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Mass Spectrometry of *vic*-Dioximate Complexes of Nickel, Palladium, and Platinum

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The nickel(II), palladium(II), and platinum(II) complexes formed from dimethylglyoxime, diphenylglyoxime, and α-furildioxime have been studied by positive ion electron-impact mass spectrometry. The molecular ions of every complex are very stable and correspond to the base peak in seven of nine spectra. Usually, the stabilities of the molecular ions are in the sequence Pt > Ni > Pd. The spectra are rather complicated, but ion types and structures of fragment ions correlate well with structures known from the condensed-phase chemistry of the metals. Some ion types are specific to certain complexes, and there are significant differences between the behaviors of the three metals. The most conspicuous trend involves the formation of fragment ions with metal–carbon σ bonds and metal–acetylene bonds. Such ions increase in prominence in the spectra of the metal complexes in the sequence Ni < Pd < Pt, consistent with the known chemistry of the metals. In contrast to the case for "classical complexes", the spectra do not show a well-defined dependence on the formal oxidation state of the metal, no doubt reflecting the extensive metal→ligand π bonding that is possible in many fragment ions.

Introduction

The mass spectra of metal-containing compounds have often been discussed in terms of the valence-change concept[1,2] for rationalizing the major fragmentation pathways. It was proposed that the odd- or even-electron character of a metal-containing ion is determined by the capacity of the metal to accept one or more electrons from the ligands (valence decrease) or to donate one or more electrons to the ligands (valence increase). Thus, ion abundances in mass spectra will be influenced by the ion structures and relative stabilities of oxidation states of metals in gaseous metal-containing ions. In the absence of substantial information on these points it has been necessary to discuss spectra in terms of the general chemistry of the particular metal. While the perhaps unwarranted assumptions inherent in this procedure are recognized, considerable success has been achieved in rationalizing ion decompositions of "classical complexes"[3,4] in this way.[5] The concept has been applied in reviews of the spectra[6] and energetics[7] of decompositions of coordination compounds of many transition and nontransition metals. However, there are many complexes for which the oxidation state of the metal is vague or ambiguous, particularly when the metal–ligand bond is highly covalent and/or multiple, e.g., when π-acceptor or π-bonded ligands are involved. In these cases the mass spectra differ in important qualitative ways from those of classical complexes and the valence-change concept becomes less useful.

In this paper we describe a systematic study of the mass spectrometry of *vic*-dioximate complexes of nickel(II), palladium(II), and platinum(II). These complexes have complicated mass spectra that are of fundamental interest because while the initial compounds may be considered as classical complexes it will be shown that many of the fragment ions have ligand residues that fall into the π-acceptor or π-bonded classifications. The spectra can be used as a sensitive probe to investigate the variations in mass spectral behavior between the metals of this group. Our studies are much more extensive than earlier reports on the nickel complexes of dimethyl- and diphenylglyoximes[8] and of nickel and palladium complexes of dialkylglyoximes.[9,10] They do, in fact, reveal significant differences between the stabilities of ions containing the three metals.

Other reports on the mass spectrometry of palladium and platinum chelates are much fewer than those for nickel. They include studies of complexes formed from derivatives of salicylaldimines (Pd and Pt),[11,12] acetylacetone ethylenediimines (Ni, Pd, and Pt),[13] Schiff bases derived, from ethylenediamine and β-diketones (Ni and Pd),[14,15] salicylaldoximes (Ni and Pd),[16] and 8-quinolinol and 2-methyl-8-quinolinol (Ni, Pd, and Pt).[17]

Experimental Section

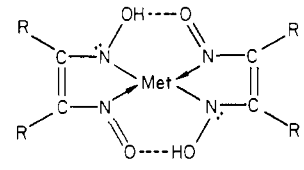
The complexes were prepared by adding alcoholic solutions of the *vic*-dioximes (Fisher Scientific Co.) to aqueous solutions of $NiCl_2$, $PdCl_2$ (acidified with HCl), and K_2PtCl_4. The precipitates were filtered off, washed thoroughly with ethanol, and dried in an oven at 60 °C. Deuteration of $Ni(DMG)_2$ was achieved by refluxing its solution in dimethyl sulfoxide with D_2O for about 1 h to give the following deuterium incorporation: d_2, 37%; d_1, 45%; d_0, 18%.

Positive ion electron-impact mass spectra of samples admitted via the direct-insertion probe were recorded with a Hitachi RMU-6D single-focusing mass spectrometer at an electron beam energy of 50 V, ion-accelerating voltage of 1200 V, and an ionization chamber temperature of 220–250 °C.

Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere with use of the TGA mode of a Perkin-Elmer DSC-1B combined differential scanning calorimeter–thermogravimetric analyzer.

