New Coordinative Compounds with 4-(4′-pyridyl)pyridinium Disubstituted Monoylides

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Abstract: The complexes with manganese(II), iron(II), cobalt(II), nickel(II) and copper(II) of 2-(4, 4'-bipyridin-1-ium-1-yl)-1-(4-bromophenyl-amino)-3-(4-methoxyphenyl)-3-oxo-1-thioxopropan-2-ide (ylide, Y) were synthesized and characterized. The obtained compounds with 1 : 2 metal/ligand ratios have been characterized by FTIR, UV Vis spectroscopy, ESI MS spectrometry, molecular conductance, magnetic measurements and thermal analysis. The ylide ligand forms chelates with metallic (II) ions through their amide nitrogen and oxygen atoms.

Keywords: *N*-ylide, complexes, ESI MS, thermal analysis.

INTRODUCTION

YLIDES are zwitterionic organic compounds, in which a carbanion is directly bond to a positive charged heteroatom (as N, P, As, S, Sb). The term "ylide" was first time introduced in literature by G. Wittig in 1944.[1] After their structures were proved by diverse chemical reactions, isolation of a stable ylide[2] opened the way to the synthesis of various ylidic structures with nitrogen, phosphorus, sulfur and arsenic as cationic heteroatoms. The nature of both the heteroatom and the groups covalently bond to the cation is an essential factor in determining the stability and reactivity of ylides. A special interest was shown in the last years for cycloimmmonium ylides, in which the nitrogen atom is involved into an *N*-heteroaromatic ring, due to their reactivity as 1,3-dipol and consequently for their use as intermediates in organic synthesis.[2,3] Thus, a series of compounds possessing antibacterial and antifungal,[4–10] anti-secretory[11] or anti-leukemic[12] properties were synthesized. On the other hand, this unique reactivity of cycloimmonium ylides made them subject for computational and experimental studies of their electro-optical molecular parameters.[3] Stable cycloimmonium ylides attracted considerable interest in chemistry and biology due to their biological activities (antibacterial, antifungal).[5–7,10]

Due to their nucleophilic character, the nitrogen, phosphorus, arsenic and sulfur ylides, are also interesting ligands toward transition metals in organometallic chemistry.[13–16] The coordination chemistry of ylides has been previously reviewed by Schimdbaur[17,18] and Kaska,[19] who described the synthesis of metal-ylide complexes from 'preformed' ylides. (Thio)carbonyl - stabilized *N*-ylides are interesting ligands because they can behave as C-, O-, S- or N- donors due to the delocalization of the ylidic negative charge. This ambidentate character facilitates the synthesis of stable metal complexes.[20]

We reported here the new coordinative compounds of manganese(II), iron(II), cobalt(II), nickel(II) and copper(II) ions with a cycloimmonium ylide, 2-(4,4'-bipyridin-1-ium-1-yl)-1-(4-bromophenylamino)-3-(4-methoxyphenyl)-3-oxo-1-thioxopropan-2-ide (**1**) (Figure 1).
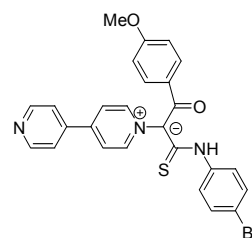

Figure 1. Molecular structure of nitrogen ylide (**1**).

Experimental

Materials and Methods

All chemicals and solvents used for the synthesis were commercially available reagents and used without any purification.

