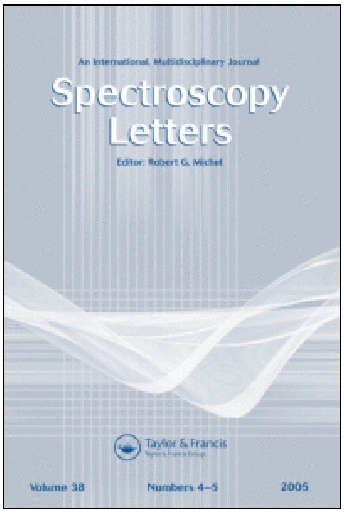

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ELECTROSPRAY MASS SPECTROMETRIC STUDY ON COMPLEXATION OF TRANSITIONAL METAL IONS WITH OLIGOBIPYRIDINE LIGAND

Key words: Electrospray Mass Spectrometry, Supramolecular chemistry, Transition metal complex, Oligobipyridine

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ABSTRACT

Positive-ion mode electrospray mass spectrometry (ES-MS) was used to investigate the reaction of oligobipyridine ligand L (L = 5,5'-bis[2-(2,2'-bipyridin-6-yl)ethyl]-2,2'-bipyridine) with $M(ClO_4)_2$ in various mole ratios [M = Fe(II), Co(II), Ni(II) and Cu(II)]. The results indicate that the oligobipyridine L coordinated to the transitional metal ions to form mononuclear complexes. The ES mass spectra of isolated complex $[FeL_3](PF_6)_2$ were measured under various electrospray conditions to examine the influence of the spray voltage, capillary temperature, capillary voltage, and tube lens offset on the fragmentation of the complex in electrospray ionization process. The results show that the fragmentation was mainly controlled by the capillary temperature, capillary voltage, and tube lens offset potential for Finnigan MAT LCQ system. The present study confirmed that the ES-MS is a powerful technique for determining the species existing in solution and for investigation of the reaction between oligobipyridine and transitional metal ions.

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INTRODUCTION

In the field of supramolecular chemistry, supramolecular units are usually constructed by the association of small molecules, and thus the characterization of the resulting supramolecules is frequently difficult. Solid state structures may be determined by X-ray crystallography, however, it is impossible to get single crystal in all cases, especially for compounds existing in liquid state or only in solution. Powerful techniques are needed for investigation of assembly species formed in solution, in particular to determine whether their structures are the same as in the solid state. Mass spectrometries such as electron ionization (EI), fast atom bombardment (FAB) are useful techniques. But EI is limited to the analysis of neutral volatile and thermally stable compounds, FAB is more successful but is still disadvantaged by the relatively high degree of fragmentation making the identification of molecular ions difficult. The soft ionization technique of electrospray (ES), which has been proven particularly beneficial to biochemists for the characterization of large biological molecules such as proteins and oligonucleotides,[1-4] gives considerable control over the degree of fragmentation by varying the experiment parameters. Furthermore, the electrospray mass spectrometry (ES-MS) has been found to be a useful method for detecting the composition of the species presented in solution and has been applied to characterize a variety of compounds including proteins, oligonucleotides, transition-metal complexes[5-7], as well as a number of supramolecular self-assemblies.[8-10] Here we report the ES-MS study of the isolated complexes $[FeL_3](PF_6)_2$ and the reaction systems between $M(ClO_4)_2$ and L in various molar ratios in solution {M = Fe(II), Co(II), Ni(II) and Cu(II), L = 5,5'-bis[2-(2,2'-bipyridin-6-yl)-ethyl]-2,2'-bipyridine}.

EXPERIMENTAL

Preparation of $[FeL_3](PF_6)_2$

Ligand L (30 mg) was suspended in 20 ml methanol with stirring, to which $FeSO_4{\cdot}7H_2O$ (20 mg) in water (2 ml) was added dropwisely. The mixture turned red immediately. After refluxed for 4 hours, the result solution was precipitated with excess of KPF_6. The isolated dark red solid was recrystallized from CH_3CN/C_2H_5OH to give red microcrystalline. Elemental analysis shows that it is a mononuclear complex $[FeL_3](PF_6)_2 \cdot C_2H_5OH \cdot 0.5H_2O$.[11]

Sample Preparation for ES-MS Spectral Measurements

The synthesized complex $[FeL_3](PF_6)_2$ was dissolved in 1:1 v/v acetonitrile-water, with the concentration of 0.01 mmol/L. The other samples were prepared *in situ* by following procedures: 1.00 ml of L in acetonitrile (1.0 mg/ml) was mixed with a predetermined portion of freshly prepared standard $M(ClO_4)_2$ solutions (M = Fe, Co, Ni, Cu) in water and the mixture was stirred for 2 hr to give a clear solution.

