

Surface vibrational study of macrocycle complexes: Co(II), Ni(II), Cu(II) and Zn(II) bis(phenylhydrazine)-1,10-phenanthroline

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Abstract

A complete assignment of the infrared spectra of the title macrocycles was carried out on the basis of well-documented references and a normal coordinate analysis based on a simplified molecular model. The structure of the complexes has been inferred from IR and UV–VIS data. Infrared reflection–absorption (IRRAS) spectra using a smooth copper surface and surface enhanced Raman spectra of samples dissolved in colloidal silver were registered. The non-planar structure of the coordination site and the sterical hindrance imposed by phenyl substituent fragments avoid any adsorbate–substrate interaction. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Bis(phenylhydrazine)-1,10-phenanthroline; Metal macrocycle Co(II), Ni(II), Cu(II) and Zn(II) complexes; Synthesis; UV–VIS and IR spectra; Normal coordinate analysis; IRRAS and SERS

1. Introduction

Vibrational spectroscopy has been used in our research group to study in the last 4 years macrocycles and its metal complexes. Lately, the aim of our work has been to determine the effect that different metal surfaces have on their structures, organization and orientation when adsorbed on metal surfaces. Macrocyces considered displayed different characteristics such as the ring and the π electronic size, the number of the metal coordinating nitrogen atoms, and the presence of substituent groups in planar macrocycles [1–9].

An additional characteristic is introduced in this work, that is macrocycles displaying a non-planar and asymmetric coordination site. Macrocycle complexes here considered are the bis(phenylhydrazine)-1,10-phenanthroline (L) and its Co(II), Ni(II), Cu(II) and Zn(II) complexes, see Fig. 1. To determine the influence that smooth copper and colloidal silver surfaces have on the molecular structure, organization and orientation of these complexes, we will use infrared, infrared reflection–absorption (IRRAS) and surface enhanced Raman scattering (SERS) spectroscopies. The complete vibrational assignment, fundamental in this kind of study, is accompanied by a normal coordinate analysis of these compounds. Their structures, not reported yet, are inferred from UV–VIS and infrared data. No surface effect study was possible to perform on the ligand

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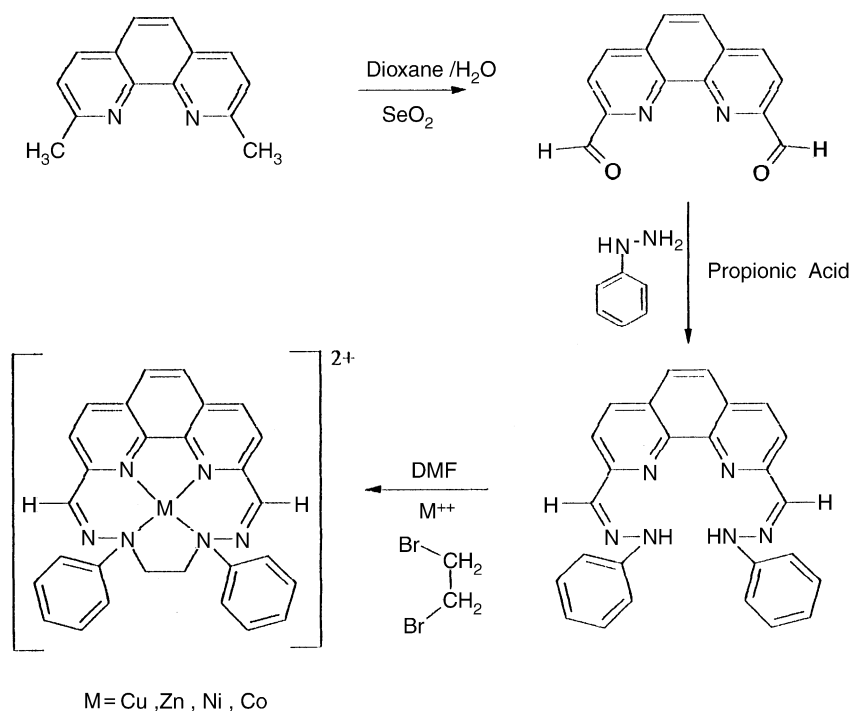


Fig. 1. Synthesis scheme and molecular diagram of the bis(phenylhydrazine)-1,10-phenanthroline metal complexes.

bis(phenylhydrazine)-1,10-phenanthroline because it is easily decomposed by solvent dilution.