Results and Discussion

The compounds chosen for study were the *vic*-dioximate complexes **1**–**3** of Ni(II), Pd(II), and Pt(II) formed from



1: $Met(DMG)_2$, $R = CH_3$
2: $Met(DPG)_2$, $R = C_6H_5$
3: $Met(AFD)_2$, $R = 2\text{-}C_4H_3O$

dimethylglyoxime (HDMG), diphenylglyoxime (HDPG), and

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Table I. Relative Abundances (RA) of Metal-Containing Ions in the Mass Spectra of Dimethylglyoximate Complexes (Base Peak 100%)

m/z	% RA			assignt
	Ni	Pd	Pt	
M[a]	100 (27.9)	100 (23.5)	100 (29.0)	$[\mathrm{MetL_2}]^+$, a
M − 17	5.6	2.0	16	$[\mathrm{MetL_2} - \mathrm{OH}]^+$, b
M − 30	4.4	7.0	7.4	$[\mathrm{MetL_2} - \mathrm{NO}]^+$, c
M − 47			5.1	$[\mathrm{MetL_2} - (\mathrm{OH} + \mathrm{NO})]^+$, x
M − 60	2.7	1.6	1.4	$[\mathrm{MetL_2} - 2\mathrm{NO}]^+$, d
M − 61			2.8	$[\mathrm{MetL_2} - (\mathrm{NO} + \mathrm{NOH})]^+$, y
M − 74	4.1	6.0		$[\mathrm{MetL(NCR)}]^+$, p
M − 75	6.3		11	$[\mathrm{Met(L - H)(NCR)}]^+$, q
M − 77			11	$[\mathrm{MetL_2} - (\mathrm{OH} + 2\mathrm{NO})]^+$, z
M − 84	34	18	7.7	$[\mathrm{Met(LH)(NO)}]^+$, e
M − 104			4.0	$[\mathrm{Met(L - NO)(NCR)}]^+$, aa
M − 105	4.4		9.1	$[\mathrm{Met(L - NOH)(NCR)}]^+$, r
M − 106			8.0	$[\mathrm{Met(N_2C_2R_2)(NCR)} + \mathrm{H}]^+$, ab
M − 114	44	97	5.1	$[\mathrm{MetLH}]^+$, f
M − 115	8.7	22	5.5	$[\mathrm{MetL}]^+$, g
M − 116			2.9	$[\mathrm{Met(L - H)}]^+$, h
M − 131	7.0	28	12	$[\mathrm{Met(LH - OH)}]^+$, i
M − 135			5.1	$[\mathrm{Met(C_2R_2)(NCR)}]^+$, ac
M − 136			5.1	?
M − 144	4.4		14	$[\mathrm{Met(LH - NO)}]^+$
M − 145	1.9		6.4	$[\mathrm{Met(L - NO)}]^+$
M − 146	9.4		16	$[\mathrm{Met(L - NOH)}]^+$, j
M − 147	3.9	7.6	5.5	$[\mathrm{Met(NCR)_2} + \mathrm{H}]^+$
M − 148	16	12	10.6	$[\mathrm{Met(NCR)_2}]^+$, k
M − 159	17	7	8.3	$[\mathrm{Met(NO)(NCR)}]^+$, s
M − 162		12	17	$[\mathrm{MetNC_2R_2}]^+$, l
M − 176	8.5	8.0	27	$[\mathrm{MetC_2R_2}]^+$, m
M − 189	38	59	5.5	$[\mathrm{MetNCR}]^+$, t
M − 203	12	17	10.6	$[\mathrm{MetCN}]^+$ or $[\mathrm{MetNC}]^+$
M − 213	11			$[\mathrm{MetOH}]^+$
M − 230	12	22	1.9	$[\mathrm{Met}]^+$
M/2	2.9		1.9	$[\mathrm{MetL_2}]^{2+}$, n
(M − 60)/2			1.4	$[\mathrm{MetL_2} - 2\mathrm{NO}]^{2+}$, o

	Ni	Pd	Pt
probe temp, °C	200 ± 10	185 ± 10	170 ± 10
dec temp,[b] °C	340 ± 10	354 ± 10	332 ± 10

[a] Molecular weights: $^{58}\mathrm{NiL_2}$, 288; $^{106}\mathrm{PdL_2}$, 336; $^{195}\mathrm{PtL_2}$, 425; L, 115. Parentheses denote the molecular ion current as a percentage of the total metal-containing ion current. [b] Determined by thermogravimetric analysis under a nitrogen atmosphere.

di-2-furanylethanedione dioxime (α-furildioxime, HAFD). This selection of compounds permits assessment of the effects of alkyl vs. aryl substitution in the ligand.