The infrared spectra were recorded on a Jasco FT-IR 660 Plus spectrometer in KBr pellets. The UV-Vis spectra were recorded in MeOH solution, $c = 10^{-3}$ M, using a Cintra 101 device. Electrospray mass spectra (ESI MS) were recorded on a Excalibrus device using as solvent a MeOH / CH$_2$Cl$_2$ (1 / 1, *v* / *v*) mixture. Thermogravimetric measurements, TG and DTG were made with a Mettler Toledo derivatograph, under air atmosphere, with a flow of 20 mL min^{-1} and heating speed of 10 °C min^{-1}, in the temperature domain of 35–900 °C. The thermal characteristics were obtained using the STAR soft from Mettler Toledo for processing the experimental curves. The molar conductance of the complexes, with concentration $c = 10^{-3}$ M in MeOH solution, was determined with a Consort K912 device. The magnetic moments were determined in solid state by Gouy method using a Magnetic susceptibility balance MSB-auto.
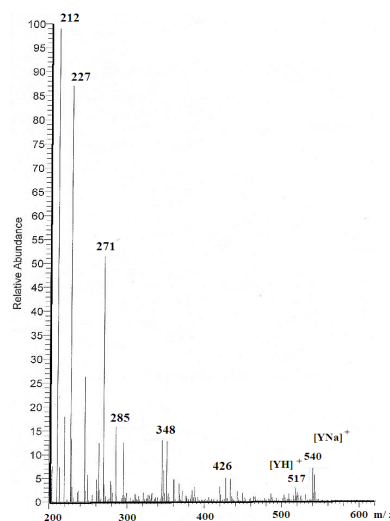
Synthesis of the Ligand

2-(4,4'-Bipyridin-1-ium-1-yl)-1-(4-bromophenylamino)-3-(4-methoxyphenyl)-3-oxo-1-thioxopropan-2-ide (**1/Y**) was synthesized in two steps.

First, the 1-(2-(4-methoxyphenyl)-2-oxoethyl-[4, 4'-bipyridin]-1-ium bromide was dissolved in water and treated with aqueous 0.2 N NaOH solution. The obtained suspension was centrifuged and the intense red monosubsituted ylide was separated and dried before used in the next step. Monosubstituted cycloimmonium ylide generated in basic media reacted with 4-bromophenyl isocyanate in dimethylformamide, affording the 1-disubstituted 4-(4'-pyridyl) pyridinium methylide **1** in good yield.[21]

Table 1. The synthesized complexes and their physical properties.

| Compounds	No.	m / z	Λ_m / μS cm^{-1}	Yield / %	μ /BM
Y	1	517	4.5		–
[Mn(Y)$_2$]	2	1089	16.1	55	5.82
[Fe(Y)$_2$]	3	1090	4.9	62	4.92
[Co(Y)$_2$]	4	1093	5.4	57	3.78
[Ni(Y)$_2$]	5	1092	9.7	54	0
[Cu(Y)$_2$]	6	1101	2.6	58	1.67

Figure 2. ESI MS spectrum of compound (**1**).

