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Synthesis, Characterization and HPLC Behaviour of Metal Complexes of Methyl Pyruvate Aroylhydrazones

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The synthesis and characterization of some transition metal complexes of methyl pyruvate N-*aroylhydrazones* $RC(O)NHN{=}C(CH_3)C(O)OCH_3$ *(*$R = C_6H_5, C_6H_4OH$*) are reported. These ligands undergo deprotonation with Co, Ni, Cu and Zn acetates to form neutral, hexacoordinate metal complexes with metal to ligand ratios of 1:2, acting as terdentate through the two carbonyl oxygens and the azomethine nitrogen. The study of the HPLC behaviour of these complexes and the results in the separation of Co, Ni, Cu chelates are also reported. The best results were obtained using an apolar stationary phase and acetonitrile–dichloromethane mixtures as mobile phase.*

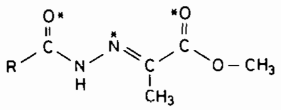
Introduction

Coordination chemistry of aroylhydrazones of the type $ArC(O)NHN{=}CR_1R_2$ shows many interesting features owing to the great chelating power of the $-C(O)NHN{=}$ group and the possibility of these ligands to act as bidentate or terdentate depending on the nature of R_1 and R_2. Moreover these ligands can undergo a variety of conformational and configurational changes, when chelate to different metal centers, forming neutral, cationic or mixed ligand metal complexes [1, 2].

Their tendency to give intensely-coloured metal chelates allow their use in analytical chemistry as extraction reagents for the spectrophotometric determination of several metals. Recent examples include the utilization of aroylhydrazones of pyridine-2-carbaldehyde and pyridine-2-acetaldehyde for the determination of iron and vanadium respectively [3, 4].

In the field of HPLC techniques some examples of the separation of substituted phenyl- and thiobenzoylhydrazones metal complexes have already been reported [5, 6].

As a part of our research programs on the chelating properties of acyl- and aroylhydrazones and the chromatographic behaviour of metal chelates, we have studied a new series of aroylhydrazones (see scheme) obtained by condensation of *N*-aroylhydrazines with methyl pyruvate



$R = C_6H_5$ (HBIPYR)
$R = o\text{-}C_6H_4OH$(HSIPYR)

These ligands undergo deprotonation with metal acetates to form neutral hexacoordinate metal complexes with metal/ligand ratio 1/2, acting as terdentate through the starred atoms.

The present paper deals with the synthesis and characterization of these neutral metal bis-chelates and with the separation of some of them *via* HPLC.

Experimental

Preparation of the Ligands

Hbipyr (Hsipyr) was prepared by heating 1:1 molar ratios of benzoylhydrazine (salicyloylhydrazine) and methyl pyruvate under reflux in ethanol for 20 min. The white microcrystalline products obtained on cooling were recrystallized from hot ethanol and identified by means of their NMR and mass spectra.

Preparation of the Complexes

$M(bipyr)_2$ ($M(sipyr)_2$) was prepared by refluxing in ethanol Hbipyr (Hsipyr) and the metal acetate in ½ molar ratio. A suspended solid began to form and precipitation was complete after cooling. The products were filtered, washed and dried *in vacuo*;

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TABLE I. Characterization Data for Hbipyr (HL), Hsipyr (HL') and their Complexes.

Compound	Color	M.P. (℃)	μ_{eff} (B.M.)	Electronic Absorptions Maxima (nm)			
				L–L*	C.T.	d–d	
HL	white	187	–	265			b
CoL_2	orange	252(dec)	4.57	270	345[b]	560, 975	c
NiL_2	yellowish orange	258(dec)	3.39	265	350[b]	580, 975	c
CuL_2	brownish yellow	201(dec)	[a]	265	340[b]	740	c
ZnL_2	pale yellow	260(dec)	–	260	345		b
HL'	white	208	–	270			b
CoL'_2	orange	282(dec)	4.91	280	350[b]	570, 950	c
NiL'_2	orange yellow	298(dec)	3.18	280	350[b]	640, 1040	c
CuL'_2	brownish yellow	242(dec)	[a]	275	345[b]	730	c
ZnL'_2	pale yellow	278(dec)	–	285	345		b

[a]Unmeasured. [b]Ethanol solution. [c]DMSO solution.

all these complexes gave satisfactory elemental (C, H, N) analyses.

