Part 1. Reactions of Zinc Bis(dithiocarbamates) and Bis(benzothiazole-2-thiolates) with Carboxylates, and the Structure of $[NBu^n_4][\{Zn(S_2CNMe_2)_2\}_2(\mu\text{-}OCOMe)]$ †

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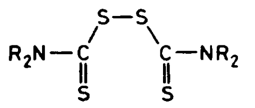
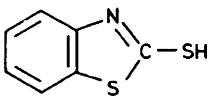
Reaction of $[Zn(S_2CNMe_2)_2]$ with $[NR_4][OCOR']$ (R = Me or $Bu^n$; R' = Me, Et, $Pr^n$, or $Bu^n$) gives $[NR_4][Zn(S_2CNMe_2)_2(OCOR')]$, but when R' = n-$C_5H_{11}$, n-$C_6H_{13}$, n-$C_7H_{15}$, n-$C_8H_{17}$, or $C_{17}H_{35}$, $[NR_4][Zn(S_2CNMe_2)_3]$ only has been isolated. Treatment of $[\{Zn(C_7H_4NS_2)_2\}_n]$($C_7H_5NS_2$ = 2-mercaptobenzothiazole) with $[NBu^n_4][OCOR']$(R' = Me or $C_{17}H_{35}$) gives only $[NBu^n_4][Zn(C_7H_4NS_2)_3(OH_2)]$. The structure of $[NBu^n_4][\{Zn(S_2CNMe_2)_2\}_2(\mu\text{-}OCOMe)]$, obtained after recrystallisation of $[NBu^n_4][Zn(S_2CNMe_2)_2(OCOMe)]$, has been determined crystallographically. The molecule consists of two five-co-ordinate zinc atoms, each having an essentially square-pyramidal geometry ($S_4O$ co-ordination), bridged by the acetato-group. The relevance of these compounds to certain aspects of the activation of sulphur in rubber vulcanisation is briefly discussed.

THE vulcanisation of rubber is a process whereby links between polymeric unsaturated hydrocarbon chains are produced chemically, leading to a network structure of high molecular weight. Rubber can be vulcanised by sulphur alone, and, using eight parts of $S_8$ per 100 parts of rubber, cross-linking may be accomplished in 5 h at 140 °C. However, when zinc oxide is added, the time for complete vulcanisation is significantly reduced (to 3 h). The further inclusion of ' accelerator ' molecules, *e.g.* organosulphur compounds such as tetra-alkylthiuram disulphides, (1), or 2-mercaptobenzothiazole, (2) ($C_7H_5NS_2$), leads to dramatically reduced vulcanisation times (5—10 min) as well as affording some control over the speed and efficiency of the vulcanisation process and effecting an improvement in the nature and stability of the cross-links.



(1)



(2)

Specific accelerator formulations include ZnO, $S_8$, fatty acids (usually stearic), and, for example, $[Me_2NC(=S)S]_2$, (1; R = Me), or (2). This mixture reacts at 120—150 °C to form a ' sulphurating system ' which, it is thought,[1] may contain $[S_xC(=S)NMe_2]^-$ or $[C_7H_4NS_x]^-$ ($x > 1$), perhaps bound to zinc. In effect, these perthio-species may be regarded as a form of ' activated ' sulphur, and attack by these or related derivatives on the rubber hydrocarbon affords an intermediate containing sulphur atoms linked to parts of the accelerator molecule and bound to the rubber hydrocarbon backbone. This intermediate, whose existence is clearly established,[2] is subsequently degraded in the presence of ZnO and/or zinc complexes to give hydrocarbon chains linked by polysulphidic groups which are themselves ultimately broken down to monosulphidic cross-links in the fully vulcanised product.

One of the, as yet, unsolved mysteries of the vulcanisation process is the precise mode of sulphur ' activation '. If perthio-species such as $[S_xC(=S)NMe_2]^-$ or $[C_7H_4NS_x]^-$ ($x > 1$) are important in this respect, then they must presumably be produced either by generation of ' free ' $[S_2CNMe_2]^-$ or $[C_7H_4NS_2]^-$ which can then nucleophilically attack $S_8$, or by insertion of $S_8$ into Zn–S or C–S bonds in $[Zn(S_2CNMe_2)_2]$ or $[\{Zn(C_7H_4NS_2)_2\}_n]$.‡ It is known that zinc oxide reacts with (1) or (2) giving $[Zn(S_2CNR_2)_2]$ or $[\{Zn(C_7H_4NS_2)_2\}_n]$ but neither of these zinc complexes has appreciable solubility in hydrocarbons or shows significant reactivity towards sulphur. In an earlier communication, we observed[3] that $[Zn(S_2CNMe_2)_3]^-$, $[Zn(C_7H_4NS_2)_3(OH_2)]^-$, and especially $[S_2CNMe_2]^-$, as their $[NR_4]^+$ salts, formed red oils when heated with $S_8$ in xylene. We further noted that neither $[Zn(S_2CNMe_2)_2]$ nor $[\{Zn(C_7H_4NS_2)_2\}_n]$ would form these red oils in the presence of sulphur in refluxing xylene. It was subsequently found that vulcanising mixtures containing $[Zn(S_2CNMe_2)_3]^-$ or $[S_2CNMe_2]^-$ are extremely fast accelerators, significantly more so than $[Zn(S_2CNMe_2)_2]$. We therefore concluded that it was possible that the red oils may contain $[S_xC(=S)NMe_2]^-$ or $[C_7H_4NS_x]^-$ ($x > 1$), either as ' free ' $[NR_4]^+$ salts or bound to zinc. Whether this is true nor not, it appears that vulcanisation, and so presumably $S_8$ activation, is greatly facilitated by the presence of *anionic* species in the ' sulphurating system '. What is not clear, however, is how such anionic species might be generated.

