

Analysis of Coordination and Organometallic Compounds Using Photoionisation Mass Spectrometric Techniques

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A range of coordination and organometallic compounds have been analysed by quadrupole ion-trap mass spectrometry using various photoionisation methods. Atmospheric-pressure photo ionisation (APPI), which combines atmospheric-pressure chemical ionisation (APCI) with a photolysis lamp, was compared with the new technique photo-assisted electrospray ionisation (PAESI). Additionally, the atmospheric-

pressure matrix-assisted laser desorption ionisation (AP-MALDI) was also evaluated and compared to MALDI quadrupole ion-trap time-of-flight (MALDI-QIT-TOF) mass spectrometry.

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Introduction

An armoury of mass spectrometric techniques is already available for determining the molecular weight and obtaining structural data on a plethora of different types of compounds. Coordination and organometallic chemists once relied almost exclusively on electron impact, chemical ionisation and fast-atom bombardment methods, but now they routinely employ electrospray ionisation (ESI) and matrix-assisted laser desorption ionisation (MALDI) techniques.^[1] Although these techniques were largely developed with biomolecules and polymers in mind, various strategies have been developed to assist the analysis of coordination and organometallic compounds. For example, MALDI is sometimes most effective in the absence of a matrix; hence, LDI is a better description of the experiment. ESI mass spectrometry seems to be ideally suited to naturally charged coordination and organometallic compounds, although variations including ambient temperature ESI^[2] and cold-spray ionisation^[3] have been applied to compounds with labile ligands and unstable reaction intermediates, and instrument modifications made for high-throughput catalyst screening.^[4] Apart from charged compounds, neutral compounds with ligands that have basic pendant groups are readily protonated and analysed; however, where such ligands are not present, a range of derivatisation reagents have been evaluated, which are now in widespread use.^[5] Clearly, chemical derivatisation complicates the experiment and

alternative ionisation sources would be advantageous. Since many coordination and organometallic compounds are photoactive, we have evaluated a series of photoionisation methods and indicate where they exhibit greatest utility.

A range of coordination and organometallic compounds, including metallocenes, phosphane compounds, metal-carbonyl complexes and clusters, porphyrin and phthalocyanine complexes, and bi- and tripyridine complexes (see Exp. Sect. for a full list), were investigated using a quadrupole ion-trap mass spectrometer. Initial experiments were carried out using an atmospheric-pressure photoionisation (APPI) source,^[6] which comprises a krypton photolysis lamp that emits photons with energies of 10.0 and 10.6 eV combined with an atmospheric-pressure chemical-ionisation (APCI) source. APCI mass spectrometry has been previously applied to the analysis of coordination^[7] and organometallic^[8] compounds and we find that essentially any compound that is amenable to APCI can be analysed by APPI. The lamp can be switched on or off as the analyte enters the mass spectrometer and in certain cases large increases in the signal intensity can be obtained when the lamp is on. Perhaps the most interesting results were provided by the analysis of ruthenocene in aromatic solvents. Figure 1 shows a series of spectra of ruthenocene in toluene recorded using APCI only, APPI (i.e. APCI with PI) and APPI in which the plasma source of the APCI unit was switched off. In the APCI spectrum the dominant peak at $m/z = 232$ corresponds to the ruthenocenium cation $[\text{Ru}(\text{C}_5\text{H}_5)_2]^+$, but in addition, a peak of quite high relative intensity is observed at $m/z = 259$ and corresponds to a complex in which one cyclopentadienyl ligand has been replaced by a toluene molecule, viz. $[\text{Ru}(\text{C}_5\text{H}_5)(\text{C}_7\text{H}_8)]^+$. This type of arene exchange reaction has been observed previously, but under very different conditions, with AlCl_3 as a Lewis acid catalyst.^[9]

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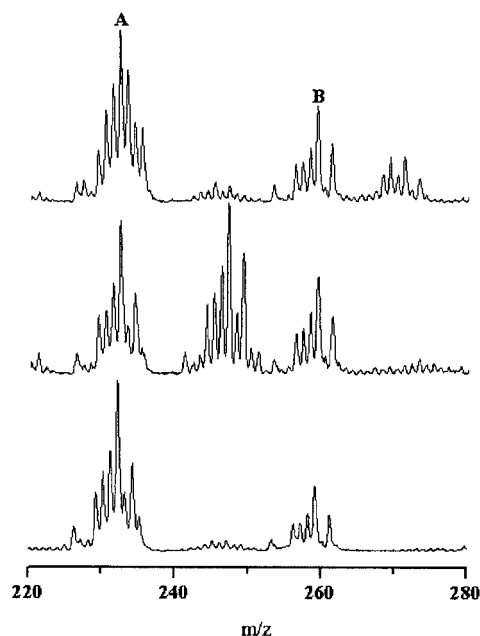