2. Experimental

2.1. Synthesis

The synthesis of the metal macrocycles was performed following the general procedure shown in Fig. 1; the ligand was synthesized following the procedure described by Anacona and coworkers [10].

2.2. UV–VIS spectra

UV–VIS spectra in solid phase (nujol mulls) were registered using a Karl-Zeiss DMR-22 model and a Varian Cary 1E model spectrophotometers.

2.3. Infrared spectra

Infrared spectra of the compounds were obtained as KBr pellets on a Perkin-Elmer series 2000 apparatus in

the range $4000\text{--}450\text{ cm}^{-1}$ and scanned with a resolution of 2 cm^{-1} . This apparatus operates with a DTGS detector. Two-hundred scans were accumulated. A beam splitter of a $6\text{ }\mu\text{m}$ stretched Mylar pellicle was used. IRRAS spectra in the region $1600\text{--}450\text{ cm}^{-1}$ were recorded with a WeeMax variable angle accessory of PIKE-Technologies mounted on the Perkin-Elmer optical bench. IRRAS measurements were performed at different incident radiation angles, in the range $30\text{--}80^\circ$. Similar spectral conditions were used to scan the spectra. The FT-IR spectra in the region $600\text{--}200\text{ cm}^{-1}$, for the samples dispersed in polyethylene were scanned by using a Bruker model Vector 22 spectrometer. Spectra were registered with a resolution of 4 cm^{-1} . Four-hundred scans were accumulated.

2.3.1. Sample preparation for IR spectra

Copper foils from Merck of 99.7% purity were used as smooth surfaces for the IRRAS experiments; in order to avoid oxidation they were manipulated under N_2 atmosphere. Samples were dissolved in chloroform and then dropped onto a smooth copper surface. The solvent was evaporated under vacuum. About 10^{-6} mol

of the compounds were spread out in 1 cm^2 of the copper surface. The same procedure was followed to deposit the compounds onto a KBr monocrystal. Also, pellets were obtained by dispersing 2 mg of the sample to study in 300 mg of KBr under pressure during 30 s.

2.4. Raman spectra

FT-SERS spectra were scanned by using a RFS 100/S Bruker spectrophotometer. The 1064 nm line, provided by a Nd:YAG laser, was used as excitation line. The resolution was set to 4 cm^{-1} and a 180° geometry was employed. The output laser power was 50–250 mW. Up to 1000 scans were accumulated for the solution samples.

2.4.1. Preparation of the Ag colloid and samples for SERS

The silver colloid for the SERS measurements was prepared by following the method reported by Lee and Meisel by using citrate as reducing agent [11]. Macrocycle solutions in ethanol (99%) were prepared at 10^{-4} M concentrations. Because of the low solubility of the macrocycles, their final concentrations are in the range 10^{-5} to 10^{-7} M . Fifty micro liters of the solutions were added to 500 μl of silver colloid. The liquid samples were placed into 1 mm optical path length capillaries.

3. Results and discussion

3.1. Structural characterization of macrocycles

3.1.1. UV–VIS spectra

UV–VIS spectra in solid phase (nujol mull) with tentative assignments are shown in Table 1. The d–d

bands position indicates a tetrahedral coordination site. The spectra taken from DMF solutions do not show major differences, which suggests minor changes upon dissolution. The UV–VIS spectra of the free macrocycle and the Zn(II) complex in DMSO solutions was already reported [10].

3.2. Vibrational assignment

The different electron donor–acceptor characteristics of the distinct fragments of the highly delocalized π electron macrocycles indicates that a rich vibrational spectra is expected. Most assignments were made by comparison with data published for related tetraaza-macrocycles [1,6,10] and precursors [12], where a detailed spectral analysis for the phenantroline, azomethine and hydrazine fragments is proposed. In particular, vibrations of the phenyl moieties will be considered under the notation proposed by Whiffen [13] for monosubstituted benzene and they are divided in two groups; the first one contains 24 phenyl vibrations which can be further subdivided from descriptions of their normal modes to vCC, out-of-plane C–H deformations, etc. The second group contains six vibrations which are dependent on the mass of the substituent, and are called X-sensitive vibrations, q, r, t, y, u and x (vide infra).

