to form hydroxy- and iodotrimethylplatinum tetramers thus becomes plausible. This reasoning is applicable to the other two intermediates if one considers distortions in the central "cubic" arrangement.

The infrared spectrum of hydroxytrimethylplatinum was found to be rather different from that reported by Hoechstetter.[6] Adams, Chatt, and Shaw[11] have reported Pt–C stretching frequencies in alkylplatinum(II) complexes in the region 500–600 cm^{-1}, and Gel'man[12] has reported the Pt–C stretching frequency in iodotrimethylplatinum at 562 cm^{-1}. Hoechstetter asserts that he did not see the slightest indication of Gel'man's Pt–C band in a series of trimethylplatinum derivatives. We, on the other hand, have observed two bands in hydroxytrimethylplatinum and also in the iodo, bromo, and chloro derivatives.[13] The reason for this disagreement must be that we used much thicker samples and a more sensitive instrument in this region.

The hydroxyl group bonded to three platinum atoms has local C_{3v} symmetry and should be expected to have four normal Pt–O modes of vibration.[14] The band at 365 cm^{-1} is assigned to the Pt–O deformation frequencies (although the weak shoulder at 382 cm^{-1} may be the unsymmetric Pt–O deformation).

The band at 721 cm^{-1} represents both symmetric and unsymmetric Pt–O stretching frequencies which often appear as one intense band.[14] This band has an overtone at 1411 cm^{-1}. The whole series of tetrameric trimethylplatinum derivatives have unsymmetric CH deformation bands in the region 1410–1420 cm^{-1},[6,13] while the aquated trimethylplatinum cation has this band at 1427 cm^{-1}.[7] Under high resolution we observed three definite bands in this region. A logical explanation for this is that the overtone of the unsymmetric Pt–O stretching frequency is in Fermi resonance with the unsymmetric CH deformation frequency, generating the bands at 1427 and 1381 cm^{-1}. The overtone of the symmetric Pt–O stretching frequency cannot take part in Fermi resonance and appears at 1411 cm^{-1}.

Clegg and Hall assigned their 1143-cm^{-1} band as a combination band of the Pt–C_3 skeletal deformation and CH_3 rocking frequencies ($259 + 882 = 1141$) and their 1194-cm^{-1} band as an overtone of the Pt–C stretching frequency ($2 \times 600 = 1200$). Since we were not able to make a choice among these overtones and combinations, the band at 1160 cm^{-1} is labeled an unidentified combination.

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High Resolution Mass Spectroscopic Studies of Metal Chelates

BY EMILY P. DUDEK AND MICHAEL BARBER[1]

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The mass spectra of 2-carbamoyldimedone and N-phenyl-2-carbamoyldimedone complexes of copper(II), zinc(II), and iron(III) ions are presented. The spectra provide valuable information, including molecular weights, metal:ligand ratios, and relative stabilities of ion fragments. The possibility of rearrangements due to radical transfer processes is depicted.

Introduction

Mass spectrometry has been used extensively over the past few years in studies of large organic molecules,[2,3] but its applicability to the investigation of transition metal complexes has yet to be firmly established. With the advent of highly efficient direct evaporation inlet systems, the problems with low volatility and thermal instability which are encountered frequently when dealing with metal complexes have to some extent been overcome. To date, only a few metal chelates have been studied by mass spectrometry, *e.g.*, metalloporphyrins,[4] a chromium complex of acetylacetone,[5] and several ferrocene derivatives.[6–8] Shannon[9] has also described in some detail the ionization and fragmentation processes in a number of inorganic complexes. Most of these compounds have, however, been of moderate volatility or of considerable thermal stability (as in the case of the metalloporphyrins). We wish to

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present here the mass spectra of some 2-carbamoyldimedone (2-carbamoyl-5,5-dimethylcyclohexane-1,3-dione) metal complexes to exemplify the detailed information which mass spectrometry offers in the analysis of metal–ligand coordinate bonding.