Many accelerator mixtures contain stearic acid and, indeed, it has been suggested[4] than zinc dithiocarbamates and benzothiazolethiolates form 1 : 2 adducts with this acid. Such adduct formation, it is postulated, may enhance the nucleophilicity of the co-ordinated dithio-

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† Tetra-n-butylammonium μ-acetato-*O,O'*-bis[bis(dimethyldithiocarbamato)zincate].

‡ The compound $[Zn(S_2CPh)_2]$ reacts with $S_8$ giving $[Zn(S_3CPh)_2]$; D. Coucouvanis, J. P. Fackler, jun., J. A. Fetchin, and W. C. Seidel, *J. Amer. Chem. Soc.*, 1968, **90**, 2784.

carbamate towards attack on $S_8$. In an earlier paper, we observed[5] that acetate forms only a 1 : 1 adduct with $[Zn(S_2CNMe_2)_2]$, *viz.* $[NR_4][Zn(S_2CNMe_2)_2(OCOMe)]$. The formation of this ***anionic*** metal complex, with its implications for sulphur activation, prompted us to investigate more fully the behaviour of $[Zn(S_2CNR_2)_2]$ and $[\{Zn(C_7H_4NS_2)_2\}_n]$ with carboxylate anions.

## RESULTS AND DISCUSSION

*Synthetic Studies.*—Treatment of $[Zn(S_2CNMe_2)_2]$ with $[NMe_4][OCOR']$ ($R' = Me$, Et, $Pr^n$, or $Bu^n$) afforded the 1 : 1 adducts $[NMe_4][Zn(S_2CNMe_2)_2(OCOR')]$. Those species containing $R' = Bu^n$ did not afford satisfactory analytical data (Table 1). Indeed, in the reactions with $[NMe_4][OCOBu^n]$ the species $[NMe_4][Zn(S_2CNMe_2)_3]$ was also formed, and attempts to separate this from the carboxylato-adduct by recrystallisation resulted only in the recovery of the tris(dithiocarbamato)zincate. In all other reactions with longer chain carboxylato-anions, only $[Zn(S_2CNMe_2)_3]^-$ was isolated. Similar results were obtained with the $[NBu^n{}_4]^+$ salts of the carboxylic acids. Occasionally, on attempted recrystallisations of the carboxylate adducts, only $[Zn(S_2CNMe_2)_2]$ could be recovered.

TABLE 1

Analytical data (%) obtained from new zinc sulphur complexes

| | Found | | | | Calc. | | | |
|---|---|---|---|---|---|---|---|---|
| Complex | C | H | N | S | C | H | N | S |
| $[NMe_4][Zn(S_2CNMe_2)_2(OCOMe)]$ | 33.0 | 5.9 | 9.6 | 31.2 | 32.8 | 6.2 | 9.6 | 29.2 |
| $[NMe_4][Zn(S_2CNMe_2)_2(OCOEt)]$ | 34.3 | 6.4 | 9.0 | 27.6 | 34.5 | 6.5 | 9.3 | 28.3 |
| $[NMe_4][Zn(S_2CNMe_2)_2(OCOPr^n)]$ | 35.9 | 6.6 | 9.0 | 27.5 | 36.0 | 6.7 | 9.0 | 27.5 |
| $[NMe_4][Zn(S_2CNMe_2)_3]\cdot H_2O$ | 30.0 | 6.0 | 10.7 | 38.5 | 30.1 | 6.2 | 10.8 | 37.1 |

When $[\{Zn(C_7H_4NS_2)_2\}_n]$ was treated with $[NBu^n{}_4][OCOR']$, only the known $[NR_4][Zn(C_7H_4NS_2)_3(OH_2)]$,[3] together with $[Zn(OCOR')_2]$ or basic zinc carboxylate, was formed, irrespective of the nature of R′ and the reaction conditions.

TABLE 2

Important i.r. spectral data (cm$^{-1}$) obtained from selected zinc sulphur complexes and related species

| Complex | Specific assignments | Other bands * (1 300—1 500 cm$^{-1}$) |
|---|---|---|
| $[NMe_4][Zn(S_2CNMe_2)_2(OCOMe)]$ | 1 570vs[ν(OCO)], 1 524vs[ν(CN)], 975m[ν(SCS)] | 1 489s, 1 430m (sh), 1 405s, 1 392s, 1 386s (sh), 1 342vw |
| $[NBu^n{}_4][Zn(S_2CNMe_2)_2(OCOMe)]$ | 1 578vs[ν(OCO)], 1 520vs[ν(CN)], 990m[ν(SCS)] | 1 481s, 1 466m, 1 461m, 1 446w, 1 409m (sh), 1 404m, 1 378s, 1 348 (sh), 1 323w, 1 314vw |
| $[NMe_4][Zn(S_2CNMe_2)_2(OCOEt)]$ | 1 568vs[ν(OCO)], 1 522vs[ν(CN)], 974m[ν(SCS)] | |
| $[NMe_4][Zn(S_2CNMe_2)_2(OCOPr^n)]$ | 1 560vs[ν(OCO)], 1 526vs[ν(CN)], 975m[ν(SCS)] | |
| $[NMe_4][Zn(S_2CNMe_2)_3]$ | 1 505vs[ν(CN)], 1 490vs[ν(CN)] | 1 483s, 1 460 (sh), 1 445m, 1 395m, 1 378 (sh), 1 366 (sh) |
| $[NBu^n{}_4][Zn(S_2CNMe_2)_3]$ | 1 505vs,br[ν(CN)] | 1 483s, 1 468m, 1 460w, 1 442w, 1 404w, 1 397m, 1 376vs, 1 316vw |
| $[Zn(S_2CNMe_2)_2]$ | 1 520vs[ν(CN)], 972m[ν(SCS)] | 1 445w, 1 405m, 1 390s, 1 340vw |
| $[NMe_4][S_2CNMe_2]$ | 1 485vs[ν(CN)] | 1 476m, 1 445w, 1 413vw, 1 385vw, 1 350s |
| $[NBu^n{}_4][Zn(C_7H_4NS_2)_3\cdot H_2O]$ | 3 900m[ν(OH)] | 3 050w, 1 450s, 1 350vs, 1 015s |

* In KBr discs.