Spectra of the ligand and the complexes in the medium and low energy region are shown in Figs. 2 and 3, respectively.

IR data in the region $1700\text{--}200 \text{ cm}^{-1}$ and the most probable spectral assignment for the ligand and complexes are collected in Table 2; in the low energy region (below 500 cm^{-1}) we observe the most important differences between the spectra of the ligand and complexes. The general aspect of the spectra of the complexes is not much different which suggests that their structures are not much different.

3.2.1. The $1700\text{--}1300 \text{ cm}^{-1}$ region

This is the region where the aromatic ring stretching vibrations are found, Fig. 2. Concerning the phenyl group of the phenylhydrazine in both the ligand and the complex, the vibrational analysis starts regarding that benzene possesses three ring stretching vibrations at 1596 cm^{-1} (e_{2g}), 1486 cm^{-1} (e_{1u}) and 1310 cm^{-1} (b_{2u}) [14]. The degeneracy of the first two vibrations is lifted upon ring substitution, and the band at

Table 1
UV–VIS spectra in solid phase (nujol mull) and tentative assignment for bis(phenylhydrazine)-1,10-phenanthroline (L) and its metal complexes

Compound	Intraligand bands $\pi\text{--}\pi^*$	$n\text{--}\pi^*$ and CT bands	d–d bands
L	312	356 (sh), 404	
CoL	280, 330 (sh)	403	580
CuL	268		480, 870
ZnL	268, 345 (sh)	395	

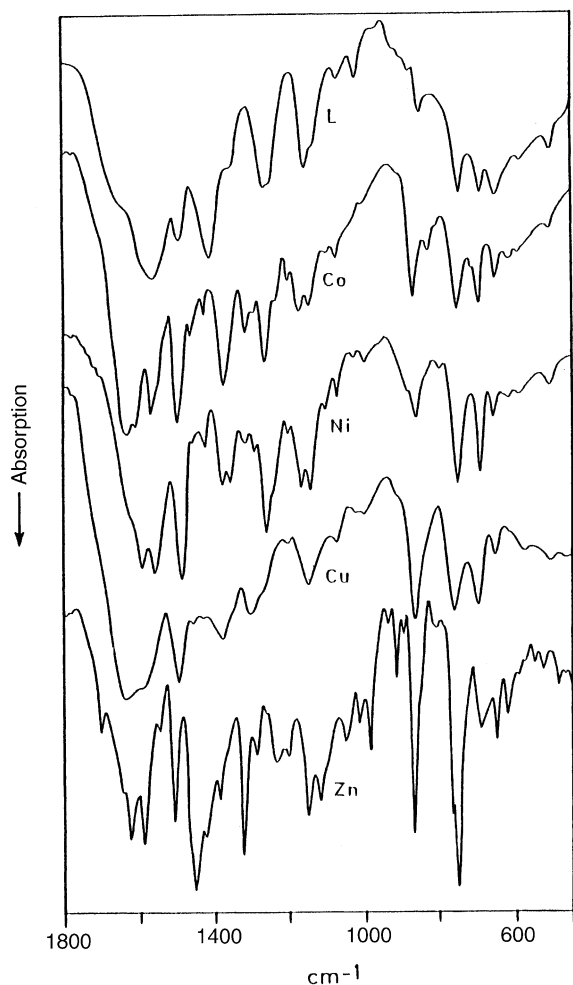


Fig. 2. Infrared spectra of bis(phenylhydrazine)-1,10-phenanthroline (L) and its metal complexes in the region 1800–450 cm^{-1} .

1596 cm^{-1} gives rise to the k and l bands (in the ranges 1589–1573 cm^{-1} and 1575–1567 cm^{-1} , respectively), whereas the band at 1486 cm^{-1} gives rise to the m and n bands. Ranges of these last bands have been set in monosubstituted benzenes of 1510–1480 cm^{-1} and 1470–1439 cm^{-1} , respectively [15]. The non-degenerate b_{2u} vibration, labelled o by Whiffen [13] remains relatively unaffected on substitution. The shoulder at 1592 cm^{-1} could be assigned to the k vibration. Meanwhile, at about 1546 cm^{-1} we can detect the presence of the l stretching vibration. Bands observed between 1600 and 1700 cm^{-1} in the ligand and complexes are assigned to νCN coming from the phenan-

