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Synthesis and Characterization by FAB Mass Spectrometry of a Series of New Polymetallic Homo- and Heteronuclear Complexes of Ruthenium(II) and Rhodium(III) with the Symmetric Bridging Ligand 1,4,5,8,9,12-Hexaazatriphenylene

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FAB (fast atom bombardment) mass spectrometry is shown to be a valuable technique for characterizing polymetallic complexes, when other methods, such as NMR spectroscopy, are not helpful due to the complexity of the NMR spectra. The studied complexes are based on the bridging ligand 1,4,5,8,9,12-hexaazatriphenylene which presents three symmetrically arranged chelating sites and allows the preparation of polymetallic homo- and heteronuclear complexes of Ru(II) and Rh(III). The major ionization mechanism under FAB conditions is shown to be a first loss of one negatively charged counterion, followed by the successive losses of other counterions, either as uncharged radicals or as negatively charged ions accompanied, in the latter case, by a one-electron reduction from the matrix; both ionization mechanisms lead to singly charged ions. Minor doubly and triply charged species are also observed, corresponding to the loss of a second and third negatively charged counterion without subsequent reduction by the matrix. Finally fragmentations of the complexes occur as demonstrated by the detection of metal–ligand moieties.

Introduction

Luminescent and redox reactive coordination compounds have received considerable attention in the design of photochemically and photophysically efficient molecular devices. In this context, several polymetallic homo- and heteronuclear complexes,[1] where the metallic centers are either assembled by a bridging ligand[2] or by bridging ions,[3] have been prepared and studied as models for larger aggregated chromophores–luminophores operating electron[4] and energy[5] transfer under illumination. The literature on these topics is too vast to be quoted exhaustively. For recent reviews, see ref 1a,c,d.

A few years ago, a new tris-chelating, highly symmetric (D_3) ligand, the dipyrazino[2,3-*f*:2′,3′-*h*]quinoxaline, also known as 1,4,5,8,9,12-hexaazatriphenylene (HAT, Figure 1a) has been complexed to Ru(BPY)$_2^{2+}$ moieties (BPY = 2,2′-bipyridine) to form the corresponding mono-, bi-, and trimetallic complexes.[6,7] More recently we have investigated the possibilities offered by this ligand to design nonsymmetric homo-[7c] and heteronuclear complexes of Ru(II) and Rh(III).

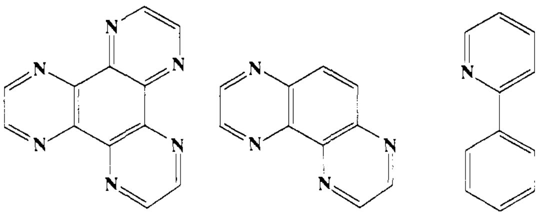
(a): HAT (b): TAP (c): PPY

Figure 1. (a) 1,4,5,8,9,12-hexaazatriphenylene (HAT or H). (b) 1,4,5,8-tetraazaphenanthrene (TAP or T). (c) 2-phenylpyridine (PPY or Py).

The major problem encountered in this study was to obtain a nonambiguous proof of the structure of the polynuclear edifice. Because of the racemic nature of the monometallic precursors (Λ and Δ forms), the resulting polynuclear complexes represent a mixture of diastereoisomers that cannot be separated by usual chromatography methods. The number of diastereoisomers obtained with the HAT ligand depends on the symmetry of the designed complex, as illustrated in Table I. Because the numerous ^{1}H and ^{13}C signals of the different ligands are multiplied by the number of diastereoisomers, the polymetallic complexes show very complicated ^{1}H and ^{13}C NMR spectra.

To some extent structural information can also be obtained from the NMR spectrum of the transition metal itself,[8] such as ^{99}Ru NMR.[9] However, because the ruthenium NMR signals

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Table I. Symmetry of the Complexes and Possible Number of Diastereoisomers

complex[a]	symmetry operations[b]	no. of diastereoisomers
$[M(L)_2]_2HAT^{n+}$	$E + 1C_2$	2
$[M(L)_2]HAT[M(L')_2]^{n+}$ or $[M(L)_2]HAT[M'(L)_2]^{n+}$	E	2
$[M(L)_2]_3HAT^{n+}$	$E + 1C_3 + 3C_2$	2
$[M(L)_2]_2HAT[M(L')_2]^{n+}$ or $[M(L)_2]_2HAT[M'(L)_2]^{n+}$	$E + 1C_2$	3

[a] M and M′ represent different metals, L and L′ represent different ligands, and *n* denotes the total charge of the complex, which depends on the nature of the metals and ligands. [b] *E* stands for the identity operation and C_2 and C_3 stand for 2- and 3-fold rotation operations, respectively.

are very broad, the available information will be limited in most of the cases to the knowledge of the number of metallic ions in the molecule and will not allow the observation of the diastereoisomers.

The use of new techniques in mass spectrometry for the characterization of transition metal complexes has rapidly developed during the last few years. When applied to coordination compounds, conventional mass spectrometry[10] has been used with limited success, while field desorption, electrohydrodynamic ionization, laser mass spectrometry, and fast atom bombardment mass spectrometry have produced significant results.[11] FAB mass spectrometry is extremely promising in view of characterizing polymetallic complexes because parent and fragmentation ions can be detected, as has been shown with some complexes of Re, Mo, and Os.[12] Despite the fact that several studies have been devoted to FAB mass spectrometry of organometallic and coordination compounds,[13] only a few reports on polymetallic compounds, especially of high molecular weights (MW ≥ 2000), are available.

In this paper we present the first FAB mass spectrometry studies of mono-, bi-, and trimetallic homo- and heteronuclear complexes of Ru(II) and Rh(III), bridged by the ligand HAT (Figure 1a), which reach molecular weights as high as 2000 Da. The nonbridging ligands (hereafter referred to as ancillary ligands) are BPY or B (2,2′-bipyridine), TAP or T (1,4,5,8-tetraazaphenanthrene, Figure 1b), PHEN or Ph (1,10-phenanthroline), HAT or H and, when Rh(III) is coordinated, PPY or Py (2-phenylpyridine, Figure 1c). All complexes correspond to the PF_6^- (or P) salts.

