cadmium ion rather than an increase in ring strain in these rigid porphyrin-like chelate ligands.

Jakobsen et al.[3] and Kennedy and Ellis[5] have shown that four-coordinate Cd–porphyrins, which bind a single axial pyridine ligand and experience a resulting displacement of the cadmium ion out of the plane of the ligand (or further displacement from the plane of the ligand), undergo a concomitant shift of all the tensor elements. However, if the axially coordinating ligand binds without perturbing the position of the Cd^{2+} in the plane, only a change in the nonunique elements should be observed. From the data in Table I, the unique tensor element, σ_{33}, is shielded for complexes **3**–**5**, 310, 310, and 319 ppm, respectively, relative to that for complex **2** (325 ppm). These observations are consistent with those for axial pyridine coordination to Cd–TPP and Cd–PPIXDME, although the roughly 100 ppm shielding that occurs for the four-coordinate porphyrin is attenuated to a 10–15 ppm effect for the cadmium complex of the "expanded" texaphyrin system. The apparent reduced sensitivity to axial pyridine ligation of the Cd complex of the expanded porphyrin as reflected in the ^{113}Cd shielding tensor prompts the suggestion that the bonding requirements of the Cd^{2+} ion have been unusually well satisfied by the texaphyrin ligand. From Table I, the σ_{33} tensor element varies over a small range from 310 to 325 ppm for all the complexes **2**–**5**. In complex **4**, the Cd^{2+} resides in the plane of the ligand. However, in complex **5**, the Cd^{2+} lies 0.338 Å out of the ligand plane. Apparently, the change in the electron distribution in **5** compensates for the pulling of the Cd^{2+} out of the plane. Upon binding of pyridine to Cd–tetraphenylporphyrin, Jakobsen et al.[3] observed the unique element to be shielded by 124 ppm (see Table I).

Conclusions

From this study of the cadmium complex of texaphyrin and its pyridyl and benzimidazole adducts, the following observations have been made. First, a clear correlation exists between Cd–N bond length associated with cadmium complexes with rigid nitrogen-chelating aromatic macrocycle ligands, namely increasing bond length leads to increased shielding. Similar observations by others[18] have been interpreted in terms of strain of the chelate ring. However, it is difficult to disentangle the influence of the varying hybridization and the possibility of increased electron density about the cadmium ion associated with increasing coordination number. Second, the sensitivity of the "in-plane" tensor elements to apical binding of π-base ligands is clearly reduced compared to those of naturally occuring tetrapyrrolic porphyrins. This phenomenon may be due to an electronic overlap of the cadmium ion with the texaphyrin ligand such that the electron density undergoes a redistribution in such a way that compensates for axial ligand binding. This change in sensitivity of "in-plane" tensor elements between tetrapyrrolic porphyrins and texaphyrin to axial ligands is of potential interest to those practitioners of qualitative MO theory.

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Chemical-Ionization and Electron-Ionization Mass Spectra of Dimethylglyoxime and Its Complexes with Nickel(II), Palladium(II), and Platinum(II)[1]

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Positive-ion methane chemical-ionization (CI) mass spectra are reported for the title compounds. Also "self-CI" is reported for dimethylglyoxime at high sample pressures with no reagent gas. For the metal complexes, the respective protonated molecules dominate the CI spectra, and higher mass peaks are observed for adducts with reagent-gas ions and for protonated dimers, whose relative abundances increase with sample pressure. Charge transfer from reagent-gas ions is seen in each case, and a small but significant abundance of only one metal-containing fragment is seen for each metal complex. In contrast, free dimethylglyoxime has a methane CI spectrum dominated by fragments, although the above-mentioned ion types are formed also, and its self-CI spectrum shows more abundant protonated monomer and dimer. Comparisons are made with electron-ionization mass spectra, which show extensive fragmentation at 70 eV, where some previously unrecognized or misassigned fragments are now assigned on the basis of isotopic peak ratios in natural-abundance and deuterated samples. Thermal reactions appear to have affected some previously reported spectra. The CI spectral assignments are verified similarly.

Introduction

Although dimethylglyoxime (2,3-butanedione dioxime or H_2dmg) has long, been used as a chelating agent for Met(II), where Met = Ni, Pd, and Pt, there has been little study of the mass spectra and gaseous ion chemistry of it or its metal complexes.

