Interpretation of EI organometallics mass spectra applying isotopic patterns

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Introduction

Mass spectrometry (MS) is dynamically developing instrumental analytical technique, which has been widely applied in many domains of science [1, 2], technology [3] and medicine [4] due to its high sensitivity and detection limit of femtogram order. The principle of MS depends on measurement of the mass to charge ratio (m/z) for molecular and fragment ions obtained during ionization of investigated sample, usually by means of high energy (70 kV) electrons (EI). The set of m/z signals versus their intensities (expressed usually in %) forms mass spectrum, in which one can differentiate clusters of signals (bands) exhibiting characteristic isotopic patterns. Their shape depends on natural isotopic abundance of elements [5] contained in the sample studied. In properly obtained spectrum, the mutual location of bands as well as their ion composition and isotopic pattern are specific for almost each individual compound, hence MS is a very suitable analytical technique for identification of compounds.

Despite several advantages, MS has two serious limitations, i.e. well known problems with obtaining a correct spectra and troubles with their interpretation. The second problem was overcome only for spectra of typical organic compounds (i.e. containing such elements like C, H, O, N, S) by registration and collection hundred thousands of them in popular data bases [6, 7]. It is also worth to note that isotopic patterns of such spectra are far simpler than those of organometallics ones. On the other hand interpretation of mass spectra of organic derivatives of multi-isotopic elements mainly the metals (e.g.: Pt, Mo, Ge, Sn and Pb) is seriously hindered by the modest representation of such spectra in available data bases as well as their wide isotopic patterns. This type of pattern, which is directly responsible for the intensive effects of overlapping of neighboring bands observed in organometallics mass spectra, requires use of non-routine methods of their interpretation. For that purpose various computer-aided chemometric methods based on analysis of isotopic patterns [8-14] appeared to be very helpful. The general idea of all those methods depends on comparison of experimental bands extracted from experimental spectra with those computer generated from natural isotopic abundance of elements contained in ions of known summary formulas.

Recently Szymura and Lamkiewicz [14] elaborated original procedure of the band composition analysis (BCA) in EI mass spectra of organometallics. Up to now its efficiency has been confirmed only for organotin spectra [14, 15]. In this work, being a natural continuation of previous research, the same authors by means of BCA performed the interpretation of several EI mass spectra of the organic derivatives of the metals representing a wide range of natural isotopes (4÷10). All organometallics were either the compounds with π or σ bonds between the metal and carbon atoms.

Mass spectra used for study

In this paper five low-resolution EI mass spectra of organic derivatives of Pt, Mo, Ge, Sn and Pb metals having 6, 7,5,10 and 4 natural isotopes [5] were used. All spectra were taken from the newest edition of NIST data base [6]. Two compounds, i.e. tris(η^4-1,3-butadiene) molybdenum (ZMo) and (η^5-2,4-cyclopentadien-1-yl)(η^3-2-propenyl) platinum (ZPt) characterized with presence of π coordination bond between metal and carbon atoms of organic part Z. The remaining

three: tetraisobutylplumbane (ZPb), tetraisobutyltin (ZSn) and 4-germaspiro[3,4]octane (ZGe) were the examples of the compounds containing typical covalent σ bond. All analyzed spectra are shown in Figure 1, together with their structural formulas and isotopic patterns of appropriate metals.
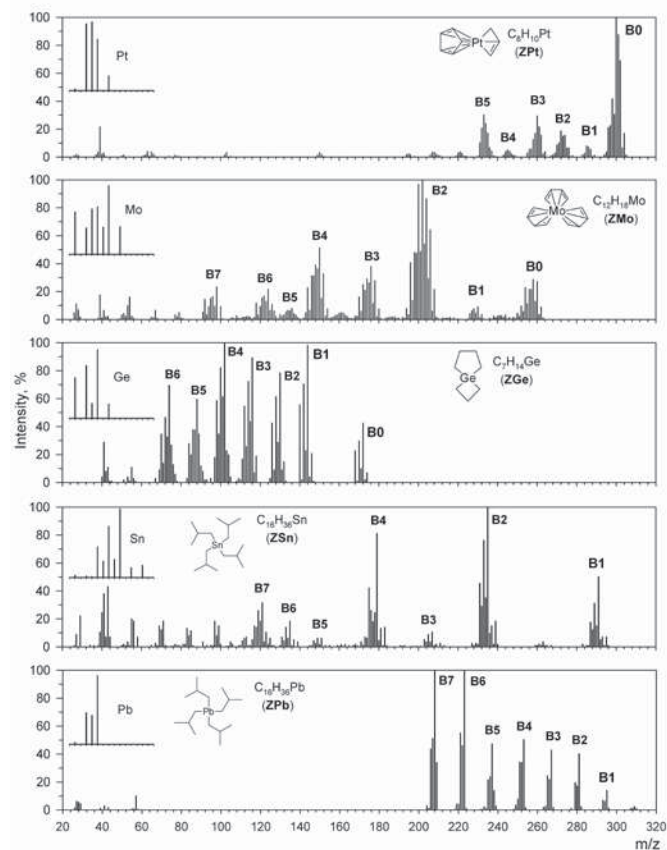
Fig. 1. EI mass spectra of organic derivatives of Pt, Mo, Ge, Sn and Pb multi-isotopic elements [6], with division on experimental bands: B0 originated from molecular ion, B1-B7 originated from fragment ions. In the left-upper corner of each spectrum the enlarged isotopic pattern of the appropriate metal is shown