These observations seem to be consistent with equilibria (1) and (2).

$$2[Zn(S_2CNR_2)_2] + 2[OCOR']^- \rightleftharpoons 2[Zn(S_2CNR_2)_2(OCOR')]^- \rightleftharpoons [Zn(S_2CNR_2)_3]^- + [Zn(OCOR')_2] + [S_2CNR_2]^- \quad (1)$$

$$[\{Zn(C_7H_4NS_2)_2\}_n] + n[OCOR']^- \rightleftharpoons n[Zn(C_7H_4NS_2)_2(OCOR')]^- \rightleftharpoons (n/2)[Zn(C_7H_4NS_2)_3(OH_2)]^- + (n/2)[Zn(OCOR')_2] + (n/2)[C_7H_4NS_2]^- \quad (2)$$

*Spectral Characterisation.*—From i.r. spectral studies of dithiocarbamato-complexes it is possible, in principle, to distinguish between symmetrically and asymmetrically bound $S_2CNR_2$ by studying the nature of the absorptions in the region around 1 000 cm$^{-1}$. The structurally characterised[3] $[Zn(S_2CNMe_2)_3]^-$, which contains one symmetric and two asymmetric sulphur ligands, exhibits two bands (KBr disc) near 1 000 cm$^{-1}$ (Table 2). These are due to the $Zn(S_2C-)$ group and are consistent with the structure of the complex. The species $[Zn(S_2CNMe_2)_2(OCOR')]^-$, however, exhibit only one band in this region, indicating that both sulphur ligands are probably bound equivalently to the metal.

In principle, it is also possible to distinguish between uni- and bi-dentate carboxylato-groups by i.r. spectroscopy, the former in general exhibiting[6] ν(OCO; asym) and ν(OCO; sym) in the ranges 1 580—1 650 and 1 310—1 390 cm$^{-1}$, respectively. The chelating mode is characterised by bands in the ranges 1 490—1 540 and 1 400—1 470 cm$^{-1}$, respectively.

An inspection of the spectra of the carboxylato-adducts (important spectral data are summarised in Table 2) in the region 1 500—1 600 cm$^{-1}$ reveals the presence of two absorptions, at *ca.* 1 565 and *ca.* 1 520 cm$^{-1}$. One of these bands must be due to $\nu(C \overset{\cdot\,\cdot}{\text{---}} N)$ of $S_2C \overset{\cdot\,\cdot}{\text{---}} NMe_2$, and the other to ν(OCO; asym) of OCOR.

By comparing the spectra of $[NMe_4][Zn(S_2CNMe_2)_3]$ [ν(CN) at *ca.* 1 482 and 1 504 cm$^{-1}$], $[\{Zn(S_2CNMe_2)_2\}_2]$ [ν(CN) at 1 522 cm$^{-1}$], and $[NMe_4][S_2CNMe_2]$ [ν(CN) at 1 486 cm$^{-1}$] with those of $[NMe_4][Zn(S_2CNMe_2)_2(OCOR')]$, we are strongly tempted to conclude that the band in the adducts at *ca.* 1 520 cm$^{-1}$ is due to ν(CN), both dithiocarbamato-ligands being chelated to the metal, while the absorption at 1 565 cm$^{-1}$ is presumably due to ν(OCO; asym). The position of this latter band implies that the carboxylato-ligand in these adducts is unidentate, and therefore that the zinc complex is five-co-ordinate. It should be possible to confirm this by identifying ν(OCO; sym) in the region 1 310—1 390 cm$^{-1}$, but an inspection of this range reveals a number of bands associated with the $S_2CNMe_2$ ligands and with $[NMe_4]^+$, and no unambiguous assignment can be made.

The $^1H$ n.m.r. spectra of $[Zn(S_2CNMe_2)_2(OCOR')]^-$ (Table 3) are unexceptional, but appear to confirm the 1 : 1 nature of these adducts.

Because we were unable to establish the structure of $[Zn(S_2CNMe_2)_2(OCOR')]^-$ unequivocally by spectral methods, we attempted to determine the crystal and molecular structure of $[NBu^n_4][Zn(S_2CNMe_2)_2(OCOMe)]$ which we thought we had obtained as suitable crystals from a mixture of acetone and light petroleum (b.p. 40—60 °C). In Tables 4, 5, and 6 we list, respectively, the bond lengths, bond angles (each with their estimated standard deviations), and selected planes of the molecule whose structure we have elucidated. The Figure shows the molecular structure and atom labelling.

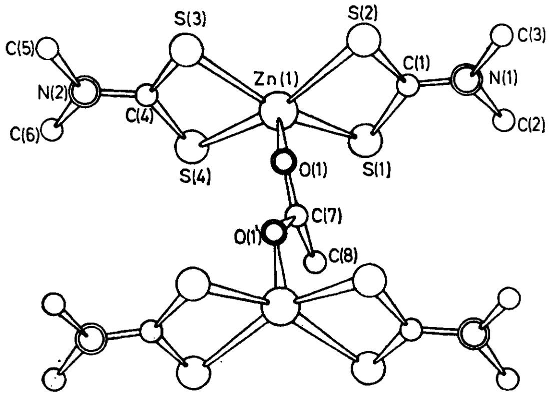
TABLE 3

Proton n.m.r. spectral data obtained from selected zinc sulphur complexes and related species