The complexes, admitted to the ion source on the heated direct-insertion probe, vaporized smoothly at temperatures far below their initial decomposition temperatures as determined in separate experiments by thermogravimetric analysis under a nitrogen atmosphere (see Tables I–III). The relative abundances of metal-containing ions in their positive ion electron-impact mass spectra, listed by ion type, are presented in Tables I–III. (The term "Met" is used to denote the metal atom; this avoids confusion with the molecular ion "$\mathrm{M}^{+\cdot}$". The ligand is denoted by "L".) Metal-containing ions are easily recognized by their characteristic isotopic patterns while mass shifts from ligand to ligand enable elemental compositions to be assigned with confidence in most cases (except as noted in the tables), even though exact mass determinations are not possible with our instrumentation. The less interesting ions that do not contain a metal have not been tabulated, but in general, the relative abundances of several of them are of magnitude comparable to those listed. In cases where two or more ion types differ by 1–3 in their *m/z* values, the Pd and Pt compounds gave a complex pattern of mass spectral peaks. The relative abundances in Tables I–III are calculated in terms of correct abundances for the principal isotopic mass in each ion type.

Table II. Relative Abundances (RA) of Metal-Containing Ions in the Mass Spectra of Diphenylglyoximate Complexes (Base Peak 100%)

m/z	% RA			assignt
	Ni	Pd	Pt	
M[a]	100 (20.1)	96 (20.7–28.2)[b]	100 (40.4)	$[\mathrm{MetL_2}]^+$, a
M − 17		6.1	20	$[\mathrm{MetL_2} - \mathrm{OH}]^+$, b
M − 30	21	3.7	16	$[\mathrm{MetL_2} - \mathrm{NO}]^+$, c
M − 60		4.1		$[\mathrm{MetL_2} - 2\mathrm{NO}]^+$, d
M − 137			3	$[\mathrm{Met(L - H)(NCR)}]^+$, q
M − 168			8	$[\mathrm{Met(N_2C_2R_2)(NCR)} + \mathrm{H}]^+$, ab
M − 197			11	$[\mathrm{Met(C_2R_2)(NCR)}]^+$, ac
M − 208	57	22	4	$[\mathrm{Met(LH)(NO)}]^+$, e
M − 238	78	100		$[\mathrm{MetLH}]^+$, f
M − 239	28	15		$[\mathrm{MetL}]^+$, g
M − 255	63	25		$[\mathrm{Met(LH - OH)}]^+$, i
M − 272	11	19	10	$[\mathrm{Met(NCR)_2}]^+$, k
M − 286	9.0	18	4.5	$[\mathrm{MetNC_2R_2}]^+$, l
M − 288	13	5.5	13	?
M − 300	29	26	30	$[\mathrm{MetC_2R_2}]^+$, m
M − 375	89	≤123[c]	22	$[\mathrm{MetNCR}]^+$, t
M/2			6	$[\mathrm{MetL_2}]^{2+}$, n

	Ni	Pd	Pt
probe temp, °C	205 ± 10	195 ± 10	265 ± 10
dec temp,[d] °C	362 ± 10	338 ± 10	388 ± 10

[a] Molecular weights: $^{56}\mathrm{NiL_2}$, 536; $^{106}\mathrm{PdL_2}$, 584; $^{195}\mathrm{PtL_2}$, 673; L, 239. Parentheses denote the molecular ion current as a percentage of the total metal-containing ion current. [b] Range limits calculated for inclusion and omission of the (M − 375) ion. [c] Interference from a non-metal-containing ion. [d] Determined by thermogravimetric analysis under a nitrogen atmosphere.

Table III. Relative Abundances (RA) of Metal-Containing Ions in the Mass Spectra of α-Furildioximate Complexes (Base Peak 100%)

m/z	RA			assignt
	Ni	Pd	Pt	
M[a]	100 (31.3)	91 (27.5)	100 (36.9)	$[\mathrm{MetL_2}]^+$, a
M − 16	1.5	19	16	$[\mathrm{MetL_2} - \mathrm{O}]^+$, u
M − 30	6.5	13	14	$[\mathrm{MetL_2} - \mathrm{NO}]^+$, c
M − 31			24	$[\mathrm{MetL_2} - \mathrm{NOH}]^+$, w
M − 60	20	16	18	$[\mathrm{MetL_2} - 2\mathrm{NO}]^+$, d
M − 88			11	?
M − 188	32	16	9.0	$[\mathrm{Met(LH)(NO)}]^+$, e
M − 218	28	100	3.0	$[\mathrm{MetLH}]^+$, f
M − 219	10			$[\mathrm{MetL}]^+$, g
M − 234		38	3.8	$[\mathrm{Met(LH - O)}]^+$, v
M − 252	19			$[\mathrm{Met(NCR)_2}]^+$, k
M − 280	25	14	34	$[\mathrm{MetC_2R_2}]^+$, m
M − 292		8.6		?
M − 293			19	?
M − 345	78	48	12	$[\mathrm{MetNCR}]^+$, t
M/2			7.2	$[\mathrm{MetL_2}]^{2+}$, n

	Ni	Pd	Pt
probe temp, °C	85 ± 10	110 ± 10	280 ± 10
dec temp,[b] °C	314 ± 10	318 ± 10	330 ± 10

[a] Molecular weights: $^{58}\mathrm{NiL_2}$, 496; $^{106}\mathrm{PdL_2}$, 544; $^{195}\mathrm{Pt}$, 633; L, 219. Parentheses denote the molecular ion currents as a percentage of the total metal-containing ion current. [b] Determined by thermogravimetric analysis under a nitrogen atmosphere.

