Synthesis and Characterization by Fast Atom Bombardment and Electrospray Mass Spectrometry of New Copper(I) Complexes with Substituted 1,4,5,8,9,12-Hexaaza-triphenylenes and Macrocycles†

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A series of new homo- and hetero-leptic copper(I) complexes have been prepared with various substituted polychelating 1,4,5,8,9,12-hexaazatriphenylene (hat) derivatives. The homoleptic complexes, the stability of which is strongly related to the number and nature of the substituents borne by their two identical acyclic hat ligands, appeared in general less stable than their corresponding heteroleptic complexes prepared with the similar hat acyclic ligand and a macrocycle derived from a 1,10-phenanthroline. The results show clearly that by tethering the first chelate to a macrocycle of adequate size, more stable complexes can be obtained. All the complexes described were characterized by fast atom bombardment and electrospray mass spectrometry.

The luminescent character of $[Cu(dmphen)_2]^+$ (dmphen = 2,9-dimethyl-1,10-phenanthroline) was observed at low temperature by Buckner and McMillin[1] in 1977. This was the beginning of photochemical studies on copper(I) complexes with various azaaromatic ligands. Unfortunately, $[Cu(dmphen)_2]^+$ has a short-lived excited state and cannot be used in polar solvents which increase the non-radiative deactivation[2] processes. This drawback is overcome in $[Cu(dpphen)_2]^+$ (dpphen = 2,9-diphenyl-1,10-phenanthroline) in which the bulky phenyl substituents efficiently shield the metallic centre[3] against deactivation by solvent molecules. The latter rigid complex has a longer excited-state lifetime than $[Cu(dmphen)_2]^+$ both at low and room temperature. This specific property of $[Cu(dpphen)_2]^+$ or related copper(I) complexes has been widely studied and is well established.[4]

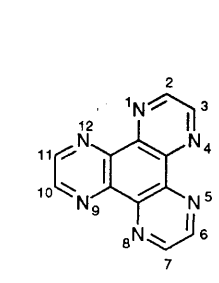
During a study on oxidizing polypyridinic mononuclear homoleptic copper(I) complexes we first used as ligands various derivatives of 1,4,5,8-tetraazaphenanthrene (tap).[5] Later, as we developed in our group the synthesis of polynucleating ligands such as substituted 1,4,5,8,9,12-hexaazatriphenylene (hat),[6] we could also envisage the formation of either homo- or hetero-nuclear polymetallic complexes. Towards such complexes, we undertook the synthesis of homo- and hetero-leptic mononuclear copper(I) complexes with various substituted hat ligands in order to test their ease of formation and their stability. In contrast to ruthenium(II),[7] copper(I) does not easily form stable heteroleptic complexes especially when the ligands are electron deficient as is the case for tap and hat: attempts to prepare $[Cu(tmtap)(dmphen)]^+$ (tmtap = 2,3,6,7-tetramethyl-1,4,5,8-tetraazaphenanthrene) led only to a mixture of complexes;[8] the labile heteroleptic complex $[Cu(tmtap)(dmphen)]^+$ equilibrates with the two homoleptic complexes [equation (1)]. However, it

$$2[Cu(tmtap)(dmphen)]^+ \rightleftharpoons [Cu(dmphen)_2]^+ + [Cu(tmtap)_2]^+ \quad (1)$$

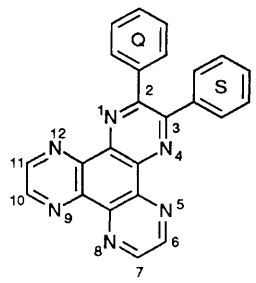
should be possible to increase the stability of hat-containing heteroleptic copper(I) complexes by means of geometrical constraints. Complexes comprising one hat ligand, one copper and one chelating macrocycle, *i.e.* with a pseudo-rotaxane or precatenate structure,[9] should fulfil such a requirement.

We report here the synthesis of such pseudo-rotaxane copper(I) complexes prepared with variously substituted electron-deficient hat ligands and two different chelating macrocycles both containing a 1,10-phenanthroline. Stabilization introduced in these heteroleptic copper(I) complexes is demonstrated by comparison with the corresponding homoleptic complexes of general formula $[Cu(hat)_2]^+$. Their synthesis is also described in the present report. Besides the synthesis itself of the complexes, another problem was their characterization. As a complete analysis of the NMR spectra was impossible for many of the studied complexes[3c] (due to paramagnetism, see Experimental section), an extensive mass spectrometry study was performed and allowed their unambiguous characterization. The use of new techniques of ionization in mass spectrometry has made possible the characterization of co-ordination compounds in the last few years. Indeed, conventional mass spectrometry can be applied to metal complexes only with limited success while laser desorption mass spectrometry,[10b] field desorption,[10d] electrohydrodynamic ionization[10c] or fast atom bombardment (FAB)[10b,d] lead to interesting results.[10a-e] The latter technique is of particular interest due to the possible detection of parent and fragment ions.[4b,11] An important drawback of this method comes from the number of peaks which can sometimes be attributed either to a fragment of the compound or to an impurity. Recently, a new technique, electrospray mass spectrometry (ESMS), has been developed and used for characterization of large biomolecules.[12] It is a mild technique which causes minimum fragmentation and has been shown to be particularly suitable for the characterization of large copper(I) polycatenates up to M 7000[13c] or ruthenium(II) complexes.[13a,b] For co-ordination compounds, ionization is not obtained by protonation of basic sites as for biomolecules[12] but by the loss of one or several counter ions. In this paper we describe, along with their synthesis, the FABMS and ESMS characterization of our hat-containing copper(I) complexes. The use of both techniques allows insight into the relative stability of the various compounds.

