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Methane Enhanced Negative Ionization Mass Spectra of some Biologically Important Chelate Compounds: Porphyrins, Dithiophosphates and Dithiolates

NEIL B. H. HENIS, KENNETH L. BUSCH and MAURICE M. BURSEY

William Rand Kenan, Jr.-Laboratories of Chemistry, University of North Carolina, Chapel Hill, N.C. 27514, U.S.A.

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The methane enhanced negative ion mass spectra of three kinds of chelate complexes are usually characterized by a stable M^- ion. Notable characteristics of porphyrin spectra include the formation of $(M + CH_3)^-$ and $(M + C_2H_5)^-$ ions and a partial replacement of the weakly bonded Cd and Pb by Ni, presumably from the source housing. Dithiophosphate complexes show less M as the alkyl groups become large, probably as a result of steric crowding. Dithiolates have negative ion spectra the extent of whose fragmentation is governed by both organic substituent and central metal; these also provide another example of $(M + CH_3)^-$ ions, probably caused by ion-radical reactions.

In the last two cases, beyond the molecular negative ion, ligand ions are also prominent and thus as a rule these negative ion spectra provide a clearer identification of the ligand than the positive ion spectra.

Introduction

In the past fifteen years, interest in negative mass spectrometry of compounds has increased greatly [1–6]. Reproducible spectra devoid of ion/molecule reactions are obtained at source pressures of 4×10^{-6} to 3×10^{-5} torr with 70 eV electrons [1–4]; sensitivity is 10% of that in positive ion experiments [2]. When the source pressure of sample is raised above 10^{-5} torr, ion/molecule reactions are observed [7].

Concomitantly high-pressure techniques have been developed to allow detection of negative molecular ions instead of small fragments. A moderator gas, such as methane at 1 torr, thermalizes energetic electrons to provide an abundant supply of low-energy electrons likely to be captured by molecules. For ligands with many electrophores [8], negative ion methods are more sensitive than positive. For structural information, the two kinds of spectra are often complementary [9].

We have applied the moderator-gas technique, methane enhanced negative ionization, to compounds with some biological applications. Trace metals from biological sources have been analyzed as chelates of synthetic porphyrins in the positive ion mode with sensitivities in the pico- and femtogram ranges using selected ion monitoring [10]. Likewise, dithiophosphate complexes have been used as fungicides and pesticides [11]. Finally, some dithiophosphates have exhibited carcinostatic properties [11].

Experimental

Negative ion experiments were carried out on a Finnigan 3300 quadrupole mass spectrometer modified to allow either positive or negative ion operation [12]. Methane was used as the moderator gas, and was admitted to the source through a Finnigan 9500 gas chromatograph at a sufficient flow rate to keep the source pressure between one and two torr. Sample was admitted to the source by direct probe. The spectrometer was tuned on background rhenium oxide (ReO_3^-, ReO_4^-) and perfluorotributylamine peaks. Spectra were generated with 100 eV electrons and 1.0 mA emission current. The source temperature was held constant at 140 °C. It is necessary to keep the temperature within a very narrow range, because negative ion spectra are often extremely sensitive to temperature fluctuations [13]. The compounds examined were prepared by standard methods [11, 14, 15].

Electron impact spectra were recorded on a Dupont 21-490-B single focusing mass spectrometer, with perfluorokerosene as a mass marker and direct probe introduction, a 100 °C source temperature and 70 eV electron energy.

Results and Discussion

Dithiolates, Dithiophosphates

The major peaks in the spectra of the dithiolate and dithiophosphate complexes are the molecular ion M^-, and in some cases, the ligand ion L^-. This can be contrasted to the EI spectra, where much fragmentation is observed: in the case of most dithiolates studied the molecular ion is of only 1% abundance. Tables I and II show the enhanced negative ionization mass spectra of the dithiophosphates and the dithiolates respectively.

The dithiophosphate spectra are divided into two groups. When the alkyl groups on the ligand are small, there are intense peaks in the molecular ion region,

TABLE I. Methane Enhanced Negative Ionization Mass Spectra of Representative Dithiophosphate Complexes.*

Compound	Ions, Approximate Relative Intensities
$[Ni[S_2P(OCH_3)_2]_2$	$(L-H)^-$, 20%; L^-, 30%; $(M-H)^-$, 10%; M^-, 100%; $(M+H)^-$, 10%
$[Ni[S_2P(OC_2H_5)_2]_2$	PS_2^-/PSO_2^-, 10%; $CH_3PS_2^-/CH_3PSO_2^-$, 10%; $(L-H)^-$, 100%; L^-, 100%; $(M-H)^-$, 10%; M^-, 70%; $(M+H)^-$, 10%
Ni[S_2P(O-*cyclo*-$C_6H_{11})_2]_2$	PS^-/PO_2^-, 10%; PSO^-/PO_3^-, 40%; PS_2^-/PSO_2^-, 100%; $P_2S_2^-$, 10%; PS_2O^-, 70%; $PS_2O_2C_6H_{11}^-$, 50%; L^-, 60%
[Ni[S_2P(O-*cyc*-2-$CH_3C_6H_{10})_2]_2$	PS^-/PO_2^-, 5%; PSO^-/PO_3^-, 10%; PS_2^-/PSO_2^-, 10%; $PS_2O_2^-$, 60%; $PO_4C_7H_{13}^-$, 10%; $PSO_3C_7H_{13}^-$, 10%; $PS_2O_2C_7H_{13}^-$, 60%; L^-, 100%; $SNiL^-$, 10%

*Instrumental resolution inadequate to establish S/O_2 identities of small fragment ions.