| Compound | δ [a] | Relative area | Assignment |
|---|---|---|---|
| $[NMe_4][Zn(S_2CNMe_2)_2(OCOMe)]$ | 3.45 [b] | 4 | s, $[N(CH_3)_4]^+$ |
| | 3.34 | 4 | s, $S_2CN(CH_3)_2$ |
| | 2.04 | 1 | s, $OCOCH_3$ |
| $[NBu^n_4][Zn(S_2CNMe_2)_2(OCOMe)]$ | 3.33 [b] | 8 | t, $[N(CH_2Pr^n)_4]^+$ |
| | 3.45 | 12 | s, $S_2CN(CH_3)_2$ |
| | 2.10 | 3 | s, $OCOCH_3$ |
| | 1.53 | 16 | m, $[N\{CH_2(CH_2)_2Me\}_4]^+$ |
| | 0.08 | 12 | t, $[N\{(CH_2)_3CH_3\}_4]^+$ |
| $[NMe_4][Zn(S_2CNMe_2)_2(OCOEt)]$ | 3.43 [c] | 12 | s, $[N(CH_3)_4]^+$ |
| | 3.39 | 12 | s, $S_2CN(CH_3)_2$ |
| | 2.15 | 2 | q, $OCOCH_2Me$ |
| | 1.02 | 3 | t, $OCOCH_2CH_3$ |
| $[NMe_4][Zn(S_2CNMe_2)_2(OCOPr^n)]$ | 3.41 [c] | 12 | s, $S_2CN(CH_3)_2$ |
| | 3.38 | 12 | s, $[N(CH_3)_4]^+$ |
| | 2.09 | 2 | m, $OCOCH_2Et$ |
| | 1.55 | 2 | m, $OCOCH_2CH_2Me$ |
| | 0.89 | 3 | t, $OCOCH_2CH_2CH_3$ |
| $[NMe_4][Zn(S_2CNMe_2)_2(OCOBu^n)]$ | 3.43 [c] | 12 | s, $S_2CN(CH_3)_2$ |
| | 3.41 | 12 | s, $[N(CH_3)_4]^+$ |
| | 2.22 | 2 | t, $OCOCH_2Pr^n$ |
| | 1.55 | 2 | m, $OCOCH_2CH_2Et$ |
| | 1.35 | 2 | sxt, $OCOCH_2CH_2CH_2Me$ |
| | 0.87 | 3 | t, $OCO(CH_2)_3CH_3$ |
| $[NMe_4][S_2CNMe_2]$ | 3.54 [b] | 1 | s, $S_2CN(CH_3)_2$ |
| | 3.48 | 1 | s, $[N(CH_3)_4]^+$ |
| $[NBu^n_4][S_2CNMe_2]$ | 3.58 [b] | | s, $S_2CN(CH_3)_2$ |
| | 3.43 | | t, $[N(CH_2Pr^n)_4]^+$ |
| | 1.55 | | m, $[N\{CH_2(CH_2)_2Me\}_4]^+$ |
| | 0.70 | | t, $[N\{(CH_2)_3CH_3\}_4]^+$ |
| $[NMe_4][Zn(S_2CNMe_2)_3]$ | 3.43 [b] | 3 | s, $S_2CN(CH_3)_2$ |
| | 3.22 | 2 | s, $[N(CH_3)_4]^+$ |
| $[NBu^n_4][Zn(S_2CNMe_2)_3]$ | 3.47 [b] | 9 | s, $S_2CN(CH_3)_2$ |
| | 3.39 | 4 | t, $[N(CH_2Pr^n)_4]^+$ |
| | 1.55 | 8 | m, $[N\{CH_2(CH_2)_2Me\}_4]^+$ |
| | 0.08 | 6 | t, $[N\{(CH_2)_3CH_3\}_4]^+$ |
| $[Zn(S_2CNMe_2)_2]$ | 3.44 [c] | | s, $S_2CN(CH_3)_2$ |

[a] In p.p.m. *vs.* $SiMe_4$. [b] In $CDCl_3$ at 100 MHz. [c] In $(CD_3)_2CO$ at 220 MHz.

As can be seen from the Figure, the molecule whose structure we actually determined was $[NBu^n_4][\{Zn(S_2CNMe_2)_2\}_2(\mu\text{-}OCOMe)]$, and not, as we had expected, $[NBu^n_4][Zn(S_2CNMe_2)_2(OCOMe)]$. The compound is binuclear with two bis(dimethyldithiocarbamato)zincate units bridged by an acetato-*O,O'* ligand. The whole



Molecular geometry and atom labelling of the anion

TABLE 4

Bond lengths (Å) and estimated standard deviations (in parentheses) for $[NBu^n_4][\{Zn(S_2CNMe_2)_2\}_2(OCOMe)]$

| | | | |
|---|---|---|---|
| (*a*) Anion | | | |
| Zn(1)–S(1) | 2.465(3) | Zn(1)–S(4) | 2.446(3) |
| Zn(1)–S(2) | 2.476(3) | Zn(1)–O(1) | 1.979(6) |
| Zn(1)–S(3) | 2.450(4) | | |
| S(1)–C(1) | 1.737(10) | N(2)–C(4) | 1.346(13) |
| S(2)–C(1) | 1.694(10) | N(1)–C(2) | 1.476(14) |
| S(3)–C(4) | 1.707(10) | N(1)–C(3) | 1.446(15) |
| S(4)–C(4) | 1.705(10) | N(2)–C(5) | 1.431(16) |
| N(1)–C(1) | 1.323(12) | N(2)–C(6) | 1.452(15) |
| O(1)–C(7) | 1.255(9) | C(7)–C(8) | 1.509(11) |
| (*b*) Cation | | | |
| N(3)–C(9) | 1.510(15) | C(11)–C(12) | 1.444(22) |
| N(3)–C(13) | 1.521(15) | C(13)–C(14) | 1.476(32) |
| C(9)–C(10) | 1.556(19) | C(14)–C(15) | 1.520 * |
| C(10)–C(11) | 1.456(21) | C(15)–C(16) | 1.520 * |