Experimental Section

Monometallic Precursors. $Ru(BPY)_2Cl_2$[14] is obtained by standard methods of preparation; the syntheses of $Ru(HAT)_3^{2+}$ and $Ru(BPY)(HAT)_2^{2+}$ have been described previously.[7a] $Ru(BPY)(TAP)_2^{2+}$ has also been prepared in a similar manner[15] using TAP instead of HAT.

For the synthesis of $Rh(PPY)_2HAT^+$, 0.1 mmol of $[Rh(PPY)_2Cl]_2$[16] in CH_2Cl_2 is added dropwise to a refluxing solution of HAT (>0.2 mmol) in a $MeOH/CH_2Cl_2$ (1:1) mixture. The solution is refluxed for 2 h, the solvent evaporated, the complex dissolved in water, and the nonsoluble HAT filtered off. The complex is precipitated as its hexafluorophosphate salt (yellow) by addition of a saturated aqueous solution of KPF_6 (yield: 80%).

The Monometallic $Ru(BPY)(TAP)(HAT)^{2+}$ Complex (A). $Ru(BPY)Cl_4^{2-}$[17] (0.5 mmol) and 0.5 mmol of TAP are suspended in 5 mL of *N,N*′-dimethylformamide (DMF) in the presence of 1.5 mmol of LiCl. The mixture is refluxed for 24 h until no further change in its visible absorption spectrum is observed. The violet solid, $Ru(BPY)(TAP)Cl_2$, is slowly precipitated from the reaction mixture by condensation of acetone vapor in DMF. An aqueous solution of $Ru(BPY)(TAP)Cl_2$ (0.1 mmol) is added to a refluxing solution of HAT (>0.5 mmol) in water, and the mixture is kept refluxing for 3 h. When no further evolution is observed in the visible absorption spectrum, the reaction mixture is chilled and the excess of HAT filtered off; the solution is then loaded on a cation-exchanger chromatography column (Sephadex SP-C25, Pharmacia) and the complex eluted by an aqueous solution of 0.1 M NaCl. The complex solution plus NaCl is evaporated to dryness, the residue is dissolved in a minimum of ethanol, the nondissolving salt filtered off, the ethanolic solution evaporated again to dryness, and the residue dissolved in a small amount of water. The complex is then precipitated by adding a saturated aqueous solution of KPF_6. The precipitate is filtered and washed with water to remove the excess of KPF_6. The overall yield, relative to $Ru(BPY)Cl_4^{2-}$, is 50%. ^1H NMR spectrum (Bruker Cryospec WM 250 MHz, dimethyl sulfoxide-d_6; δ (ppm); (J, Hz)): 9.61, d (2.09); 9.59, d (2.07); 9.42, d (2.9); 9.33, d (2.8); 9.21, d (2.9); 9.12, d (2.8); 9.01–9.98 (poorly resolved); 8.80, d (9.3); 8.75, d (9.3); 8.56, d (2.9); 8.55, d (2.9); 8.53, d (2.8); 8.46, d (2.8); 8.36, dd (7.8, 4.8); 8.33, dd (8.0, 4.8); 8.02, d (5.7); 7.97, d (5.4); 7.58, dd (6.8, 2.4) and 7.55, dd (6.6, 3). The integration of each peak corresponds to one proton, and all the protons are identified on the basis of a ^1H–^1H COSY correlation spectrum.

Homonuclear Bimetallic Complexes. $[Ru(TAP)_2]HAT[Ru(BPY)_2]^{4+}$ (B), $[Ru(HAT)_2]HAT[Ru(BPY)_2]^{4+}$ (C), and $[Ru(HAT)(BPY)](HAT)[Ru(BPY)_2]^{4+}$ (D). These binuclear complexes are prepared by refluxing an aqueous solution of $Ru(BPY)_2Cl_2$ (0.1 mmol) with an excess (>0.2 mmol) of the corresponding monometallic precursor: $Ru(TAP)_2(HAT)^{2+}$, $Ru(HAT)_3^{2+}$, and $Ru(HAT)_2(BPY)^{2+}$ respectively.

The evolution of the reaction mixture is followed by visible absorption spectroscopy; after 2 days when the spectrum shows no further changes, the solution is allowed to cool and the mixture of mono- and binuclear compounds is separated on a Sephadex SP C-25 column, eluted by aqueous NaCl solutions, with increasing concentrations of salt. The remaining excess of monometallic precursor (yellow) is first eluted at a salt concentration of 0.1 M, followed by the binuclear complex (purple) (salt concentration of 0.2 M). The complexes are isolated as described above, and the overall yields reach 80%, relative to the amount of $Ru(BPY)_2Cl_2$.

$[Ru(PHEN)_2]HAT[(Ru(BPY)_2]^{4+}$ (E). The chloride salt of $Ru(BPY)_2HAT^{2+}$ (0.1 mmol) is dissolved in refluxing water with 0.5 mmol of $Ru(PHEN)_2Cl_2$, prepared according to standard methods,[18] and the mixture is refluxed for 16 h. The bimetallic complex (purple colored) is isolated and purified as described above.

$[Rh(PPY)_2]_2HAT^{2+}$ (F). $[Rh(PPY)_2Cl]_2$ (0.1 mmol) in 15 mL of CH_2Cl_2 is added dropwise to a refluxing solution of 0.1 mmol HAT, also in 15 mL of CH_2Cl_2. The reaction mixture is refluxed for 5 h, the solvent is evaporated, and the complex is dissolved in water and loaded on a Sephadex LH-20 column. The complex (orange) is eluted with water and isolated with a yield of 80%.

Homonuclear Trimetallic Complexes. $[Ru(TAP)_2]HAT[(Ru(BPY)_2]_2^{6+}$ (G). This trinuclear complex is prepared by the condensation of $Ru(TAP)_2(HAT)^{2+}$ (0.1 mmol) with an excess of $Ru(BPY)_2Cl_2$ (>0.4 mmol) in water, and purified and isolated as described for the bimetallic compounds. The remaining excess of monometallic precursor (red) is eluted first, followed by the trinuclear complex (violet). The overall yield is 80%, relative to $Ru(TAP)_2(HAT)^{2+}$.

