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Gas-phase Electron Attachment to Metal Complexes: The Influence of Oxygen and Sulphur Donor Atoms on the Electron Attachment Reactions of Bis-chelates of Nickel(II)

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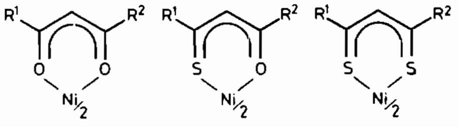
As part of an extended gas-phase ion chemistry programme which encompasses the generation of negatively charged metal containing ions as well as the investigation of their modes of decomposition and ion/molecule reactions [1–5], we report details of the effects of oxygen and sulphur donor atoms on the electron attachment reactions of a number of bis-chelates of nickel(II):



$R^1 = R^2 =$ Me; I II III
$R^1 = R^2 =$ t-Bu; IV V VI

This is an important series of nickel(II) complexes for which a considerable amount of structural and physical data have been accumulated, particularly for the compounds in the solution and solid phases [6–9]. Whereas II–VI are isostructural, being square planar and monomeric [6, 9–12], I, in its anhydrous form, is trimeric [13], although it is known to be monomeric and square planar in the gas-phase [14]. Scant attention has been given to studies of the gas-phase ion chemistry of this series, and such reports as exist, in the main, only give details of UV photoelectron and positive ion mass spectra of some of the compounds [15–19]. However, electron attachment in the gas-phase, under solvent free conditions, with such a series of structurally similar complexes is seen as a unique method for obtaining fundamental data on the effect of different ligand donor atoms on the electron capture process, the generation of molecular negative ions, as well as the subsequent decompositions of such species. In addition, as gas-phase electron attachment, in a classical sense, may be regarded as a reduction process, data so obtained might be expected to be complementary to those derived from related solution phase electrochemical reductions with this series of compounds [20, 21].

To this end, we have applied the technique of negative ion mass spectrometry to our electron attachment study with these complexes as this is an instrumental method particularly suited to the examination of low energy electron attachment processes, the gas-phase synthesis of molecular negative ions, as well as the determination of their fragmentation pathways and reactivities [1–5, 22, 23].

Experimental

The complexes were prepared by established methods [24–26], and were purified by recrystallisation as well as vacuum sublimation before insertion into the mass spectrometer. All compounds gave satisfactory analyses and were further characterised from their NMR and positive ion mass spectra [8, 15, 16].

The electron attachment reactions and negative ion mass spectra reported in this paper were obtained on a modified VG MM-16F single focusing mass spectrometer, which was fitted with an E.I./C.I. ion source. Generation of low energy secondary electrons of near thermal energies independently of each compound was achieved by interaction of the primary electron beam with methane (Matheson Gas Products, UHP grade, 99.97%), which functioned as an electron energy moderating gas [27], and which was introduced into the ion source via a Drierite/5A molecular sieve tower and a Negretti and Zambra precision pressure regulator valve to give constant ion source pressures of c. 0.5 torr. For convenience in routine operation of the mass spectrometer methane gas pressures were usually monitored via the ion source housing ionisation gauge, and were typically in the range 2–5 $\times 10^{-5}$ torr. All spectra were recorded by evaporating the samples directly within the ion source at the minimum temperatures necessary to obtain reproducible ion intensities, which were 150–190 °C, depending on the sample volatility, and the other ion source parameters were as follows: total emission current 500 μA, primary electron energy 50 eV, repeller voltage relative to ionisation chamber −1 to −2 V, ion accelerating voltage 4 kV. The detectable yield of negative ions for each complex was quantified by evaporating a small known sample in the high pressure ion source while integrating the signal corresponding to the ^{58}Ni peak in the molecular ion isotopic cluster.

Results and Discussion

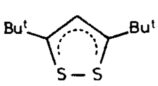
From the negative ion mass spectral data which are summarised in Table I, it is apparent that high yields of molecular negative ions relative to other species can be obtained by low energy electron attachment to I–VI. The degree of fragmentation given by such $[NiL_2]^{-\bullet}$ species is low, and ligand ions, L^-, in general make the next highest contributions to the total ion currents. While contributions to the L^- ion yields cannot be excluded from dissociative electron capture processes [5, 22], resolution of metastable peaks has indicated that decomposition of molecular ions to give ligand ions is a process which contributes, at least in part, to the L^- ion yields: $[NiL_2]^{-\bullet} \xrightarrow{*} L^- + Ni^IL$. Resolution of metastable peaks has also accounted for the origin of the other ions listed in Table I.

TABLE I. Negative Ion Mass Spectra of Bis-Chelates of Nickel(II), I–VI: Intensities of Principal Ions.[a,b,c]

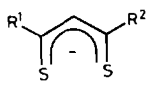
Ion	Intensity (%Σ)[e]					
	I	II	III	IV	V	VI
$[NiL_2]^{-\bullet}$	92	88	72	94	88	73
$[NiL_2 - \ddot{C}H_2]^{-\bullet}$	1	<1	0	1	<1	1
$[NiL_2 - CH_4]^{-\bullet}$	0	0	0	0	0	4
$[NiL_2 - C_4H_8]^{-\bullet}$	–	–	–	<1	1	1
$[NiLSH]^{-\bullet}$	–	2	3	–	<1	<1
$[NiLCH_3]^{-\bullet}$	1	0	0	0	0	0
$[L]^-$	3	5	8	<1	4	7
$[L - H]^{-\bullet}$	0	0	2	0	3	0
$[NiL_2 + X]^-$[d]	2	<1	3	4	2	12

[a] Intensities were found to be reproducible to within 2% of the listed values. [b] All isotopes of all atoms are considered. [c] Minor non-metal containing ions for III, $\Sigma = 12\%$. [d] Summation of intensities of adduct ions, where X = H, H_2, CH_2, CH_3. [e] Similar negative ion mass spectral data were also obtained on a Hitachi RMU-6L instrument under E.I. conditions as described previously [3–5]. Such minor differences as were observed in the data are described in detail in a forthcoming publication [28].