* Constrained during the later stages of least-squares refinement (see Experimental section).

anion possesses crystallographically imposed $C_2$ symmetry (passing through the μ-acetato-ligand) as does the tetra-n-butylammonium cation. The co-ordination geometry around the zinc atom is five-co-ordinate square-based pyramidal with the sulphur atoms occupying the basal sites and the oxygen atom of the bridging acetate slightly asymmetrically occupying the axial site. All zinc–sulphur bond lengths are similar and the dimethyldithiocarbamato-ligands are approximately planar (the small deviations from perfect planarity being a combination of twist about the C–N bond and a slight pyramidalisation at the carbon and nitrogen atoms). The zinc atom is displaced significantly from the mean plane of each of the chelating ligands (Table 6). The acetate group is constrained to be planar and has unexceptionable geometry. One butyl group of the cation is accurately anti-periplanar in conformation (but with the nitrogen atom deviating significantly from the mean plane of the carbon atoms), whereas the second n-butyl group shows a less favourable conformation for the terminal carbon atom (Table 6) but an otherwise approximately coplanar nitrogen atom. These distortions are presumably a consequence of intermolecular crystal-packing forces. The zinc–oxygen bond length of 1.98 Å compares with similar values in the polymeric zinc propionate [7] for which a spread of values between 1.89 and 1.98 Å has not been explained.

TABLE 5

Bond angles (°)[a] and estimated standard deviations (in parentheses) for $[NBu^n_4][\{Zn(S_2CNMe_2)_2\}_2(OCOMe)]$

| | | | |
|---|---|---|---|
| (*a*) Anion | | | |
| S(1)–Zn(1)–S(2) | 72.5(1) | S(2)–Zn(1)–S(3) | 102.3(1) |
| S(3)–Zn(1)–S(4) | 72.8(1) | O(1)–Zn(1)–S(1) | 106.9(2) |
| S(1)–Zn(1)–S(3) | 155.1(1) | O(1)–Zn(1)–S(2) | 98.1(2) |
| S(2)–Zn(1)–S(4) | 153.2(1) | O(1)–Zn(1)–S(3) | 97.9(2) |
| S(1)–Zn(1)–S(4) | 100.7(1) | O(1)–Zn(1)–S(4) | 108.6(2) |
| Zn(1)–S(1)–C(1) | 84.6(3) | Zn(1)–S(3)–C(4) | 85.0(4) |
| Zn(1)–S(2)–C(1) | 85.1(3) | Zn(1)–S(4)–C(4) | 85.1(3) |
| S(1)–C(1)–N(1) | 120.0(7) | C(1)–N(1)–C(2) | 123.1(8) |
| S(2)–C(1)–N(1) | 123.2(7) | C(1)–N(1)–C(3) | 120.9(9) |
| S(1)–C(1)–S(2) | 116.8(6) | C(2)–N(1)–C(3) | 116.0(8) |
| S(3)–C(4)–N(2) | 121.3(7) | C(4)–N(2)–C(5) | 123.1(9) |
| S(4)–C(4)–N(2) | 121.9(7) | C(4)–N(2)–C(6) | 121.6(9) |
| S(3)–C(4)–S(4) | 116.8(6) | C(5)–N(2)–C(6) | 115.3(9) |
| Zn(1)–O(1)–C(7) | 137.8(5) | O(1′)–C(7)–O(1) | 119.4(7) |
| O(1)–C(7)–C(8) | 120.3(7) | | |
| (*b*) Cation | | | |
| C(9)–N(3)–C(9″) | 105.8(8) | C(9)–N(3)–C(13″) | 111.2(8) |
| C(9)–N(3)–C(13) | 111.1(8) | C(13)–N(3)–C(13″) | 106.5(8) |
| N(3)–C(9)–C(10) | 115.9(10) | N(3)–C(13)–C(14) | 114.8(9) |
| C(9)–C(10)–C(11) | 114.8(11) | C(13)–C(14)–C(15) | 106.4(18) |
| C(10)–C(11)–C(12) | 115.9(13) | C(14)–C(15)–C(16) | 113.0 [b] |

[a] Superscripts indicate atoms which are symmetry related to those labelled by the application of the $C_2$ axis at 0, *y*, 0.25 for O(1′) and 0.5, *y*, 0.25 for C(9″) and C(13″). [b] Constrained during the later stages of least-squares refinement (see Experimental section).

The square-pyramidal co-ordination geometry of the zinc atom in this binuclear species may be compared with that of the metal in $[Zn(py)(S_2CNMe_2)_2]$.[8] In this pyridine adduct the zinc atom has an only slightly distorted trigonal-bipyramidal configuration, in which the pyridine occupies an equatorial site and there are two long axial Zn–S (2.60 Å) and two short equatorial Zn–S (2.33 Å) distances.