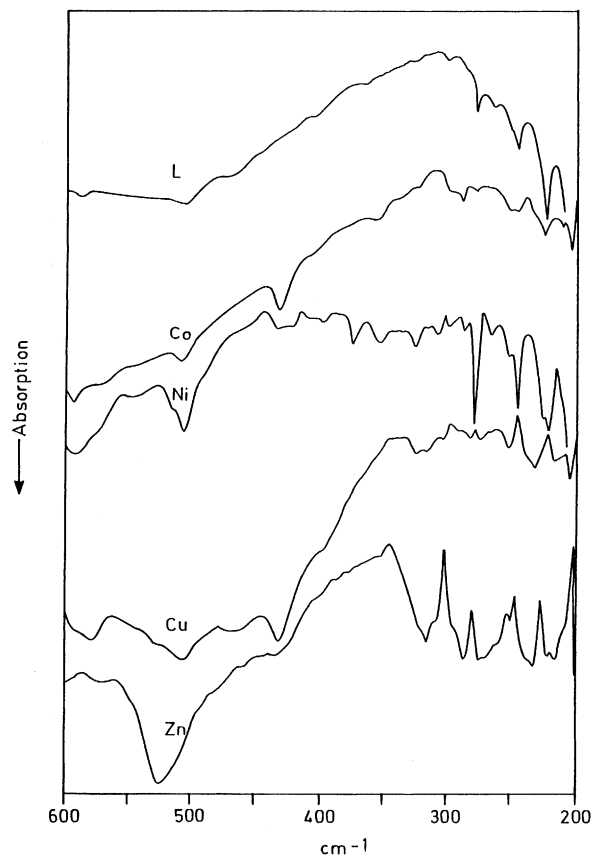


Fig. 3. Infrared spectra of bis(phenylhydrazine)-1,10-phenanthroline (L) and its metal complexes in the region 600–200 cm^{-1} .

throline moiety [16]. The band at 1567 cm^{-1} in the spectrum of the ligand is ascribed to a νCN mode of the azomethine fragment (vide infra).

At 1495 cm^{-1} is observed the m component of the phenyl ring stretching, while the very weak n component which should appear at about 1470 cm^{-1} is not observed in our spectra. As a consequence of the scissoring and wagging modes of the methylene groups we observe a significant difference between the spectra of the ligand and the complexes. Weak bands at about 1460 cm^{-1} in the complexes are easily recognizable as the CH_2 scissoring mode, while the wagging modes appears in the region of 1420 cm^{-1} [17]. The band at 1415 cm^{-1} is metal sensitive and is observed in the complexes at lower energy (about 1377 cm^{-1}). In this region, we also expect to observe νCN aromatic modes, which enhance the relative

Table 2

Observed infrared data (cm^{-1}) and the most probable vibrational assignment for bis(phenylhydrazine)-1,10-phenanthroline (L) and its Co(II), Ni(II), Cu(II) and Zn(II) complexes^a