TABLE II. Methane Enhanced Negative Ionization Mass Spectra of Representative Dithiolate Complexes.

Compound	Ions, Approximate Relative Intensities
$Ni[C_2S_2H_2]_2$	M^-, 100%
$Ni[C_2S_2(CH_3)_2]_2$	M–, 100%; L^-, 50%
$Ni[C_2S_2(C_6H_5)_2]_2$	M–, 100%; L^-, 50%; $(M+CH_3)^-$, 5%; $(L+CH_3)^-$, 5%; $HC_2S(C_6H_5)_2^-$, 10%
Ni[$C_2S_2(C_6H_4$-*p*-Cl$)_2]_2$	M–, 100%; L^-, 80%; $(L+CH_3)^-$, 60%; $HC_2S(C_6H_4$-*p*-Cl$)_2^-$, 20%; $HC_2S(C_6H_4Cl)(C_6H_4)^-$, 10%
$Pt[C_2S_2(CH_3)_2]_2$	M–, 100%
$Pt[C_2S_2(C_6H_5)_2]_2$	M–, 100%; $(M+CH_3)^-$, 80%

moderate peaks in the ligand ion region, and little else. On the other hand, the cyclohexyl derivatives yield small or no molecular ion peaks, but numerous fragment peaks related to the ligand. A complex combination of steric and electronic effects is evident here. Where the alkyl groups are large, the phosphorus atom is forced to assume a more nearly tetrahedral arrangement, thus straining the metal–sulfur bond. Apparently then, the compound then decomposes in the source. The stepwise replacement of sulfur by oxygen fragment ions is analogous to observations in the spectra of organic dithio- and monothiophosphates because of trace oxygen in the source [16].

Peak intensities are semiquantitative; reproducibility is affected by pyrolysis on the direct probe.

For the dithiolates, the intensity of the ligand peaks parallels the ability of the ligand ion to accommodate the negative charge as size increases, and the ability of the central metal in the negative molecular ion to stabilize the negative charge (Pt > Ni). That the central metal should markedly affect the appearance of the negative ion spectra is expected. Molecular orbital calculations for dithiolate compounds demonstrate that the LUMO which an electron would enter upon undergoing resonance capture is based significantly on the metal ion [17]. These results have been confirmed as well by electronic and UV photoelectron spectroscopic studies with compounds of similar structure [18, 19]. The negative ion spectra of other metal compounds have also been explained by electron addition to metal-centered orbitals [6, 20, 21].

TABLE III. Methane Enhanced Negative Ionization Mass Spectra of Representative Metalloporphyrins*.

Compounds	Ions, Approximate Relative Intensities
CuTPP	M^-, 10%; $(M+H)^-$, 100%
ZnTPP	M^-, 10%; $(M+H)^-$, 100%
CdTPP	$(M+H)^-$, 100%; $(M-Cd+NiH)^-$, 20%; $(M-Cd+Ni)^-$, 20%; $(M-Cd)^-$, 10%; $(M+CH_3)^-$, 10%
PbTPP	$(M+H)^-$, 100%; $(M-Pb+NiH)^-$, 50%; $(M-Pb+H)^-$, 10%
CuOEP	M^-, 40%; $(M+H)^-$, 100%; $(M+CH_3)^-$, 15%; $(M+C_2H_5)^-$, 10%

*TPP, tetraphenylporphyrin; OEP, octaethylporphyrin.

The presence of $(M + CH_3)^-$ ions in the dithiolate spectra is analogous to a similar observation in other negative ion spectra of metal complexes [22, 23]. They are attributed to reactions of the molecular ion with the methane moderator gas [22]. Addition of CH_3 and C_2H_5 radicals produced from the methane to molecular negative ion has been established as the mechanism in other negative ion systems [24].

Metalloporphyrins

Table III shows the ions observed in the negative ionization mass spectra of metalloporphyrins. In all cases, molecular ion peaks were the most abundant. Perhaps the most interesting feature of the spectra is the exchange reaction of the Pb and Cd tetraphenylporphyrins. Both Pb and Cd are too large to fit into the porphyrin cavity, and consequently occupy positions above the plane of the rings. Since the bonds between porphyrin and metal are then weak, decomposition of these metalloporphyrin occurs during EI analysis [25]. In the negative ion spectra, small peaks are due to exchange of the central metal (Cd or Pb) with H, probably from trace water or from methane, and Ni from the source housing. Nickel undergoes more facile exchange reactions in porphyrin systems than other metals [26]. On the other hand, in field desorption mass spectrometry, nickel surfaces are quite inert to exchange reactions of porphyrins but cobalt surfaces are not [27]. Fe exchange reactions have been observed during negative ion analyses of other chelates [22]. The ions $(M + CH_3)^-$ and $(M + C_2H_5)^-$ presumably are also the products of ion-radical reactions, as those discussed earlier.

Conclusions

The particular merit of methane enhanced negative ionization for structural determination for these three kinds of chelate compounds is the ready identification of both the mass of the complex and that of the ligand; the largest peaks present were the molecular ion (M^-), and/or the ligand ion (L^-). The fragmentations seen in these negative ion spectra were thus far more useful than the corresponding positive ion spectra for analysis. The interesting additions and exchanges, while not unique, are characteristic of rare processes.

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