Synthesis of the Complexes

Complexes **2**–**6** (Table 1) were synthesized using a general method reported by R. M. Ma and collab.[22,23] To a solution of ligand (**1**) (38 mg, 0.1 mmol) in 5 mL chloroform and triethylamine (14 μL, 0.1 mmol), metal(II) chloride (7.5 mg for CoCl$_2$·6H$_2$O, 0.05 mmol) dissolved in ethanol (5 mL) was added dropwise. The solution was stirred for 4 hours at room temperature and then allowed to precipitate. The precipitate was filtered, dried and crystallized from an appropriate solvent giving the desired compounds in moderate yields.
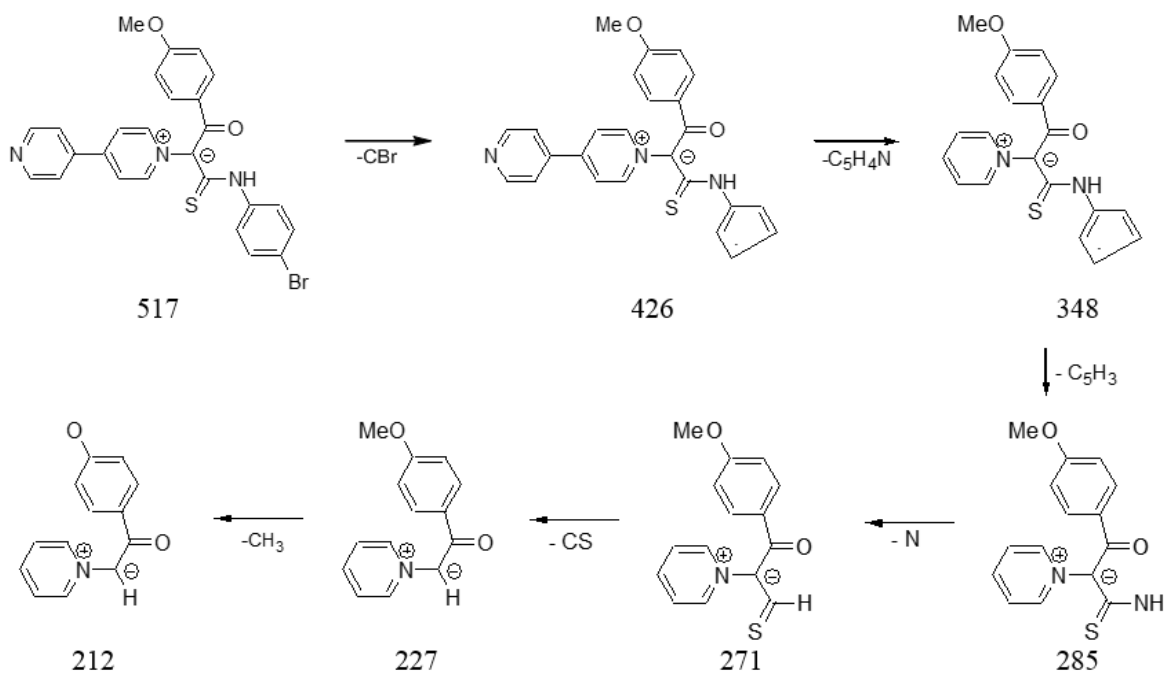
RESULTS AND DISCUSSIONS

ESI MS Spectra

ESI MS spectrum of compound **1** provides useful information about the exact mass and its fragmentation mode. The mass spectrum of the ligand (Figure 2) presents a molecular peak at $m / z = 540$, corresponding to [YNa]$^+$. The peak at 518 corresponds to the protonated species [YH]$^+$.
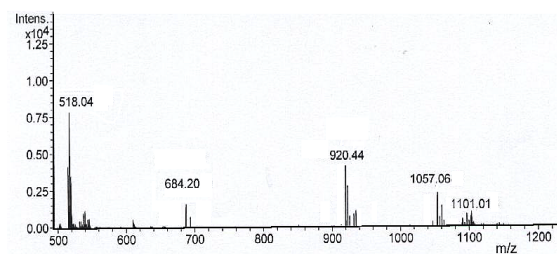
Figure 3. ESI MS spectrum of complex **6** [Cu(Y)$_2$].

Scheme 1. Possible fragmentation pathways of ligand (**1**).
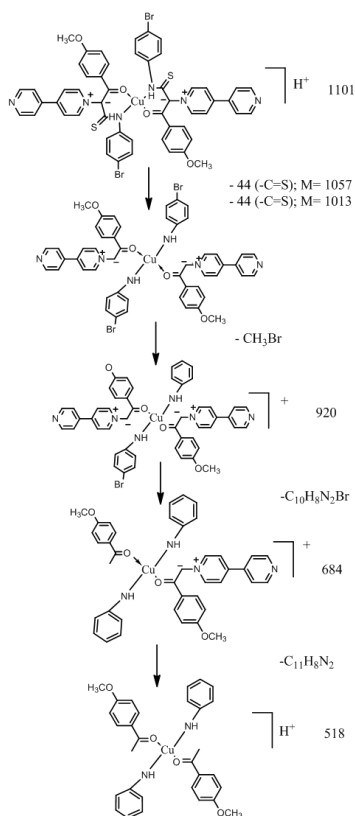
Scheme 2. Possible fragmentation pathways of complex **6** [Cu(Y)$_2$].

Few possible fragmentation ways of the ligand (**1**) are shown in Scheme 1.