$[Ru(HAT)_2]HAT[Ru(BPY)_2]_2^{6+}$ (H) and $[Ru(HAT)(BPY)]HAT[Ru(BPY)_2]_2^{6+}$ (I). These trinuclear complexes are prepared by refluxing aqueous solutions of $Ru(HAT)_3^{2+}$ (0.1 mmol) or $Ru(HAT)_2(BPY)^{2+}$ (0.1 mmol), with 0.2 mmol of $Ru(BPY)_2Cl_2$. The trimetallic complexes are isolated and purified on a Sephadex SP C-25 column as described above. Small amounts of binuclear compounds are eluted first, followed by the trinuclear complexes (violet), and afterward by traces of polynuclear

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species of higher charges. The complexes are obtained with an overall yield of 70%. It is important to note that once two Ru moieties have been coordinated to a same HAT ligand, the third Ru species may chelate the same bridging HAT ligand or a remaining ancillary HAT ligand. The visible absorption spectra of the obtained blue complexes show however the typical MLCT (metal to ligand charge transfer) band centered at 600 nm for a trimetallic complex where the three Ru metals are fixed on the same bridging HAT ligand.[6] This indicates that at least H and I have been formed but the presence of isomers may not be excluded at this stage.

[Rh(PPY)$_2$]$_3$HAT^{3+} (J). To prepare this polymetallic homonuclear complex, [Rh(PPY)$_2$Cl]$_2$ ($^3/_2$ equiv) is refluxed together with 1 equiv of HAT in dichloromethane for 5 h. The solvent is evaporated and the complex dissolved in water and precipitated by the addition of a saturated aqueous solution of KPF$_6$. The resulting precipitate is dissolved in a minimum amount of acetone and loaded on a Sephadex LH-20 column; the complex (orange) is eluted with a water/acetone (1:1) mixture and isolated with a yield of 85%.

Heteronuclear Bi- and Trimetallic Complexes. [Rh(PPY)$_2$]HAT[Ru(BPY)$_2$]$^{3+}$ (K) and [Rh(PPY)$_2$]$_2$HAT[Ru(BPY)$_2$]$^{4+}$ (L). These bimetallic and trimetallic complexes are prepared by heating [Rh(PPY)$_2$Cl]$_2$ (0.05 mmol and 0.1 mmol respectively) with the chloride salt of Ru(BPY)$_2$HAT^{2+} (0.1 mmol) in a dichloromethane/methanol (1:1) solution under reflux for 6 h. After solvent evaporation, the complex is dissolved in water and purified by ion-exchange chromatography (Sephadex SP-C25). The fraction containing the desired complex (orange and red respectively) is treated as described above, and the compound is isolated by precipitation of its hexafluorophosphate salt with a yield of 60% for both K and L.

[Rh(PPY)$_2$]HAT[Ru(BPY)$_2$]$_2$$^{5+}$ (M). This trimetallic compound is prepared in a similar fashion, by mixing [Ru(BPY)$_2$]$_2$HAT^{4+} (0.1 mmol) with 0.05 mmol of [Rh(PPY)$_2$Cl]$_2$. The desired complex (red) is eluted after the unreacted purple bimetallic Ru(II)–Ru(II) precursor, with a yield of 60%.

FAB Mass Spectrometry. The complexes are directly deposited as a solid on the stainless steel target coated with *m*-nitrobenzyl alcohol (*m*-NBA) as a matrix in a ZAB HF from VG analytical (Manchester U.K.) used at full accelerating voltage (8 kV) with a FAB source in the positive mode. Ionization is performed with the standard FAB gun fitted on the mass spectrometer and the bombardment carried out with Xe (1 mA at 8 kV). The mass spectrometer scans from m/z 100 to m/z 2700 at 10 sper/decade. Calibration of the mass spectrometer is performed using CsI clusters and a VG II/250 data system. Resolution is 2500 at 5% valley, and therefore all isotopic peaks are separated.

Mass-analyzed ion kinetic energy spectra (MIKES) are performed in the classical way, usually without gas in the collision cell. A resolution of 100 is used because the slits are fully opened in order to allow all the peaks of the molecular clusters to be selected. In some cases however the intensities of the fragments in the spectra are increased using collisional activated decomposition (CAD), after having verified that the observed fragments are identical to the ones observed in non CAD conditions. In the MIKES technique the parent ion is selected at constant magnetic field, and the fragment ions produced by its decomposition are identified by measuring their kinetic energy in the electrostatic sector of the mass spectrometer. The decomposition of the parent ion is usually spontaneous (except for CAD) and of monomolecular type with no possible interaction with the *m*-NBA matrix. The molecular masses of the fragment ions are expressed in terms of the largest isotopic peak (LIP), calculated with the most abundant isotope for each element. The monoisotopic peak is of little use in the description of the mass spectra of these compounds because it is always minor and difficult to detect. The expected isotopic patterns are calculated using the following abundances for the Ru and Rh isotopes: ^{96}Ru (5.68%), ^{98}Ru (2.22%), ^{99}Ru (12.81%), ^{100}Ru (12.70%), ^{101}Ru (16.98%), ^{102}Ru (31.34%), ^{104}Ru (18.27%), and ^{103}Rh (100%).

Results

1. Synthesis. All of the bi- and trimetallic compounds of Ru(II) (B–E, G–I) are obtained by condensing one or two RuL$_2$Cl$_2$ species (L = BPY, PHEN, TAP) with the monometallic trischelated complexes Ru(HAT)L$_2$$^{2+}$ (L = BPY, TAP, HAT) according to

$$\mathrm{Ru(HAT)L_2^{2+} + RuL_2Cl_2 \rightarrow [RuL_2]HAT[RuL_2]^{4+} + 2Cl^-} \quad (1)$$

$$\mathrm{Ru(HAT)L_2^{2+} + 2RuL_2Cl_2 \rightarrow [RuL_2]HAT[RuL_2]_2^{6+} + 4Cl^-} \quad (2)$$

The nature of the ligands of the monometallic trischelated precursor seems to have little influence on the yields of the complexation with a second Ru(II) ion, while the nature of the ligands in RuL$_2$Cl$_2$ is more critical. The reactions are indeed faster and give better yields when the ligands are better σ donors such as BPY or PHEN, as compared to TAP or HAT which are better π-acceptor ligands.

The homonuclear complexes of Rh(III) (F and J) are easily synthesized by the reaction of [Rh(PPY)$_2$Cl]$_2$ with the HAT ligand; this shows, as claimed in the literature,[19] that the chloro-bridged dimer is an excellent precursor for the synthesis of Rh(III) trischelated complexes.

