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Effects of Metal-Ligand Charge Transfer on the Mass Spectra of Bis(N,N-diethyldithiocarbamato) Complexes. An Application of the Shannon-Swan Rule

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The mass spectra fragmentation patterns of bis(N,N,-diethyldithiocarbamato)copper(II) and zinc(II) follow the Shannon-Swan rule, apparently because of the ability of copper(II) to be reduced to copper(I) in contrast to zinc(II). It is also observed that the short out-of-plane bonds between the two halves of the zinc dimer are strong enough for ions containing two zinc atoms to be observed under the severe experimental conditions employed, while the out-of-plane bonds in the copper dimer are too weak for species containing two copper atoms to be observed.

Introduction

In a continuation of our studies of the mass spectra of compounds interesting for the possibility of detection of weakly linked dimers in the gaseous phase,[1,2] we have examined the spectra of bis(N,N,-diethyldithiocarbamato) complexes of copper(II) and zinc(II) [$Cu(edtc)_2$ and $Zn(edtc)_2$]. In the present case, we consider the evaluation of the role of low-energy oxidation states of the metal in controlling fragmentation patterns of these complexes, as first generalized by Shannon and Swan.[3]

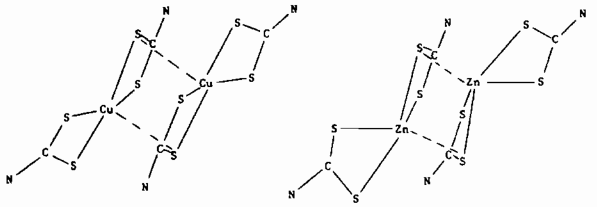

Figure 1. Schematic representation of the Cu^{II} and Zn^{II} complexes of N,N-diethyldithiocarbamic acid. Hydrogen and some carbon atoms were left out for clarity.

A schematic of the structure of these compounds is shown in Figure 1. The out-of-plane copper-sulphur bonds are shown by the dotted lines and as can be observed, the structures are rather similar except in the length of the out-of-plane bonds (Cu–S = 2.85 Å, Zn–S = 2.38 Å).[4,5]

Results and discussion

Our mass spectral results strikingly confirm the importance of the possibility of one-electron transfer between the metal and the ligand in the copper(II) complex but not in the case of the zinc(II) complex. The experimental data for the two complexes between the mass of the free ligand and the mass of the monomer complex $M(edtc)_2$ are given in Table I. The metastable ions are not shown, but those observed were used to infer some of our assignments.

From a simple inspection of the decomposition patterns (Table I) it can be noticed that they parallel each other except for one key point: copper-containing fragments contain one more hydrogen than their zinc counterparts. For example, the first loss from the molecular ion of $Cu(edtc)_2$ is of C_2H_4, but that of the molecular ion of $Zn(edtc)_2$ is of C_2H_5. Other losses may be similarly correlated. These observations may be rationalized in the following fashion: if the first ionization potentials are taken as a rough guide, the copper(I) state is more stable than the zinc(I) by 1.7 eV[6] [in fact, there are only isolated unconfirmed reports of zinc(I) compounds[7,8] while there are many known stable compounds of copper-(I)[9,10]]. This indicates that the copper(II) compound, but not the zinc(II) analog, has the ability to undergo the metal reduction step shown in Figure 2. Therefore, the zinc(II) complex will fragment by the typical[11] $[O.E.^{+\cdot} \rightarrow E.E.^{+} + O.E.^{\cdot}]$ routes usual of organic radical ions; that is, radicals are lost, not molecules, from the molecular ion. In contrast, the organic ligand[(II) in Figure 2], produced in the

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[5] M. Bonamico, G. Mazzone, A. Vaciago, and L. Zambonelli, *Acta Crystallogr.*, *19*, 898 (1965).

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[10] Ref, 8, pp. 894 - 898.

[11] See F. W. McLafferty, « Interpretation of Mass Spectra », W.A. Benjamin, Inc., 1967, p. 30. O.E. = odd-electron; E.E. = even-electron.

Table I. Comparative Mass Spectra of $Zn(edtc)_2$ and $Cu(edtc)_2$. Only principal isotopic peaks above 2% are indicated.

m/e	rel inten	$M = Zn(edtc)_2$	m/e	rel inten	$M = Zn(edtc)_2$
360	100	$M^{+\cdot}$ (molecular ion)	359	100	$M^{+\cdot}$
331	5	$[M—C_2H_5]^+$	331	16	$[M—C_2H_4]^{+\cdot}$
299	6	$[M—C_2H_5S]^{+\,a}$	299	2	$[M—C_2H_4S]^{+\cdot}$
283	8	$[H—CHS_2]^{+\,a}$	283	2	$[M—CS_2]^{+\cdot}$
271	6	$[M—C_2H_5S—C_2H_4]^{+\,a,b}$	271	2	$[M—C_2H_4S—C_2H_4]^{+\cdot}$
244	30	$[M—(C_2H_5)_2NCS]^+$	244	10	$[M—(C_2H_5)(C_2H_4)NCS]^{+\cdot}$
212	33	$[M—(C_2NCS_2]^+$	212	44	$[M—(C_2H_5)(C_2H_4)NCS_2]^{+\cdot}$

[a] Assignments confirmed by high resolution data. [b] Principal peak of a triplet at this mass.