Mass spectra of complexes **2–6** provided as expected molecular peaks at the same ratio 1 : 2 metal / ligand, Table 1.

The mass spectrum of compound **6** shows a complex isotopic pattern due to the presence of two bromine and one copper atoms as can be seen in Figure 3 (the most intense peaks are $m / z = 1097 / 1099 / 1101$). Fragmentation of the complex [CuY$_2$]$^+$ leads to a series of peaks corresponding to different fragments.

Three possible fragmentations of the copper complex are represented in Scheme 2.

Molar conductance (Λ_m) of the complexes shows that all are non-electrolytes. Magnetic moments (μ) indicate a diamagnetic behavior for Ni(II) complex, therefore complex **5** has a square planar structure. The other complexes are paramagnetic and magnetic moments correspond to 5 unpaired electrons for Mn(II) complex, 4 unpaired electrons for Fe(II) complex, 3 unpaired electrons for Co(II) complex and 1 unpaired electron for Cu(II) complex.

Infrared Spectra

The FTIR spectrum of the ligand shows few characteristic bands. Absorption band of N-H bending appears at 1628 cm^{-1}. The band corresponding to $v_{C=O}$ carbonyl group appears at 1490 cm^{-1} while the C=S vibration can be associated with several combination bands.

Table 2. Relevant FTIR frequencies of the synthesized complexes (cm^{-1}).

Compounds	ν_{HOH}	δ_{NH}	$\nu_{C=O}$	ν_{M-N}	ν_{M-O}
1	–	1628	1490	–	–
2	3437	1624	1487	505	451
3	3436	1623	1487	506	453
4	3434	1626	1488	504	455
5	3438	1626	1488	504	449
6	3438	1619	1484	504	451

Table 3. UV VIS data for the obtained compounds in MeOH.

Compounds	λ_1 / nm (lg ε_1)	λ_2 / nm (lg ε_2)	λ_3 / nm (lg ε_3)	λ_4 / nm (lg ε_4)	λ_1 / nm (lg ε_1)
2	264 (3.41)	282[a] (3.29)	340[a] (2.73)	412[a] (2.27)	264 (3.41)
3	270 (3.45)	296 (3.44)	339 (2.95)	377 (2.87)	270 (3.45)
4	266 (3.42)	288 (3.35)	335 (2.83)	380 (2.80)	266 (3.42)
5	268 (3.40)	286 (3.32)	341 (3.00)	374 (2.91)	268 (3.40)
6	241 (3.36)	267 (3.35)		381 (2.79)	241 (3.36)

[a] Shoulder.

By coordination, the characteristic bands of the ligand were modified in position and intensity. In addition, in the range 500–400 cm^{-1} there are a series of new absorption bands, corresponding to the newly formed bonds.[24,25] These changes indicate the formation of the metal complexes and that metal ions bind to ligands through oxygen (O) and nitrogen (N) atoms. The most important IR bands for ligand and the new complexes are given in Table 2.

The electronic spectra of the free ligand in MeOH show one absorption bands in UV-Vis at 264 nm, that could be attributed to π→π* transitions. The free ligand also exhibited several shoulders at 282, 340 and 412 nm that can be attributed to π→π* and n→π* transitions.[26,27] Comparing to UV-Vis spectra of the ligand, the spectra of corresponding M(II) complexes, show important changes in position and intensity of the absorption bands (Figure 4). In addition, the spectra of complexes also present new bands in visible region (not well defined, because of the low solubility of the complexes) (Table 3). The shifts and intensity modification for absorption bands are the evidence of coordination of *N*-ylide ligand **(1)** towards metallic ions.[27,28]

Thermal Analysis

The TG and DTG studies for complex **6** [Cu(Y)$_2$], were carried out to in the range of temperature 35–900 °C providing information about decomposition and the relative volatility of the complexes (Figure 4).