Even their initial visual evaluation discloses the presence of isotopic patterns characteristic for Pt, Mo, Ge, Sn and Pb. One can also notice the highest condensation of bands for ZMo spectrum in comparison to all others. For ZMo, ZPt and ZGe spectra the bands of appropriate molecular ions, marked as B0 are clearly visible in Figure 1. They are absent in case of ZSn and ZPb, since molecular ions of those derivatives decompose easily under the conditions of ionization chamber of mass spectrometer (low pressure, high temperature). All the remaining bands B1-B7 in Figure 1 were left by fragment ions originated from decomposition of molecular or other fragment ions. The signal intensities in bands of ZPb spectrum remind those characteristic for fragmentation of typical organic compounds [16] having long aliphatic chains, since their intensities increase with decrease in ion mass.

The most stable fragment ions can be observed in ZGe spectrum. Generally, the highest signal intensities (over 50%) visible in ZGe spectrum point to the highest stability of the fragment ions originated from this derivative. Another significant observation is that among all

spectra interpreted, only those for ZMo and ZPt contain bands wider than the width of „pure" isotopic patterns of Mo and Pt, respectively. This can be an evidence of overlapping of fragment bands, which originate from numerous ions formed during extensive fragmentation of those compounds in ionization chamber of mass spectrometer.

Interpretation procedure

All mass spectra in this work were analyzed by means of modified version (v.3.0) of computer-aided chemometric method called band composition analysis (BCA) [14]. At the beginning it automatically divides investigated spectrum on experimental bands E (marked as B0-B7 in Figure 1) and generates theoretical multi-isotopic bands T of ions, using natural isotopic abundances of the elements[5]. Next BCA combines them to obtain a model band M, which is finally compared with the appropriate experimental band E. The method uses two classifiers: theoretical variance (s^2_{theor}) and fit factor (α). The first one expresses the fit between E and T:

$$s^2_{theor} = \Sigma(E-T)^2 \qquad (1)$$

For $s^2_{theor} < 20$, the experimental band is called "simple" since in was left by the single ion, whereas for $s^2_{theor} > 20$, the band is called "complex" as that originated from more than one ion. The complex band needs modeling for determination of its ionic composition. Modeling depends on the search for optimal values of theoretical ions contributions (x), for which the second classifier (α) given by the equation:

$$\alpha = \frac{s^2_{theor} - \Sigma(E-M)^2}{s^2_{theor}} \qquad \text{where:} \quad M = \Sigma\, T \cdot x \qquad (2)$$

exceeds 90%. This second classifier expresses matching between E and M bands.

After the division of given spectrum on several individual experimental bands, for each of them BCA chooses the signal of the highest intensity (so called „main signal") to build a fragmentation table helpful for determination of summary formulas of the main ions. The term „main ion" denotes the ion, whose mass corresponds to the m/z position of the main signal. In this work only the bands left by metal containing ions, whose signal intensities exceeded 5% were taken into account.