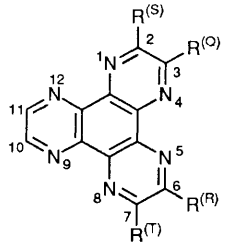
† *Supplementary data available* (No. SUP 56990, 3 pp.): mass spectral data for heteroleptic complexes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

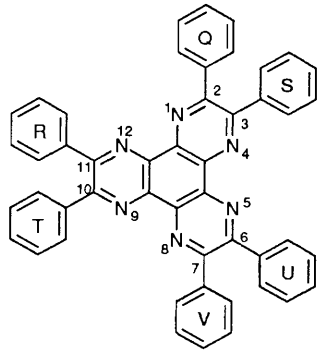


hat



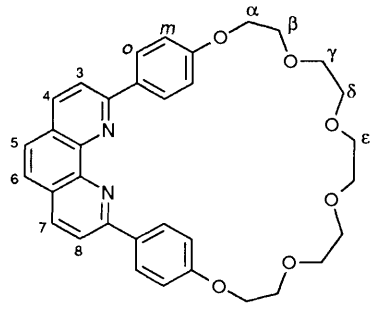
dphat



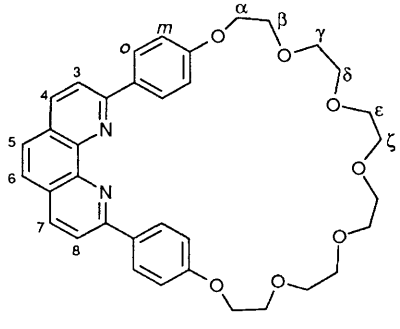


tmhat R = Me
tphat R = Ph

hphat



L^1



L^2

Experimental

Materials and Methods.—Acetonitrile was dried and purified by distillation (normal pressure) from $CaCl_2$. The complex $[Cu(MeCN)_4]BF_4$ was prepared as described.[14] All other chemicals were of the best commercially available grade and were used without further purification. Proton NMR spectra of macrocycles were recorded with a Bruker WP 200 SY spectrometer and ^1H NMR spectra of other ligands and copper(I) complexes with a Bruker Cryospec WM instrument at 250 MHz.

Precursors.—(*a*) *Macrocycles.* The synthesis of macrocycle L^1 has been described previously and the larger macrocycle L^2 was prepared in a similar way from 2,9-di(*p*-hydroxyphenyl)-1,10-phenanthroline and the diiodo derivative of hexaethylene glycol instead of pentaethylene glycol.[15] Starting with the phenanthroline derivative (0.939 g, 2.6 mmol) and the diiodo derivative of hexaethylene glycol (1.298 g, 2.6 mmol) we obtained 0.760 g (48% yield) of pure macrocycle L^2 as pale yellow crystals. ^1H NMR ($CDCl_3$): δ 8.43 (4 H, d, *J* 8.9, H_o), 8.30 (2 H, d, *J* 8.5, H^4 and H^7), 8.10 (2 H, d, *J* 8.5, H^3 and H^8), 7.76 (2 H, s, H^5 and H^6), 7.17 (4 H, d, *J* 8.9, H_m), 4.31 (4 H, t, α-CH_2), 3.90 (4 H, t, β-CH_2) and 3.79–3.67 (16 H, m, γ,δ,ε,ξ-CH_2).

(*b*) *1,4,5,8,9,12-Hexaazatriphenylene derivatives.* The unsubstituted compound hat was prepared as described.[6,16] The syntheses of 2,3-diphenyl-1,4,5,8,9,12-hexaazatriphenylene (dphat) and 2,3,6,7-tetraphenyl-1,4,5,8,9,12-hexaazatriphenylene (tphat) have also been described previously.[6] 2,3,6,7-Tetramethyl-1,4,5,8,9,12-hexaazatriphenylene (tmhat) has been prepared in a similar way to the tetraphenyl derivative using diacetyl instead of benzil for the condensations. ^1H NMR ($CDCl_3$): δ 2.99 (12 H, s, 2,7- and 3,6-CH_3, accidental isochronism) and 9.24 (2 H, s, $H^{10,11}$). 2,3,6,7,10,11-Hexaphenyl-1,4,5,8,9,12-hexaazatriphenylene (hphat)[17,18] was prepared similarly to unsubstituted hat using benzil instead of glyoxal.[6]

Homoleptic Complexes of Copper(I).—The general procedure used for preparing the homoleptic copper(I) complexes was as follows. By the double-ended needle-transfer technique, the appropriate quantity of $[Cu(MeCN)_4]BF_4$ in degassed acetonitrile (10 cm^3) was added under argon at room temperature to a stirred and degassed solution of the corresponding hat derivative in anhydrous dichloromethane. The mixture was stirred under argon during the indicated time (complex formation is evidenced by TLC), after which the solvents were removed and the residue was chromatographed on silica gel (eluent CH_2Cl_2 containing 0.1–5% MeOH). The results of these different syntheses are collected in Table 1. The ^1H NMR spectrum of $[Cu(hat)_2]BF_4$ was not recorded due to the instability of this complex in solution and that of $[Cu(dphat)_2]BF_4$ has only very broad signals which are not interpretable.

$[Cu(tmhat)_2]BF_4$: ^1H NMR (CD_2Cl_2) (peaks not well resolved) δ 9.36 (2 H, s, $H^{10,11}$), 2.93 (6 H, s, 2,7-CH_3) and 2.83 (6 H, s, 3,6-CH_3).

$[Cu(tphat)_2]BF_4$: ^1H NMR (CD_2Cl_2) (no peaks, only broad signals observed) δ 9.3 ($H^{10,11}$), 8.0–7.1 (H_o^{QRST}, $H_{m,p}^{ST}$) and 6.9–6.4 ($H_{m,p}^{QR}$).

$[Cu(hphat)_2]BF_4$: ^1H NMR (CD_2Cl_2) δ 7.85 (H_o^{UV}), 7.58 (H_o^{ST}), 7.50 ($H_{m,p}^{UV}$), 7.43 (H_p^{ST}), 7.36 (H_m^{ST}), 7.05 (H_o^{QR}), 6.80 (H_p^{QR}) and 6.67 (H_m^{QR}).

Heteroleptic Complexes of Copper(I).—The general procedure used for preparing the heteroleptic complexes was as follows. By the double-ended needle-transfer technique, the indicated amount of $[Cu(MeCN)_4]BF_4$ in degassed acetonitrile (10 cm^3) was added under argon and at room temperature to a stirred degassed solution of the chosen macrocycle (L^1 or L^2) in anhydrous dichloromethane (20 cm^3). The instantaneous appearance of an orange coloration in the solution was due to the formation of $[CuL^1(MeCN)_2]BF_4$ or $[CuL^2(MeCN)_2]$-BF_4. After 0.5 h at room temperature, a solution of the appropriate chelate (hat, dphat, tmhat, tphat or hphat) in anhydrous dichloromethane (30 cm^3) was added. The mixture was stirred under argon at room temperature for the indicated time, after which the solvents were removed under vacuum. The solid obtained was chromatographed on silica gel (eluent CH_2Cl_2 containing 0.1–5% MeOH). The excess of free ligand was eluted prior to the complex. The complexes can be recrystallized from CH_2Cl_2–toluene. The results of these different syntheses are collected in Table 2 and ^1H NMR data for the heteroleptic complexes are collected in Table 3.