There are reports of positive-ion electron-ionization (EI) mass spectra for H_2dmg[2] and its chelates (Figure 1) $Met(Hdmg)_2$.[2-6] Because of possible interference from thermal reactions or of incomplete data analysis, some of these studies of the complexes show disagreements in assignments and presence or absence of certain mass spectral peaks. In the most thorough of these and the only one to consider the Pt complex and the deuterated $Ni(Ddmg)_2$, Westmore and Fung[5] suggested structures for the fragment ions, concluding that the molecular ions of the complexes are very stable and that metal-to-ligand π bonding in the fragments prevents a simple rationalization of the fragmentation pathways in terms of formal oxidation states accessible by the metal. The latter approach has been used successfully with other coordination compounds.[7] Positive-ion chemical-ionization (CI) mass spectra

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(1) Presented in part at the 194th National Meeting of the American Chemical Society, New Orleans, LA, Aug 30–Sept 4, 1987.

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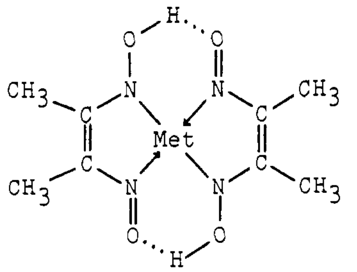

Figure 1. Structure of Met(Hdmg)$_2$.

had not been reported for any of the title compounds until the present work was near completion, when Charalambous et al. reported ammonia CI spectra for H$_2$dmg and Ni(Hdmg)$_2$. They stated also that the methane CI spectrum of H$_2$dmg is dominated by $[MH]^+$ and $[M]^{\bullet+}$ with large abundances of unspecified low-mass fragments.[8]

The present work was undertaken to obtain, excluding thermal reaction products, positive-ion methane CI spectra of H$_2$dmg and its complexes with Ni(II), Pd(II), and Pt(II), to obtain EI spectra of these compounds in order to resolve the previous discrepancies and for comparison with the CI, and to elucidate the gaseous ion chemistry that gives rise to these spectra.

Experimental Section

H$_2$dmg (mp 242–244 °C) was obtained commercially. Ni(Hdmg)$_2$ was prepared from aqueous $NiSO_4$ and ethanolic H$_2$dmg, adjusting to pH 6 with ammonia. The mixture was filtered to obtain the red precipitate. The yellow Pd complex was made similarly from hot aqueous $PdCl_2$. From a published procedure,[9] the violet Pt(Hdmg)$_2$ was obtained. D$_2$dmg was prepared by dehydrating Na$_2$dmg·8H$_2$O at 130 °C for 15 h and then dissolving it in D_2O. Acidification with 10% H_2SO_4 in D_2O gave the D$_2$dmg precipitate, which was filtered, washed with D_2O, and dried. To make Ni(Ddmg)$_2$, ethanolic D$_2$dmg was mixed with $NiCl_2$ in D_2O. Although these procedures do not strictly exclude protium, the extent of deuteration, as evidenced in the mass spectra, depended strongly on the pretreatment with D_2O of the Pyrex sample tubes for the direct probe. For each spectrum of a deuterated sample, the extent of deuteration was determined from the isotopic cluster of the molecular ion and, for CI, of the $[MH]^+$ and $[MC_2H_5]^+$ ions. In each case, deuteration was sufficient (45–70% for the two active hydrogens in each molecule) to calculate unambiguously the degrees of deuterium retention in the fragment ions relative to that in the unfragmented ions.

The instrument is a Finnigan MAT 1020B GC/MS with CI and EI ion sources and direct probe inlet. H$_2$dmg was introduced typically by injecting into the GC about 100 ng in 0.5 μL of diethyl ether. The capillary column leads directly into the ion source. For D$_2$dmg and the metal chelates, several micrograms were introduced via the direct probe ramped at 2°/s.

Ionizing energy was 70 eV and the ion-repeller potential was 3 V. The CI reagent gas was ultrahigh-purity methane at 50 Pa. Self-CI spectra were obtained with the CI ion source but without methane. The quadrupole mass analyzer, with an upper limit of m/z 800, was operated at unit resolution. It was tuned and calibrated daily with perfluorotributylamine (FC-43) and was used for repetitive full scans typically at 2 s per scan.

Results and Discussion

Spectrum averaging with background subtraction was carried out with the data system. In order to avoid interference from possible products of thermal reactions, peaks were further verified as arising from the same compound by the similarity of their intensity-versus-time profiles as the sample eluted from the GC (mass chromatograms) or vaporized from the direct probe.