Experimental Section

The mass spectra of 2-carbamoyldimedone and N-phenyl-2-carbamoyldimedone complexes of copper(II), zinc(II), and iron(III) have been obtained with an A.E.I. MS9 double focusing mass spectrometer using 70 ev electrons and 8 kv accelerating voltage. The compounds were introduced by direct evaporation. The temperature required to obtain an adequate signal was approximately 300°.

The synthesis and properties of the compounds have been reported.[10]

Results and Discussion

The spectra obtained can be divided into two main classes. In the first class can be placed the bis-2-carbamoyldimedone complexes. Considerable intermolecular bonding occurs in these compounds as is shown by melting point, solubility, spectroscopic, and magnetic measurements; as a result their volatility is extremely low.[10] Nevertheless, the spectrum of each of these complexes is sufficiently intense to reveal a parent ion and an ion corresponding to the ligand. Aside from the parent peak no other identifiable metal-containing ions are evident in the spectra, even though the spectra were taken at a resolution sufficient to distinguish metal-containing ions with characteristic large mass deficiencies from background or other species occurring at the same integral mass number. Thus it would appear that the only information which can be obtained from the mass spectra of such compounds is the molecular weight and the ligands present.

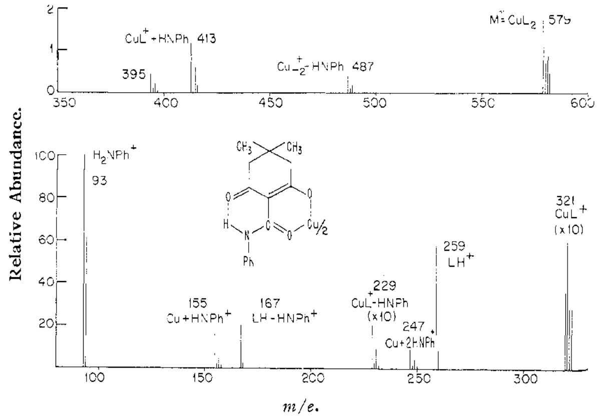

Figure 1.—The mass spectrum of bis(N-phenyl-2-carbamoyldimedonato)copper(II); LH = N-phenyl-2-carbamoyldimedone.

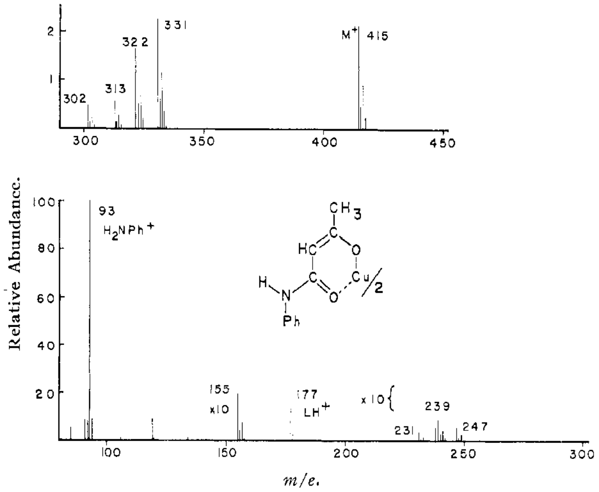

Figure 2.—The mass spectrum of bis(acetoacetanilidato)copper(II); LH = acetoacetanilide. Peak assignments: $(CuL_2 + HNC_6H_5)^+$ *m/e* 331, $(CuL_2 - H_2NC_6H_5)^+$ *m/e* 322, $(Cu + 2HNC_6H_5)^+$ *m/e* 247, $(CuL)^+$ *m/e* 239, $(Cu + HNC_6H_5)^+$ *m/e* 155.