TABLE 6

Mean planes through selected fragments of $[NBu^n_4][\{Zn(S_2CNMe_2)_2\}_2(OCOMe)]$. Planes are defined by the formula $lX + mY + nZ = d$, where *l*, *m*, and *n* are the direction cosines of the normal to the mean plane referred to orthogonal crystal axes *a*, *b*, *c*. The deviations (Å) of specified atoms from the mean planes are given in parentheses

| | *l* | *m* | *n* | *d* |
|---|---|---|---|---|
| Plane A: S(1), S(2), S(3), S(4) | −0.9235 | 0.0581 | 0.3792 | −1.6960 |
| [S(1) 0.020, S(2) −0.020, S(3) 0.020, S(4) −0.020, Zn(1) 0.549, O(1) 2.508] | | | | |
| Plane B: S(1), S(2), N(1), C(1), C(2), C(3) | −0.9530 | 0.0708 | 0.2945 | −1.8869 |
| [S(1) −0.000, S(2) −0.004, N(1) −0.006, C(1) 0.008, C(2) −0.001, C(3) 0.003, Zn(1) 0.373] | | | | |
| Plane C: S(3), S(4), N(2), C(4), C(5), C(6) | −0.8409 | 0.0326 | 0.5403 | −0.5727 |
| [S(3) −0.012, S(4) 0.008, N(2) 0.005, C(4) 0.004, C(5) 0.009, C(6) −0.014, Zn(1) 0.196] | | | | |
| Plane D: O(1), C(7), C(8) | −0.4889 | 0.0000 | −0.8724 | −4.1654 |
| [O(1) 0.000, C(7) 0.000, C(8) 0.000, Zn(1) −0.244] | | | | |
| Plane E: C(9), C(10), C(11), C(12) | −0.3013 | −0.0678 | 0.9511 | 2.9262 |
| [C(9) −0.004, C(10) 0.004, C(11) 0.004, C(12) −0.004, N(3) 0.129] | | | | |
| Plane F: N(3), C(13), C(14), C(15) | −0.9091 | −0.0334 | −0.4153 | −7.3307 |
| [N(3) 0.021, C(13) −0.024, C(14) −0.017, C(15) 0.020, C(16) 0.511] | | | | |

Selected interplanar angles (°): A–B 5.2; A–C 10.5; B–C 15.7; A–D 83.1.

*Conclusions.*—As mentioned earlier, we believe that the systems $[\{Zn(S_2CNMe_2)_2\}]$–$[OCOR']^-$ and $[\{Zn(C_7H_4NS_2)_2\}_n]$–$[OCOR']^-$ may be defined as a series of equilibria. Our adventitious extraction of $[NBu^n_4][\{Zn(S_2CNMe_2)_2\}_2(\mu\text{-}OCOMe)]$, from what we believed was recrystallised and apparently analytically and spectroscopically pure $[NBu^n_4][Zn(S_2CNMe_2)_2(OCOMe)]$, underlines this point, and demonstrates the lability of these systems. Presumably the binuclear species is produced by dissociation of acetate from the 1 : 1 adduct, followed by recombination of $[Zn(S_2CNMe_2)_2]$ with undissociated $[Zn(S_2CNMe_2)_2(OCOMe)]^-$ in which the acetate ligand is unidentate.

Our original aim in this work was to discover whether anionic species could be readily produced from $[Zn(S_2CNR_2)_2]$ and $[\{Zn(C_7H_4NS_2)_2\}_n]$. We have shown that tetra-alkylammonium stearate reacts with the bis(dithiocarbamate) and its $C_7H_4NS_2$ analogue, causing labilisation of the systems and formation, amongst other compounds, of $[Zn(S_2CNR_2)_3]^-$ and $[Zn(C_7H_4NS_3)_3(OH_2)]^-$. That the carboxylic acid must be in the form of an ammonium salt is clearly demonstrated by the inability of HOCOR′ or M(OCOR′) (M = alkali metal) to form either an adduct or anionic complex with $[Zn(S_2CNMe_2)_2]$ or $[\{ZnC_7H_4NS_2)_2\}_n]$.

In the ' sulphurating systems,' an ammonium stearate could be formed by neutralisation of the added acid by amines which either occur naturally in rubber latex or which are formed by acid decomposition of (1) or $[Zn(S_2CNR_2)_2]$. In the benzothiazole-activated system, (2) is frequently used as a sulphenamide derivative, $C_7H_4NS_2NR''_2$ (R″ = alkyl), and treatment of these with acids readily affords $[NH_2R''_2]^+$.

Thus, the production of $[Zn(S_2CNMe_2)_3]^-$ and $[Zn(C_7H_4NS_2)_3(OH_2)]^-$ in ' sulphurating systems ' containing ZnO, (1) or (2), $S_8$, and stearic acid is distinctly possible, and these species may be important precursors in the activation of sulphur in zinc-assisted vulcanisation.

## EXPERIMENTAL

Infrared spectra were recorded using Perkin-Elmer 457 and 180 spectrophotometers. The $^1H$ n.m.r. spectra were obtained using JEOL PFT-100 and Perkin-Elmer R-34 instruments. Elemental analyses were determined by the Microanalytical Laboratory of this Department.

The species $[NR_4][S_2CNMe_2]$ (R = Me or Bu$^n$), $[NBu^n_4][Zn(S_2CNMe_2)_3]$, and $[NBu^n_4][Zn(S_2CNMe_2)_2(OCOMe)]$ were prepared as described previously.[5] The complex $[NMe_4][Zn(S_2CNMe_2)_3]$ was prepared by the same route as its $[NBu^n_4]^+$ analogue using $[NMe_4][S_2CNMe_2]$. The species $[NBu^n_4][Zn(C_7H_4NS_2)_3(OH_2)]$ is described elsewhere.[9]

*Tetramethylammonium Bis(dimethyldithiocarbamato)propionatozincate*, $[NMe_4][Zn(S_2CNMe_2)_2(OCOEt)]$.—A mixture of $[NMe_4][OH]$ (4.8 cm³, 25% solution) and propionic acid (1.0 g) in acetone (50 cm³) was evaporated to dryness *in vacuo* at 60 °C. The oil which had formed was redissolved in acetone (100 cm³) and $[Zn(S_2CNMe_2)_2]$ (4.0 g) was added. The mixture was refluxed for 2 h, cooled, filtered, and the filtrate dried over $Mg[SO_4]$. On addition of light petroleum (b.p. 40—60 °C), white crystals precipitated which were filtered off, washed with cold light petroleum, and dried *in vacuo*.