The heteronuclear complexes of Ru(II) and Rh(III) (K–M) are prepared by the reaction of the mono- or bimetallic complex, Ru(BPY)$_2$HAT^{2+} or [Ru(BPY)$_2$]$_2$HAT^{4+}, with [Rh(PPY)$_2$Cl]$_2$. An alternative way to synthesize complexes K and M would consist in condensing one or two Ru(BPY)$_2$Cl$_2$ with the monometallic Rh precursor Rh(PPY)$_2$HAT$^+$. However this synthetic route leads to the formation of small amounts of trimetallic Ru(II) complex, indicating that Ru(II) is able to expel Rh(III) from the complex.

2. FAB Mass Spectrometry. The Monometallic Complex Ru(BPY)(TAP)(HAT)$^{2+}$ (A). This complex is easily characterized by its ^{1}H NMR spectrum which is in full agreement with its expected structure (see Experimental Section). As in this case we have the unambiguous spectroscopic proof of the formation of this compound, it has been used as a standard for the study of the FAB mass spectra.

Figure 2 presents the FAB mass spectrum obtained in *m*-NBA at unit resolution. The spectrum is characterized by several isotopic clusters covering about 10 m/z units, due to the presence of the numerous ruthenium isotopes. In Figure S1, the theoretical isotopic distribution has been calculated (Figure S1a) and compared to the experimental one (S1b). As the monoisotopic peak is minor it will not be detected easily; therefore, for a matter of convenience the spectrum will be interpreted using mainly the largest isotopic peak (LIP) for each isotopic cluster, the LIP being calculated by using the atomic mass of the most abundant isotope for each element.

In spectrum of compound A (Figure 2), no protonated molecular ion [M + H]$^+$ is detected at the expected value m/z = 964.9 for the LIP peak, but a clear signal at m/z = 986.7 corresponds to a cationized [M + Na]$^+$ complex (calculated m/z = 986.9).

An intense fragment ion at m/z = 818.8 (calculated m/z = 818.9), bearing a single positive charge, corresponds to the loss of one PF$_6^-$. A second loss of PF$_6$ produces the major ion of the spectrum at m/z = 673.9 (calculated m/z = 673.9). In this case either a loss of a counterion PF$_6^-$ with an addition of one electron from the matrix, or the loss of a radical PF$_6^\bullet$, is needed to observe a singly charged ion. The loss of a protonated form of PF$_6^-$ from the ion at m/z = 818.8 is not possible because the mass difference is exactly 144.9 (PF$_6$) and not 145.9 (HPF$_6$). If there were a loss of two counterions PF$_6^-$, without reduction by the matrix, a doubly charged ion at m/z = 336.9 would be expected (see below). The small peak at 972.2 corresponds to the addition of one molecule of *m*-NBA to the ion at m/z = 818.8.

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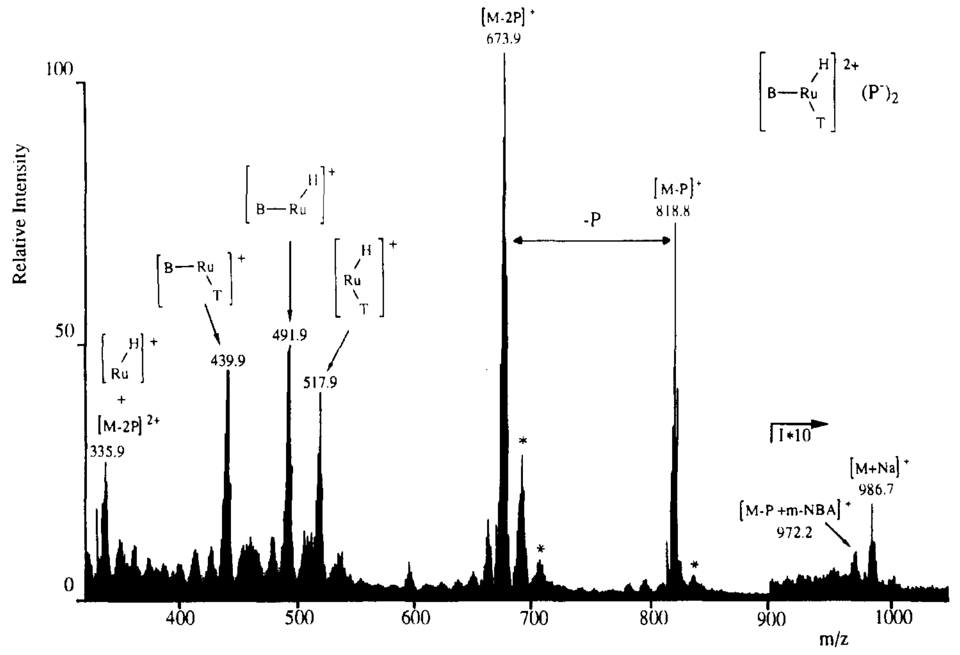

Figure 2. Positive ion FAB mass spectrum of $Ru(BPY)(TAP)(HAT)^{2+}(PF_6^-)_2$ (A). An asterisk denotes peaks due to the addition of oxygen.

The peak corresponding to the loss of one PF_6^- ($m/z = 818.8$) is accompanied by a peak at +16 ($m/z = 834.8$) which represents about 5% of the intensity of the ion at $m/z = 818.8$. The major peak at $m/z = 673.9$ is also accompanied by peaks at +16 ($m/z = 689.8$) and +32 ($m/z = 705.8$) that represent 27% and 6% respectively of the intensity of the major peak at $m/z = 673.9$. It is probable that all these peaks at $m/z = 834.8$, 689.8, and 705.8 (marked with an asterisk in the spectrum) correspond to the addition of one and two oxygen atoms. The ratios between the peaks corresponding to an oxygen addition and the parent peak remain constant over a period of 10 min for a single introduction of the sample in the mass spectrometer and, as can be clearly seen from Figure 2, increase with the number of lost PF_6 species.

The part of the spectrum at lower masses is dominated by three ions at $m/z = 517.9$, 491.9, and 439.9. These peaks correspond to the loss of one of the three possible ligands from the fragment ion at $m/z = 673.9$, and are all singly charged; thus the loss of BPY produces the ion at $m/z = 517.9$ (calculated value: 517.9), the loss of TAP corresponds to the ion at $m/z = 491.9$ (calculated value: 491.9), and the loss of HAT gives rise to the ion at $m/z = 439.9$ (calculated value: 439.9). It is interesting to note that these three peaks have about the same intensity, which suggests that in FAB conditions the coordination bonds of these three ligands fragment in a similar way.