Fast Atom Bombardment Mass Spectrometry.—The complexes were directly deposited as solids on the stainless-steel

Table 1 Synthesis of homoleptic complexes of copper(I) with hat derivatives

$[Cu(MeCN)_4]BF_4$		Ligand derived from hat			Reaction time		Yield[a]
mg	10^{-4} mol	Type	mg	10^{-4} mol	(h)	Product	(%)
37	1.18	hat	59[b]	2.52	22	$[Cu(hat)_2]BF_4$	< 10
56	1.78	dphat	143[b]	3.70	21	$[Cu(dphat)_2]BF_4$	19
25	0.795	tmhat	47[c]	1.62	4	$[Cu(tmhat)_2]BF_4$	42
27	0.858	tphat	95[c]	1.76	22	$[Cu(tphat)_2]BF_4$	85
35	1.11	hphat	160[b]	2.32	26	$[Cu(hphat)_2]BF_4$	84

[a] After chromatography. [b] Dissolved in CH_2Cl_2 (50 cm^3). [c] Dissolved in CH_2Cl_2 (30 cm^3).

Table 2 Synthesis of heteroleptic complexes of copper(I)

(*a*) With L^1 as macrocycle

$[Cu(MeCN)_4]BF_4$		L^1		Ligand derived from hat			Reaction time		Yield[a]
mg	10^{-4} mol	mg	10^{-4} mol	Type	mg	10^{-4} mol	(h)	Product	(%)
59	1.9	110	1.9	hat	47	2.2	22	$[CuL^1(hat)]BF_4$	39
61	1.9	115	2.0	dphat	76	2.0	17	$[CuL^1(dphat)]BF_4$	61
59	1.9	113	2.0	tmhat	56	1.9	17	$[CuL^1(tmhat)]BF_4$	46
34[b]	1.1	69[c]	1.2	tphat	66	1.2	18	$[CuL^1(tphat)]BF_4$	> 71
59	1.9	112	2.0	hphat	133	1.9	22	$[Cu(hphat)_2]BF_4$	80

(*b*) With L^2 as macrocycle

$[Cu(MeCN)_4]BF_4$		L^2		Ligand derived from hat			Reaction time		Yield[a]
mg	10^{-4} mol	mg	10^{-4} mol	Type	mg	10^{-4} mol	(h)	Product	(%)
57	1.8	117	1.9	hat	44	1.9	24	$[CuL^2(hat)]BF_4$	71
57	1.8	117	1.9	dphat	74	1.9	17	$[CuL^2(dphat)]BF_4$	> 70
59	1.9	122	2.0	tmhat	57	2.0	17	$[CuL^2(tmhat)]BF_4$	66
53	1.7	121	2.0	tphat	106	2.0	23	$[CuL^2(tphat)]BF_4$	92
59	1.9	121	2.0	hphat	133	1.9	22	$[CuL^2(hphat)]BF_4$	80

[a] After chromatography. [b] Dissolved in MeCN (6 cm^3). [c] Dissolved in CH_2Cl_2 (10 cm^3).

target coated with *m*-nitrobenzyl alcohol or 2-nitrophenyl octyl ether as a matrix. The mass spectrometer was a ZAB-HF from VG Analytical (Manchester) used at full accelerating voltage (8 kV) with a xenon FAB source in the positive-ion mode. Resolution was 1800 at 10% valley and therefore all isotopic peaks were separated.

Electrospray Mass Spectrometry.—Mass spectrometry using electrospray ionization was performed on a VG BIO-Q quadrupole mass spectrometer with a m/z range of 0–4000. The samples were dissolved in dichloromethane and the resulting solution (10 μl, about 10–50 pmol μl^{-1}) was introduced into the ion source at a flow rate of 5 $\mu l\ min^{-1}$ and the spray pneumatically assisted. The electrostatic spray ion source was operated at atmospheric pressure at 3200 V. The extraction cone voltage (V_c) was 40 V except where indicated. Resolution was about 800 and therefore average masses were measured. The molecular masses of the fragment ions which appeared below m/z = 1000 are expressed in terms of the largest isotopic peak, calculated with the most abundant isotope for each element.[11]

Results

Synthesis.—(*a*) *Ligands.* The synthesis of macrocycle L^1 was described in detail in 1990.[15] By treating 2,9-di(*p*-hydroxyphenyl)-1,10-phenanthroline with 1,17-diiodo-3,6,9,12,15-pentaoxaheptadecane in dimethylformamide (dmf) in the presence of a large excess of Cs_2CO_3[19] at 60 °C under high-dilution conditions and under argon, a 48% yield of L^2 was obtained. The syntheses of unsubstituted and hexasubstituted hat were performed as described in the literature.[6,17] 2,3-Diphenyl-1,4,5,8,9,12-hexaazatriphenylene (dphat) can be synthesised by the direct condensation of hexaaminobenzene with 2 equivalents of glyoxal (added in two steps) and 1 equivalent of benzil.[6] Similarly, 2,3,6,7-tetraphenyl- (tphat) and 2,3,6,7-tetramethyl-1,4,5,8,9,12-hexaazatriphenylene (tmhat) can be prepared by adding 2 equivalents of benzil or diacetyl (in two steps) and 1 equivalent of glyoxal.

(*b*) *Complexes. Homoleptic complexes of copper*(I). All the homoleptic complexes of copper(I), $[Cu(hat)_2]BF_4$, $[Cu(dphat)_2]BF_4$, $[Cu(tmhat)_2]BF_4$, $[Cu(tphat)_2]BF_4$ and $[Cu(hphat)_2]BF_4$, were obtained by adding an acetonitrile solution of $[Cu(MeCN)_4]BF_4$[14,15] under argon to a dichloromethane solution of ligand L with stirring (L = hat, dphat, tmhat, tphat or hphat) according to equation (2). The

$$[Cu(MeCN)_4]BF_4 + 2L \xrightarrow[MeCN,\ Ar]{CH_2Cl_2} [CuL_2]BF_4 \quad (2)$$

best yields after purification were obtained with 2,3,6,7-tetraphenyl- and 2,3,6,7,10,11-hexaphenyl-1,4,5,8,9,12-hexaazatriphenylenes (see Scheme 1). The synthesis performed with tmhat gave a lower yield than that obtained from the phenyl analogue, in agreement with the observation made with $[Cu(dmphen)_2]^+$ and $[Cu(dpphen)_2]^+$. Hindered chelates bearing bulky substituents α to the nitrogen atoms (phenyl) lead to stable copper(I) complexes. It is therefore expected that phenylated hat ligands lead to better yields than their methylated or unsubstituted analogues. Indeed, 2,3-disubstituted or unsubstituted hexaazatriphenylenes provided only poor yields of complexes.