L	Co	Ni	Cu	Zn	Assignment
1650 sh	1629 s	1626 sh	1642 bs	1647 s 1623 s	vCC phenanthroline + vCN phenanthroline
1592 sh	1606 sh	1600 s	1600 sh	1588 s	vCC phenyl
1567 s	1564 s	1563 s	1566 sh		vCN azomethine
	1546 sh	1546 sh		1546 w	
1495 ms	1493 s	1493 s	1496 ms	1506 s	vCC phenyl
	1461 w	1457 vw	1457 vw	1452 ds	CH ₂ scissoring
	1424 w	1424 wm	1431 vvw	1421 sh	CH ₂ wagging + vCN aromatic
1415 sb	1373 s	1378 md	1377 ms	1385 w	metal sens.
1358 w		1357 m	1360 sh	1355 vvw	vCC aromatic
	1314 mw	1317 w	1302 mb	1321 s	vCC aromatic
	1293 vw	1294 w		1285 w	δ CH ring
1265 ds	1263 ms	1263 s	1260 sh		δ CH ring
1252	1233 vw	1240 sh	1268	1235 bm	
	1202 w	1205 w	1208 vw	1200 w	δ CH ring
1156 ds	1172 dm	1168 dms	1149 mb	1150 dms	δ CH ring
1134 sh	1146 w	1144 ms		1117 mb	
	?	1102 w			vNN
1069 w	1074 w	1073 w	1076 w	1049 m	δ CH ring + vPh-N + vCN
1021 m		1026 vw	1024 dw	1015 wm	ϕ breath.
		996 wb	1000 wb	985 m	δ NCC macrocycle ring
				940 w	
				917 m	CH ₂ rock + vCN
		888 sh		896 w	ρ CH
852 m	871 s	862 m	868 s	867 s	ρ CH + v ϕ N
	831 w			849 sh	
		801 vw		807 vwd	
				764 sh	
748 m	754 s	754 s	760 msb	748 vs	ρ CH + CH ₂ rock
	715 vw				
691 m	696 s	695 s	697 ms	691 mb	deformation NCCN + ρ CH
651 m	654 m	660 wm	653 mb	650 m	deformation NCCN
	619 w	619 vw		621 m	aromatic ring deformation
587 vw	594 vw	590 vw	575 vw	591 vvw	deformation NCCN
				574 vvw	
				548 vw	
510 vw	509 vw	508 w	510 vw	527 w	ρ CH ring
			469 bv		
	433 m	435 dw	433 m	433 m	macrocycle ring deformation
		423 w			$\chi\phi$
	358 vw	353 bw			macrocycle ring deformation
		325 m	326 dvw		macrocycle deformation + $\chi\phi$ + δ Ph-N
302 vw	291 wd	300 w			$\chi\phi$ + δ Ph-N
	291 ^b		283 m		vMN

^a Abbreviations: w, weak; vw, very weak; m, medium; mw, medium weak; s, strong; br, broad; sh, shoulder; shp, sharp; i.p., in-plane; o.p., out-of-plane; sens., sensitive; as, asymmetric; d, double; t, triple; χ , out-of-plane ring deformation.

^b Used twice.

band intensity. A band at about 1310 cm^{-1} can be assigned to the o stretching vibration of the aromatic ring, which is recognized to give rise to a weak band in the IR spectrum.

3.2.2. The $1300\text{--}1000\text{ cm}^{-1}$ region

Randle and Whiffen [18] showed that the five in-plane CH bending fundamentals a, b, c, d, and e occur in this region. Their infrared intensity is generally weak [19]. Bands c, a, and e are found in the ranges $1161\text{--}1150\text{ cm}^{-1}$, $1187\text{--}1175\text{ cm}^{-1}$, and $1275\text{--}1264\text{ cm}^{-1}$, respectively. Assignment of d, $1072\text{--}1064\text{ cm}^{-1}$, is more difficult owing to its weak intensity as well as to the close proximity of the highest X-sensitive (weak-medium) vibration q, a vibration with C–H in-plane bending contribution which also should involve the stretching of the Ph–hydrazinic bond. At about 1000 cm^{-1} it is expected to observe the totally symmetric ring *breathing* vibration (a_{1g}) of benzene [20], and the macrocycle ring deformation. The actual situation is that in substituted benzenes, this vibration is far from 1000 cm^{-1} . In fact, for monosubstituted benzenes, Varsanyi [21] placed it in the range $1100\text{--}1060\text{ cm}^{-1}$ for heavy substituents (mass attached atom greater than 25 amu) and in the range $830\text{--}620\text{ cm}^{-1}$ for light substituents. Further, these band should be coupled to the rocking modes of the close methylene groups. Also at about 1100 cm^{-1} should appear the totally symmetric mode $\nu(\text{N–N})$ of the hydrazine, which loose symmetry in phenylhydrazine and consequently, can be observed with poor intensity in the IR spectrum. Following our works in ethylenediamine complexes [22], bands at about 1070 cm^{-1} in ligand and complexes and the band observed at 917 cm^{-1} in the spectrum of the Zn complex, are assigned to stretching vibrations of the single CN bonds adjacent to the N–Ph fragment.