Isotopic clusters were compared with calculated patterns to verify elemental compositions of the ions and to determine relative abundances of chemically different ions whose isotopic clusters overlapped. In Table I is the example of m/z 333–342 in the CI spectrum of Pd(Hdmg)$_2$. The observed relative intensities of these peaks are consistent with the presence of the molecular ion $[M]^{\bullet+}$ and the protonated molecule $[MH]^+$ in the ratio 20/97 = 21% (using the values in columns 2 and 3 for the ^{106}Pd species), although the errors show that a small contribution from $[M - H]^+$ cannot be ruled out.

Table I. Analysis of the $[M]^{\bullet+}$ and $[MH]^+$ Isotope Cluster in the CI Mass Spectrum of Pd(Hdmg)$_2$

	rel abundance[a]				
m/z	obs[b]	$[M]^{\bullet+}$ calc	$[MH]^+$ calc	tot. calc	obs − tot. calc
333	4 ± 1	0	3	3	1
334	10 ± 1	8	0	8	2
335	57 ± 2	16	36	52	5
336	100	20	76	97	3
337	99 ± 4	2	97	99	(0)
338	29 ± 2	18	11	29	(0)
339	89 ± 4	2	87	89	−1
340	18 ± 2	8	9	18	0
341	39 ± 2	1	39	40	−1
342	4 ± 1	0	4	4	−1

[a] Abundances in columns 2–6 are relative to that observed at m/z 336. Values in columns 3 and 4 were calculated from accepted natural isotopic abundances and were scaled to force agreement with observed values at m/z 337, which is predominantly $[MH]^+$ (^{106}Pd), and at m/z 338, which is predominantly $[M]^{\bullet+}$ (^{108}Pd). [b] Observed mean and standard deviation for five runs carried out on four different days.

Table II. Relative Abundances of Ions in the Methane CI Mass Spectra of Dimethylglyoxime and Its Metal Complexes[a]

	rel ion abundance (mass no.)			
ion	H$_2$dmg	Ni(Hdmg)$_2$	Pd(Hdmg)$_2$	Pt(Hdmg)$_2$
$[M_2H]^+$	var[b] (233)	var (577)	var (673)	?
$[MC_3H_5]^+$	5 (157)	1.8 (329)	2.1 (377)	2.7 (466)
$[MC_2H_5]^+$	11 (145)	14 (317)	15 (365)	17 (454)
$[MH]^+$	100 (117)	100 (289)	100 (337)	100 (426)
$[M]^{\bullet+}$	13 (116)	21 (288)	21 (336)	27 (425)
$[MetH_2dmgNO]^+$		2.7 (204)	3.5 (252)	0.8 (341)
$[CH_3CNOH]^+$	460 (58)			

[a] Contributions from isotopic peaks have been subtracted but are consistent with calculated natural abudances for the given ions. Ion abundances (not peak intensities) are shown relative to that of $[MH]^+$; these are followed in parentheses by the mass number of the dominant isotopic peak for ^{58}Ni, ^{106}Pd, or ^{195}Pt. [b] var = variable.

Methane Chemical Ionization. A comparison of principal ion abundances from the methane CI spectra is in Table II. Each complex shows $[MH]^+$ to be the most abundant ion, but for H$_2$dmg the most abundant is at m/z 58, taken as the "half-molecular" ion $[CH_3CNOH]^+$ related to acetaldoxime. This ion shows the corresponding retention of one deuterium from D$_2$dmg, as with EI, while the other listed ions retain both. Each compound shows a protonated dimer $[M_2H]^+$, whose relative abundance increases with sample size or partial pressure, except the Pt complex, for which this ion's mass would be beyond the range of the present instrument. This ion must be an adduct of $[MH]^+$ with neutral M. No evidence was found for any other ions containing more than one metal atom. The methane plasma adducts $[MC_2H_5]^+$ and $[MC_3H_5]^+$ were observed in each case with similar relative abundances for the ethyl adducts, but with a somewhat more abundant propenyl adduct for H$_2$dmg than for Met(Hdmg)$_2$.

An abundant molecular ion $[M]^{\bullet+}$ was seen for each compound. For the present conditions, direct EI of M should be negligible, but a molecular ion can arise by electron transfer if the vertical ionization energy (IE) of M is less than the recombination energy of reagent-gas ions, 810 kJ/mol for $C_2H_5^+$ or 770 kJ/mol for CH_5^+.[10] The observation of the molecular ions implies that the present compounds have IEs below the former value. The greater relative abundances of these ions from the complexes than from H$_2$dmg suggests that the Met(Hdmg)$_2$ have smaller IEs than H$_2$dmg. This agrees with a simple MO model of the metal complexes that gives the HOMO (a_{1g}) as metal-localized (d_{z^2}).