Heteroleptic complexes of copper(I). By adding an acetonitrile solution of $[Cu(MeCN)_4]BF_4$ to a stoichiometric amount of macrocycle L′ = L^1 or L^2 in dichloromethane under argon, a yellow air-sensitive solution of $[CuL'(MeCN)_2]BF_4$ was formed (see Scheme 2). Addition of 1 equivalent of L (hat, dphat, tmhat, tphat or hphat) in dichloromethane to the solution of $[CuL'(MeCN)_2]BF_4$ leads to an immediate colour change, with

Table 3 Proton NMR spectral data for copper(I) heteroleptic complexes: δ in CD_2Cl_2 (internal reference $CDHCl_2$ at δ 5.32)

H(hat derivative) H(phen)	H^2 $H^{4,7}$	H^3 $H^{5,6}$	H^6 $H^{3,8}$	H^7 H_o	H^{10} H_m	H^{11}	H_o^S	H_o^T	H_p^{ST}	H_m^T	H_m^S	H_o^R	H_p^R	H_m^R	H_o^Q	H_p^Q	H_m^Q	3,6-CH_3, α,β,γ,δ,ε(ξ)-CH_2
Compounds																		
$[CuL^1(hat)]^+$	9.42	8.76	8.76	9.42	9.42	9.42	—	—	—	—	—	—	—	—	—	—	—	
	8.76	8.23	8.23	7.38	6.23													3.88–3.31
$[CuL^1(dphat)]^+$	—	—	8.52		9.81	9.81	6.7–6.2	—	6.7–6.2	—	6.7–6.2	—	—	—	6.7–6.2	6.7–6.2	6.7–6.2	—
	8.46	7.92	7.95	7.38	6.25													3.78–3.47
$[CuL^1(tmhat)]^{+a}$	—	—	—	—	9.51	9.51	—	—	—	—	—	—	—	—	—	—	—	2.28
	8.74	8.21	8.17	7.26	6.08													3.88–3.00
$[CuL^1(tphat)]^+$	—	—	—	—	9.73	8.29	7.82	7.82	7.6–6.2	7.6–6.2	7.6–6.2	7.6–6.2	7.6–6.2	7.6–6.2	7.6–6.2	7.6–6.2	7.6–6.2	—
	8.49	7.95	7.99	7.41	6.25													3.92–3.55
$[CuL^2(hat)]^+$	9.5–9.4	8.73	8.73	9.5–9.4	9.5–9.4	9.5–9.4	—	—	—	—	—	—	—	—	—	—	—	—
	8.73	8.21	8.21	7.39	6.14													3.74–3.45
$[CuL^2(dphat)]^+$	—	—	8.72	9.65	9.51	9.51	7.35	—	7.35	—	7.35	—	—	—	6.74	6.55	6.27	—
	8.52	8.00	7.94	7.37	6.27													3.78–3.54
$[CuL^2(tmhat)]^{+b}$	—	—	—	—	9.52	9.52	—	—	—	—	—	—	—	—	—	—	—	2.27
	8.75	8.21	8.16	7.38	6.06													3.74–3.23
$[CuL^2(tphat)]^+$	—	—	—	—	10.04	8.89	7.76	7.98	7.5–6.1	7.5–6.1	7.5–6.1	7.5–6.1	7.5–6.1	7.5–6.1	7.5–6.1	7.5–6.1	7.5–6.1	—
	8.44	7.90	7.90	7.29	6.36													3.96–3.28
$[CuL^2(hphat)]^{+c}$	—	—	—	—	—	—	7.45	7.63	7.45	7.45	7.32	7.08	6.94	6.69	6.65	6.48	6.19	—
	8.49	7.98	7.91	7.30	6.28													3.80–3.30

For each complex, the first line collects chemical shifts for the hat ligand and the second one shows data for L^1 or L^2.

[a] δ(2,7-CH_3) 2.92. [b] δ(2,7-CH_3) 2.89. [c] δ 7.9–7.8 ($H_o^{U,V}$), 7.45 ($H_p^{U,V}$ and $H_m^{U,V}$).

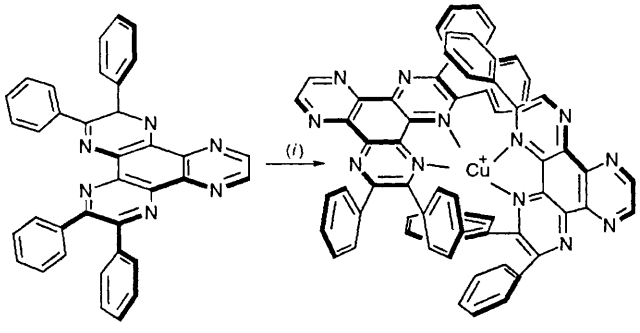
formation of the deep red-violet complex $[CuL'(L)]BF_4$ (see Scheme 2) according to equations (3) and (4). The

$$[Cu(MeCN)_4]BF_4 + L' \xrightarrow[MeCN,\ Ar]{CH_2Cl_2} [CuL'(MeCN)_2]BF_4 \quad (3)$$

$$[CuL'(MeCN)_2]BF_4 + L \xrightarrow[MeCN,\ Ar]{CH_2Cl_2} [CuL'(L)]BF_4 \quad (4)$$

$[CuL'(L)]BF_4$ could all be isolated as dark red-violet air-stable solids. The results obtained for the different syntheses are shown in Table 2.

The large macrocycle L^2 provided in every case the desired heteroleptic complex. The same syntheses performed with the smaller macrocycle L^1 gave the heteroleptic complexes except with hphat, affording only the homoleptic complex $[Cu(hphat)_2]BF_4$. Clearly, threading hphat of the large molecule into the smaller system containing L^1 is unfavourable. In each series, the highly rigid and encaged complexes are easier to isolate than their analogues synthesised from only partially phenylated ligands. The decrease in yields after chromatography follows the sequence $[CuL^2(tphat)]BF_4$ > $[CuL^2(hphat)]BF_4$ > $[CuL^2(dphat)]BF_4$ > $[CuL^2(hat)]BF_4$. The replacement of phenyl by methyl groups in hexaazatriphenylene derivatives results in a decrease in yields after purification. Comparison of yields obtained for the heteroleptic complexes with those obtained for the corresponding homoleptic complexes shows that encircling hat or dphat by a macrocycle stabilizes the heteroleptic complex compared to the corresponding homoleptic complex, which partly decomposes on the column (see Table 4).