3.2.3. The $1000\text{--}700\text{ cm}^{-1}$ region

In this region, there occur five modes f, g, h, i and j, which are attributable to out-of-plane C–H deformations of the phenyl ring [13]. The f strong band falls in the range $758\text{--}731\text{ cm}^{-1}$. Bands g and i arise from the e_{1g} C–H deformation of benzene 849 cm^{-1} and occur in the ranges $864\text{--}843\text{ cm}^{-1}$ and $920\text{--}905\text{ cm}^{-1}$, respectively. We have assigned bands at about 860 cm^{-1} to other C–H out-of-plane bending of the phenyl groups along with that observed at about

750 cm^{-1} , while a medium doublet observed at about 920 cm^{-1} in the complexes can be ascribed to the CH_2 rocking mode.

3.2.4. The $700\text{--}450\text{ cm}^{-1}$ region

In the $706\text{--}691\text{ cm}^{-1}$ region appears the out-of-plane ring deformation mode labelled v by Whiffen [13] and derived from the inactive b_{2g} mode of benzene, as a group of intense bands in the infrared spectrum. Close to this mode lies the X-sensitive in-plane ring bending mode r, which involves appreciable Ph–hydrazine stretching, which presents weak intensity in the spectrum. Further, medium-weak IR bands at $630\text{--}605\text{ cm}^{-1}$ have been recognized as the in-plane ring deformation s [23,24] for monosubstituted benzenes, being at 606 cm^{-1} for benzene itself.

Near 500 cm^{-1} , it is observed a strong band of the free phenylhydrazine molecule. This band appears weak in phenanthroline as a consequence of the fusion of the rings. Between 550 and 450 cm^{-1} , we expect to observe phenyl out-of-plane deformations with influence of the Ph–N stretching.

3.2.5. The $450\text{--}100\text{ cm}^{-1}$ region

In this region have been reported most of the coordination ring vibrations directly related to the metal, see Fig. 3.

The complex formation is verified in this spectral region by the appearance of several bands. Bands at about 430 , 350 and 325 cm^{-1} only observed in the complexes are ascribed to metal sensitive vibrations; they are probably macrocycle ring deformations. The band at about 291 cm^{-1} in the spectrum of the Co complex is assigned to a νCoN mode following reported data on Schiff base complexes [25]. The band of the Ni complex at 435 cm^{-1} is ascribed to a νNiN mode following the assignment proposed in azabipiridyl and Schiff base Ni complexes [1,26]. Two bands were identified as νCuN modes in the spectrum of the Cu complex at 326 and 283 cm^{-1} ; this assignment is based on that proposed in a Schiff base Cu complex [27]. Data of azabipiridyl complexes [1], suggest that we should expect $\nu\text{Zn–N}$ modes between 320 and 275 cm^{-1} . The observed frequency shift to lower energy of the M–N bands at 291 and 283 cm^{-1} for the Co and Cu, is in agreement with the mass increasing.

Concerning the phenyl bands, in this region appears the w out-of-plane ring deformation. It is derived from

the e_{2u} torsional mode of benzene (404 cm^{-1}) and exhibit a very weak intensity in the infrared spectra. This absorption has been estimated from combination bands at about 400 cm^{-1} [14] for monosubstituted benzenes. The u X-sensitive mode, which is related essentially to the Ph–hydrazine bending, appears at about 330 cm^{-1} . Finally, at about 300 cm^{-1} , it is expected the x, X-sensitive mode, which is another out-of-plane ring deformation also with participation of the Ph–hydrazine bending. These bands are easily identified as giving rise to bands in both the infrared and Raman spectra, as is the case of the very weak band observed in all the spectra at about 300 cm^{-1} .

On this basis, bands under 300 cm^{-1} can be assigned to deformations of the coordinating site. Since we do not expect highly characteristic metal–ligand vibrations but rather simultaneous contributions of distinct normal modes, a detailed discussion of the assignment of those bands presented in this part of the spectra of both complexes under study would be too speculative at this stage of the work. In this sense, the assignment should be clarified by a normal coordinate analysis.

