Mass Spectrometric Evidence for Out-of-plane Bonding in Bis-(*NN*-diethyldithiocarbamato)zinc(II) Dimers

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Summary The first evidence for out-of-plane interactions in the gas phase is reported from the mass spectrum of the dimer $[Zn(edtc)_2]_2$.

WE have been interested in properties of metal complexes where there are interactions between the unpaired spins.[1,2] We have recently demonstrated the existence of a triplet ground state for some copper dimers, particularly in bis-(*NN*-diethyldithiocarbamato)copper(II), $[Cu(edtc)_2]_2$, where the spin coupling occurs through the out-of-plane bonds between a sulphur atom of one monomeric unit and the copper ion of the neighbouring unit.[3,4] We report now the mass spectrum of the zinc analogue, $[Zn(edtc)_2]_2$, whose crystal structure[5] is very similar to that of the copper compound (see Figure 1), which demonstrates the importance

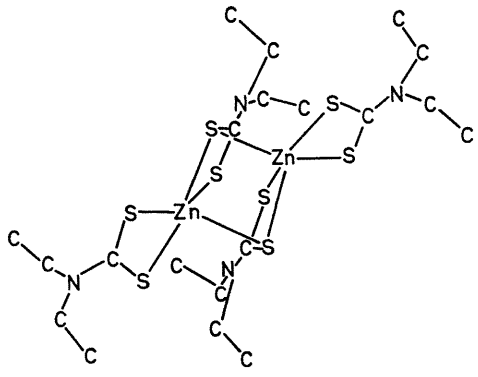

FIGURE 1. *Schematic structure of* $[Zn(edtc)_2]_2$. *Hydrogens were left out for clarity.*

of these bonds even in the gas phase. There has been only one previous report of mass spectral evidence for gas-phase dimers of copper compounds, these being carboxylates,[6] where the crystal structure[7] indicates bidentate-chelating bridging ligands. These new results, however, are the first evidence for out-of-plane dimerisation in the gas phase where the two portions of the molecule are not held together by a chelate bridge in the solid phase.

Spectra of $[Zn(edtc)_2]_2$ were obtained with a direct probe at 180° on a Hitachi–Perkin-Elmer RMU-6E mass spectrometer; peaks above the monomer molecular ion were about 1% of the intensity of the molecular ion peak, but were easily identified as containing two Zn atoms because of the characteristic isotopic distribution expected (*M*, 71; *M* + 2, 81; *M* + 4, 100; *M* + 6, 33; *M* + 8, 22), though they are distorted by the large amount of sulphur present. The peaks were too weak to peak-match by high-resolution techniques, but the addition of a standard (high-boiling perfluorokerosene) permitted identification of the masses of four clusters. These were found to have the lightest isotope peak at *m/e* 604, 572, 491, and 459, respectively. The relative intensities of these clusters are indicated in Figure 2, together with a tracing of the most intense cluster. The data indicate that the dimeric molecular ion is not maintained, but most of the fragments observed can be explained by logical losses from it. The *m/e* 604 peak

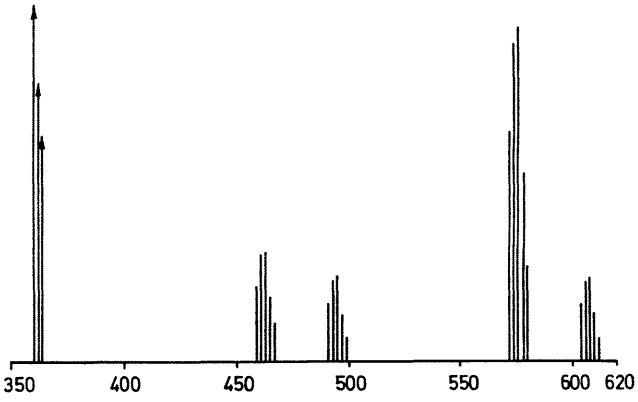

FIGURE 2. *Mass spectrum of* $[Zn(edtc)_2]_2$.

corresponds to the loss of $(C_2H_5)_2NCS$ from the dimer molecular ion and that at *m/e* 572 corresponds to the loss of $(C_2H_5)_2NCS_2$, that is, one entire ligand. This assignment is corroborated by a comparison of the statistically predicted and found isotopic distributions, as shown in the Table.

Isotopic distributions for the m/e 572 *peak* (*for* $C_{15}H_{30}N_3S_6Zn_2$; *all isotopes of all atoms were considered*)

Mass	Calc.	Exp.	Mass	Calc.	Exp.
572	67	67	578	58	58
573	16	15	579	19	18
574	96	96	580	24	24
575	33	33	581	6	7
576	100	100	582	5	5
577	32	32	583	1	1

Likewise, the other two clusters are separated by 32 mass units and most likely correspond to similar cleavages as the first two plus the loss of C_8H_{17} or $C_7H_{15}N$. Several possible pathways could account for these latter losses.

Thus, the interactions between single units of $Zn(edtc)_2$ in the crystalline state, which are so important in determining the magnetic properties of the copper compound, are shown to hold even in the gaseous state; the bond strengths of the out-of-plane bonds are obviously rather strong in order for even a small amount of product to be observed at the pressures employed (2×10^{-7} torr) where ion-molecule reactions are unlikely. We have also observed clusters above the monomer molecular ion in the spectra of the copper analogue but withhold a discussion until further studies have been made.

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Added in proof. A recent observation of metal dimers in the gas phase is afforded by the *o*-benzoquinone monooxime complexes.[8] *X*-Ray structurali nformation on these is not available.

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