Scheme 1 (*i*) $[Cu(MeCN)_4]BF_4$, CH_2Cl_2, Ar

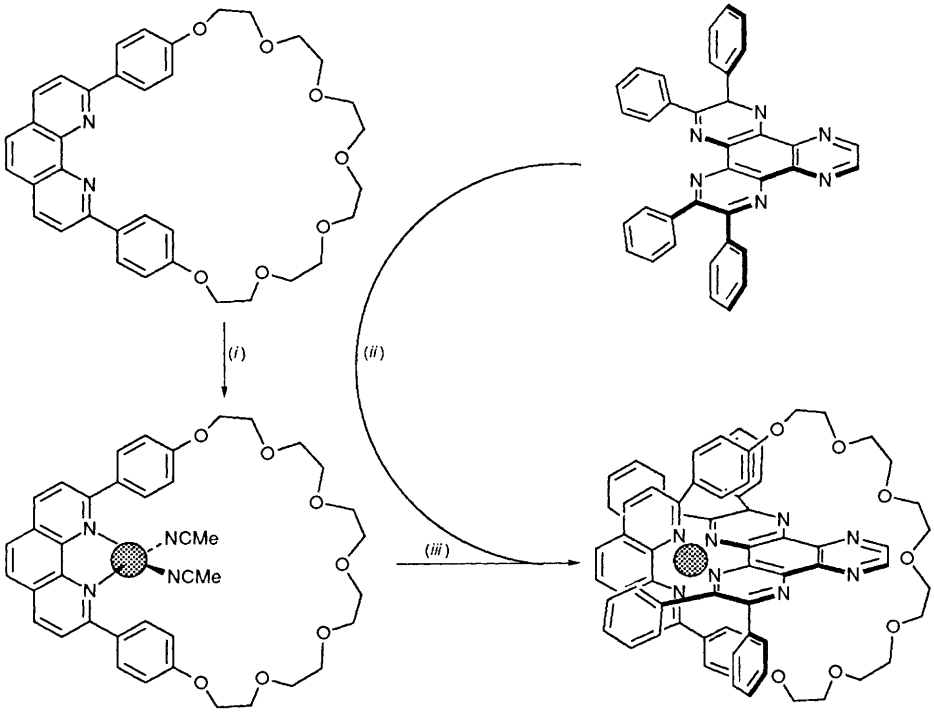
Mass Spectrometry.—Identification of these complexes was achieved using both FAB and electrospray mass spectrometry.

(*a*) *Homoleptic complexes*. Fig. 1 shows the positive FAB and ES mass spectra obtained for $[Cu(hphat)_2]BF_4$. In the FAB spectrum [Fig. 1(*a*)] an intense singly charged ion appears at m/z = 1444.2. This peak is accompanied by a small (7%) peak at +16 (m/z = 1460.2). Such a +16 peak is not observed in the ES spectrum. It can therefore be attributed to an artefactual addition of one oxygen atom during the FAB process in the matrix. This phenomenon has been observed in another FAB mass spectral study of complexes[11] and occurs for most of the complexes studied here. Peaks corresponding to the addition of one oxygen are marked by a star (★) in Fig. 1(*a*). The most intense peak of the spectrum (m/z = 751.9) corresponds to the loss of one ligand. The fragment appearing at m/z = 690.9 (calculated largest isotopic peak m/z 691.2) corresponds to the free protonated ligand $[hphat + H]^+$. In the ES mass spectrum of this hphat complex [Fig. 1(*b*)] only the peak at m/z = 1444.6, corresponding to $[M - BF_4]^+$, is observed.

Table 5 summarizes the data obtained for the five homoleptic complexes. The fragmentation patterns for all these complexes in FAB mass spectra are similar to those described for $[Cu(hphat)_2]BF_4$. In most cases adducts with the matrix were

Table 4 Comparative yields (%) of isolated homo- and hetero-leptic complexes

Acyclic ligand L	Homoleptic series $[CuL_2]BF_4$	Heteroleptic series $[CuL^1(L)]BF_4$	$[CuL^2(L)]BF_4$
hat	< 10	39	71
dphat	19	61	70
tmhat	42	46	66
tphat	85	71	92
hphat	84	0	80



Scheme 2 (*i*) $[Cu(MeCN)_4]BF_4$ in MeCN; CH_2Cl_2, Ar; (*ii*) CH_2Cl_2, Ar; (*iii*) CH_2Cl_2, MeCN, Ar

Table 5 Main peaks observed in the ES and FAB mass spectra of homoleptic complexes

Complex	M^a	ESMS[b]	Main fragments	FAB[b]	Main fragments
$[Cu(hat)_2]BF_4$	618.8	531.2^{100} (531.1) 356.2^{42} (355.5) 235.2^{76} (234.7)	$[M - BF_4]^+$ $[Cu_4(hat)_5]^{4+}$ $[hat + H]^+$	531.0^{68} (531.1) 235.0^{100} (234.7)	$[M - BF_4]^+$ $[hat + H]^+$
$[Cu(dphat)_2]BF_4$	923.2	835.3^{100} (835.2)	$[M - BF_4]^+$	[c]834.9^{75} (835.2) 448.8^{71} (449.1) 387.0^{100} (387.1)	$[M - BF_4]^+$ $[Cu(dphat)]^+$ $[dphat + H]^+$
$[Cu(tmhat)_2]BF_4$	731.0	643.4^{100} (643.2) 499.3^{8} (498.2)	$[M - BF_4]^+$ $[Cu_2(tmhat)_3]^{2+}$	643.1^{44} (643.2) 353.0^{100} (353.1) 291.1^{50} (291.1)	$[M - BF_4]^+$ $[Cu(tmhat)]^+$ $[tmhat + H]^+$
$[Cu(tphat)_2]BF_4$	1227.6	1139.8^{100} (1139.3)	$[M - BF_4]^+$	1140.1^{22} (1139.3) 601.0^{44} (601.1) 539.1^{26} (539.2)	$[M - BF_4]^+$ $[Cu(tphat)]^+$ $[tphat + H]^+$
$[Cu(hphat)_2]BF_4$	1532.0	1444.6^{100} (1443.4)	$[M - BF_4]^+$	1444.2^{58} (1443.4) 751.9^{100} (753.2) 690.9^{32} (691.2)	$[M - BF_4]^+$ $[Cu(hphat)]^+$ $[hphat + H]^+$

[a] Calculated chemical mass. [b] m/z observed for the largest isotopic peaks with relative intensities as superscripts and calculated values in parentheses. Matrix is *m*-nitrobenzyl alcohol unless otherwise stated. [c] Matrix is 2-nitrophenyl octyl ether.