Results forthcoming from electronic and UV photoelectron spectroscopic studies with I–III indicate that the lowest unoccupied molecular orbitals in these complexes are metal-based [17, 19]. Thus, it may be envisaged that the electron attachment process could involve electron capture into a metal-based LUMO, with an attendant reduction in the oxidation state of the metal as well as a decrease in its coordination number and the formation of the reduced Ni^IL species together with L^-. Such an electronic and reaction sequence may be contrasted with that given by electron detachment from these complexes, which may be considered, overall, to be an oxidative process. Indeed, the positive ion mass spectra of IV–VI, which were obtained [16], as a result of electron detachment reactions, have been rationalised in terms of the stability of the oxidised ligands, especially that of the highly stable [8, 16] dithiolium ion of VI, *viz.*, VII:



VII



VIII

Although it is possible to envisage an anion with a similar cyclic structure to the dithiolium ion, electrochemical evidence suggests that such a species is short-lived relative to the dithioenolate form, VIII, which is stable enough to be isolated in solution [29]:

Additionally, it is known that β-diketones themselves exist in the enol form in the gas-phase [30, 31] and can readily eliminate $H^\bullet$ as a consequence of electron attachment or thermolysis to give $[M - 1]^-$ species, which may be presumed to be enolate ions [32].

Table I shows that decreased molecular ion yields are given with an increased sulphur donor atom incorporation into the complexes for both groups of compounds within this series, I–III; IV–VI. This points to a greater ease of reduction occurring as a consequence of electron capture as the number of sulphur atoms bonded to nickel increases. A similar conclusion has been reached for the electrochemical reductions of IV–VI [21]. It is noteworthy, too, that results forthcoming from UV photoelectron spectroscopic studies with I–III show that, in agreement with the lower electronegativity of sulphur compared with oxygen, there is a trend towards a higher electron density on the nickel atom as the number of sulphur atoms in the complexes increases [17]. This, undoubtedly in an important contributory factor in any reduction process, as is, too, the influence of the ligand substituent groups R^1, R^2 on any such process. This latter effect has been examined electrochemically [33], and is now receiving increasing attention in an extension to this present gas-phase electron attachment investigation [28].

Table I also indicates that fragment ions of formulation $[NiLSH]^{-\bullet}$ are given for II, III, V, VI. These species owe their origin to $H^\bullet$ rearrangements within the decomposing $[NiL_2]^{-\bullet}$ ions and it is presumed that nickel is sulphur bonded in these $[NiLSH]^{-\bullet}$ species which would be consistent with the known class (b) characteristics of this metal [34]. The yields of these fragment ions is lower for V, VI because of the increasing facility for the formation of elimination and rearrangement ions which derive from $[NiL_2]^{-\bullet}$ ions as a result of the participation of the t-Bu substituent groups.

Quantitative determinations designed to give some measure of the efficiency of electron attachment for I–VI have been made. The results are given in Table II in terms of the number of negative ions reaching the electron multiplier per 10^9 molecules introduced into the ion source. Such measurements provide a useful index and guide as to the potential of the electron attachment process and negative ion monitoring for trace and ultra-trace analysis of metals derivatised with a suitable chelating agent. The results show that the complexes which contain oxygen donor atoms give a much higher apparent electron attachment efficiency than do the dithio-derivatives. The precise reason for this is difficult to establish at this juncture, but a number of contributory factors would seem to be of importance. These could include the differences in electron capture cross sections [35] of the complexes, the relative stabilities and lifetimes of the negative ions formed from them, as well as the effects exerted on the electron attachment by the electron density differences on the nickel atoms on the various complexes [17]. Further surveys of these and similar types of metal complexes are underway in an effort to obtain a better understanding of the chemical and structural characteristics of such molecules which favour electron attachment.

TABLE II. Negative Ion Detection Efficiencies.[a,b]

I	II	III	IV	V	VI
3500	8200	140	9000	8000	80

[a] Results are expressed as the number of negative ions detectable at the electron multiplier of the mass spectrometer for 10^9 molecules introduced into the ion source. [b] The relative standard deviations for these results were less than 20%.

Negative ions which owe their origin to ion/molecule reactions have also been observed in low yields in our negative ion mass spectra, Table I. In particular, $[M + 1]^-$, $[M + 2]^{-\bullet}$, $[M + 14]^{-\bullet}$ and $[M + 15]^-$ species have been identified. It is of great significance that we have been able to detect with ease, in the VG MM-16F instrument, relatively constant but low abundances of $C^{-\bullet}$, CH^-, $CH_2^{-\bullet}$, CH_3^-, $O^{-\bullet}$ and OH^- in the methane electron energy moderating gas and instrument air/water background spectra. The carbon containing ions are well established products of dissociative electron capture processes involving methane, whose relative abundances are known to be pressure dependent [35]. Significantly too, we have noted that the abundances of $CH_2^{-\bullet}$ and $[M + 14]^{-\bullet}$ ions in the various negative ion mass spectra were very similar, and at this stage venture to suggest that the adduct ions are formed, at least in part, as a result of ion/molecule processes which involve the interaction of certain of these highly reaction nucleophiles with metal complex molecules. Such a suggestion is consistent with the well established solution phase Lewis acid properties exhibited by divalent transition metal β-keto-enolate complexes as well as their mono- and dithio-analogues [8, 36]. However, we note that recently an alternative explanation has been offered for the observance of $[M + 14]^-$ and other similar species, under different instrumental conditions, with various transition metal Schiff base complexes [37].

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