Physical Measurements

The IR spectra (KBr disks) were recorded on a Perkin-Elmer 283B instrument. Electronic spectra were run on a Cary 14 and a Jasco 505 spectrophotometers. Magnetic susceptibilities were measured, by the Gouy methods, on a Newport Instruments balance at 30 ℃.

High-Pressure Liquid Chromatography

A Perkin-Elmer series 3B liquid chromatograph, equipped with a variable wavelength spectrophotometric detector, was used (full scale 0.01 absorbance units, flow cell volume 8 μl). The column was Hibar Lichrosorb RP-8 (25 cm × 0.4 cm i.d.); flow rate of mobile phase: 1 cm^3 min^{-1}; Lichrosolv solvent (E. Merck, Darmstadt) were used as mobile phases, without further purification. Metals, in column eluates, were checked by means of flameless atomic absorption spectroscopy. A Perkin Elmer mod. 303 spectrophotometer equipped with a graphite furnace HGA-72 atomizer was used.

Results and Discussion

The reaction of methyl pyruvate aroylhydrazones, Hbipyr and Hsipyr, with some first row transition metal acetates gives the corresponding bis-chelates of general formula $M(bipyr)_2$ and $M(sipyr)_2$, respectively. They are coloured, high melting solids, poorly soluble in all common solvents (chiefly $M(sipyr)_2$), but soluble in DMSO and DMFA.

In Table I characterization data, together with electronic absorption maxima, are given whereas Table II states the most important infrared bands in the region 4000–250 cm^{-1}.

Both these ligands exhibit moderately intense NH stretching bands which disappear in the spectra of the complexes as a consequence of the deprotonation. The position of these bands in Hbipyr is consistent with the formation in the solid state of N–H···O=C hydrogen bonds, as it occurs in secondary amides [7]; whereas the IR spectrum of Hsipyr, in the 3300–2500 region, suggests the same N–H···O–H···O=C network that was found in pyridine-2-carbaldehyde salicyloylhydrazone [8, 9], involving the *o*-hydroxyl group of the salicyloyl moiety.

The IR spectra of the complexes show many interesting features arising from the relevant shifts of the ν(CO), amide I and amide II bands resulting from the coordination on the metal centers of the starred atoms in the scheme.

The lowering of the ν(CO), due to the ester grouping, is to some extent dependent on the nature of the metal, being more relevant (~55 cm^{-1}) in the case of nickel and cobalt, for both the ligands.

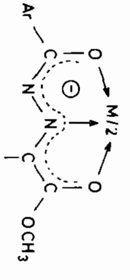
More pronounced is the lowering (80 cm^{-1} in $M(bipyr)_2$) of the amide I band, mainly due to ν(CO); this lowering is among the more considerable observed for similar systems [10, 11] and it appears to be unaffected by the nature of the metal. The amide II band, which, in the free ligand results from interaction between δ(NH) and ν(CN), shifts to lower frequencies, probably as a consequence of the coupling of the amide bands with those of the coordinated azomethine group, as has been found for other similar systems [12–14].

TABLE II. Characteristic IR Bands (cm^{-1}) of Hbipyr (HL), Hsipyr (HL′) and Their Complexes.

Assignments	HL	CoL$_2$	NiL$_2$	CuL$_2$	ZnL$_2$	HL′	CoL′$_2$	NiL′$_2$	CuL′$_2$	ZnL′$_2$
ν(NH)	3240m 3200sh					3260m				
ν(OH)						2840w,br 2700w,br	2720w,br 2630w,br	2720w,br 2620w,br	2720w,br 2620w,br	2720w,br 2620w,br
ν(CO) ester	1710vs	1658s	1653s	1662s	1680s	1710vs	1660s	1660s	1665s	1680s
Amide (I) ν(CO)	1672vs	1590s	1590s	1590s	1595s	1648vs	1590s	1590s	1588s	1588s
Ring	1600m 1580mw	1600sh 1578sh	1600sh 1575sh	1600sh 1575sh	1600sh 1575sh	1600ms	1620m	1620m	1620m	1620m
Amide II δ(NH) + ν(CN)	1535s	1500s	1498s	1500s	1500s	1560s	1515ms	1515ms	1520ms	1520ms
Ring and δ$_{as}$(CH$_3$)	1445m 1430s	1445m 1435sh	1440m 1430sh	1445m 1435sh	1445ms 1435sh	1455ms 1445ms	1490ms 1460s	1490ms 1460s	1490ms 1460s	1490ms 1460s
δ$_s$(CH$_3$)	1370m	1370ms	1370m	1368ms	1368s	1370m	1375m	1375m	1370m	1370m
C–C(=O)–O system	1300sh 1270vs 1190ms 1153sh 1138vs	1320s 1285vs 1223mw 1170sh 1145vs	1315s 1280vs 1220m 1165sh 1140vs	1315s 1280vs 1220mw 1170sh 1145vs	1315vs 1280vs 1220w 1168sh 1145vs	1310ms 1290m 1230s 1190ms 1150vs	1305vs 1255ms 1225ms 1185s 1155vs	1305vs 1255ms 1225ms 1190s 1155vs	1302vs 1255ms 1225ms 1185s 1155vs	1300vs 1250ms 1220ms 1180s 1150vs
γ(CH) ring	720ms 700s	710ms 685 m	710ms 685m	710s 685m	710s 685w	750s	765m 750ms	765m 750ms	765m 750ms	760m 750ms