Figure 1. The positive ion mass spectra of ruthenocene in toluene recorded using (top) APCI, (middle) APPI and (bottom) APPI without the plasma: **A** corresponds to $[\text{Ru}(\text{C}_5\text{H}_5)_2]^+$ and **B** to $[\text{Ru}(\text{C}_5\text{H}_5)(\text{C}_7\text{H}_8)]^+$

Other peaks are also present, but these are less readily assigned. Using APPI the same two peaks are present, but the most intense is observed at $m/z = 247$ which cannot be assigned to any simple species (see below). However, if the APCI plasma is turned off and PI is used alone, the spectrum becomes much cleaner with the dominant peaks corresponding to $[\text{Ru}(\text{C}_5\text{H}_5)_2]^+$ and $[\text{Ru}(\text{C}_5\text{H}_5)(\text{C}_7\text{H}_8)]^+$. If the PI lamp is switched off, no peaks are observed. Clearly, the PI lamp has a significant effect, but it is very difficult to separate from the thermal effect of the APCI source (even when the plasma is off the source is maintained at a very high temperature) and the ligand exchange reaction is thermally driven. The same arene exchange process occurs with other arenes when these are used as the solvent. Solvent has already been shown to be very important in APPI mass spectrometry,^[6] and here it seems probable that the PI source ionises the solvent molecules, and the solvent ions then ionise the ruthenocene. The peak of highest relative intensity obtained under APPI conditions is 15 mass units above the parent ion and might correspond to the parent ion with a methyl group attached, possibly arising from a side reaction related to the primary ionisation mechanism.

In general, most of the compounds analysed by APPI afforded spectra, but the effect of PI was minimal compared to the effect of the APCI source, which is too harsh for most coordination and organometallic compounds, resulting in extensive fragmentation and reactivity. As such, we combined PI with the considerably softer ESI source, which, as far as we are aware, has not been attempted before, and we term the technique photo-assisted ESI (PAESI). In keeping with ESI, no peaks were observed when neutral compounds were studied using PAESI mass spectrometry, but any compound that can be analysed with

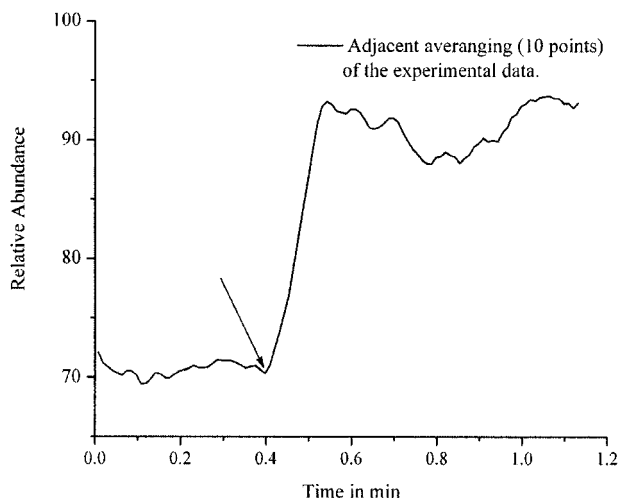


Figure 2. The effect of PI on ESI; the arrow indicates when the PI lamp was switched on, resulting in a higher ion current and hence an improved signal-to-noise ratio

ESI mass spectrometry, can be analysed by PAESI. The main effect was found for some positively and negatively charged coordination and organometallic compounds which tended to give higher ion currents, and hence improved the signal-to-noise ratio (Figure 2). However, characteristic photolysis products, such as carbonyl dissociation products, were not observed. In comparison to APPI, where photoionisation takes place in the gas-phase, in the PAESI experiment the analyte remains in the solvent during photolysis. As such, it is likely that the PI effect will be relatively dilute, since the exposure of the ions in the solvent spray is very short. As in APPI, it is likely that the solvent will play an important role and further experiments are required in this respect.

MALDI mass spectrometry, in which a laser is used to photolyse the analyte, has been used for the analysis of coordination and organometallic compounds. Atmospheric-pressure MALDI has been developed recently,^[10] but the types of compounds considered here have not been analysed using this method. Since the AP-MALDI source is compatible with the quadrupole ion-trap instrument, we evaluated the method for coordination and organometallic compounds. The same method was used to great success for coordination and organometallic compounds, (viz. when no matrix^[11] was present). In general, the only compounds that could be detected were those with strong chromophores such as porphyrin and phthalocyanine complexes. Metal-carbonyl compounds, for example, gave only very weak signals in AP-LDI in contrast to those in spectra obtained from LDI-TOF experiments, which reveal extensive gas-phase reaction products.^[12] In the LDI-TOF experiments, the energetic ions formed by the laser desorption process undergo gas-phase reactions with little interference from other molecules or ions, because the experiment is conducted under a high vacuum. In contrast, the ions formed in the AP-LDI experiment may undergo collisional deactivation by reaction with the gas molecules present in the source. Porphyrin and phthalocyanine complexes have also

been shown to dimerise and oligomerise in LDI mass spectrometry,^[12] although no MS/MS experiments have been conducted on the gas-phase products, which would help to confirm their identity.