The ion at $m/z = 335.9$, which belongs to an isotopic cluster separated by half m/z units, is identified as an overlapping between the $Ru(HAT)^+$ fragment (calculated value: 335.9) and the doubly charged ion $Ru(BPY)(TAP)(HAT)^{2+}$ (calculated value: 336.9); the latter does indeed show peaks at half mass units.

A MIKES analysis of the peak at $m/z = 818.8$ (data not shown), thus in the absence of a matrix, shows a peak at $m/z = 672.9$; this latter could correspond to the loss of HPF_6 or, since resolution in a MIKES is weaker than in the original FAB mass spectrum, to the loss of a radical PF_6. Minor peaks observed at masses higher than $m/z = 672.9$ in the MIKES analysis may correspond to the loss of fragmented PF_6 from the parent compound.

The Homonuclear Bimetallic Complexes $[Ru(TAP)_2]HAT[Ru(BPY)_2]^{4+}$ (B), $[Ru(HAT)_2]HAT[Ru(BPY)_2]^{4+}$ (C), $[Ru(HAT)(BPY)](HAT)[Ru(BPY)_2]^{4+}$ (D), $[Ru(PHEN)_2]HAT[(Ru(BPY)_2]^{4+}$ (E), and $[Rh(PPY)_2]_2HAT^{2+}$ (F). Table II summarizes the spectroscopic data for the complexes B–F (for the spectrum of compound B, see Figure S2).

Spectra at unit resolution (resolution 2500) of the five compounds (B–F) contain a series of peaks separated by m/z units of 144.9, corresponding to the loss of one, two, three, and four PF_6 species. This series of peaks will be referred to as pseudomolecular peaks throughout the rest of this paper. No $[M + H]^+$ or $[M + Na]^+$ peak is detected but the intense pseudomoleculr fragment ions are all singly charged and are always observed together with peaks corresponding to one or several additions of 16 mass units. The intensities of the peaks containing 16 supplementary mass units become higher when several PF_6 moieties are lost. For the different compounds, fragment ions corresponding to monometallic species with three ligands (one HAT and two of the ancillary ligands) or with two ligands (one HAT and one of the ancillary ligands or two ancillary ligands) are observed. In the spectra of complexes D and E, in addition to the series of pseudomolecular peaks separated by masses corresponding to the loss of PF_6, a similar series of peaks at $m/z = 1494.0$ and 1350.9 and, for compound D only at $m/z = 1207.0$, is observed. These peaks have been identified as originating from the complex $[Ru(BPY)_2]_2HAT^{4+}(PF_6^-)_4$, present as an impurity in the samples D and E. For complexes B–F doubly charged ions are also observed, but with very low intensities.

The Homonuclear Trimetallic Complexes $[Ru(TAP)_2]HAT[(Ru(BPY)_2]_2^{6+}$ (G), $[Ru(HAT)_2]HAT[Ru(BPY)_2]_2^{6+}$ (H), $[Ru(HAT)(BPY)]HAT[Ru(BPY)_2]_2^{6+}$ (I), and $[Rh(PPY)_2]_3HAT^{3+}$ (J). Table III summarizes the data obtained with compounds G–J. The spectrum of compound G shows the expected pseudomolecular peaks (Table III) together with a second similar series of peaks at $m/z = 2143$, 1934, and 1849 that indicate the presence of a chloride ion as counterion instead of a PF_6^- ion. For complex I none of the pseudomolecular peaks are observed.

For compounds G, H and I, at lower m/z, monometallic fragments with two ligands (none with three ligands) are detected.

Complex J (Figure 3) shows pseudomolecular peaks at $m/z = 1757.0$, 1612.0, and 1467.0 and two fragment ions at $m/z = 1201.1$ an 1056.1 composed of two metal centers with their ancillary ligands PPY; one of them ($m/z = 1201.1$) contains a PF_6^- counterion. A MIKES spectrum of the pseudomolecular peak at $m/z = 1757.0$ (Figure S3) leads to the following fragmentation pattern: (i) a peak at $m/z = 1612$, which corresponds to the loss of a PF_6 entity from the ion at $m/z = 1757.0$ (a peak at +16 from 1612 is observed because a small amount of ions at +16 from 1757 is allowed to be selected due

Table II. Main Peaks Observed in the FAB Mass Spectra of Compounds B–F

complex	mass[a]	$[M-P]^{+\,b}$	$[M-2P]^{+\,b}$	$[M-3P]^{+\,b}$	other main fragments[b]
$[Ru(T)_2]H[Ru(B)_2]^{4+}(P^-)_4$ (B)	1692.9	1549.0^{8} (1548.8)	1404.1^{40} (1403.8)	1259.1^{42} (1258.8)	$[M-4P]^+$, 1114.1^{18} (1113.9); $[M-2P]^{2+}$, 702^{15} (702.0); $[M-3P]^{2+}$, 692.0^{20} (629.4); $[M-4P]^{2+}$, 557.0^{15} (556.9); $[Ru(B)_2H]^+$, 648.1^{38} (647.9); $[Ru(T)H]^+$, 518.0^{45} (517.9); $[Ru(B)H]^+$, 492.0^{75} (491.9); $[Ru(T)_2]^+$, 466.1^{65} (465.9); $[Ru(B)_2]^+$, 413.0^{100} (413.9)
$[Ru(H)_2]H[Ru(B)_2]^{4+}(P^-)_4$ (C)	1797.0	1653.0^{2} (1652.8)	1508.0^{7} (1507.8)	1363.0^{4} (1362.9)	$[M-2P]^{2+}$, 755^{2} (754.4); $[Ru(H)_2]^+$, 570.0^{15} (569.9);$[Ru(B)H]^+$, 491.0^{15} (491.9); $[Ru(B)_2]^+$, 413^{15} (413.9)
$[Ru(H)(B)]H[Ru(B)_2]^{4+}(P^-)_4$ (D)	1718.9	1574.9^{2} (1574.7)	1429.9^{4} (1429.7)	1285.0^{2} (1284.8)	$[[Ru(B)_2]_2HP_3]^+$, 1494.0^{2} (1496.7); $[[Ru(B)_2]_2HP_2]^+$, 1350.9^{4} (1351.7); $[[Ru(B)_2]_2HP]^+$, 1207.0^{4} (1209.8); $[M-2P]^{2+}$, 714.0^{2} (714.8); $[Ru(B)H]^+$, 492.0^{30} (491.9); $[Ru(B)_2]^+$, 413^{30} (413.9)
$[Ru(Ph)_2]H[Ru(B)_2]^{4+}(P^-)_4$ (E)	1688.9	1544.0^{30} (1544.7)	1399.0^{45} (1399.8)		$[[Ru(B)_2]_2HP_3]^+$, 1494.0^{5} (1496.7); $[[Ru(B)_2]_2HP_2]^+$, 1350.9^{10} (1351.7); $[Ru(Ph)H]^+$, 516^{28} (515.9); $[Ru(B)H]^+$, 491.1^{40} (491.9); $[Ru(Ph)_2]^+$, 460.0^{55} (461.9); $[Ru(B)(Ph)]^+$, 437.1^{50} (437.9); $[Ru(B)_2]^+$, 413^{55} (413.9)
$[Rh(Py)_2]_2H^{2+}(P^-)_2$ (F)	1346.7	$1207.8^{0.5}$ (1200.8)	1055.8^{1} (1055.9)		$[Rh(Py)_2H]^+$, 644.9^{1} (644.9); $[Rh(Py)_2]^+$, 410.9^{100} (410.9); $[Rh(Py)]^+$, 256.9^{15} (256.9)