For electron-bookkeeping purposes and for the assignment of formal oxidation states to the metal the following conventions have been adopted. Ion types have been written with even-electron structures having appropriate changes in the formal oxidation state of the metal to accommodate this, with use of valence bond canonical forms (except in a few cases where molecular orbital descriptions have been used). The symbol → represents a coordinate bond to the metal with both electrons of the bond originating from, and assigned to, the donor atom (two-electron donor). The symbol — represents a coordinate bond to the metal with one electron being contributed by each partner but with both electrons being assigned to the donor atom (one-electron donor), resulting in a unit increase in formal valence state of the metal. This method of assignment of the oxidation state of the metal is, of course, a gross approximation to the charge distribution in the ion (particularly when, as here, extensive metal–ligand π bonding occurs) but is, nevertheless, a convenient way of assessing the influence of metal oxidation state on the fragmentation pathways.

The mass spectra shown in Tables I–III reveal a marked dependence on the identity of the metal. As a first step in understanding the differences between the spectra, it is necessary to identify the ion types present and to assign probable structures to them. In the ensuing discussion the ion types characteristic of most spectra are first presented. This is followed by an examination of features specific to certain spectra. Detailed fragmentation pathways could not be confirmed because the spectra were almost completely devoid of metastable peaks. The only decompositon supported by a metastable peak corresponded to the trivial $M^+ \rightarrow (M - 17)^+$ in several spectra.

Characteristic Ion Types That Are Present in Several Spectra and Whose Formation Does Not Require Fission of the Carbon–Carbon Bond of the Chelate Ring. The molecular ions have high stability. They are the base peaks in all spectra except those of $Pd(DMG)_2$ and $Pd(DPG)_2$ and carry a substantial proportion of the total current of metal-containing ions. This proportion is normally in the sequence Pt > Ni > Pd. In structure a (Chart I) the positive charge has been formally placed on the metal, resulting in an increase in its formal oxidation state to +3.

Loss of a neutral hydroxyl radical from the molecular ion results in an ion formulated as b. The molecular ion of deuterium-labeled $Ni(DMG)_2$ eliminates OD·, thus confirming the loss of the labile H atom. The relative abundance of ion b for a given ligand is normally in the sequence Pt > Pd > Ni. It is absent from the spectra of the AFD complexes. For ion b, and for many ions yet to be discussed, both intact chelate rings and ring-opened forms are equally acceptable. For example, stable ions might have structure b_1 while decomposing forms might have structure b_2. Subsequently, ring-opened structures will not be shown. In the formation of ion b we have assumed facile interring transfer of the labile H atom. This is logical in view of the strong interring hydrogen bonding observed in the neutral complexes, and the transfer will be again invoked in assigning other ion structures. Elimination of a neutral radical from an even-electron metal-containing ion can only give an even-electron daughter ion if a unit change (oxidation or reduction) in the formal oxidation state of the metal occurs. In this case the metal has formally reverted to its +2 oxidation state.

Elimination of a neutral NO· radical from the molecular ion leads to an ion that has been assigned structure c (note the formal *increase* in oxidation state). It is particularly prominent in the spectra of the phenyl- and furyl-substituted complexes. Its assigned structure, containing a metal–carbon σ bond, is consistent with the stabilizing influence of these substituents (illustrated by the canonical forms c′ and c″ for the furyl-substituted complexes) and with the formation of fragment ions containing acetylenic groups (see below), for which it is a potential precursor. Furthermore, there are many examples of metal–carbon σ bonds in the known chemistry of palladium and platinum.[4,18] In particular, a four-membered chelate ring isostructural and isoelectronic with c″ has been observed when two molecules of cyclohexyl isocyanide insert into a palladium(II)–carbon σ bond.[19]