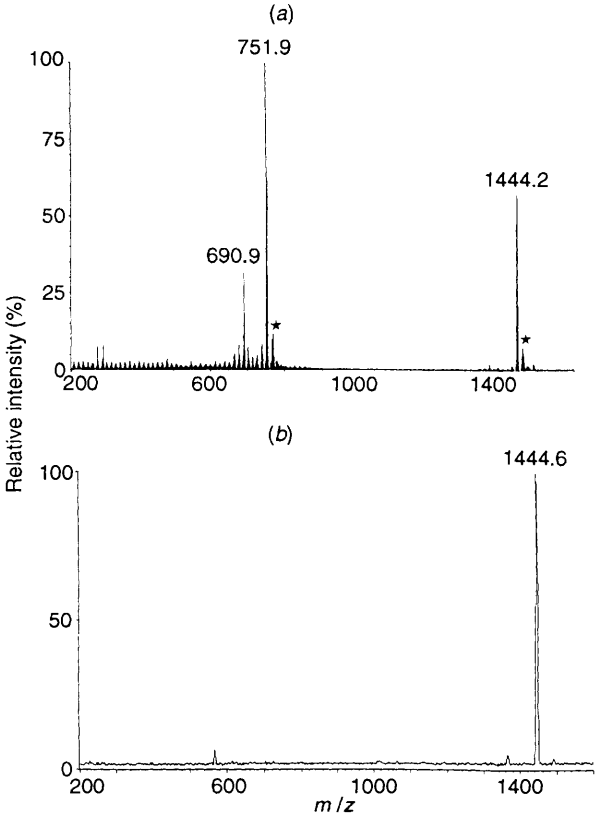


Fig. 1 (*a*) The FAB mass spectrum of the homoleptic complex $[Cu(hphat)_2]BF_4$ in *m*-nitrobenzyl alcohol; ★, peak corresponding to addition of one oxygen. (*b*) The ES mass spectrum of the same complex

observed and also peaks corresponding to the addition of one oxygen. The ES mass spectra of all homoleptic complexes are characterized by an intense signal corresponding to the cationic part of the complex $[M - BF_4]^+$. No fragments were observed except for the less-stable complex $[Cu(hat)_2]BF_4$ which presents an intense fragmentation peak (76%) at m/z = 235.2 attributed to a free protonated ligand $[hat + H]^+$. This observation corroborates well the known stabilization effect of substituents α to nitrogen in polyimine ligands.[3,4] Also noteworthy is the fact that ESMS, due to its very mild ionization technique, allowed the detection of small amounts of polynuclear complexes. Indeed the peak observed for $[Cu(hat)_2]BF_4$ at m/z = 356.2 can be attributed to the fragment $[Cu_4(hat)_5]^{4+}$, indicating the presence of a tetrametallic complex, whereas that at m/z = 499.3 in the spectrum of $[Cu(tmhat)_2]BF_4$ can reasonably be attributed to the doubly charged fragment $[Cu_2(tmhat)_3]^{2+}$ originating from a bimetallic complex. Such labile entities could not be observed under much harsher FAB conditions.

(*b*) *Heteroleptic complexes.* Collected in Table 6 are the mass spectrometry data for all the heteroleptic complexes prepared from the small macrocycle L^1. All the spectra of these complexes show a clear signal corresponding to the loss of BF_4 {m/z = 863 for $[CuL^1(hat)]BF_4$, 1015 for $[CuL^1(dphat)]BF_4$, 919 for $[CuL^1(tmhat)]BF_4$ and 1167 for $[CuL^1(tphat)]BF_4$} either in ESMS or FABMS. In FABMS, these four compounds present intense fragmentation peaks at m/z = 629 corresponding to $[CuL^1]^+$ and also peaks corresponding to $[CuL]^+$ (L = hat, dphat, tmhat or tphat). The compounds $[CuL^1(hat)]BF_4$ and $[CuL^1(tmhat)]BF_4$ give peaks corresponding to both $[M + Na]^+$and $[M - BF_4 + Na]^+$.[11] The presence of peaks at m/z values for singly charged entities $[M - BF_4 + Na]^+$ suggests that, under FABMS conditions, ionization is accompanied by a reduction of the fragment. This occurs most probably on the ligands.

The ESMS spectrum of $[CuL^1(dphat)]BF_4$, taken at an extraction cone voltage of 40 V, shows, besides the expected $[M - BF_4]^+$ ion (m/z = 1015.5), an intense signal at m/z = 823.4. This peak corresponds to a doubly charged fragment $[Cu_2L^1_2(dphat)]^{2+}$ (calculated largest isotopic peak m/z = 822.2). The corresponding bimetallic complex $[Cu_2L^1_2(dphat)][BF_4]_2$ was probably formed as a side product along with the expected mononuclear $[CuL^1(dphat)]BF_4$. Owing to steric hindrance, the dinuclear complex is expected to be quite unstable. This is confirmed by the decrease in intensity for the peak at m/z = 823.4 when high V_c (80 V) is used. The latter compound was not detected at all by FAB. In the ES mass spectrum of the supposed compound $[CuL^1(hphat)]BF_4$ no peak corresponding to $[M - BF_4]^+$ was detected but an intense signal appeared at m/z = 1443.6 attributed to the homoleptic complex $[Cu(hphat)_2]^+$. Another signal of high intensity could be attributed to the protonated $[L^1 + H]^+$ macrocycle. Similarly, the FAB spectrum reveals no peak corresponding to a heteroleptic complex but shows again an intense signal attributed to the homoleptic compound $[Cu(hphat)_2]^+$ (m/z = 1444.2). Both these observations show clearly that hphat was too bulky to thread through the small L^1 macrocycle and form $[CuL^1(hphat)]BF_4$.