Using AP-LDI, the mass spectrum of manganese phthalocyanine showed four main peaks, the parent ion $[\text{Mn}(\text{phthalocyanine})]^+$ at $m/z = 567$ and the dimeric species $[\{\text{Mn}(\text{phthalocyanine})\}_2]^+$ at $m/z = 1134$, (Figure 3). In addition, a peak centred at $m/z = 1153$ corresponds to two overlapping species, these being the hydroxide $[\{\text{Mn}(\text{phthalocyanine})\}_2(\text{OH})]^+$ and $[\{\text{Mn}(\text{phthalocyanine})\}_2(\text{H}_3\text{O})]^+$, and the peak at $m/z = 1168$ corresponds to $[\{\text{Mn}(\text{phthalocyanine})\}_2(\text{O}_2\text{H}_3)]^+$, (i.e. probably an adduct with both OH and H_2O interactions). Oxidation products such as these are not unexpected for these types of compounds.^[13] These products result from the presence of oxygen and water in the source, which are removed in conventional MALDI since it operates under high vacuum. In Figure 3 spectrum (ii) was obtained using exactly the same conditions, except the source was purged with nitrogen for five minutes before acquiring the data, and during data acquisition. The amount of products resulting from reactions with oxygen and water is reduced considerably. MS/MS of the simple dimer product resulted in regeneration of the parent ion only (A; Figure 3) indicating that the aggregate is held together by noncovalent interactions.

The same compound was analysed by MALDI quadrupole ion-trap time-of-flight (MALDI-QIT-TOF) mass spectrometry without matrix. Like the AP-MALDI experiment, a parent ion peak was observed at $m/z = 567$; however, a

dimer was observed at $m/z = 1132$, which corresponds to the dimer with loss of two hydrogen atoms, probably corresponding to the formation of a C–C bond. This hypothesis is given greater weight as the MS/MS of the dimer does not result in the reformation of the monomer, but instead, a complicated series of fragmentation products are observed.

Again, the differences between the LDI-QIT-TOF and AP-LDI experiments may be attributed to the differences in pressure at which these experiments take place (see above).

Overall, the new techniques described herein cannot be applied to a wide range of coordination and organometallic compounds; APPI and PAESI give good spectra for any compound that can be analysed by APCI and ESI mass spectrometry, respectively. In addition, LDI-QIT-TOF can also be applied to any sample which is amenable to LDI, whereas AP-LDI is only suited to compounds with very strong chromophores. These various photoionisation techniques also give rise to some interesting features not accessible with other techniques currently used. For example, certain gas-phase products that form can be deciphered using the ion-trap, which allows information to be gained that would otherwise be inaccessible. We also found that for best results with AP-MALDI it is essential that the source is purged with nitrogen or another inert gas in order to reduce gas-phase reactions with oxygen or other reactive contaminants in the atmosphere. As yet, we have not evaluated in detail the influence of matrices in AP-MALDI and it is possible that their application may increase the range of compounds that can be studied.