The complexes $[NMe_4][Zn(S_2CNMe_2)_2(OCOR)]$ (R = Me, Pr$^n$, or Bu$^n$) were obtained similarly. Reactions between $[Zn(S_2CNMe_2)_2]$ and $[NR_4][OCOR']$ (R = Me or Bu$^n$; R′ = $C_5H_{11}$, $C_6H_{13}$, $C_7H_{15}$, $C_8H_{17}$, $C_9H_{19}$, or $C_{17}H_{35}$) were carried out as described above, but only $[NR_4][Zn(S_2CNMe_2)_3]$ and small amounts of $[Zn(OCOR')_2]$ were recovered.

*Zinc Bis(benzothiazole-2-thiolate)*, $[\{Zn(C_7H_4NS_2)_2\}_n]$.—To a solution of 2-mercaptobenzothiazole (16.7 g) in hot ethanol (250 cm³) was added K[OH] (5.7 g) in aqueous solution (30 cm³). The clear orange-yellow solution which formed was filtered and a solution of $[Zn(OCOMe)_2]\cdot 2H_2O$ (10.9 g) in ethanol (100 cm³) was added to the filtrate. After cooling, the pale yellow precipitate of the compound was filtered

TABLE 7

Atomic positional parameters (and estimated standard deviations) for $[NBu^n_4][\{Zn(S_2CNMe_2)_2\}_2(OCOMe)]$

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|
| Zn(1) | 0.227 10(9) | 0.045 20(6) | 0.184 12(5) |
| S(1) | 0.200 6(3) | −0.027 5(1) | 0.082 2(1) |
| S(2) | 0.217 2(3) | 0.116 0(2) | 0.078 8(2) |
| S(3) | 0.334 4(3) | 0.113 3(2) | 0.265 3(2) |
| S(4) | 0.322 4(3) | −0.029 6(1) | 0.264 5(2) |
| O(1) | 0.078 3(5) | 0.064 4(3) | 0.222 3(4) |
| N(1) | 0.154 9(7) | 0.044 0(4) | −0.030 7(4) |
| N(2) | 0.427 9(6) | 0.038 6(5) | 0.363 8(4) |
| N(3) | 0.5000 | −0.242 4(6) | 0.2500 |
| C(1) | 0.186 2(7) | 0.045 5(5) | 0.035 6(5) |
| C(2) | 0.128 5(10) | −0.017 5(5) | −0.068 3(6) |
| C(3) | 0.142 3(12) | 0.104 3(6) | −0.070 3(6) |
| C(4) | 0.367 9(7) | 0.040 4(5) | 0.304 4(5) |
| C(5) | 0.466 8(12) | 0.096 6(7) | 0.398 7(7) |
| C(6) | 0.458 9(11) | −0.023 2(6) | 0.396 4(6) |
| C(7) | 0.0000 | 0.033 2(6) | 0.2500 |
| C(8) | 0.0000 | −0.041 1(7) | 0.2500 |
| C(9) | 0.406 9(12) | −0.197 6(6) | 0.227 4(7) |
| C(10) | 0.298 6(12) | −0.232 3(6) | 0.203 5(8) |
| C(11) | 0.206 6(15) | −0.188 2(6) | 0.188 5(8) |
| C(12) | 0.105 5(13) | −0.219 3(7) | 0.165 4(9) |
| C(13) | 0.463 9(12) | −0.287 2(5) | 0.309 6(8) |
| C(14) | 0.416 8(23) | −0.252 8(17) | 0.370 8(12) |
| C(15) | 0.380 0(20) | −0.306 0(6) | 0.421 7(11) |
| C(16) | 0.295 5(19) | −0.281 7(19) | 0.474 7(10) |
| H(2A) | 0.1365 | −0.0543 | −0.0377 |
| H(2B) | 0.0511 | −0.0171 | −0.0837 |
| H(2C) | 0.1731 | −0.0232 | −0.1081 |
| H(3A) | 0.1561 | 0.1420 | −0.0427 |
| H(3B) | 0.1872 | 0.1051 | −0.1110 |
| H(3C) | 0.0646 | 0.1087 | −0.0873 |
| H(5A) | 0.4214 | 0.1060 | 0.4397 |
| H(5B) | 0.4878 | 0.0876 | 0.4469 |
| H(5C) | 0.5416 | 0.0923 | 0.4150 |
| H(5D) | 0.5289 | 0.1154 | 0.3759 |
| H(5E) | 0.4625 | 0.1338 | 0.3687 |
| H(5F) | 0.4087 | 0.1291 | 0.4006 |
| H(6A) | 0.4969 | −0.0168 | 0.4409 |
| H(6B) | 0.4261 | −0.0297 | 0.4409 |
| H(6C) | 0.3984 | −0.0513 | 0.4040 |
| H(6D) | 0.4416 | −0.0600 | 0.3670 |
| H(6E) | 0.5125 | −0.0471 | 0.3670 |
| H(6F) | 0.5402 | −0.0255 | 0.4040 |
| H(8A) | 0.0568 | −0.0581 | 0.2801 |
| H(8B) | −0.0129 | −0.0581 | 0.2962 |
| H(8C) | −0.0697 | −0.0581 | 0.2660 |
| H(9A) | 0.3841 | −0.1689 | 0.2637 |
| H(9B) | 0.4300 | −0.1705 | 0.1879 |
| H(10A) | 0.3147 | −0.2575 | 0.1590 |
| H(10B) | 0.2774 | −0.2652 | 0.2363 |
| H(11A) | 0.1898 | −0.1646 | 0.2302 |
| H(11B) | 0.2259 | −0.1580 | 0.1525 |
| H(12A) | 0.0781 | −0.2532 | 0.1994 |
| H(12B) | 0.0420 | −0.1897 | 0.1605 |
| H(12C) | 0.1108 | −0.2428 | 0.1216 |
| H(13A) | 0.4070 | −0.3171 | 0.2912 |
| H(13B) | 0.5272 | −0.3171 | 0.3198 |
| H(14A) | 0.4855 | −0.2254 | 0.3921 |
| H(14B) | 0.3662 | −0.2231 | 0.3622 |
| H(15A) | 0.3659 | −0.3420 | 0.3947 |
| H(15B) | 0.4568 | −0.3204 | 0.4473 |