Instrumentation

Electrospray ionization mass spectra were recorded in positive-ion mode on a Finnigan MAT LCQ ES Mass spectrometer with a mass to charge (m/z) range of 2000. Mobile phase is MeOH and entered the ESI interface at a flow-rate of 300 μl/min with a syringe pump. The experiment parameters, e.g. spray voltage, capillary temperature, capillary voltage and tube lens offset were varied to investigate the influence of them on the fragmentation of the isolated complex $[FeL_3](PF_6)_2$. The spray voltage, capillary temperature, capillary voltage and tube lens offset were set at 5.0 kV, 100 °C, 7.0 V and 0 V respectively, for the measurements of the other samples. The m/z values listed below are the most intense peak in the isotopic distribution pattern, and all the assignments were confirmed by good agreement between the calculated and the experimental isotopic distribution patterns.

RESULTS AND DISCUSSION

ES-MS of isolated complex $[FeL_3](PF_6)_2$ — Influence of experimental parameters on the fragmentation

In order to investigate the influence of the experimental conditions such as: spray voltage, capillary temperature, capillary voltage and tube lens offset on the fragmentation of the parent ions of the isolated complex $[FeL_3](PF_6)_2$, the parameters were varied and the related mass spectral data are summarized in Table 1. When the capillary temperature was set at 100 °C, molecular ion $[FeL_3]^{2+}$ at m/z = 808.9 is the base peak, the peak at m/z = 1762.5 corresponds to the species $[FeL_3](PF_6)^+$, the fragment peaks at m/z = 548.9 and 288.3 corresponding to $[FeL_2]^{2+}$ and $[FeL]^{2+}$ respectively, are small. The relative percentage of the fragments at m/z = 548.9 and 288.3 increased when the capillary temperature was set at 200 °C although the base peak did not change. However, when the capillary temperature was 250 °C, the fragment at m/z = 548.9 became the base peak. It is obvious that the lower capillary temperature is useful to observe the original molecular ions formed in solution. It can also be found that the higher capillary voltage is less favorable to the fragmentation. For the tube lens offset, however, either positive or negative value increased the relative percentage of the fragment ions, the fragmentation was minimized only when it was set at 0.0 V. As shown in Table 1, no significant influence was observed for the spray voltage on the fragmentation of the complex. According to the above experimental results, the fragmentation of the parent ion was limited only when the capillary temperature, capillary voltage, spray voltage and tube lens offset were set at 100 °C, 7.0 V, 5.0 kV and 0.0 V, respectively. It means that the fragmentation is controlled by three parameters: capillary temperature, capillary voltage and tube lens offset. The mass spectra of $[FeL_3](PF_6)_2$ under the selected experimental conditions is shown in Figure 1(a).

ES-MS investigation of the reaction between the L and $M(ClO_4)_2$ *in situ*

The distribution of various species in solutions containing L and $M(ClO_4)_2$ (M = Fe, Co, Ni and Cu) in different molar ratios are listed in Table 2 and the related species were assigned as shown in Table 3. Different molar ratios between L and M cause the variation of the distribution of the species presented in solution, which was reflected by the relative percentage of the species in the mass spectra. For example, in the Fe(II)-L system, a peak due to the free ligand L was observed as LH^+ at m/z 521.5, the base peak at m/z = 808.9 corresponds to the main species

Table 1. The relative abundance of the fragments of the complex $[FeL_3](PF_6)_2$ under different ES-MS experimental conditions

species	m/z	[a]capil. temp.°C			[b]capil. volt. V			[c] spray volt. kV			[d]tube lens offset V		
		100	200	250	-7	0	7	2	5	8	-60	0	40
$[FeL_3(PF_6)]^+$	1762.5	10	24	24	35	34	24	16	24	20	0	24	38
$[FeL_3]^{2+}$	808.9	100	100	47	100	100	100	100	100	100	0	100	46
$[FeL_2]^{2+}$	548.9	4	38	100	56	55	37	32	37	38	100	37	100
$[FeL]^{2+}$	288.3	4	6	13	8	70	6	5	6	6	84	6	18
$[FeL_2(OH)]^+$	1115.3	0	10	62	20	17	10	4	10	10	0	10	52
LH^+	521.5	0	0	0	0	0	0	0	0	0	28	0	5

[a] The capillary voltage, spray voltage and tub lens offset were set at 7 V, 5 kV and 0 V. [b] The capillary temperature, spray voltage and tube lens offset were set at 150 °C, 5.0 kV and 0 V. [c]The capillary temperature, capillary voltage and tube lens offset were set at 150 °C, 7V and 0 V. [d] The capillary temperature, capillary voltage and spray voltage were set at 150 °C, 7V and 5 kV.