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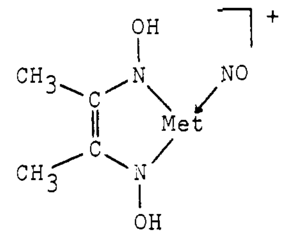

Figure 2. Structure of $[MetH_2dmgNO]^+$.

Table III. Relative Abundances of Ions in the EI Mass Spectrum of Dimethylglyoxime[a]

m/z	rel abundance	assignt
116 (2)[b]	29	$[M]^{\bullet +}$
99 (1)	22	$[M - OH]^+$
68	12	$[M - OH - NOH]^+$
58 (1)	32	$[CH_3CNOH]^+$
57	7.4	$[CH_3CNO]^{\bullet +}$
54	9.3	$[CH_3C{=}CCH_3]^{\bullet +}$
52	6.9	$[C_2N_2]^{\bullet +}$
43	13	$[CHNO]^{\bullet +}$
42 (<1)	100	$[CNO]^+$ or $[CH_3CNH]^+$
41 (<1)	53	$[CH_3CN]^{\bullet +}$ or $[CH_2CNH]^{\bullet +}$
40	32	$[CH_2CN]^+$
39	16	$[C_3H_3]^+$
38	7.0	$[C_3H_2]^{\bullet +}$
31 (1)	20	$[NOH]^{\bullet +}$
30	11	$[NO]^+$
28	26	$[C_2H_4]^{\bullet +}$ or $[HCNH]^+$
27	14	$[C_2H_3]^+$ or $[HCN]^{\bullet +}$
15	16	$[CH_3]^+$

[a] Ionizing energy is 70 eV. Only those ions with abundances >5% are shown. [b] The number of deuterium atoms, if any, retained in each ion from D_2dmg is shown in parentheses.

A CI fragment must be formed with small endothermicity. The only metal-containing CI fragment ion detected from the three complexes is $[MetH_2dmgNO]^+$, which is also seen in the EI spectra but was not reported in the previous CI study of the Ni complex.[8] Its relative abundance is lowest for the Pt complex in both CI and EI modes. It was suggested that the EI fragment arises by loss of NO$^\bullet$ and 2-butyne from the molecular ion to give predominantly a structure with another neutral NO$^\bullet$ ligand bonded to Met(I).[5] If, however, the ion is represented as in Figure 2 with a NO^+ ligand, then the metal may be considered to retain its favored Met(II) state. The ion may arise similarly in CI from $[M]^{\bullet +}$ in accord with the present observation that the CI fragment retains both deuteriums from $Ni(Ddmg)_2$. The CI fragment could arise also from $[MH]^+$ by loss of even-electron neutral C_4H_7NO if the proton from the reagent gas remains with the neutral, not the ionic, fragment.

All the compounds show ions with low abundances (<3%) that might seem to involve loss of an oxygen atom from the protonated molecule (retaining both deuteriums from D_2dmg), but these ions are considered to arise from the product of thermal reaction preceding ionization. In an EI study of aldoximes it was concluded that they lose O to give imines by a thermal process.[11]

Although not indicated in Table II, loss of H_2O from $[MH]^+$ is seen in the CI spectrum of only H_2dmg, with 6% relative abundance at m/z 99, retaining one deuterium from D_2dmg. The absence of this process in the metal complexes may be explained by their interligand hydrogen bonding, but $Ni(Hdmg)_2$ reportedly[8] gives $[M - H_2O]^{\bullet +}$ under ammonia CI. The purported loss of H_2O from H_2dmg by EI is considered next.

Electron Ionization of H_2dmg. The EI data observed for H_2dmg and the ion assignments, based on the known structure of the molecule and deuteration experiments, are in Table III. These agree substantially with those of Charalambous et al.,[2] but with several significant exceptions. The peak they reported at m/z 98, corresponding to $[M - H_2O]^{\bullet +}$, is detected here with irreproducible and smaller relative intensities than previously given. Its mass chromatogram does not match those of other ions coming from H_2dmg. Although previous workers[2] reported the metastable process from the parent ion at m/z 116, the peak at m/z 98 must result, to a large extent, from the molecular ion of a compound, apparently 3,4-dimethylfurazan, formed by thermal dehydration of neutral H_2dmg. This supports the EI study of aldoximes by Vijfhuizen et al., who argued, contrary to earlier supposition, that the analogous dehydration is largely a heterogeneously catalyzed thermal process.[11] The *E*,*E* configuration of H_2dmg keeps the two active hydrogens well separated; maintenance of this configuration in the molecular ion should preclude its unimolecular dehydration.