On the other hand, the second class, which contains the N-phenyl-2-carbamoyldimedone and tris-2-carbamoyldimedone metal complexes, shows significant fragmentation. In comparison with class one, these compounds exhibit less intermolecular bonding and hence would be expected to possess a greater volatility.[10] The mass spectrum of bis(N-phenyl-2-carbamoyldimedonato)copper(II) is shown in Figure 1.[11] As is true of all these complexes, a small but nevertheless quite distinct parent peak is exhibited. Both the copper and zinc complexes lose a fragment corresponding to HNC_6H_5, and the spectrum of the copper complex exhibits a $CuL_2^+ - 2HNC_6H_5$ ion at *m/e* 395, which suggests that the carbamoyl oxygen and not the nitrogen is coordinated to the metal. This is borne out by other physical measurements.[10] However, there is a peak at *m/e* 413 in the spectrum of the copper complex (this is shifted to *m/e* 414 in the case of the zinc complex) which corresponds to an ion containing the metal attached to one ligand plus HNC_6H_5. A metastable ion peak is observed at *m/e* 294.6 which is due to the transition $M^+ \rightarrow (\text{metal–ligand} + HNC_6H_5)^+$, and thus *m/e* 413 must arise in a one-step process from the parent molecular ion. The one-step fragmentation suggests that the carbamoyl nitrogen is coordinated to the metal, unless some form of radical-transfer reaction can be invoked. Mandelbaum has reported that significant rearrangement reactions occur in substituted ferrocenes,[8] and numerous other radical-transfer processes have been discovered recently in the mass spectra of organic molecules. The mass spectrum of bis(acetoacetanilidato)copper(II) (see Figure 2) was therefore obtained since this is an analogous complex of ostensibly known structure.[12,13] In addition to a parent peak, peaks in the 331 region correspond to $(CuL + HNC_6H_5)^+$ and peaks at 322 are due to the loss of $H_2NC_6H_5$. Since bis(acetoacetanilidato)copper(II) is all-oxygen coordinated, some molecular rearrangement must be postulated to account for *m/e* 331 and by analogy used to explain such peaks in the spectra of the carbamoyldimedone complexes. The mechanism for the formation of the (metal–ligand + HN-

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[10] E. P. Dudek and M. L. Snow, *Inorg. Chem.*, in press.

[11] Each figure presents all the ion currents which were observed above the background in the given *m/e* range. The numbers ×10, ×20, or ×100 indicates that the peak intensities have been magnified by a factor of 10, 20, or 100, respectively.

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[13] R. L. Belford, E. A. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).

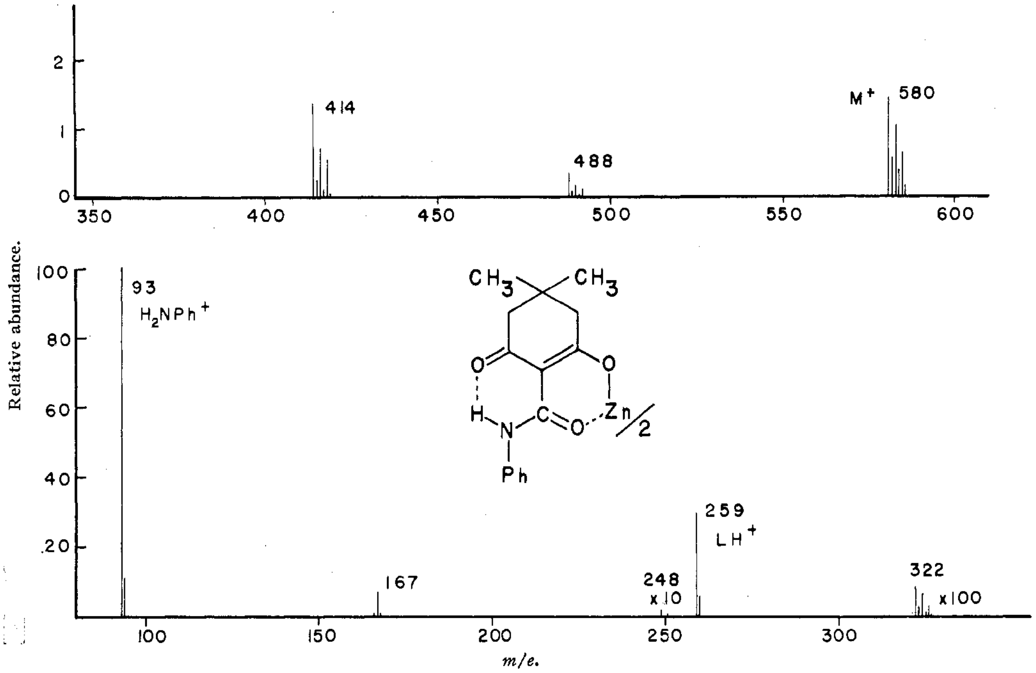
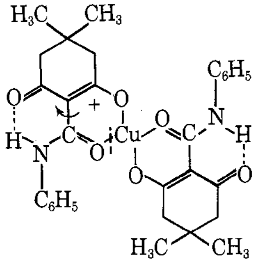
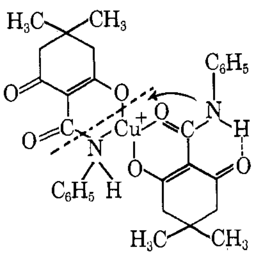