[a] Calculated chemical mass. [b] m/z observed for the largest isotopic peaks with relative intensities in superscript and calculated values for m/z in parentheses. Key: H, 1,4,5,8,9,12-hexaazatriphenylene; B, 2,2′-bipyridine; T, 1,4,5,8-tetraazaphenanthrene; Py, 2-phenylpyridine; Ph, 1,10-phenanthroline; P, PF_6^-.

Table III. Main Peaks Observed in the FAB Mass Spectra of Compounds G–J

complex	mass[a]	$[M-P]^{+\,b}$	$[M-2P]^{+\,b}$	$[M-3P]^{+\,b}$	other main fragments[b]
$[Ru(T)_2]H[(Ru(B)_2]_2^{6+}(P^-)_6$ (G)	2396.3	2254.5^{4} (2252.6)	2107.6^{5} (2104.6)	1962.9^{3} (1962.7)	$[[Ru(T)_2]H[Ru(B)_2]_2P_4Cl]^+$, 2143^{1} (2142.6); $[[Ru(T)_2]H[Ru(B)_2]_2P_3Cl]^+$, 1934^{4} (1997.6); $[[Ru(T)_2]H[Ru(B)_2]_2P_2Cl]^+$, 1849^{5} (1852.6); $[Ru(B)H]^+$, 492^{15} (491.9); $[Ru(B)_2]^+$, 413^{55} (413.9)
$[Ru(H)_2]H[Ru(B)_2]_2^{6+}(P^-)_6$ (H)	2500.3	$2357^{1\,c}$ (2356.6)	$2213^{1\,c}$ (2211.6)	$2067^{1\,c}$ (2066.7)	$[Ru(B)H]^+$, 492^{30} (491.9); $[Ru(B)_2]^+$, 413^{55} (413.9)
$[Ru(H)(B)]H[Ru(B)_2]_2^{6+}(P^-)_6$ (I)	2422.3				$[Ru(B)H]^+$, 492^{20} (491.9); $[Ru(B)_2]^+$, 413^{20} (413.9)
$[Rh(Py)_2]_3H^{3+}(P^-)_3$ (J)	1902.9	1757.0^{6} (1756.7)	1612.0^{7} (1611.8)	1467.0^{5} (1466.8)	$[[Rh(Py)_2]_2HP]^+$, 1201.1^{6} (1200.8); $[[Rh(Py)_2]_2H]^+$, 1056.1^{4} (1055.8); $[[Rh(Py)_2]H]^+$, 645.1^{55} (644.9); $[Rh(Py)_2]^+$, 411.0^{100} (410.9); $[RhPy]^+$, 257.0^{80} (256.9)

[a] Calculated chemical mass. [b] m/z observed for the largest isotopic peaks with relative intensities in superscript and calculated values for m/z in parentheses. Key: H, 1,4,5,8,9,12-hexaazatriphenylene; B, 2,2′-bipyridine; T, 1,4,5,8-tetraazaphenanthrene; Py, 2-phenylpyridine; P, PF_6^-. [c] Hardly greater than the background noise.

to the low resolution used); (ii) a peak at $m/z = 1201$, which is formed by the loss of $[Rh(PPY)_2PF_6]$ from the pseudomolecular peak at $m/z = 1757.0$ and which corresponds to the $[[Rh(PPY)_2]_2HAT\,PF_6]^+$ moiety, still containing one PF_6^- counterion; (iii) peaks at $m/z = 1056$ and $m/z = 645$ that correspond to $[Rh(PPY)_2]_2HAT]^+$ and to the monometallic fragment $[Rh(PPY)_2HAT]^+$ respectively. All these fragments are consistent with the structure proposed for compound J.

The Heteronuclear Bi- and Trimetallic Complexes $[Rh(PPY)_2]HAT[Ru(BPY)_2]^{3+}$ (K), $[Rh(PPY)_2]_2HAT[Ru(BPY)_2]^{4+}$ (L), and $[Rh(PPY)_2]HAT[Ru(BPY)_2]_2^{5+}$ (M). In Table IV are collected the main fragments observed for these three heteronuclear complexes. The fragmentation patterns are similar to those described for the homonuclear compounds. As observed before, the additions of one and two oxygen atoms accompanying the loss of PF_6 and increasing with the number of PF_6 moieties are again clearly detected in spectra of K (Figure S4) and L (Figure S5). Moreover bimetallic fragments corresponding to the loss of one metal with its ancillary ligands and associated with one or two PF_6^- counterions are also observed.

Discussion

The pseudomolecular peaks and fragment ions containing ruthenium are easily identified by the presence of a characteristic cluster of isotopic peaks. For all the spectra, we observe an isotopic distribution for each pseudomolecular peak, which agrees well with the calculated one.