Hydrogen atoms are labelled according to the carbon atoms to which they are attached, with further alphabetic symbols to indicate different hydrogen atoms (or partial occupancy sites) on the same carbon atom. The positional parameters for hydrogen atoms associated with C(5), C(6), and C(8) are for sites of 50% occupancy (see Experimental section). Atoms N(3), C(9)—C(12), and C(13)—C(16) comprise the independent atoms of the tetra(n-butyl)ammonium cation.

off, washed with ethanol, and dried ***in vacuo*** (16.7 g, 84% yield).

*Reactions of* [NBu$^n_4$][OCOR′] ***with*** [$\{Zn(C_7H_4NS_2)_2\}_n$].—Solutions of [NBu$^n_4$][OCOR′] (R = Me or $C_{17}H_{35}$) in acetone were added to [$\{Zn(C_7H_4NS_2)_2\}_n$] suspended in acetone. Dissolution immediately occurred and the mixtures were refluxed for various lengths of time (2—16 h), but only [NBu$^n_4$][$Zn(C_7H_4NS_2)_3(OH_2)$] was isolated from the pale yellow solutions. The product was identified by analysis and by comparison of its i.r. spectrum with an authentic sample of [NBu$^n_4$][$Zn(C_7H_4NS_2)_3(OH_2)$].[39]

*Crystallographic Studies.*—Crystals of [NBu$^n_4$][$\{Zn(S_2CNMe_2)_2\}_2$(μ-OCOMe)] were obtained from acetone–light petroleum (b.p. 40—60 °C) mixtures as colourless needles (the chosen crystal had dimensions 0.15 × 0.14 × 0.48 mm).

*Crystal data.* $C_{30}H_{63}N_5O_2S_8Zn_2$, $M = 913.11$, Orthorhombic, $a = 12.081(10)$, $b = 20.306(16)$, $c = 19.099(12)$ Å, $U = 4\,685(6)$ Å$^3$, $D_m = 1.284$, $Z = 4$, $D_c = 1.295$ g cm$^{-3}$, $F(000) = 1\,928$, Mo-$K_\alpha$ radiation, $\lambda = 0.710\,69$ Å, $\mu$(Mo-$K_\alpha$) = 14.22 cm$^{-1}$, space group *Pbcn* from systematic absences $0kl$, for $k = 2n + 1$, $h0l$, for $l = 2n + 1$, and $hk0$, for $h + k = 2n + 1$.

Three-dimensional *X*-ray data with $6.5 < 2\theta < 50°$ were collected on a Stöe Stadi-2 two-circle diffractometer by the rotating-crystal–stationary-counter method and the 1 243 independent reflections with $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects and for absorption. The structure was solved by conventional Patterson and Fourier methods and refined by block-diagonal least-squares methods to *R* 0.052, allowing anisotropic thermal vibration for all non-hydrogen atoms. Further refinement with geometric constraints on the last three carbon atoms [C(14)—C(16)] of one n-butyl group reduced *R* to 0.053 2. Refinement was completed with inclusion of contributions from hydrogen atoms (*B* 10.0 Å$^2$) in calculated positions (for $CH_2$ groups) and in positions indicated by an electron-density synthesis (for $CH_3$ groups) with C–H 0.95 Å, X–C–H 109.5°. The hydrogens of three methyl groups, those associated with C(5), C(6), and C(8), did not show localised maxima and were approximated by half-population hydrogen atoms distributed around the annulus; no attempt was made to assign the hydrogen atoms on C(16). After allowance for the anomalous scattering of zinc, convergence was achieved at $R = 0.042\,8$. Table 7 lists the atomic positional parameters with their estimated standard deviations. Observed structure amplitudes, calculated structure factors, and thermal parameters are deposited in Supplementary Publication No. SUP 22801 (13 pp.).* Atomic scattering factors were taken from ref. 10; unit weights were used throughout the refinement, and the computer programs used form part of the Sheffield *X*-ray system.

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* For details see Notices to Authors, *J.C.S. Dalton*, 1979, Index issue.

REFERENCES

[1] M. Porter, 'The Chemistry of Sulphur Vulcanisation of Natural Rubber,' in 'The Chemistry of Sulphides,' ed. A. Tobolsky, Interscience, New York, 1968.

[2] C. G. Moore and A. A. Watson, *J. Appl. Polymer Sci.*, 1964, **8**, 581.

[3] C. C. Ashworth, N. A. Bailey, M. Johnson, J. A. McCleverty, N. J. Morrison, and B. Tabbiner, *J.C.S. Chem. Comm.*, 1976, 743.

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

[5] J. A. McCleverty and N. J. Morrison, *J.C.S. Dalton*, 1976, 2169.

[6] S. D. Robinson and M. F. Uttley, *J.C.S. Dalton*, 1973, 1912; K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' Wiley, New York, 1963, and refs. therein.

[7] E. Goldschmied, A. D. Rae, and N. C. Stephenson, *Acta Cryst.*, 1977, **B33**, 2117.

[8] K. A. Fraser and M. M. Harding, *Acta Cryst.*, 1967, **22**, 75.

[9] J. A. McCleverty, N. J. Morrison, N. Spencer, C. C. Ashworth, N. A. Bailey, J. M. A. Smith, B. Tabbiner, and C. R. Taylor, following paper.

[10] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.