Figure 3.—The mass spectrum of bis(N-phenyl-2-carbamoyldimedonato)zinc(II); LH = N-phenyl-2-carbamoyldimedone. Peak assignments: $(ZnL_2 - HNC_6H_5)^+$ *m/e* 488, $(ZnL + HNC_6H_5)^+$ *m/e* 414, $(ZnL)^+$ *m/e* 322, $(Zn + 2HNC_6H_5)^+$ *m/e* 248, $(LH - HNC_6H_5)^+$ *m/e* 167.

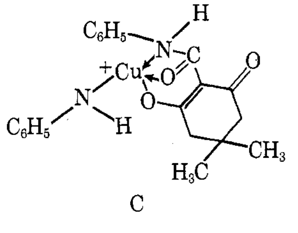
$C_6H_5)^+$ ion is presumably as follows. In the original metal complex the zinc or copper is in a +2 oxidation state, the compounds being outer orbital or ionic complexes,[10,14] hence on electron impact an electron is removed from the π system of the chelate ring rather than the metal cation. On the loss of the electron, the bond between the carbamoyl oxygen and the metal ion breaks, allowing the amide group to rotate about the C–C bond between the carbamoyl moiety and the 2-carbon of dimedone (structure A). On rotation the nitrogen of the carbamoyl group comes within bonding distance of the metal (structure B). The ligand then cleaves, leaving an HNC_6H_5 group joined to the metal. The charge on the ion could then produce a distortion in the remaining chelate ring to give rise to a quasi-tetracoordinated metal ion (structure C).



A



B



C

The mass spectrum of the copper complex shown in Figure 1 contains peaks which are noticeably absent or much less intense in the spectrum of the analogous zinc compound shown in Figure 3. Thus the ions of copper for which there are no comparable zinc ions are $CuL_2^+ - 2HNC_6H_5$, $CuL^+ - H$, $CuL^+ - HNC_6H_5$, and $Cu^+ + HNC_6H_5$, and the ions of copper which are much more intense than the corresponding zinc ions are CuL^+ and $Cu^+ + 2HNC_6H_5$. All of the ions listed contain copper(I). We believe that this difference between the analogous copper and zinc spectra is due to the fact that copper can readily assume a +1 oxidation state whereas zinc cannot. It is noted that the $CuL^+ - HNC_6H_5$ ion, *m/e* 229, is produced in a one-step fragmentation of the CuL^+ ion, *m/e* 321, as verified by the appearance of a metastable peak at *m/e* 163.4. The 259, 167, and 93 mass peaks in Figures 1 and 3 do not contain metal ions but are due instead to ligand fragments.

A comparison of the mass spectra of bis-N-phenyl-2-carbamoyldimedone metal complexes with that of tris-(N-phenyl-2-carbamoyldimedonato)iron(III) presented in Figure 4 reveals several significant differences. The relative intensities of the metal-containing ion fragments of bis(N-phenyl-2-carbamoyldimedonato)copper-(II) and tris(N-phenyl-2-carbamoyldimedonato)iron-(III) may be tabulated as in Table I, the parent peaks being assigned an abundance of 1%. The high intensity of the FeL_2^+ peak is indicative of the stability of the +2 oxidation state of iron. A metastable species at *m/e* 394.2 shows that the loss of one ligand from the parent ion, *m/e* 830, to form the FeL_2^+ species, *m/e* 572, is a one-step process. The low abundance of the FeL_2^+

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[14] Esr results to be published.

