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Molecular Anion Formation in the Gas-Phase by Bis-(dimethylglyoximato) Complexes of Nickel(II), Palladium(II) and Platinum(II)

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Examination of low energy electron attachment reactions in the gas-phase, under solvent free conditions, is assuming increasing importance for the assessment of the role of metal/ligand combinations, donor atom sets, metal oxidation state and metal complex stereochemistry on the electron capture process. In addition, estimations can be made of the stabilities of molecular negative ions so formed, and their decomposition products may be identified [1–7]. The instrumental technique of high pressure negative ion mass spectrometry is particularly valuable for such studies. In particular, this technique allows steady fluxes of low energy or thermalised electrons to be generated in mass spectrometer high pressure ion sources, independently of the compounds undergoing electron attachment, by the use of electron energy moderating gases such as methane [8–9]. Several novel features have emerged in relation to the gas phase electron attachment reactions of the title compounds $[Ni(HDMG)_2]$, $[Pd(HDMG)_2]$ and $[Pt(HDMG)_2]$, I–III, which have prompted this communication.

Experimental

The complexes were prepared and purified by established methods and gave satisfactory analyses [10–11]. The electron attachment reactions and negative ion mass spectra were obtained with a modified VG MM-16F single focusing mass spectrometer fitted with an E.I./C.I. ion source. Matheson Gas Products UHP grade (99.97%) methane was used as the electron energy moderating gas, and the instrumental conditions and parameters used were similar to those reported previously [3]. Since the metal complexes used in this study all contain polyisotopic metal atoms, elucidation of the contributions of $[M + 1]^-$, $[M]^{-\bullet}$ and $[M - 1]^-$ species to the actual observed mass spectral clusters has been achieved by recourse to comparisons with computer simulated clusters based on normal isotopic distributions.

TABLE I. Negative Ion Mass Spectra of $[Ni(HDMG)_2]$, $[Pd(HDMG)_2]$ and $[Pt(HDMG)_2]$, I–III: Intensities of Principal Ions.[a,b]

Ion	Intensity (% Σ)		
	I	II	III
$[M]^{-\bullet}$	61	16	13
$[M - H_2O]^{-\bullet}$	32	69	71
$[M - CH_4O]^{-\bullet}$ [e]	3	6	8
$[HDMG]^-$	–	0.1	–
Other ions[c,d] (Σ)	4	7	8

[a] Ion Intensities were found to be reproducible to within 2% of the listed values, and are reported as percentages of the total ion current (% TIC) carried by each ion. [b] All isotopes of all atoms in the various ion clusters are considered. [c] These include species such as $[M + 14]^{-\bullet}$, $[M + 2]^{-\bullet}$, $[M + 1]^-$, $[M - 1]^-$, $[M - 2]^{-\bullet}$, $[M - HDMG]^-$, $[M - H_2DMG]^{-\bullet}$, $[DMG]^-$. [d] No polymeric ions were observed for I–III. [e] This ion corresponds to a loss of the elements of CH_3OH from $M^{-\bullet}$. No metastable peak could be detected to account for its origin, which could be accounted for by either a direct elimination of CH_3OH from $M^{-\bullet}$, or alternatively elimination of CH_2 from the $[M - H_2O]^{-\bullet}$ ion. Eliminations of this latter type have been reported previously by us [3].

Results and Discussion

Results of low energy electron attachment to I–III are given in Table I in terms of the negative ion mass spectra of these compounds. These data differ significantly from negative ion mass spectra and results of electron attachment reactions with other series of metal(II) bis-chelates, and specifically those which contain O_4, O_2S_2 and S_4 donor atom sets [2, 3, 5, 6]. Molecular negative ions were observed for I–III and a ligand ion, $HDMG^-$ or L^-, could only be detected for II in very low abundance (0.1% TIC). This may be taken to indicate the reluctance of the molecular negative ions of I–III to decompose in a reductive process of the type $Ni^{II}L_2^{-\bullet} \xrightarrow{*} L^- + Ni^IL$, which has been deduced for other series of nickel(II) complexes [2, 5]. The virtual absence of L^- ions in the various negative ion mass spectra may also be interpreted to be indicative of the instability of such a species containing a N_2 donor atom set, at least under the solvent free conditions prevailing within the mass spectrometer ion source. Instead, the principal molecular negative ion decomposition pathway found for I–III is one which involves the elimination of a water molecule from $M^{-\bullet}$ in processes for which metastable peaks have been assigned, *viz.*: $M^{-\bullet} \xrightarrow{*} [M - H_2O]^{-\bullet}$. This, to our knowledge, is the first