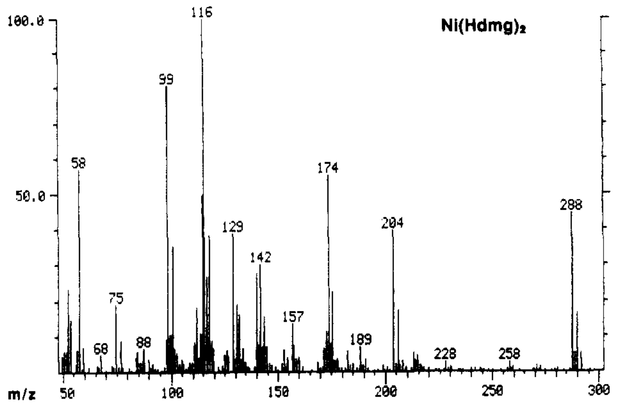

Figure 3. Example of a 70-eV electron-ionization mass spectrum of $Ni(Hdmg)_2$.

Another difference is that the previous study[2] gave the base peak for H_2dmg at m/z 41 for $[CH_3CN]^{\bullet +}$ and did not report m/z 42, but here the intensity at m/z 42 is twice that at m/z 41. Also the ion at m/z 57 is much less abundant here than previously. These differences are understood if fragments at m/z 57 and 41 arise from the parent ion at m/z 98, as Charalambous et al.[2] supposed, but now, as discussed above, this parent ion is *not* attributed primarily to H_2dmg. Ions at m/z 57 and, to a lesser extent, m/z 41 were reported[12] as abundant fragments in the EI spectrum of dimethylfurazan, the presumed dehydration product of H_2dmg.

The species giving rise to m/z 41 and 42 in H_2dmg show only partial retention of a deuterium atom from D_2dmg. This implies that the hydrogens in $[CH_3CN]^{\bullet +}$ at m/z 41 do not come only from the methyl groups of H_2dmg and that $[CH_2CNH]^{\bullet +}$ may contribute. At m/z 42, $[CH_3CNH]^+$ formation may involve hydrogen participation from both methyl groups, or $[CNO]^+$ may contribute.

Besides m/z 42, ions now observed at m/z 52, 40, 38, 31, 30, 28, 27, and 15 were not previously reported.[2]

Electron Ionization of $Met(Hdmg)_2$. An example EI spectrum of $Ni(Hdmg)_2$ is in Figure 3 for illustration, but isotopic analyses were based on more precise numerical printouts of relative abundances. The principal ions and their abundances for the three metal complexes are in basic agreement with those reported by Westmore and Fung.[5] Points of disagreement with previous reports will be discussed for each complex.

For $Ni(Hdmg)_2$ the abundant ion at m/z 116 contains a Ni atom according to isotopic analysis and is taken to be $[Ni(OH)NCCH_3]^+$ in agreement with Charalambous et al.[2] and with Ablov et al.[4] but contrary to Westmore and Fung,[5] who omitted it as a metal-containing ion, and Isa and Yamada,[6] who presumed it to be $[H_2dmg]^+$ although their spectrum implies that it contains Ni. Conversely m/z 58 was taken as Ni^+ in the three reports in which an identity for it was proposed, but Ablov et al.[13] noted

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a slightly distorted Ni^+ peak shape in other nickel dialkylglyoximates and attributed it to superposition of an organic fragment. Isotopic analysis here shows both $[CH_3NOH]^+$, a fragment from H_2dmg also, and Ni^+ in a 3:2 ratio. Minor nickel-containing ions not previously reported are taken as $[NiNO]^+$ at m/z 88 and $[NiNCH]^+$ at m/z 85. Isotopic ratios confirm the formulation $[NiNCCH_3]^+$ for m/z 99, although it was previously reported[6] as $[H_2dmg - OH]^+$. An early report[3] showed abundant fragments at m/z 115, 173, and 203, but these were apparently misassignments of m/z 116, 174 or $[NiH_2dmg]^+$, and 204 or $[NiH_2dmgNO]^+$, respectively, as given in later reports and found in the present work.