Ionization is performed by the loss of one PF_6^- counterion rather than by protonation of the parent complex as observed for other compounds in the literature.[11e] For compound A a peak at the mass $[M + Na]^+$, corresponding to a monocationized form of the parent compound is observed. The presence of sodium can easily be explained by taking into account the different preparation and purification steps of the complex. For the polymetallic complexes the loss of up to four counterions can be detected, giving rise to a series of pseudomolecular peaks that are all singly charged. The presence of peaks expected at m/z values for doubly charged pseudomolecular peaks indicates that some of the analyzed ions originate also from the loss of two negatively charged PF_6^- counterions.

In conclusion the main ionization mechanism corresponds first to the loss of a negatively charged counterion; this step is followed by the successive loss of the other PF_6 species, either as uncharged radicals $PF_6^{\bullet}$ or as negatively charged PF_6^-; in the latter case the ionization should be accompanied by a reduction of the fragment by the matrix since the resulting ion is singly charged.

When a MIKES experiment is performed, no reduction of the fragment may be assumed since there is no matrix. Consequently the fragmentation can only be due in that case to the loss of a neutral species such as $PF_6^{\bullet}$ or HPF_6, as observed in the MIKES spectrum of the peak $[M - P]$ for compound A. However the distinction between PF_6 and HPF_6 is not possible because of the poor resolution in a MIKES analysis.

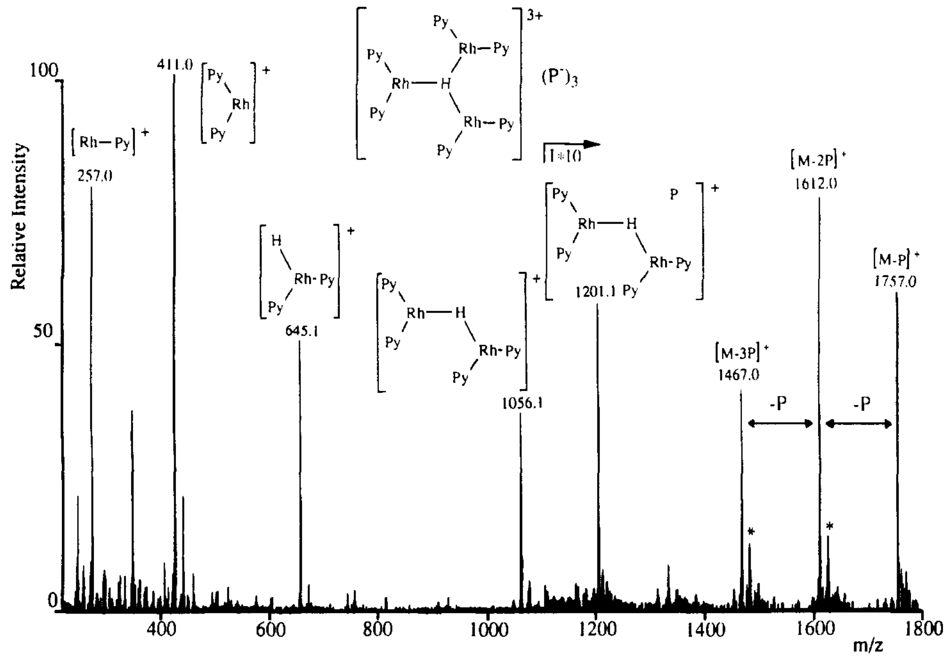

Figure 3. Positive ion FAB mass spectrum of $[Rh(PPY)_2]_3HAT^{3+}(PF_6^-)_3$ (J). An asterisk denotes peaks due to the addition of oxygen.

Table IV. Main Peaks Observed in the FAB Mass Spectra of Compounds K–M

complex	mass[a]	$[M - P]^{+\,b}$	$[M - 2P]^{+\,b}$	$[M - 3P]^{+\,b}$	other main fragments[b]
$[Rh(Py)_2]H[Ru(B)_2]^{3+}(P^-)_3$ (K)	1493.8	1348.8^{7} (1348.8)	1203.8^{6} (1203.8)	1058.9^{2} (1058.9)	$[[Ru(B)_2H]P]^+$, 793.1^{5} (792.9); $[Ru(B)_2H]^+$,[c] 647.9^{8} (647.9); $[Ru(B)H]^+$, 492.1^{15} (491.9); $[Rh(Py)_2]^+$, 410.9^{100} (410.9); $[RhPy]^+$, 256.9^{95} (256.9)
$[Rh(Py)_2]_2H[Ru(B)_2]^{4+}(P^-)_4$ (L)	2050.1	1904.8^{2} (1904.7)	1759.9^{4} (1759.7)	$1614.9^{1.5}$ (1614.7)	$[Rh(Py)_2HRu(B)_2P_2]^+$, 1348.8^{4} (1345.8); $[Rh(Py)_2HRu(B)_2P]^+$, 1203.8^{4} (1203.8); $[[Rh(Py)_2]_2H]^+$, $1055.9^{1.5}$ (1055.9); $[Rh(Py)_2HRu(B)_2]^+$, $1058.9^{1.5}$ (1058.9); $[Ru(B)_2HP]^+$, 792.9^{3} (792.9); $[Ru(B)_2H]^+$, 647.9^{7} (647.9); $[Ru(B)H]^+$, 492.0^{10} (491.9); $[Rh(Py)_2]^+$, 410.9^{100} (410.9); $[RhPy]^+$, 256.9^{25} (256.9)
$[Rh(Py)_2]H[Ru(B)_2]_2{}^{5+}(P^-)_5$ (M)	2197.2	$2053.0^{1.5}$ (2052.6)	$1908.9^{1.5}$ (1907.7)	1764.1^{1} (1762.7)	$[Rh(Py)_2]H[Ru(B)_2]P_2]^+$, $1349.0^{2.5}$ (1348.8); $[Rh(Py)_2]H[Ru(B)_2]P]^+$, 1204.0^{1} (1203.8); $[Ru(B)_2H]^+$, 647.9^{3} (647.9); $[Rh(Py)_2H]^+$, 644.9^{2} (644.9); $[Rh(Py)_2]^+$, 411^{100} (410.9); $[RhPy]^+$, 257^{40} (256.9)

[a] Calculated chemical mass. [b] *m*/*z* observed for the largest isotopic peaks with relative intensites in superscript and calculated values for *m*/*z* in parentheses. Key: H, 1,4,5,8,9,12-hexaazatriphenylene; B, 2,2′-bipyridine; Py, 2-phenylpyridine; P, PF_6^-.