Similarly, spectroscopic data were collected for the heteroleptic complexes prepared from the large macrocycle L^2 (SUP 56990). The ES mass spectra of the five complexes show their

Table 6 Main peaks observed in the ES and FAB mass spectra of the heteroleptic complexes

Complex	M^a	ESMS[b]	Main fragments	FAB[b]	Main fragments
$[CuL^1(hat)]BF_4$	951.2	863.4^{100} (863.2)	$[M - BF_4]^+$	973.0^{18} (973.5)	$[M + Na]^+$
		567.5^{21} (567.2)	$[L^1 + H]^+$	886.1^{19} (886.2)	$[M - BF_4 + Na]^+$
				863.1^{37} (863.2)	$[M - BF_4]^+$
				629.0^{92} (629.2)	$[CuL^1]^+$
				567.1^{100} (567.2)	$[L^1 + H]^+$
				297.0^{39} (297.0)	$[Cu(hat)]^+$
				235.0^{66} (235.1)	$[hat + H]^+$
$[CuL^1(dphat)]BF_4$	1103.4	$V_c = 40$ V		1015.3^{18} (1015.3)	$[M - BF_4]^+$
		1015.5^{100} (1015.3)	$[M - BF_4]^+$	629.1^{100} (629.2)	$[CuL^1]^+$
		823.4^{87} (822.2)	$[Cu_2L^1{}_2(dphat)]^{2+}$	449^{22} (449.1)	$[Cu(dphat)]^+$
		567.6^{11} (567.2)	$[L^1 + H]^+$	387^{18} (387.1)	$[dphat + H]^+$
		$V_c = 80$ V			
		1015.5^{100} (1015.3)	$[M - BF_4]^+$		
		823.4^{28} (822.2)	$[Cu_2L^1{}_2(dphat)]^{2+}$		
		629.5^{18} (629.2)	$[CuL^1]^+$		
		567.6^{20} (567.2)	$[L^1 + H]^+$		
$[CuL^1(tmhat)]BF_4$	1007.3	919.5^{100} (919.3)	$[M - BF_4]^+$	1029.2^{11} (1029.3)	$[M + Na]^+$
		567.5^{5} (567.2)	$[L^1 + H]^+$	942.2^{15} (942.3)	$[M - BF_4 + Na]^+$
				919.2^{60} (919.3)	$[M - BF_4]^+$
				629.1^{100} (692.2)	$[CuL^1]^+$
				567.2^{95} (567.2)	$[L^1 + H]^+$
				471.0^{12} (471.2)	$[M - BF_4 + Na]^{2+}$
				353.0^{70} (353.1)	$[Cu(tmhat)]^+$
				291.0^{39} (291.1)	$[tmhat + H]^+$
$[CuL^1(tphat)]BF_4$	1255.6	1167.8^{100} (1167.4)	$[M - BF_4]^+$	1167.2^{40} (1167.4)	$[M - BF_4]^+$
		567.5^{20} (567.2)	$[L^1 + H]^+$	629.1^{100} (629.2)	$[CuL^1]^+$
				601.1^{36} (601.1)	$[Cu(tphat)]^+$
				576.2^{35} (567.2)	$[L^1 + H]^+$
				539.1^{12} (539.2)	$[tphat + H]^+$
'$[CuL^1(hphat)]BF_4$'[c]	1407.8	1443.6^{100} (1443.4)	$[Cu(hphat)_2]^+$	1444.2^{51} (1443.4)	$[Cu(hphat)_2]^+$
		567.5^{80} (567.2)	$[L^1 + H]^+$	753^{100} (753.2)	$[Cu(hphat)]^+$
				691.1^{36} (691.2)	$[hphat + H]^+$
				567.1^{55} (567.2)	$[L^1 + H]^+$

[a] Calculated chemical mass. [b] m/z observed for the largest isotopic peaks with relative intensities as superscripts and calculated values in parentheses. Matrix is *m*-nitrobenzyl alcohol. [c] This complex was not formed.

most intense signals at m/z corresponding to the loss of BF_4^- {907.4 for $[CuL^2(hat)]BF_4$, 1059.5 for $[CuL^2(dphat)]BF_4$, 963.5 for $[CuL^2(tmhat)]BF_4$, 1211.8 for $[CuL^2(tphat)]BF_4$ and 1364.6 for $[CuL^2(hphat)]BF_4$}. In addition, $[CuL^2(hat)]BF_4$, $[CuL^2(tphat)]BF_4$ and $[CuL^2(hphat)]BF_4$ give a peak of low intensity at $m/z = 611.5$ corresponding to the free protonated macrocycle L^2, which also appears in the corresponding FAB mass spectrum, but is more intense.

The ES mass spectrum of $[CuL^2(tphat)]BF_4$ reveals the presence of a bimetallic complex $[Cu_2L^2{}_2(tphat)]^{2+}$ at $m/z = 943.3$. This observation is supported by the presence, in the FAB spectrum, of a peak of low intensity at $m/z = 1276.4$, which can be attributed to $[M - BF_4 + Cu + e^-]^+$ (calculated largest isotopic peak m/z 1274.4). The theoretical isotopic distribution has been calculated for $[M - BF_4 + Cu]^+$ and compared to the experimental one. The good agreement between the calculated isotopic distributions of $[M - BF_4]^+$ and $[M - BF_4 + Cu]^+$ and the experimental ones confirms our suggestion.

In FABMS the fragmentations are similar to those described for the heteroleptic complexes prepared from the smaller macrocycle L^1: intense fragment ions of $[M - BF_4]^+$ at expected values. In all cases, the major peaks correspond to $[CuL^2]^+$ ions ($m/z = 673.1$). The $[M - BF_4]^+$ ion is accompanied by peaks at +23 for compounds $[CuL^2(hat)]BF_4$ ($m/z = 930.1$), $[CuL^2(dphat)]BF_4$ ($m/z = 1082.4$) and $[CuL^2(tmhat)]BF_4$ ($m/z = 986.2$), which are attributed to the addition of a sodium cation and a one-electron reduction. Besides these peaks corresponding to singly charged fragments $[M - BF_4 + Na]^+$, clear signals appear at the expected values for the doubly charged fragments $[M - BF_4 + Na]^{2+}$ {m/z = 465.0 for $[CuL^2(hat)]BF_4$, 541.2 for $[CuL^2(dphat)]BF_4$ and 493.0 for $[CuL^2(tmhat)]BF_4$}. For these three compounds, FAB spectra moreover show a clear signal corresponding to the positively charged $[M + Na]^+$ complex (m/z = 1017.1, 1169.4 and 1073.2 respectively). In addition, all these FAB mass spectra show a peak at $m/z = 611$ corresponding to the free protonated macrocycle L^2, one attributed to the free protonated acyclic ligand HL^+ as well as a signal corresponding to $[CuL]^+$ arising from the loss of BF_4^- and the macrocycle.