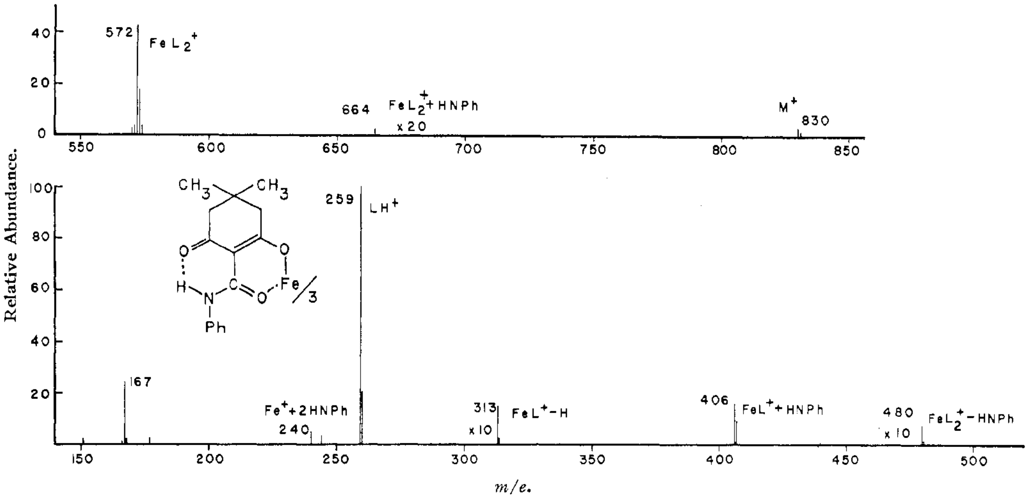

Figure 4.—The mass spectrum of tris(N-phenyl-2-carbamoyldimedonato)iron(III); LH = N-phenyl-2-carbamoyldimedone.

TABLE I

	$(ML_3)^+$	$(ML_2 + HNC_6H_5)^+$	$(ML_2)^+$	$(ML_2 - HNC_6H_5)^+$	$(ML + HNC_6H_5)^+$	$(ML - H)^+$	$(M + 2HNC_6H_5)^+$	$(ML - HNC_6H_5)^+$	$(M + HNC_6H_5)^+$
Fe	1%	0.03%	10%	0.2%	5%	0.4%	1%	0	0
Cu	...	...	1%	0.5%	0.4%	3.5%	5%	1%	8%

$+ HNC_6H_5$ fragment is due presumably to the steric difficulty in rotating a carbamoyl group about a carbon–carbon bond in an octahedral complex. The rotation is not hindered in the four-coordinate FeL_2^+ ion, and hence a sizable $FeL^+ + HNC_6H_5$ peak, *m/e* 406, is observed. Furthermore, since there is a metastable species at *m/e* 288.2, the 406 fragment must result from a one-step cleavage of the FeL_2^+ ion.

The remainder of the tris(N-phenyl-2-carbamoyldimedonato)iron(III) spectrum, including the ions, $FeL_2^+ - HNC_6H_5$ (*m/e* 480), $FeL^+ - H$ (*m/e* 313), and $Fe^+ + 2HNC_6H_5$ (*m/e* 240), is comparable to the copper spectrum of Figure 1. The intensities of the iron species are, however, considerably less than those of the analogous copper ions, supporting the fact that the +1 oxidation state is a more stable electronic configuration for copper than for iron.

Conclusions

It is evident from the preliminary studies of the 2-carbamoyl- and N-phenyl-2-carbamoyldimedone metal complexes that mass spectroscopy readily provides information pertaining to molecular weight, metal: ligand ratio, and the relative stabilities of the ion fragments of metal complexes. Furthermore, since the 2-carbamoyldimedone complexes discussed here melt with decomposition above 300°, it is apparent that mass spectral analysis is applicable to a wide range of metal complexes. However, due caution must be exercised when conclusions concerning the nature of the coordinate bonding are being made, since, as we have demonstrated above, quite complex rearrangements can occur. Use is therefore advised of running model compounds of known structure so that such rearrangements can be discovered and rationalized.