An ion at (M − 60), observed in most spectra, is a minor species except in the case of the AFD complexes, for which it is prominent. It has been assigned as $[MetL_2 - 2NO]^+$, of structure d. Since the ligand residue is now an acetylene, a feature that persists in several other fragment ions, the nature of the metal–acetylene bond for platinum-group metals deserves comment. The ligand in metal–acetylene complexes is known to be nonlinear.[20,21] For example, the substituents are bent away from the multiple-bond axis and away from the metal by 40° in the case of $[(PPh_3)_2Pt^0(PhC{\equiv}CPh)]$[22] and by 16.5° for *trans*-$[Pt^{II}(t\text{-}BuC{\equiv}C\text{-}t\text{-}Bu)(p\text{-toluidine})Cl_2]$.[23] In the Dewar–Chatt–Duncanson model,[24,25] which is described in molecular orbital terms, the acetylene ligand is regarded as a neutral, but poor, ligand $\pi \rightarrow$ metal σ donor (structures d′ and d″) and the structural results indicate substantial π back-donation from metal to ligand, the extent of π back-donation increasing with decreasing oxidation state of the metal, as expected. The stabilizing influence of a furyl substituent can now be understood in terms of contributions from structures such as d‴, in which electron release from the furyl group in the intact ligand reduces the charge on the metal and increases the π-donation capabilities of the metal to the acetylenic ligand. In equivalent valence bond terms, structure d⁗, the acetylenic ligand is regarded formally as a dianion. For ion d, and others yet to be described, the oxidation state of the metal is not readily defined. Thus, canonical forms d′ (valence increase) and d″ (valence decrease) appear equally consistent with accepted bonding conventions. Metal → ligand π back-bonding to the acetylene will be stronger for form d″.

An ion corresponding to $[M - (NO + C_2R_2)]^+$, i.e. $[Met(LH)(NO)]^+$, has been assigned structure e, in which the residue of one ligand is NO. The mass spectrum of the deuterated $Ni(DMG)_2$ complex confirms the retention of both labile H atoms. The relative abundance of e in all mass spectra increases in the sequence Pt < Pd < Ni, being prominent for the nickel complexes. Following the recommendation of a leading textbook,[26] we have regarded nitric oxide as a neutral ligand for electron-bookkeeping purposes. It is described as a σ donor that has its π^* electron paired with a $d\pi$ electron of the metal. NO is effective in stabilizing lower oxidation states of metals, suggesting that ion e″ is the dominant form.

The group of ions $[MetLH]^+$, $[MetL]^+$, and $[Met(L - H)]^+$, assigned the structures f, g, and h, respectively, exhibits marked variations in abundance in the spectra of complexes of the three metals. In the case of the platinum complexes they are all of low abundance in all spectra. For the other metals $[MetLH]^+$ is generally the most abundant, especially for palladium complexes, where it is the base peak in two spectra, namely, those of $Pd(DPG)_2$ and $Pd(AFD)_2$. The spectrum of the deuterated $Ni(DMG)_2$ complex confirms the retention of both

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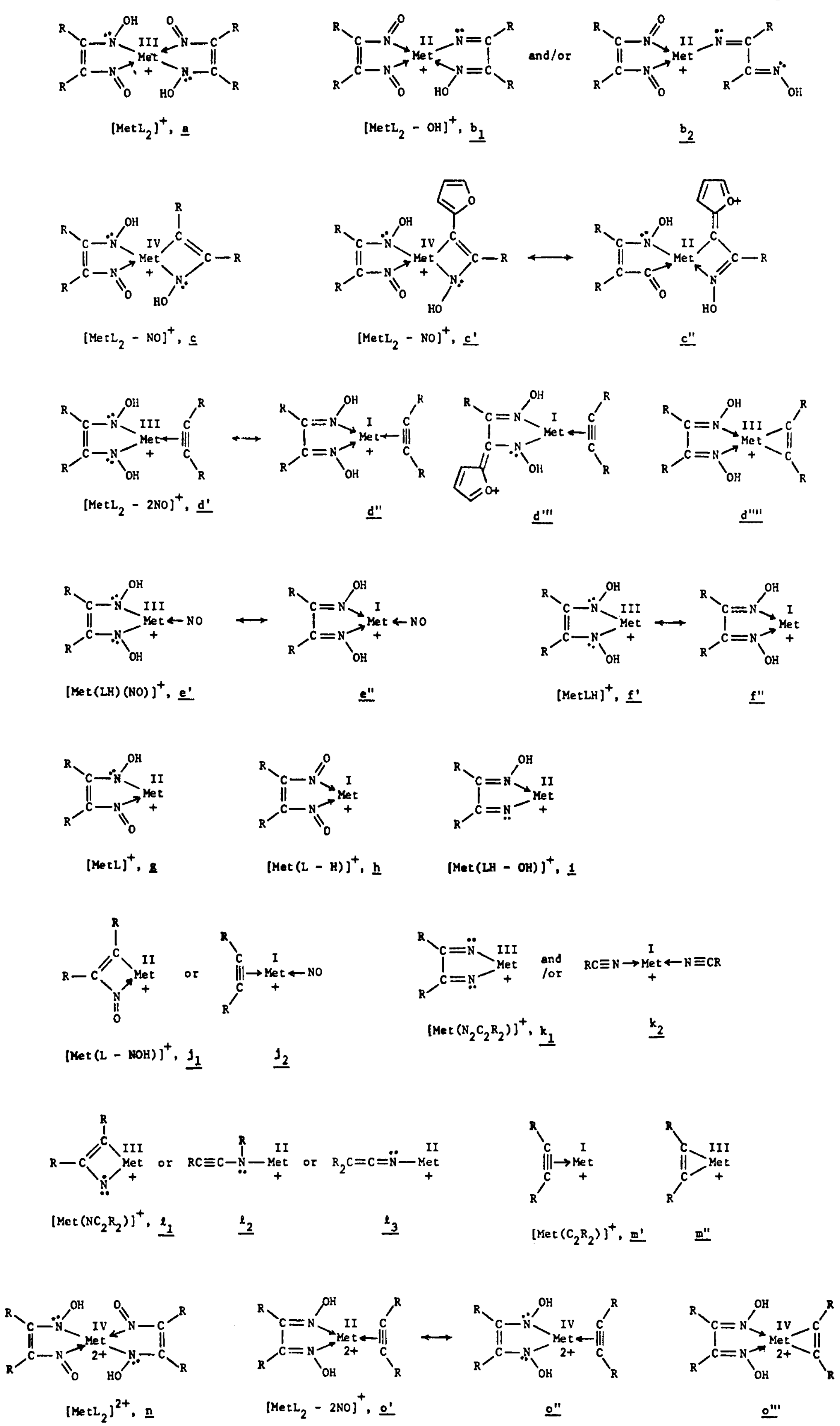
Chart I. Common Ion Types Whose Formation Does Not Require Fission of the Carbon–Carbon Bond of the Chelate Ring (Structures a–o)



