Anionic Dithiocarbamato-complexes of Zinc(II) and a Trithiocarbamate Ion

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Summary Reaction of $[\mathrm{ZnI_2\{Me_2NC(:S)S_2C(:S)NMe_2\}}]$ with $\mathrm{PPh_3}$ afforded, *inter alia*, $[\mathrm{Ph_3PC(:S)NMe_2}][\mathrm{ZnI_2(S_2CNMe_2)}]$, and $[\mathrm{Ph_3PC(:S)NMe_2}][\mathrm{ZnI_3(PPh_3)}]$; the anions $[\mathrm{ZnX_2(S_2CNR_2)}]^-$ (X = halide) and $[\mathrm{Zn(S_2CNR^1{}_2)_2(S_2CNR_2)}]^-$ were obtained by addition of $(\mathrm{S_2CNR_2})^-$ to $\mathrm{ZnX_2}$ and $[\mathrm{Zn(S_2CNR^1{}_2)_2}]$ respectively, while addition of $(\mathrm{S_2CNMe_2})^-$ to $[\mathrm{Ni\{S_2CNH}(p\text{-tolyl})\}_2]$ afforded the trithiocarbamate ion, $\{\mathrm{S_3CNH}(p\text{-tolyl})\}^-$.

IT is known[1] that tetramethylthiuram disulphide [TMTD ≡ $\mathrm{Me_2NC(:S)S_2C(:S)NMe_2}$] reacts with $\mathrm{PPh_3}$ in boiling benzene giving $\mathrm{Ph_3PS}$ and tetramethylthiuram monosulphide [TMTM ≡ $\mathrm{Me_2NC(:S)SC(:S)NMe_2}$]. During studies of this reaction in the presence of zinc salts we found that although the TMTM complex was formed initially, other novel zinc dithiocarbamates were readily produced.

Thus, as expected, $[\mathrm{ZnI_2}$ (TMTD)] reacted with 1 mol. equiv. of $\mathrm{PPh_3}$ giving $[\mathrm{ZnI_2}$ (TMTM)]. The species $[\mathrm{ZnX_2}$(TMTM)] (X = Cl, Br, or I) could be obtained independently from $\mathrm{ZnX_2}$ and TMTM in acetone. However, with 2 mol. equiv. of $\mathrm{PPh_3}$, $[\mathrm{ZnI_2}$(TMTD)] afforded $[\mathrm{Ph_3PC(:S)NMe_2}][\mathrm{ZnI_2\ (S_2CNMe_2)}]$ while with 3 mol. equiv of $\mathrm{PPh_3}$ the species $[\mathrm{Ph_3PC(:S)NMe_2}][\mathrm{ZnI_3(PPh_3)}]$† was produced. In all of these reactions, only small amounts of $[\mathrm{ZnI_2(PPh_3)_2}]$ were formed, whereas treatment of $[\mathrm{ZnI_2}$(TMTD)] with pyridines, isocyanides (L), or $(\mathrm{S_2CNMe_2})^-$ resulted in quantitative displacement of the TMTD from the zinc, and formation of $[\mathrm{ZnI_2L_2}]$ or $[\mathrm{ZnI_2(S_2CNMe_2)}]^-$.

The cation $[\mathrm{Ph_3PC(:S)NMe}]^+$ was prepared independently from $\mathrm{Me_2NC(:S)Cl}$ and $\mathrm{PPh_3}$, as the $\mathrm{PF_6}^-$ or I^- salts, using $\mathrm{AgPF_6}$ or NaI, respectively. Quaternisation was not achieved in the absence of a metal ion. Reaction of $[\mathrm{Ph_3PC(:S)NMe_2}][\mathrm{PF_6}]$ with $[\mathrm{Bu^n{}_4N}][\mathrm{S_2CNMe_2})$ yielded $\mathrm{Ph_3P}$, TMTM, and $[\mathrm{Bu^n{}_4}][\mathrm{PF_6}]$. The yellow phosphonium cation is stereochemically rigid up to *ca.* 100 °C, when rotation about the $\mathrm{C}\underline{\cdots}\mathrm{N}$ bond causes collapse of the methyl doublet observed in the ^{1}H n.m.r. spectrum. The anions $[\mathrm{ZnX_2(S_2CNMe_2)}]^-$ were prepared from an equimolar mixture of $[\mathrm{Bu^n{}_4N}][\mathrm{S_2CNMe_2}]$ and $\mathrm{ZnX_2}$ in acetone. By carrying out this reaction in water or methanol, or upon addition of a second mole of $(\mathrm{S_2CNMe_2})^-$, precipitation of $[\mathrm{Zn(S_2CNMe_2)_2}]$ was effected.