The results for $Pd(Hdmg)_2$ and $Pt(Hdmg)_2$ are analogous to those above in that neither of these shows a fragment at m/z 116, but both show an abundant one at m/z 58, which cannot contain these metals and must be $[CH_3NOH]^+$ only. The earlier works on the Pd complex[4,5] did not report the now-observed metal-containing fragments at m/z 261 (with apparent formula $[Pd(dmg)NCCH_3]^+$), 191 ($[PdC_4H_7NO]^+$), 190 ($[PdC_4H_6NO]^+$), 164 ($[C_2H_4NO]^+$), 163 ($[PdC_2H_3NO]^+$), 159 ($[PdC_4H_5]^+$), 136 ($[PdNO]^+$), 133 ($[PdNCH]^+$), and 121 ($[PdNH]^+$ or $[PdCH_3]^+$) or the doubly charged molecular ion at m/z 168. Analysis of a spectrum from another report[6] implies the formation at 15 eV of all these ions except those at m/z 168, 164, 159, and 133, which may have higher appearance energies.

A list of only metal-containing ions from an EI spectrum of $Pt(Hdmg)_2$ was given previously.[5] The present work shows that the ion at m/z 58 ($[CH_3CNOH]^+$) is much more abundant than any of those containing Pt. Of the three complexes, this one shows the most extensive fragmentation and the highest relative abundance of $[M]^{2+}$, consistent with the familiar stability of Pt(IV). It is noted here, but not previously, that both $[PtNC]^+$ at m/z 221 and $[PtNCH]^+$ at m/z 222 have comparable high abundances, although $[MetNC]^+$ is not detected for the Ni or Pd complexes. Other newly reported Pt-containing ions are at m/z 252 ($[PtC_2H_3NO]^+$), 250 ($[PtC_4H_7]^+$), and 247 ($[PtC_4H_4]^+$).

Self Chemical Ionization of H_2dmg. As noted above, under EI conditions, where the partial pressure of H_2dmg is relatively low, the mass spectrum is dominated by the fragments at m/z 42 and 41. When larger sample pressures are used in the absence of methane, $[H_3dmg]^+$ at m/z 117 gives the base peak, with high abundances also at m/z 58, 42, and 15. The protonated dimer $[H_5(dmg)_2]^+$ at m/z 233, observed also with methane CI, grows with an even stronger positive pressure dependence, reaching an abundance as high as 50% of that of $[H_3dmg]^+$. The high abundance of $[H_3dmg]^+$ implies that neutral H_2dmg is protonated by its primary fragment ions as well as, possibly, the molecular ion. At higher pressures $[H_3dmg]^+$ reacts with H_2dmg to form the protonated dimer under self-CI or methane CI conditions.

With the present apparatus, it was not possible to achieve pressures of the metal complexes high enough to detect self-CI or clustering processes in the absence of methane, although this has been done with metal β-diketonates[14-16] and acetates.[17] In an olefin CI study of Cu(II) β-diketonate complexes, it was suggested that the high pressure of reagent gas increases the residence time of sample molecules in the ion source, favoring ion–molecule clustering.[18] This or a similar increase in *ion* residence time is consistent with the present observations.

Conclusions

Methane CI spectra of the metal complexes are dominated by $[MH]^+$ with important contributions from $[M]^{\bullet+}$ and methane plasma adducts. These are abundant also for H_2dmg, but the base peak here is due to the "half-molecular" fragment $[CH_3CNOH]^+$. Protonated dimers are apparently adducts of $[MH]^+$ with M. $[M]^{\bullet+}$ is taken as resulting from electron transfer from M to the reagent gas, since it occurs more readily for the complexes than for H_2dmg. The only fragment from the complexes is $[MetH_2dmgNO]^+$, also seen in EI, where the favored Met(II) state may be retained.

The previously reported[2] EI spectrum of H_2dmg appears to have been affected by thermal dehydration. The base peak is now found at m/z 42. For the metal complexes, a consideration of intensities of natural-abundance isotopic peaks shows that several EI fragment peaks were incorrectly assigned in previous reports.

As H_2dmg pressure increases in the absence of methane, the spectrum is dominated by $[MH]^+$, with $[M_2H]^+$ becoming strong.

When the attempt is made to interpret a compound's mass spectrum, it should be standard procedure to exclude interference from other compounds by comparing mass chromatograms, when GC introduction is used, or the analogous intensity-versus-time plots, when a direct probe is used, for each peak in the spectrum. For low-resolution spectra of polyisotopic metal compounds, ion assignments should be confirmed by agreement between observed and calculated isotopic peak intensities.

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