labile hydrogens in this ion. In the spectra of nickel and palladium compounds the abundance of $[MetL]^+$ varies strongly from complex to complex. $[Met(L - H)]^+$, assumed present for purposes of calculating abundances of ion types contributing to the complex pattern of peaks, was of low abundance in all cases. While the reasons for all of these variations are not obvious, some rationalizations can be given. Canonical forms f′ and f″ indicate extensive π stabilization for $[MetLH]^+$. Also, both phenyl and furyl substituents can stabilize $[MetLH]^+$ and $[MetL]^+$ from contributions of canonical forms having the positive charge on the phenyl or furyl substituent, analogous to structure d‴ discussed above. Similar stabilizations of $[Met(L - H)]^+$, structure h, are not possible.

An ion at $[Met(LH - OH)]^+$ has been assigned the structure i. It is not observed in the spectra of any of the AFD complexes, and its relative abundance is usually low for platinum complexes. For the remaining complexes its relative abundance varies strongly from spectrum to spectrum. Its abundance in the spectrum of the $Ni(DMG)_2$-d_2 complex was too low for reliable determination of the extent of deuterium incorporation.

The group of ions $[Met(LH - NO)]^+$, $[Met(L - NO)]^+$, $[Met(L - NOH)]^+$, and $[Met(N_2C_2R_2) + H]^+$, observed only for DMG complexes, gives a complicated pattern of overlapping peaks in the mass spectra of the Ni and Pt compounds. In the case of $[Met(L - NOH)]^+$ structures j_1 and j_2 can be assigned. Evidence to support the proposed four-membered chelate ring in j_1 has been cited above for structure c, while the alternative structure, j_2, contains familiar ligands.

An ion of elemental composition $[Met(NCR)_2]^+$ can be assigned structure k_1, in which the chelate ring remains intact, or k_2, in which the carbon–carbon bond has been broken. Support for the latter structure is given by the ion $[Met(NCR)]^+$, which is very prominent in most spectra and which can only reasonably be assigned structure t (see below).

The species $[MetNC_2R_2]^+$, observed only in the spectra of DMG and DPG complexes, can be a prominent ion. Difficulties arise with structure assignment, e.g. l_1 is an odd-electron ion, unless migration of an R group (i.e., CH_3 or C_6H_5) to N or C, structures l_2 and l_3, respectively, is postulated.

The ion $[Met(C_2R_2)]^+$, assigned structure m, is prominent in all spectra except those of $Ni(DMG)_2$ and $Pd(DMG)_2$. Its stability can be understood in terms of the discussion above for ion d. Additionally, in the case of zerovalent platinum complexes the thermodynamic stabilities of platinum–acetylene bonds were shown to be greater for phenylacetylenes than for alkylacetylenes[27] and platinum(0) has a greater ability than palladium(0) to donate electrons to the acetylene π^* orbital[28] and thus to stabilize the Pt–acetylene bond. The relative abundances of the $[Met(C_2R_2)]^+$ ion in the various spectra are entirely consistent with these relative bond stabilities.