Results and discussion

The final results of interpretation performed in presented research are collected in Table 1. It contains the ions formulas together with their contributions in all simple and complex bands of investigated spectra of organometallics. Careful analysis performed on data in this table

disclosed a several interesting effects, trends and regularities. Among all spectra studied, those corresponding to the compounds containing π bonds (ZPt and ZMo) showed a predominant number of ions (up to 5) in their bands. Generally, almost all their bands (except B1 and B7 for ZMo) appeared to be complex, in contrast to those identified in spectra of other organometallics (ZGe, ZSn and ZPb) containing σ bond.

Interpretation of ZPb and ZSn spectra showed that despite the presence of common i-Bu substituent, fragmentation of their molecular ions proceeds in different way. For both spectra B7 complex band originates from 2 and 3 ions, respectively, however Pb^+ (x=0.73) is the main ion in case of ZPb in contrast to SnH^+ (x=0.62) for ZSn. A similar trend in these spectra shows another complex band B5, which contains 3 ions. Their main ions $C_2H_5Pb^+$ (x=0.77) and $C_2H_5SnH_2^+$ (x=0.71) are also different.

Further consideration on ZPb and ZSn interpreted pair of spectra provides evidence that fragmentation of their molecular ions proceeds through splitting of carbon-carbon bond of substituent rather than that of metal-carbon in both organometallics. This is supported by the presence as well as high intensities (40-50%) of the main signals of B1, B4, B5 and B6 bands in ZPb spectrum. The similar, however less distinct trend is manifested in B3, B5 and B6 bands of ZSn spectrum, where the intensities of main bands do not exceed 18%. Moreover, the presence of SnH_3^+ ion in B7 band of ZSn spectrum and simultaneous lack of PbH_3^+ ion in B7 band of ZPb spectrum reveals the greater ability of tin for hydrogenation than that for lead. Such process common in mass spectrometry is known to be responsible for difficulties in the interpretation of organometallics mass spectra [11].

The ZGe mass spectrum contains 5 complex and 2 simple bands (B0 and B1). For this spectrum, the highest value of the fit factor (α=99.61 %) was obtained for its complex band B4 left by a following ions: $C_2H_5Ge^+$ (x=0.10), $C_2H_4Ge^+$ (x=0.69) and $C_2H_3Ge^+$ (x=0.21). Moreover, it was shown that germanium in comparison to tin and lead does not form ions of $RGeH^+$ type (where R denotes alkyl substituent), with the only exception of GeH^+, whose contribution x=0.29 in B6 band. This study confirmed the occurrence of almost all ions mentioned earlier in literature for mass spectrum of ZGe [17], with the exception of: $C_5H_9Ge^+$, $C_3H_7Ge^+$ and $CHGe^+$.

Conclusions

The method of band composition analysis (BCA) used in this study for interpretation of organometallics mass spectra enabled qualitative and quantitative identification of the ions forming spectral bands (both simple and complex), no matter on the degree of complexity of spectra and number of natural isotopes of metals.

Table 1

Results of interpretation of EI mass spectra of organic derivatives ZPt, ZMo, ZGe, ZSn and ZPb (Z denotes organic part of compound) [6] showing all ions identified in bands (x denotes ion contributions)

Bands	ZPt Ions	x	s^2_{theor} α, %	ZMo Ions	x	s^2_{theor} α, %	ZGe Ions	x	s^2_{theor} α, %	ZSn Ions	x	s^2_{theor} α, %	ZPb Ions	x	s^2_{theor} α, %
B0	$C_8H_{10}Pt^+$	0.61	872.18	$C_{12}H_{18}Mo^+$	0.57	647.81	$C_7H_{14}Ge^+$	1.00	15.12	-	-	-	-	-	-
	$C_8H_9Pt^+$	0.04	99.80	$C_{12}H_{16}Mo^+$	0.23	99.09			-		-		-	-	-
	$C_8H_8Pt^+$	0.18		$C_{12}H_{15}Mo^+$	0.04										
	$C_8H_6Pt^+$	0.17		$C_{12}H_{14}Mo^+$	0.16										
B1	$C_7H_7Pt^+$	0.70	754.38	$C_{10}H_{12}Mo^+$	1.00	20.27	$C_5H_{10}Ge^+$	1.00	4.06	$C_{12}H_{27}Sn^+$	1.00	4.90	$C_6H_{15}Pb^+$	1.00	3.67
	$C_7H_6Pt^+$	0.11	99.52			-			-			-			-
	$C_7H_5Pt^+$	0.18													
B2	$C_6H_8Pt^+$	0.18	800.00	$C_8H_{12}Mo^+$	0.37	692.52	$C_4H_9Ge^+$	0.05	33.69	$C_8H_{18}SnH^+$	1.00	1.46	$C_5H_{12}PbH^+$	1.00	2.11
	$C_6H_6Pt^+$	0.43	99.25	$C_8H_{10}Mo^+$	0.13	98.37	$C_4H_8Ge^+$	0.88	94.09			-			-
	$C_6H_5Pt^+$	0.08		$C_8H_8Mo^+$	0.44		$C_4H_7Ge^+$	0.06							