Discussion

Synthesis.—Homoleptic copper(I) complexes were synthesised with five ligands derived from hat. After purification, poor yields were obtained with unsubstituted or 2,3-disubstituted hat. On the contrary, with tetra- and hexa-phenyl derivatives good yields were obtained even after purification. In other terms, the more hindered the ligand, the higher the yield. Changing phenyl for methyl groups in 2,3,6,7-tetrasubstituted hat results in a decrease in yields after purification: this can be explained by a less-effective shielding of the complex from its environment in the latter case, $[Cu(tphat)_2]BF_4 > [Cu(tmhat)_2]BF_4$, in agreement with the observation made with $[Cu(dmphen)_2]^+$ and $[Cu(dpphen)_2]^+$.[1,3a,c]

Heteroleptic complexes were synthesised with two macrocycles and five hexaazatriphenylene derivatives. All were successful except for the complex with L^1 and hphat. In the latter case the size limit for the synthesis of a heteroleptic complex seems to be reached when L^2 is replaced by L^1. As for the homoleptic complexes, the best yields are obtained when bulky substituents are present in *ortho* positions to the chelating nitrogens. Comparison of yields of the homo- and hetero-leptic complexes leads to the conclusion that tethering

hat or polysubstituted hat to a macrocycle provides a more stable complex than the corresponding homoleptic one, at least as far as the hat substituents do not introduce too much steric hindrance and the macrocycle chosen is of adequate size (see Table 4).

Mass Spectrometry.—All complexes were successfully characterized by both FABMS and ESMS. Both ionization methods yielded useful different but complementary structural information. For all complexes, FABMS produced a spectrum characterized by the presence of a pseudo-molecular ion $[M - BF_4]^+$ and intense fragments which allowed an accurate characterization of the different subunits of the complexes. The background was always high and this technique is obviously not useful for purity evaluation. For the L^2 heteroleptic series of complexes we have observed that, compared to the fragment ions, the cationic part of the heteroleptic complex $[M - BF_4]^+$ was small for unsubstituted or poorly substituted hat (dphat) complexes. These fragments became larger for more substituted hat (tmhat) and became small again for highly and fully substituted hat (tphat, hphat) complexes. This observation may give an indication of the relative stability of the series of complexes as a function of the rate and nature of substitution. Similar observations were made for the homoleptic and heteroleptic (L^1) series but to a lesser extent.

For the homoleptic complexes $[CuL_2]BF_4$ the major peak in the FAB mass spectra corresponds either to the fragment $[CuL]^+$ or the protonated ligand HL^+ whereas for the heteroleptic complexes $[CuL'(L)]BF_4$ the peak of highest intensity corresponds in most cases to the fragment $[CuL']^+$, that corresponding to $[CuL]^+$ always being smaller (about 35% of the major peak). It is interesting that the two sets of peaks obtained for the heteroleptic complexes (fragments $[CuL']^+$ and $[CuL]^+$) have different intensities. Indeed, this observation suggested that under FABMS conditions the co-ordination bonds of the two types of ligands (macrocycle and acyclic hat derivative) do not dissociate with the same ease: the link between the copper(I) ion and each of the five studied hat ligands seems easier to break than that between the same ion and macrocycle L^1 or L^2.

The behaviour of all our complexes appears to be very different under ESMS conditions: in all cases, the major peak corresponds to the single loss of the counter ion BF_4^- which allows very easy identification of the target compound. Owing to the mild ionization technique used in ESMS, no, or only minor, fragmentation was observed. In addition, ESMS allowed the detection of minor, unstable compounds for example the bimetallic complexes $[Cu_2L^1{}_2(dphat)][BF_4]_2$ and $[Cu_2L^2{}_2(tphat)][BF_4]_2$ which formed along with the major complexes $[CuL^1(dphat)]BF_4$ and $[CuL^2(tphat)]BF_4$ respectively.

The synthesis of the homoleptic complexes can also lead to polynuclear complexes as minor components. This is clearly evidenced in the case of $[Cu(hat)_2]BF_4$ for which the ES mass spectrum showed an intense peak at m/z 356.2 corresponding to the fragment $[Cu_4(hat)_5]^{4+}$ originating from a tetrametallic complex. The FABMS technique, which is more destructive than ESMS, used with a low extraction cone voltage, did not allow the unambiguous detection of the latter polynuclear complexes.

Conclusion

This work concerns the preparation of homoleptic copper(I) complexes with variously substituted electron-withdrawing polychelating 1,4,5,8,9,12-hexaazatriphenylene (hat) derivatives. We have shown that the nature and the number of the substituents in α position to the chelating nitrogens strongly influence the yields. Only the compounds bearing several bulky substituents lead to good yields even after purification by chromatography. Our study also demonstrates that it is possible to synthesise hat-containing heteroleptic copper(I) complexes. Encircling the electron-poor acyclic hat ligand by a chelating macrocycle stabilizes the resulting complex relative to the corresponding homoleptic one. The size of the macrocycle clearly plays an important role in the formation of the heteroleptic complexes studied: the macrocycle must be as small as possible in order to induce a favourable geometrical constraint, but sufficiently large to allow the complexation and the tethering of the acyclic ligand. For the bulky hphat, the size limit of the macrocycle seems to be reached when L^1 replaces L^2; in this case, only the homoleptic complex $[Cu(hphat)_2]BF_4$ is formed.

The results obtained by mass spectrometry demonstrate that ESMS is a very mild technique which not only allows the unambiguous detection of the target molecule (intense peak corresponding to the cationic part of the complex) but also, in some cases, the identification of labile polymetallic species obtained as by-products. This latter possibility significantly increases the application field of ESMS which so far has been essentially devoted to the study of biomolecules. The FABMS technique, with its much more drastic ionization, did not allow the definitive detection of polymetallic impurities but gave on the other hand information concerning the fragmentation of the various complexes and hence also about their relative stability. Thus ESMS and FABMS appear to be complementary, the first allowing easy identification of the target molecule and possible detection of unstable impurities, the second gives, owing to the fragmentation pattern, useful structural information.

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