The double charged ions $[MetL_2]^{2+}$ and $[MetL_2 - 2NO]^{2+}$, have been assigned the structures n and o, respectively. Abundances, although low, are usually greatest for the platinum complexes. The participation of canonical forms in which the formal oxidation state of the metal is +4 could account for this, reflecting the known stability sequence Ni < Pd < Pt for the +4 valence state of these metals.[29]

Chart II. Ion Types Whose Formation Requires Fission of the Carbon–Carbon Bond of the Chelate Ring (Structures p–t)

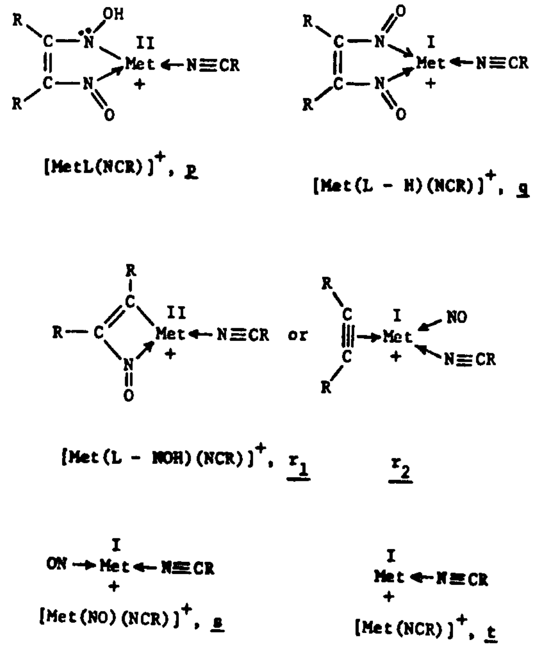
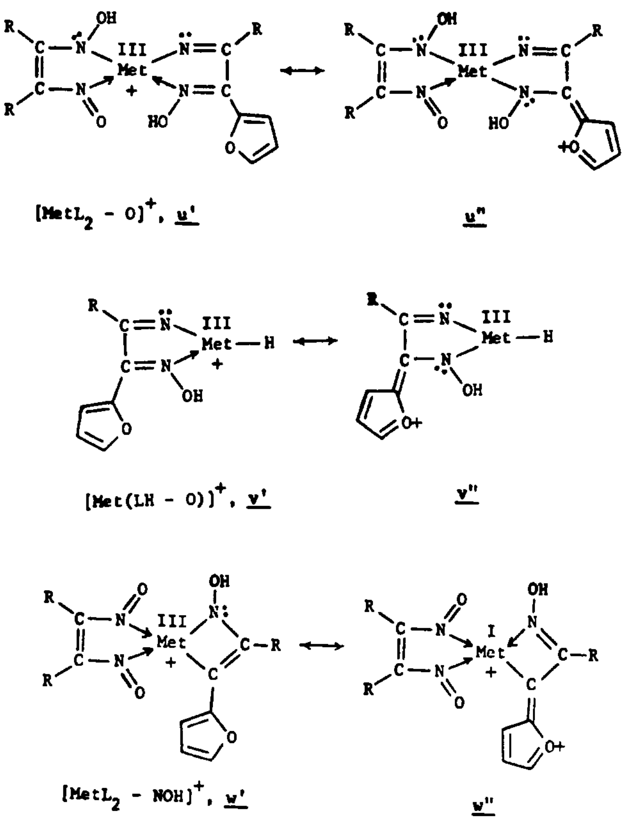


Chart III. Ion Types Specific to the Mass Spectra of AFD Complexes (Structures u–w)



Ion Types Whose Formation Requires Fission of the Carbon–Carbon Bond of the Chelate Ring. The ion types in this classification share a common feature, namely, a coordinated nitrile as the residue of an original ligand. Structures p–t (Chart II) have been assigned to them. The relative abundances of p–s are quite variable from spectrum to spectrum, while $[MetNCR]^+$, structure t, is very abundant in nearly all spectra. This suggests, perhaps, parallel fragmentation pathways terminating at a common stable ion t. If so, the suggestion is interesting because nitriles are regarded as weakly coordinating ligands for palladium and platinum[30] and can be readily displaced by, for example, olefins.[31]

Ion Types Specific to the Mass Spectra of AFD Complexes. An ion at (M − 16) in the mass spectra of AFD complexes

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(27) Chatt, J.; Rowe, G. A.; Williams, A. A. *Proc. Chem. Soc., London,* **1957**, 208.

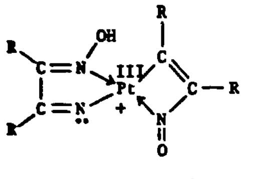
(28) Reference 18, p 405.

(29) Reference 4, p 783, 951.

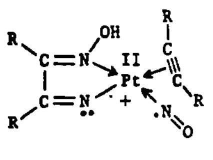
(30) Reference 18, p 362.

(31) Doyle, G. R.; Slade, P. E.; Jonasson, H. B. *Inorg. Synth.* **1960**, *6*, 216.