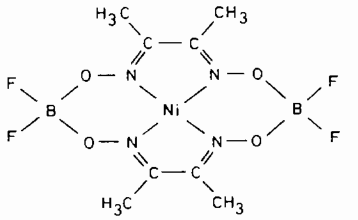
TABLE II. Negative Ion Mass Spectrum of $Ni(BF_2DMG)_2$, IV.[a]

Ion	$[M]^{-\bullet}$	$[M-CH_3]^-$	$[M-HOBF_2]^{-\bullet}$
Intensity (% Σ)	67	6	27

[a]Obtained under identical conditions to the spectra reported in Table I.

such example of a water molecule elimination from a metal containing molecular negative ion. Its occurrence may be ascribed, in qualitative terms at least, to the electron attachment taking place into a predominantly ligand-based orbital together with an intramolecular rearrangement related directly to the structure of the gas phase molecular negative ion. Although gas phase structural data do not appear to be available for I–III, planar structures may be assumed by extrapolation from solid state data [12, 13] and also by analogy with reported gas phase structural data for nickel(II) bis-chelates containing O_4 donor atom sets [14]. Implicit in these assumptions are increasing O–H···O distances for I–III in the gas phase, which are known in the solid state to be for the O······O separation respectively 2.44, 2.62 and 2.63 Å, and with the strongest H···O bond being given by I where the H atom is symmetrically located between the O atoms [15]. We may interpret the higher ion currents carried by the $[M-H_2O]^{-\bullet}$ ions of II and III, and thus their greater stabilities relative to their precursor $M^{-\bullet}$ ions, as being consistent with a greater ease of hydrogen bond rupture in the rearrangement and decomposition processes of their parent molecular ions. This is consistent too with the presence of asymmetric O–H···O bonds in the gas phase structures of II and III which is known to be the case for their solid state structures [16–18]. By comparison, the most stable $M^{-\bullet}$ and the least stable $[M-H_2O]^{-\bullet}$ species were given by I.

Another example of a similar rearrangement and elimination reaction has been observed with the $O–BF_2–O$ bridged nickel(II) macrocyclic analogue of I, *viz.*, $Ni(BF_2DMG)_2$, IV:



IV

Only three significant ion clusters were observed in the negative ion mass spectrum of IV, and these are listed in Table II. Assignments of metastable peaks indicated that both fragments ions were derived directly from $M^{-\bullet}$.

The most significant feature of the negative ion mass spectrum of IV is the observation of the rearrangement ion $[M-HOBF_2]^{-\bullet}$ which may be attributed to a molecular ion decomposition and rearrangement process similar to that operative in the formation of the $[M-H_2O]^{-\bullet}$ species for I–III. It is noteworthy too that the total ion currents carried by $[M]^{-\bullet}$ and $[M-HOBF_2]^{-\bullet}$ ions, respectively 67 and 27% are very similar to those ion currents carried by the $[M]^{-\bullet}$ and $[M-H_2O]^{-\bullet}$ species for I, which were 61 and 31%. Again, although gas phase structural data are not available for IV, it is known from solid state data that the molecular geometry is unaffected by the BF_2 substitution for the proton and that there is no significant change from the average O···O interatomic distance of 2.44 Å for $Ni(HDMG)_2$ [19]. We therefore suggest that the O–H···O or $O–BF_2–O$ structural units are the major contributing factors to the stabilities of the molecular negative ions and the formation of their decomposition products. In addition, we suggest that the chelate rings and bridges may constitute a structural barrier to a reductive electron attachment process for these compounds. In contrast, electron detachment and positive ion formation by I and II is known to be a significantly different process, and numerous metal-containing ions have been identified in the positive ion mass spectra of these compounds [20].

Current studies of electron attachment reactions with metal derivatives of both symmetrical and unsymmetrical *vic*-dioximes are designed to establish clearer criteria for molecular anion formation and stability and also the mechanism of H_2O elimination.

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