The successful synthesis of $[\mathrm{ZnX_2(S_2CNMe_2)}]^-$ suggested that $[\mathrm{Bu^n{}_4N}][\mathrm{S_2CNMe_2}]$ might have more general application in the preparation of anionic zinc complexes. Thus addition of $[\mathrm{Bu^n{}_4N}][\mathrm{S_2CNMe_2}]$ to $[\mathrm{Zn(S_2CNR\ )_2}]$ afforded $[\mathrm{Bu^n{}_4N}][\mathrm{Zn(S_2CNR_2)_2(S_2CNMe_2)}]$ (R = Me or Et) and $[\mathrm{Bu^n{}_4N}][\mathrm{Zn(S_2CNMe_2)_2(S_2CNR_2)}]$ (R = $\mathrm{Bu^n}$); iodine oxidation of $[\mathrm{Zn(S_2CNMe_{2\ 3}}]^-$ afforded TMTD and $[\mathrm{ZnI_2(S_2CNMe_2)}]^-$. Attempts to prepare similar complexes of nickel(II) by addition of $(\mathrm{S_2CNMe_2})^-$ to $[\mathrm{Ni(S_2CNR_2)_2}]$ (R = Me, Et or $\mathrm{Bu^n}$) were unsuccessful. However, treatment of $[\mathrm{Ni\{S_2CNH}(p\text{-tolyl})\}_2]$ with $[\mathrm{Bu^n{}_4N}][\mathrm{S_2CNMe_2}]$ afforded $[\mathrm{Ni(S_2CNMe_2)_2}]$ and yellow needles of the previously unknown trithiocarbamate ion, $[\mathrm{Bu^n{}_4N}][\mathrm{S_3CNH}(p\text{-tolyl})]$.‡

The discovery of the trithiocarbamate ion is of considerable significance with respect to the mechanisms of rubber vulcanisation accelerated by zinc dithiocarbamato-compounds. It has been proposed[2] that perthiocarbamates $[\mathrm{S}_n\mathrm{C(:S)NMe_2}]^-$ ($n > 1$) are the source of the sulphidic cross-links in the vulcanised rubber matrix. We have observed that $[\mathrm{Bu^n{}_4N}][\mathrm{S_2CNMe_2}]$ reacts with $\mathrm{S_8}$ giving a red oil, but have so far been unable to characterise it. However in certain rubber mixtures, in the presence of ZnO and $\mathrm{S_8}$, both $[\mathrm{Bu^n{}_4N}][\mathrm{S_2CNMe_2}]$ and $[\mathrm{Bu^n{}_4N}][\mathrm{Zn(S_2CNMe_2)_3}]$ are faster vulcanisation accelerators than $[\mathrm{Zn(S_2CNMe_2)_2}]$, the simple anion being the most rapid.

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† A single crystal *X*-ray diffraction study of this compound (N. A. Bailey and N. W. Walker, of this department) has confirmed our formulation.

‡ Excellent analytical data have been obtained for this and the other complexes described herein. There are also significant spectral differences between $[\mathrm{Bu^n_4N}][\mathrm{S_3CNH}(p\text{-tolyl})]$ and conventional dithiocarbamates.

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[2] A. A. Watson, Ph.D. Thesis, University of London, 1965; P. W. Allen, D. Barnard and B. Saville, *Chem. in Brit.*, 1970, **6**, 382.

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