The results obtained from thermo-gravimetric analyses (Table 4) were in agreement with the suggested theoretical formula. Thermal analysis of copper complex **6** indicates the decomposition in six steps. The activation energy corresponding to every decomposition step was determined using Freeman Carroll method.[29]

In the first step, in the range 35– 140 °C, the loss of 2.43 %, corresponds to the physically retained water release (calculated for 1.5 H$_2$O the loss is 2.40 %). The activation energy for this range is 17.23 kJ mol^{-1}, specific for the cleavage of physical bonds. In the second step, in the range

of 140–264 °C, the loss of 19.61 % (calculated 19.70 %) corresponds to the elimination of 2 Br atoms and 2 OMe groups. The activation energy (E_a = 38.29 kJ mol^{-1}) corresponds to C–Br bond cleavage. In the next step, the loss of 5.62 % (calc. 5.68 %), in the range 264–323 °C for elimination of two sulfur atoms needs the highest value of the activation energy (E_a = 478.12 kJ mol^{-1}). In the fourth stage in the range of 323– 464 °C, a big loss of 48.12 % (calculated 48.09 %), corresponds to the elimination of two important parts of the molecule, including the bipyridil and phenyl rings. Between 464–672 °C the loss is 7.85 % (calculated
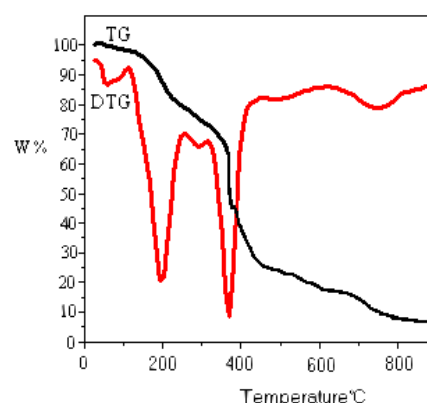
Figure 4. TG and DTG curves of complex 6.
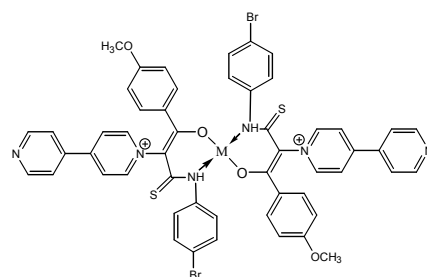
Figure 5. Proposed structure for obtained complexes.

Table 4. Thermogravimetric data results of the complex **6**.

Steps	Temperature range / °C	Mass loss found / %	Mass loss calculate / %	Assigments	E_a / kJ mol^{-1}
I	35–140	2.43	2.40	1.5 H$_2$O	17.23
II	140–264	19.61	19.70	2 Br + 2 OCH$_3$	38.29
III	264–323	5.62	5.68	2 S	478.12
IV	323–464	48.12	48.09	2 (C$_{10}$H$_8$N$_2$ −CH−C−N−C$_6$H$_4$)	191.47
V	464–672	7.85	7.81	C−C$_6$H$_4$	76.58
VI	672–820	9.25	9.23	C$_6$H$_4$−C=O	123.30
Residue	over 820	7.12	7.10	CuO	

7.81 %), which corresponds to the elimination of C$_7$H$_4$. In the final decomposition step, in the range 672–820 °C, the last organic groups (C$_6$H$_4$–C=O) are eliminated (found loss 9.25 %, calculated loss 7.23 %). The amount of residue 7.12 % over 820 °C is in agreement with the calculated value for CuO (7.10 %).[30]

The proposed structure of these complexes is presented in Figure 5.

CONCLUSIONS

The 2-(4,4'-bipyridin-1-ium-1-yl)-1-(4-bromophenylamino)-3-(4-methoxyphenyl)-3-oxo-1-thioxopropan-2-ide acts as bidentate *N*-ylide ligand and coordinates in 1 : 2 molar ratio M : L with manganese(II), iron(II), cobalt(II), nickel(II) and copper(II). The coordination chemistry of the resulting complexes **2**, **3**, **4**, **5**, **6** has been investigated, and it has been shown that ligand **1** promotes a square-planar geometry for the complexes.

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