As is shown by the values quoted in Table II, coordination slightly affects other IR bands of the ligands, particularly those attributable to ν(CO) of ester grouping.

All the evidence strongly suggests a terdentate behaviour of the deprotonated ligands, in which the negative charge appears to be delocalized over the whole chelating system, as depicted in the following scheme



The R substituent on the hydrazide group seems to play an important role in favouring this behaviour. In fact when R = C_6H_5, HO-C_6H_4 (Hbipyr and Hsipyr), deprotonation occurs and the bis-chelate complexes are formed. When R = CH_3, deprotonation does not occur and the ester grouping undergoes, in the presence of metals, complete hydrolysis [15].

The coordination mode of these ligands, depicted in the scheme (2), together with the stoichiometry of these chelates, requires an octahedral coordination for the metals, which is in agreement with the magnetic [16] and electronic absorption data [17] found in the case of nickel and cobalt complexes.

The chromatographic behaviour of some of these complexes has been studied with the aim of verifying the possibility of analytical applications of these ligands.

The formation of neutral molecular complexes with a saturated coordination sphere suggests the possibility of using the ligands Hbipyr and Hsipyr for the separation of metals as chelates, with a medium or low-polarity system. Moreover the intense absorption of the complexes in the UV-visible region allows the use of commercial spectrophotometric detectors.

Preliminary results in the study of the chromatographic behaviour of complexes of these ligands have been achieved with reversed phase partition chromatography, using an apolar stationary phase and acetonitrile–dichloromethane mixtures as mobile phase.

With this chromatographic system the Co, Ni, Cu(bipyr)$_2$ complexes were successfully separated, while with Hsipyr only one peak (corresponding to the free ligand) was observed. This different behaviour could be explained by intermolecular interaction, in which the uncoordinated phenolic hydroxile of Hsipyr could be involved.

The best results in the separation of Co, Ni, Cu(bipyr)$_2$ complexes have been obtained by dissolving the free ligand (0.04 *M*) in the mobile phase, to prevent tailing of peaks. The addition of the ligand on the mobile phase does not interfere with the UV-detection, because the absorption of the complexes is sensitively shifted towards higher wavelength; elution of the chelates can be monitored at λ = 360 nm, without spectral interference by the free ligand.

Under isocratic elution (CH_3CN/CH_2Cl_2 = 90/10 v/v) the Cu complex is separated from those Co and Ni, which are not separated from each other.

The separation of the three chelates is achieved by using a solvent gradient, with linearly variable composition of the mixture CH_3CN/CH_2Cl_2 from 90/10 to 50/50 volume ratio, running time 10 min. The retention volumes are: Cu: 3.0, Ni: 6.1, Co: 7.2 cm^3.

The presence of the metals in the effluents of the column was tested by means of flameless atomic absorption spectroscopy, in order to find out if elution of complexes occurred without decomposition. Portions of 10 μl of dichloromethane solutions of the metal chelates (~100 ppm of metal) were separately injected into the column; 5 cm^3 of the effluents in correspondence to the peak were collected and the atomic absorption of the metal was measured; a portion of the mobile phase was used as blank.

The absorbance values observed for the metals in the column eluate were found to be equal, within experimental error, to those measured in solutions obtained by directly adding 10 μl of the CH_2Cl_2 solutions of the chelates to 5 cm^3 of the mixture used as mobile phase.

This result confirms that the separation of the chelates occurs without decomposition.

Further research on the possibility of application of these ligands for the extraction and chromatographic separation of metals is in progress.

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