$[FeL_3]^{2+}$ in solution, and the cation $[FeL_2]^{2+}$ is observed at m/z 548.5 as a small peak when Fe(II)/L = 1/4. As shown in Figure 1(b), in addition to the species $[FeL_3]^{2+}$ and $\{[FeL_3](ClO_4)\}^+$, the species $[FeL_2(OH) + 2CH_3CN]^+$ and $[FeL_2]^{2+}$ were also observed, but no free ligand was detected when L:M = 3:1. The distribution of the species in solution had no significant change during the variation of the L/M molar ratio from 3:1 to 2:3. In the case of Ni(II), when L:M = 4:1, free ligand L was observed as LH^+, the base peak is at m/z = 810.4 ($[NiL_3]^{2+}$), the relative abundance of $[NiL_2(OH) + 2CH_3CN]^+$ (m/z = 1199.3) is poor. While in the case of L:M = 3:1, as shown in Figure 1(c) the species $[NiL_2]^{2+}$, $[NiL_2(OH) + CH_3CN]^+$, and $[NiL_2(OH) + 2CH_3CN]^+$ were observed in addition to the molecular ions $[NiL_3]^{2+}$ and $[NiL_3](ClO_4)^+$ and no free ligand was detected. With the increasing of Ni(II) concentration, the species $[NiL(OH) + CH_3CN]^+$, $[NiL(OH) + 2CH_3CN]^+$, $[NiL_2(OH) + CH_3CN]^+$ and $[NiL_2(OH) + CH_3CN]^+$ become the main components. The peak at m/z = 637.3 $\{[NiL (OH) + 2CH_3CN]^+\}$ becomes the base peak when L:M =3:3 and 2:3, and the species $[NiL_3]^{2+}$ (m/z = 809.9) disappeared.A similar situation was observed for Co(II) [Figure 1(d)]. In Cu(II)/L