In the FAB mass spectra at unit resolution on the other hand, the difference in mass between two pseudomolecular peaks corresponds exactly to the loss of a $PF_6^\bullet$ ($m = 144.9$) and not of a HPF_6 ($m = 145.9$). Therefore we assume that the main ionization mechanism consists in losing an uncharged radical $PF_6^\bullet$ from the first pseudomolecular peak, rather than a loss of a negative counterion with a reduction of the remaining complex by the matrix. As a minor mechanism, the loss of a second negatively charged counterion may occur and generate doubly charged fragments observable with very low intensities.

The smaller fragments that are detected may be explained by the loss of either neutral moieties or of negatively charged species followed, in the latter case, by a reduction of the fragment complex by the matrix, which we may not exclude as a secondary reaction pathway. The secondary peaks accompanying the pseudomolecular peaks at +16 and +32 mass units become more intense with each loss of PF_6 species. The fact that the ratio of these additional peaks relative to the parent peaks is independent of the time the sample spent in the ionization chamber of the mass spectrometer rules out a possible contamination of the sample by air traces remaining in the spectrometer. This suggests an addition of atomic oxygen from the matrix. The MIKES experiment on the pseudomolecular peak at $m/z = 1757.0$ of complex J (Figure S3) shows indeed that, in the absence of a matrix, the fragment at $m/z = 1201.1$ is not accompanied by a peak at +16 mass units, which is not the case in the FAB mass spectrum in the presence of *m*-NBA (Figure 3).

The FAB mass spectra of the complexes containing Rh show peaks at *m*/*z* values corresponding to fragments which are still associated to one or two counterions and are generated from the loss of one metal center with its ancillary ligands. The hypothesis that these fragments could originate from another complex present as an impurity in the sample, such as a mono- or bimetallic complex in the bi- or tri-metallic compounds, respectively, and showing its own series of pseudomolecular peaks, cannot be confirmed; indeed the results of a MIKES analysis on the pseudomolecular peak of compound J (Figure S3) demonstrate the ability of the $[M - P]^+$ ion to lose one of its metal centers while remaining associated to one counterion. Moreover as such behavior is not observed for the ruthenium complexes, this fragmentation mechanism would indicate that the Rh–HAT coordination bonds are more easily cleaved than the Ru–HAT bonds under FAB conditions.

FAB mass spectrometry reveals the presence of small amounts of impurities in some of the examined complexes although they have been purified on a Sephadex cation exchanger column. Thus the mass spectrum of complex D shows the presence of fragments originating from the complex $[Ru(BPY)_2]_2HAT^{4+}$. The presence of this complex can be explained by the fact that the monometallic precursor $Ru(BPY)HAT_2^{2+}$ used for the synthesis could contain small amounts of $Ru(BPY)_2HAT^{2+}$, which is not that easily separated from $Ru(BPY)HAT_2^{2+}$.

The FAB mass spectrum of $[Ru(PHEN)_2]HAT[(Ru(BPY)_2]^{4+}$ (E) shows peaks corresponding to the fragments $[[Ru(BPY)_2]_2HAT(PF_6^-)_3]^+$, $[[Ru(BPY)_2]_2HAT(PF_6^-)_2]^+$ and $[Ru(BPY)(PHEN)]^+$; they indicate that PHEN and BPY ligands may interchange during the synthesis, generating small amounts of the complex $[Ru(BPY)_2]_2HAT^{4+}$. In complex G the presence of some fragments clearly demonstrates that all of the chloride counterions have not been exchanged by PF_6^- ions during the precipitation of the complex by the addition of a KPF_6 solution.

The polymetallic complexes $[Ru(HAT)_2]HAT[Ru(BPY)_2]_2^{6+}$ (H) and $[Ru(HAT)(BPY)]HAT[Ru(BPY)_2]_2^{6+}$ (I), built from the monomeric units $Ru(HAT)_3^{2+}$ and $Ru(HAT)_2(BPY)^{2+}$, respectively, seem to be very unstable, as indicated by the very low intensity of the pseudomolecular peaks in complex H and by their absence in complex I. That is probably related to the instability of the central building blocks $Ru(HAT)_3^{2+}$ and $Ru(HAT)_2(BPY)^{2+}$. This conclusion is also in accordance with the fact that it has not been possible to characterize by FAB mass spectrometry the heptametallic complex $[Ru(HAT)_3[Ru(BPY)_2]_6]^{14+}(PF_6^-)_{14}$, where six $Ru(BPY)_2^{2+}$ moieties are bridged to the central $Ru(HAT)_3^{2+}$ species. As the spectrum of complex H shows only the pseudomolecular peaks together with fragments of lower masses, corresponding to bischelated ions, one cannot draw any conclusion on the structure of this compound and thus differentiate between possible structural isomers (cf. Experimental Section). For the compound I the lack of pseudomolecular peaks rules out the identification of the trimetallic complex.

Conclusion

The results of this study show that the FAB mass spectrometry is an extremely valuable technique for proving structures of large nonvolatile polymetallic transition metal complexes. For these compounds spectroscopic techniques such as the NMR are not adequate, due to the complexity of the spectra. The simultaneous presence of pseudomolecular peaks and of fragment ions in the mass spectra allows not only a clear identification and structural characterization of the compounds but also the detection of unexpected counterions and of small amounts of impurities, such as complexes formed as secondary products during the synthesis.

Although in the FAB mass spectra all the studied complexes are initially ionized according to the same mechanism (loss of a counterion) and show similar series of pseudomolecular peaks (generated by the loss of radicals $PF_6^{\bullet}$), no general rule may be established which might explain all the observed fragments. Indeed for the trimetallic complexes of Ru(II) no bimetallic fragment ions are observed, while for the Rh(III) complexes some bimetallic fragments and even fragments associated with one or two counterions appear clearly in the spectra. For all polymetallic homonuclear complexes of Ru(II), only for compound B is a trischelated fragment discernible in the spectrum, while such fragments are detected repeatedly for the heteronuclear complexes containing rhodium. The observed fragmentation patterns show thus a strong dependence on the nature of the metals and of the ligands forming the different building blocks of the polymetallic complexes.

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Supplementary Material Available: Figure S1, showing isotopical distribution of the molecular peak of compound A and Figures S2–S5, showing the mass spectrum of compound B, the MIKES spectrum of compound J, and mass spectra of compounds K and L (5 pages). Ordering information is given on any current masthead page.