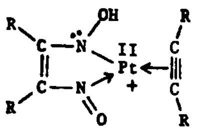
Chart IV. Ion Types Specific to the Mass Spectra of Platinum Complexes (Structures x-ac)



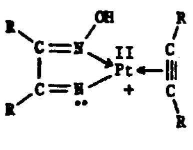
or

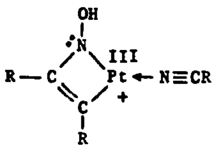


$[PtL_2 - (OH + NO)]^+$, $\underline{x_1}$ $\underline{x_2}$

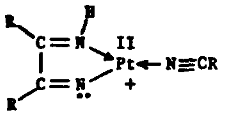


$[PtL_2 - (NO + NOH)]^+$, $\underline{y}$

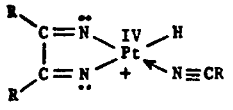




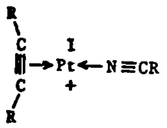
$[PtL_2 - (OH + 2NO)]^+$ $\underline{z}$ $[Pt(L - NO)(NCR)]^+$, $\underline{aa}$



or



$[Pt(N_2C_2R_2)(NCR) + H]^+$ $\underline{ab_1}$ $\underline{ab_2}$



$[Pt(C_2R_2)(NCR)]^+$, $\underline{ac}$

of Pd and Pt can only be reasonably assigned to elimination of atomic oxygen from the molecular ion. To explain the influence of the furyl substituent in enhancing the normally unfavorable elimination, we propose structure u′ ↔ u″ (Chart III). A similar stabilization by the furyl group is also proposed for the $[Met(LH - O)]^+$ ion, structure v′ ↔ v″. (Not illustrated are similar structures in which the rearranged H is placed instead on the upper N atom.)

An abundant ion at (M − 31) in the spectrum of $Pt(AFD)_2$, assigned as $[MetL_2 - NOH]^+$, is observed in no other spectrum. Structure w′ ↔ w″ rationalizes the stabilizing influence of the furyl group.

Ion Types Specific to the Mass Spectra of Platinum Complexes. The ions $[PtL_2 - (OH + NO)]^+$, $[PtL_2 - (NO + NOH)]^+$, $[PtL_2 - (OH + 2NO)]^+$, and $[Pt(L - NO)(NCR)]^+$, assigned structures x, y, z, and aa, respectively (Chart IV), are observed only in the spectra of the $Pt(DMG)_2$ complexes. The ions $[Pt(N_2C_2R_2)(NCR) + H]^+$ and $[Pt(C_2R_2)(NCR)]^+$, observed in the spectra of the $Pt(DMG)_2$ and $Pt(DPG)_2$ complexes, have been assigned structures ab and ac. No new features are invoked in assigning any of these structures. Most of them involve formation of platinum–carbon σ bonds or platinum–acetylene bonds, a characteristic feature that is important particularly in the chemistry of platinum.[18]

Influence of the Metal on the Mass Spectra. The discussion to this point has centered mainly upon correlating the compositions and structures of the ions observed in the mass spectra. We now attempt to assess the effects of the metal on the spectra. The ordinary chemistry of nickel is dominated by the +2 oxidation state, the higher oxidation states occurring in very few compounds, while the lower oxidation states require the presence of π-acceptor ligands.[4] The principal oxidation states of Pd and Pt are +2 and +4, though Pd(IV) is less stable than Pt(IV).[4] Neither element readily assumes an odd oxidation state, the +3 state being virtually unknown and the +1 state being extremely rare.[4,18] The zerovalent state occurs with π-acceptor ligands. All three metals have a strong affinity for nitrogen ligands while the stability of metal–carbon σ bonds and of metal–acetylene bonds increases in the order Ni < Pd < Pt.[4,18]

For the interpretation of the mass spectra, several ion structures have been proposed. While no direct proof for these structures can be given, they are largely based on structures established in the condensed-phase chemistry of these metals. On the basis of these structures, formal oxidation states have been assigned to the metals. In contrast to the mass spectra of "classical complexes" the spectra show no well-defined dependence on the metal oxidation state. Prominent ions with the metal formally in an odd or an even oxidation state are found in the spectra of all three metals, no doubt reflecting the extensive metal→ligand π bonding, which is important here. In particular, the stability of the molecular ions appears remarkable.

The most conspicuous trend in the spectra is the increasing prominence of fragment ions involving metal–carbon or metal–acetylene bonding in the sequence Ni → Pd → Pt. This trend is sufficiently marked that the spectra of platinum compounds differ substantially from those of nickel and palladium and contain ions absent from the spectra of the latter compounds.

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Registry No. **1** (Met = Ni), 13478-93-8; **1** (Met = Pd), 14740-97-7; **1** (Met = Pt), 17632-92-7; **2** (Met = Ni), 14286-61-4; **2** (Met = Pd), 16049-94-8; **2** (Met = Pt), 55660-52-1; **3** (Met = Ni), 14462-73-8; **3** (Met = Pd), 18534-81-1; **3** (Met = Pt), 84254-44-4.