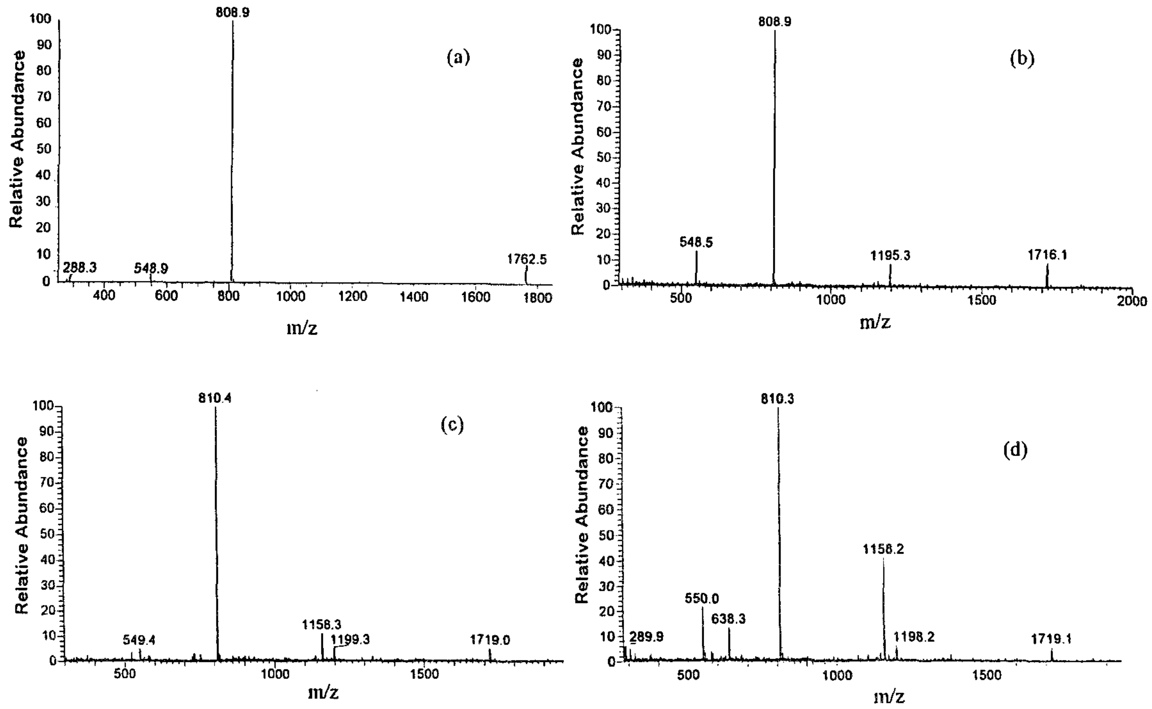

Figure 1. Electrospray mass spectra of the complexes measured in CH_3CN/H_2O, the capillary temperature, capillary voltage, spray voltage and tube lens offset were set at 100 °C, 7.0 V, 5.0 kV and 0.0 V, respectively.

(a). $[FeL_3](PF_6)_2 \cdot C_2H_5OH \cdot 0.5H_2O$, (b). $Fe(ClO_4)_2/L(1{:}3)$,

(c). $Ni(ClO_4)_2/L(1{:}3)$, (d). $Co(ClO_4)_2/L(1{:}3)$.

Table 2. Electrospray mass spectral data for $M(ClO_4)_2$ and L systems.

L:M	Fe(II) m/z (%)	Co(II) m/z (%)	Ni(II) m/z (%)	Cu(II) m/z (%)
4:1	521.5(18)	521.5(15)	521.5(13)	521.5(35)
	548.5(13)	549.9(28)	810.1(100)	642.3(38)
	808.9(100)	810.3(100)	1719.1(6)	812.3(46)
	1716.7(7)	1158.2(25)	1199.3(6)	1103.2(100)
		1198.3(6)		1162.1(54)
		1718.9(8)		1722.7(5)
3:1	548.5(14)	289.9(6)	549.4(5)	521.5(45)
	808.9(100)	550.0(22)	810.4(100)	642.3(66)
	1195.3(10)	638.3(14)	1158.3(12)	812.3(40)
	1716.1(10)	810.3(100)	1199.3(5)	1103.2(64)
		1198.2(8)	1719.0(5)	1162.1(100)
		1158.2(44)		
		1719.1(7)		
3:2	548.5(12)	289.7(35)	549.4(40)	642.3(100)
	808.9(100)	549.9(80)	579.5(48)	812.2(32)
	1195.2(6)	538.4(56)	637.4(62)	1103.2(33)
	1716.1(12)	809.9(100)	677.3(25)	1162.2(56)
		1158.2(84)	810.3(100)	1722.7(10)
		1198.2(12)	1158.3(60)	
		1718.9(8)	1199.4(30)	
			1719.2(10)	
3:3	548.3(10)	289.9(51)	549.4(23)	642.2(100)
	808.9(100)	550.0(30)	579.3(40)	812.3(42)
	1195.2(11)	638.4(100)	637.3(100)	1103.2(30)
	1716.2(10)	678.2(22)	677.3(36)	1162.2(20)
		1158.1(42)	810.4(35)	
		1198.2(10)	1158.3(44)	
			1199.3(30)	
2:3	548.3(14)	289.7(45)	579.3(30)	642.2(100)
	808.9(100)	638.3(100)	637.3(100)	812.3(22)
	1195.3(8)	678.2(30)	677.3(60)	1103.2(10)
	1716.1(8)	1158.1(12)	1158.3(12)	1162.0(10)
		1198.4(6)	1199.5(14)	

Table 3. The assignments of the observed species in Table 2.

M	m/z [a]	species
Fe	521.5	LH^+
	548.5	$[FeL_2]^{2+}$
	808.9	$[FeL_3]^{2+}$
	1195.3	$[FeL_2(OH) + 2CH_3CN]^+$
	1716.1	$[FeL_3](ClO4)^+$
Co	289.9	$[CoL]^{2+}$
	521.5	LH^+
	549.9	$[CoL_2]^{2+}$
	638.3	$[CoL(OH) + CH_3CN]^+$
	678.2	$[CoL(OH) + 2CH_3CN]^+$
	810.3	$[CoL_3]^{2+}$
	1158.2	$[CoL_2(OH) + CH_3CN]^+$
	1198.2	$[CoL_2(OH) + CH_3CN]^+$
	1718.9	$[CoL_3](ClO_4)^+$
Ni	521.5	LH^+
	549.4	$[NiL_2]^{2+}$
	579.3	$[NiL_2(H_2O) + CH_3CN]^{2+}$
	637.4	$[NiL(OH) + CH_3CN]^+$
	677.3	$[NiL(OH) + 2CH_3CN]^+$
	810.4	$[NiL_3]^{2+}$
	1158.3	$[NiL_2(OH) + CH_3CN]^+$
	1199.4	$[NiL_2(OH) + 2CH_3CN]^+$
	1719.1	$[NiL_3](ClO_4)^+$
Cu	521.5	LH^+
	642.3	$[CuL(OH) + CH_3CN]^+$
	812.3	$[CuL_3]^{2+}$
	1103.2	$[CuL_2]^+$
	1162.2	$[CuL_2(OH) + CH_3CN]^+$
	1722.7	$[CuL_3](ClO_4)^+$