Experimental Section

The compounds evaluated $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]$, $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{H}_4\text{BOH}_2)]$, $[\text{Ru}(\eta\text{-C}_5\text{H}_5)_2]$, $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$, $[\text{RhCl}(\text{PPh}_3)_3]$, $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$, $[\text{Ru}(\eta\text{-}p\text{-cymene})(\text{dppe})]^+$,^[14] $[\text{RuCl}_2(\eta\text{-}p\text{-cymene})(\text{pta})]$,^[15] $\text{Mo}(\text{CO})_6$ and $\text{M}_2(\text{CO})_{10}$ ($\text{M} = \text{Mn}$ or Re), $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Fe}$, Ru or Os), $[\text{Cr}(\eta\text{-C}_6\text{H}_6)(\text{CO})_3]$, $[\text{Cr}(\eta\text{-C}_{10}\text{H}_{16})(\text{CO})_3]$,^[16] $[\text{Cr}(\eta\text{-C}_7\text{H}_{10})(\text{CO})_3]^+$, $\text{Rh}(\text{Me})\text{O}_3$, [phthalocyaninato manganese(II)], [chloro(5,10,15,20-tetraphenylporphyrinato) $k^4\text{N}^{21,22,23,24}$ iron(III)], [(5,10,15,20-tetraphenylporphyrinato) $k^4\text{N}^{21,22,23,24}$ nickel(II)], [(5,10,15,20-tetraphenylporphyrinato) $k^4\text{N}^{21,22,23,24}$ zinc(II)], *cis*- $\text{PtCl}_2(\text{NH}_3)_2$, auranofin (ICN Biomedicals Inc), ruthenium(II)tris(2,2'-bipyridyl-4,4'-dicarboxylato) dichloride (Solaronix), ruthenium(II)*cis*-bis(isocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato) (Solaronix), tris(isothiocyanato)-ruthenium(II)-2,2':6',2''-terpyridine-4,4',4''-tricarboxylic acid (Solaronix), ruthenium(II)*cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) (Solaronix) and tris(isothiocyanato)-ruthenium(II)-2,2':6',2''-terpyridine-4,4',4''-tricarboxylic acid (Solaronix) were obtained from commercial sources (indicated when not a common supplier) or prepared by literature methods (indicated). Mass spectra were collected on a ThermoFinnigan LCQ DecaXP Plus quadrupole ion-trap instrument (APPI, APCI, PAESI and AP-MALDI) or a Shimadzu AXIMA-QIT (MALDI-OTI-TOF) mass spectrometer.

APPI, APCI and PAESI: All sources are commercially available from Thermo-Finnigan, although the PAESI must be constructed by combining the PI lamp with the ESI source. This is straightforward given the similar designs of the APCI and ESI sources. The

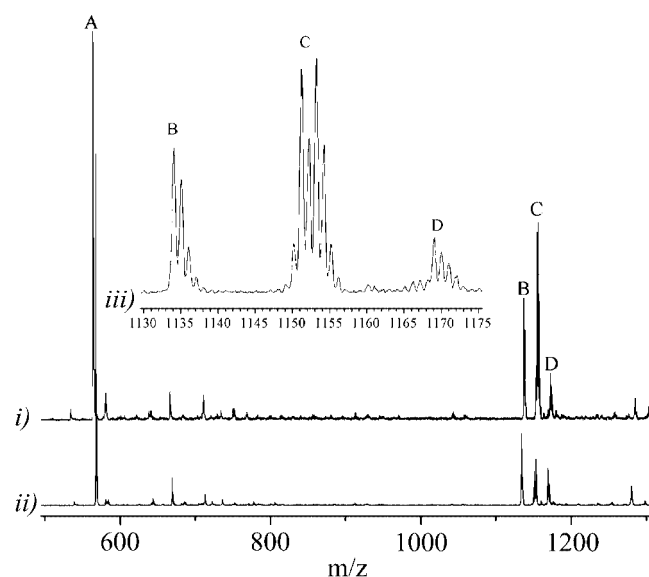


Figure 3. The positive ion AP-MALDI mass spectrum of $\text{Mn}(\text{phthalocyanine})$: (i) corresponds to the spectrum recorded under ambient atmospheric pressure, (ii) is the spectrum recorded when the source is purged with N_2 : A corresponds to $[\text{Mn}(\text{phthalocyanine})]^+$, B to $[\{\text{Mn}(\text{phthalocyanine})\}_2]^+$, C to two overlapping ions $[\{\text{Mn}(\text{phthalocyanine})\}_2(\text{O})(\text{H})]^+$ and $[\{\text{Mn}(\text{phthalocyanine})\}_2(\text{H}_3\text{O})]^+$, D to $[\{\text{Mn}(\text{phthalocyanine})\}_2(\text{O})(\text{H}_3\text{O})]^+$; note that the amount of oxide and H_3O adducts reduced when the system is purged with N_2 ; trimers of low relative intensity are also observed (not shown)

PI lamp is based on a photo-Mate ion source using a Krypton lamp which emits photons at 10.0 and 10.6 eV. Samples were infused directly into the source at $5 \mu\text{L}\cdot\text{min}^{-1}$ using a syringe pump with nitrogen as drying gas. For the ESI source the temperature was set to 50°C and the cone voltage within the range 4.50–5 kV. The MS detector was tuned automatically on the base peak, which optimised the remaining parameters. Samples were prepared by dissolving the complex (10–100 mg) in the appropriate mobile phase (1 mL).

AP-MALDI and MALDI-QIT-TOF: Samples were dissolved in dichloromethane solvent and deposited onto the sample probe. The solvent was allowed to evaporate leaving a thin layer of the pure sample. Several layers were added in this manner. The laser power was optimised for each sample. The spectra were recorded under air or N_2 at atmospheric pressure.

Peaks were assigned from the m/z values and from the isotope distribution patterns which were simulated using the ISOTOPE program.^[17] The m/z values given are for the most intense peak in the envelope in each case.

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