Table II. Mass Spectra of $Zn(edtc)_2$ and $Cu(edtc)_2$. *A*.[a] Area above parent monomer molecular ion, M^+. *B*. Area below free ligand. Only principal isotopic peaks are reported.

A m/e (Zn)	rel inten	$M_2 = [Zn(edtc)_2]_2$
612	10	$[M_2—(C_2H_5NCS)]^{+\cdot}$
610	14	
608	24	
606	24	
604	19	
580	29	$[M_2—(C_2H_5NCS_2)]^{+\cdot}$
578	57	
576	100	
574	95	
572[b]	67	
499	10	$[M_2—(C_2H_5NCS)(C_7H_5N)]^{+\cdot}$?
497	14	
495	24	
493	24	
491	14	
467	10	$[M_2—(C_2H_5NCS_2)(C_7H_5N)]^{+\cdot}$?
465	19	
463	33	
461	29	
459	24	

B m/e	rel inten (Zn)	rel inten (Cu)	assign
148	30	19	$(C_2H_5)_2NCS_2^+$
118	9	19	$(C_2H_4)NCS_2^+$
117	15	32	$(C_2H_5)_2NHCS^+$
116	130	370	$(C_2H_5)_2NCS^+$
115	12	5	$(C_2H_4)(C_2H_5)NCS^+$?
114	24	13	$(C_2H_4)_2NCS^+$
88	73	165	$(C_2H_5)NHCS^+$
86	51	35	$(C_2H_4)NCS^+$
76	3	9	CS_2^+
72	40	57	$(C_2H_5)_2N^+$
70	9	10	$(C_2H_5(C_2H_3)N^+$?
60	57	95	H_2NCS^+?
56	2	18	$C_3H_6N^+$?
43	34	—	$(C_2H_5)N$

[a] For copper data see text [b] Intensity of 572 cluster was about 1% of M^+ intensity. Relative intensities of area *B* reported relative to M^+.

reduction step for the copper(II) complex acts like an even-electron ion. These species almost always decompose according to the scheme $[E.E.^+ \rightarrow E.E.^+ + E.E.]$,[11] and the species lost as a neutral fragment is therefore a small stable molecule, for example C_2H_4. This difference in behavior is observed in every similar decomposition of $Cu(edtc)_2$ and $Zn(edtc)_2$.

It should be noticed that the reduction mechanism proposed in Figure 2 carries a concomitant weakening of the metal-sulphur bond in the case of the copper complex. This is what is observed, by the generally greater fragmentation of the copper complex; while the molecular ion of $Zn(edtc)_2$ accounts for 18% of the total ion current, the molecular ion of $Cu(edtc)_2$ accounts for only 11%. Similarly, reaction corresponding to the loss of an entire ligand to produce the ion of *m/e* ratio contains several of the fragments expected from the decomposition patterns shown in Table I. The regions above the monomer parent ion are distinctly different for these compounds. The zinc complex shows several clusters which have the isotopic distribution expected for dimer species in the gas phase. For the copper complex, however, the only ions obtained above the molecular ion of the copper complex are of very low intensity and do not contain two copper atoms, as could be judged from isotopic distributions, and might be assigned to impurities. This observation is consistent with the generally weaker out-of-plane bonding in the copper complex, reflected in the bond lengths in the copper and zinc crystal structures: the Cu–S out-of-plane distance is 2.85 Å against 2.38Å for the Zn–S out-of-plane distance. Apparently the Cu–S bonds are sufficiently weakened that no gaseous dimers exist capable of being maintained on electron impact.[11a]

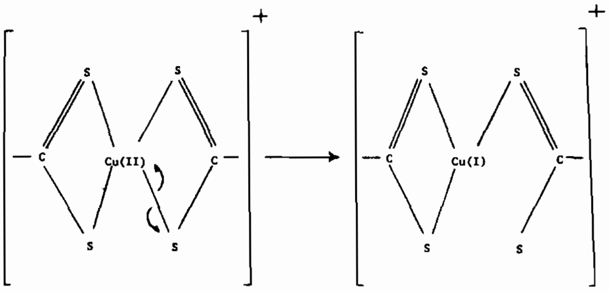

Figure 2. Metal reduction pattern used to interpret the mass spectral data for $Cu(edtc)_2$.

Experimental

The compounds were prepared as previously reported[12] and they analyzed correctly. The medium resolution spectra were obtained in a Hitachi RMU-6E single focusing mass spectrometer at 75 eV using a T2M ion source and a 10 stage detection multiplier. The samples were introduced through the direct probe

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(11a) *Note added in Proof*: Prof. J. S. Shannon has pointed out the possibility of product of these ions by ion-molecule processes. Our source pressures were *ca.* 10^{-7} torr, so that these processes are unlikely, but even if they were important formation of our products still reflects stronger interaction in the Zn than in the Cu complex.

(12) J.F. Villa and W.E. Hatfield, *Inorg. Chem. 10,* 2038 (1971).

at 425°K and a source temperature of 450°K was used. High boiling perfluorokerosene was used as internal standard. Finally, the high resolution spectra were obtained in an MS902 mass spectrometer under normal experimental conditions.

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