Crystal and Molecular Structure of the Bis-piperidine Adduct of Bis(pentamethylenethiocarbamato)zinc(II)

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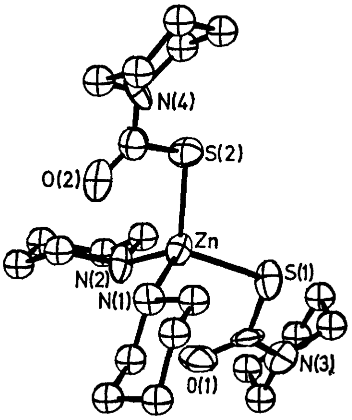
Summary The structure of the bis-piperidine adduct of bis(pentamethylenethiocarbamato)zinc(II) is reported together with a discussion of bond delocalization in the thiocarbamate ligand.

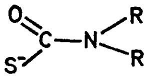
WHILE dithiocarbamate ligands have long been of interest as chelating agents, complexes of related thiocarbamate ligands have only been investigated recently.[1–4] They exist as polymers both in solution and in the solid state. Unlike their dithiocarbamate analogues, no simple monomeric thiocarbamate complexes have yet been reported. Structural studies[1,2,5] have indicated that the thiocarbamate ligand bonds terminally to the metal through the oxygen atom, bridging two adjacent metal atoms through the sulphur donor to form the polymeric linkage. On adduct formation with nitrogenous bases these polymeric units generally form discrete monomeric complexes.[3,4]

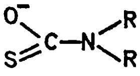
We now report a crystallographic determination of the molecular structure of bis(pentamethylenethiocarbamato) bis(piperidine)zinc(II). *Crystal data:* $Zn(SOCN[CH_2]_5)_2(NC_5H_{11})_2$ (from benzene–hexane) space group $P\bar{1}$; $a = 10{\cdot}279(5)$, $b = 12{\cdot}690(5)$, $c = 12{\cdot}161(5)$ Å, $\alpha = 107{\cdot}44(5)°$, $\beta = 92{\cdot}67(5)°$, $\gamma = 117{\cdot}27(5)°$, $U = 1313$ Å^3; $D_m = 1{\cdot}31(1)$ g cm^{-3}, $Z = 2$, $D_c = 1{\cdot}32$ g cm^{-3}. Intensity data were collected on a Picker automated diffractometer (θ–2θ scans) using Zr-filtered Mo-K_α radiation. The Zn atom was located by a Patterson map, and the remaining atoms were located by standard Fourier and least-squares techniques. The R value, after refinement of all non-hydrogen atoms using anisotropic thermal parameters, is 0·079. A perspective view of the molecular geometry is shown in the Figure.

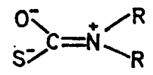
The co-ordination geometry about zinc is essentially tetrahedral with the thiocarbamate groups bonding as monodentate ligands through sulphur. The molecule possesses approximate two-fold symmetry with no significant differences between bond distances and angles within similar ligands. The average Zn–S distance is 2·311(5) Å, significantly shorter than average distances of 2·35, 2·36, and 2·46 Å found for the zinc dithiocarbamate complexes[6] $Zn_2(S_2CNMe_2)_4$, $Zn_2(S_2CNEt_2)_4$, and $Zn(S_2CNMe_2)_2(NC_5H_5)$, respectively. The average S–C bond length is 1·80(2) Å, reasonable for a S–C single bond,[7] and is significantly longer than S–C bond lengths in most 1,1-dithiolato-complexes.[6] The average C–O and C–N bond lengths are 1·22(2) and 1·36(2) Å, respectively, comparable to values found for organic amides where the double bond is delocalized over the C–O and C–N bonds.[7] The average Zn–N distance for the co-ordinated piperidine groups is 2·07(1) Å, which agrees well with Zn–N distances observed for other amine complexes.[8]



FIGURE


(I)


(II)


(III)

Surprisingly, the observed distances and angles within the ligand are not significantly different from those found in the polymeric thiocarbamate complexes previously studied, and it is clear that the structure of the ligand is essentially independent of the mode of bonding to the metal. The present results also confirm previous proposals[3] on the relative importance of resonance forms (I), (II), and (III) to the overall structure of thiocarbamate complexes. The long C–S and short C–O distances indicate that form (II) is of little importance, accounting for the mercaptide-like behaviour of the sulphur donor. The short SO(C–N) distance suggests that form (III) is of comparable importance to similar resonance structures that have been shown to be highly significant in dithiocarbamate chemistry.[9]

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