[a] The quoted m/z values are attributed with the error no more than ± 0.4.

system however, the species $[CuL_2]^{2+}$ and $[CuL]^{2+}$ were not observed in all the cases, and the species $[CuL_2]^{+}$ (m/z = 1103.2) was detected in addition to the Cu(II) complexes. The existence of the Cu(I) species indicates that the Cu(II) may be partially reduced to Cu(I) under the electrospray conditions. The data of ES-MS spectra indicate that all the species presented in the reaction mixtures are mononuclear complexes, and no polynuclear species were formed.

As shown in Table 1 and 2, the species containing OH^- group were observed in the solution of the isolated complex $[FeL_3](PF_6)_2$ and the reaction mixtures between L and $M(ClO_4)_2$. These species were considered to be produced by two possible processes, one is that the basicity of the oligobipyridine L in solution could supply OH^- group which coordinates to the metal ions as our previous reports,[12, 13] the other is the hydrolysis of the complexes under the electrospray conditions as follows:

$$[ML_3]^{2+} + H_2O \rightleftharpoons [ML_2(OH)]^{+} + LH^{+}$$

$$[ML_2]^{2+} + H_2O \rightleftharpoons [ML(OH)]^{+} + LH^{+}$$

The hydrolysis products $[ML_2(OH)]^{+}$ and $[ML(OH)]^{+}$ combine with one or two CH_3CN molecules resulting in the observed species: $[ML_2(OH) + CH_3CN]^{+}$, $[ML(OH) + CH_3CN]^{+}$, $[ML_2(OH) + 2CH_3CN]^{+}$, and $[ML(OH) + 2CH_3CN]^{+}$.

The formation of the mononuclear rather than multinuclear complexes of L with M^{2+}

Oligobipyridine ligands containing bipyridine units linked by CH_2OCH_2 or CH_2CH_2 have been shown to coordinate to copper(I),[10, 14-16] silver(I),[17] nickel(II)[18] and iron(II)[19, 20] forming double or triple helicates by self-assembly processes. In order to investigate the effect of the different linkage modes between bipyridine units, we designed and synthesized the new ligand L, in which three bipyridine units are linked by CH_2CH_2 spacer group. In this ligand L, the two terminal bipyridine units are 6-monosubstituted and the central bipyridine unit is 5,5'-disubstituted. The results of electrospray mass spectrometry indicate that the species presented in the solutions are mononuclear complexes in all cases, no multinuclear product was observed. According to the argument[10] that the steric hindrance of the substituents α to the coordinating nitrogens inhibits the formation of square pyramidal, triangle pyramidal and octahedral complexes, the terminal 6-monosubstituted bipyridine units are considered to be free of coordination while the central 5,5'-disubstituted bipyridine unit coordinated to the metal ions to give the mononuclear complexes, as mentioned above. This was supported by the crystal structure of $[FeL_3](PF_6)_2 \cdot C_2H_5OH \cdot 0.5H_2O$.[11] The results indicate that the linkage mode between the bipyridine units in oligobipyridine plays an important role in the formation of metal helical complexes.

CONCLUSION

The present study indicates that the fragmentation of the complexes was controlled by three experiment parameters: the capillary temperature, the capillary voltage, and the tube lens offset potential for Finnigan MAT LCQ system. The results confirmed that the ES-MS is a powerful technique for determining the species existing in solution and for the investigation of the reaction between oligobipyridine and transitional metal ions. The solution ES-MS data show that the oligobipyridine ligand L coordinated to transitional ions with octahedral geometry to form mononuclear complexes. The study supports that the formation of an inorganic helix is partially controlled by the linkage mode between the bipyridine units,in addition to the flexibility of the spacer group in oligobipyridine ligand and the coordination geometry of the metal ions.

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