Bands	ZPt			ZMo			ZGe			ZSn			ZPb		
	Ions	x	s^2_{theor} α, %	Ions	x	s^2_{theor} α, %	Ions	x	s^2_{theor} α, %	Ions	x	s^2_{theor} α, %	Ions	x	s^2_{theor} α, %
	$C_6H_4Pt^+$	0.21		$C_8H_7Mo^+$	0.05										
	$C_6H_3Pt^+$	0.10													
B3	$C_5H_6Pt^+$	0.42	537.84	$C_6H_8Mo^+$	0.37	302.02	$C_3H_6Ge^+$	0.77	217.52	$C_6H_{15}Sn^+$	1.00	14.90	$C_4H_9PbH_2^+$	0.86	31.12
	$C_5H_5Pt^+$	0.19	97.70	$C_6H_7Mo^+$	0.02	99.61	$C_3H_5Ge^+$	0.23	97.01			-	$C_4H_9PbH^+$	0.07	97.98
	$C_5H_4Pt^+$	0.24		$C_6H_6Mo^+$	0.46								$C_4H_9Pb^+$	0.07	
	$C_5H_2Pt^+$	0.15		$C_6H_5Mo^+$	0.06										
				$C_6H_4Mo^+$	0.09										
B4	$C_4H_5Pt^+$	0.05	313.85	$C_4H_6Mo^+$	0.28	259.18	$C_2H_5Ge^+$	0.10	371.98	$C_4H_9SnH_2^+$	0.87	27.57	$C_3H_7PbH_2^+$	0.73	171.95
	$C_4H_4Pt^+$	0.08	98.74	$C_4H_5Mo^+$	0.05	99.41	$C_2H_4Ge^+$	0.69	99.61	$C_4H_9Sn^+$	0.13	93.36	$C_3H_7PbH^+$	0.18	99.76
	$C_4H_3Pt^+$	0.26		$C_4H_4Mo^+$	0.56		$C_2H_3Ge^+$	0.21					$C_3H_7Pb^+$	0.09	
	$C_4H_2Pt^+$	0.38		$C_4H_3Mo^+$	0.12										
	C_4HPt^+	0.23													
B5	$C_3H_4Pt^+$	0.13	450.33	$C_3H_4Mo^+$	0.11	422.55	CH_3Ge^+	0.41	724.52	$C_2H_5SnH_2^+$	0.71	1056.17	$C_2H_5PbH^+$	0.22	102.35
	$C_3H_3Pt^+$	0.31	98.97	$C_3H_3Mo^+$	0.34	97.63	CH_2Ge^+	0.59	99.07	$C_2H_5Sn^+$	0.23	99.30	$C_2H_5Pb^+$	0.77	93.00
	$C_3H_2Pt^+$	0.27		$C_3H_2Mo^+$	0.55					$C_2H_4Sn^+$	0.06		$C_2H_4Pb^+$	0.01	
	$C_3H_1Pt^+$	0.28													
B6				$C_2H_6Mo^+$	0.08	168.57	GeH^+	0.29	348.91	CH_3Sn^+	1.00	12.12	CH_3Pb^+	1.00	19.86
				$C_2H_5Mo^+$	0.11	95.40	Ge^+	0.71	98.46			-			-
				$C_2H_3Mo^+$	0.08										
				$C_2H_2Mo^+$	0.64										
				C_2HMo^+	0.09										
B7				Mo^+	1.00	0.81				SnH_3^+	0.15	144.58	PbH^+	0.28	207.58
						-				SnH^+	0.62	98.86	Pb^+	0.72	98.54
										Sn^+	0.23				

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