3.3. Macrocycle ring metal complexation

Several structural modifications of the macrocycle ring by complexation can be inferred from the spectral analysis and the proposed band assignment, Table 2. In particular, in the case of the Co, Ni and Cu complexes, the band at 587 cm^{-1} of the ligand assigned to the deformation mode of the $\text{NCH}_2\text{CH}_2\text{N}$ group and the bands at 651 and 691 cm^{-1} ascribed to the CCN deformation mode of the hydrazine fragment shift by complexation to lower and higher energy, respectively. The frequency shift to higher energy by complexation of the $\nu\phi\text{-N}$ mode ascribed to the band at 852 cm^{-1} indicates the participation of the hydrazinic N in the metal coordination. The frequency shift by complexation of the band at 1415 cm^{-1} assigned previously as metal sensitive, can be explained by a reorganization of the $\text{NCH}_2\text{CH}_2\text{N}$ fragment in the complexation process. Moreover, the aromatic CN mode is observed in the spectrum of the complexes at about 1424 cm^{-1} and in the ligand is observed at lower frequency. The azomethine CN stretching mode ascribed to the band

observed at 1567 cm^{-1} remains at about the same frequency in the spectrum of the complexes, which is expected for a non-coordinated nitrogen atom [25]; in fact, the metal coordination through this azomethinic N atom causes a shift to lower energy of the $\nu\text{C=N}$ mode. Vibrations of the CH_2 group, in particular the rocking ones (748 cm^{-1}) are very sensitive to the metal complexation which is probably due to slight conformational changes in the ethylene diamine fragment. This set of spectral modifications suggest an electronic energy redistribution by complexation and a modification of the hybridization of the macrocycle ring N atoms; the aromatic and azomethinic nitrogen atoms should not be exactly sp^2 , and those of the hydrazine moiety not exactly sp^3 . Similarity of the ligand and Zn complex spectra is probably due to the size of the Zn ion, which constrains this atom to adopt a position slightly out of the coordination site. A similar situation was observed in azabipiridyl metal complexes where the Zn^{2+} ion is out of the plane of the coordination site, which makes the surface macrocycle interaction negligible [1].

3.4. Normal coordinate analysis

The normal coordinate analysis for the complexes was performed by assuming a 35 atom planar model of C_{2v} symmetry (see Fig. 4), in which the phenyl groups were deleted for the sake of simplicity and taking into account that the presence of these substituents do not mainly affect the vibrations of the rest of the molecule

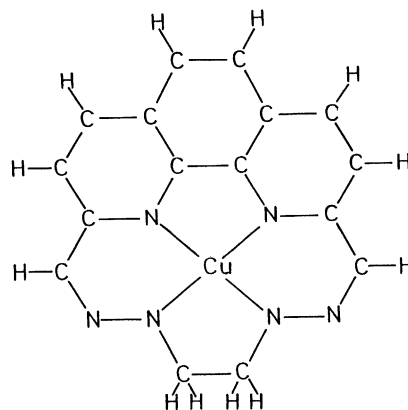


Fig. 4. Molecular model for the normal coordinate analysis of the complexes.

Table 3

Diagonal (F) and interaction (f) force constants (m dyn/Å), for Cu(II) bis(phenylhydrazine)-1,10-phenanthroline complex

Diagonal force constants				Interaction force constants	
Bonds	F	Torsion angles	F	Bond/bond	f
CC	6.100	NCCN	0.082	CC/CC _{ortho}	0.750
CN	6.100	CCNN	0.120	CC/CC _{meta}	-0.320
NN	5.700	NCuNN	0.100	CC/CC _{para}	0.190
CH	5.100			CC/CN	0.100
CuN	1.000			CN/NN	0.100
				CC/NN	0.200
Angles		Bond-plane angles		Bond/angle	
HCH	0.520	HCCC	0.300	CC/NCN	0.090
CCH	0.540			CC/CNC	0.120
CCC	1.000			CC/CCC	0.082
CNC	0.950				
CCN	0.960				
NCN	1.100				
CuNN	0.200				

[28]. The model has $3N-6$ degrees of internal freedom which classify as $\Gamma_{\text{vib}}=33A_1 + 17A_2 + 32B_1 + 17B_2$.

The secular equation was set up according to the Wilson's FG method [29]. In absence of X-ray diffraction studies for our complexes, the geometrical parameters needed to build the G matrix were taken from those obtained throughout the molecule built with the Hyperchem package and optimized by using a semiempirical INDO/1 method. The calculated parameters are similar to those currently observed for the ligands, that is bonds and angles for the phenanthroline moiety are typical of condensed fully conjugated systems with sp^2 hybridization (CC about 1.39 Å and CCC about 120°). In the case of the phenylhydrazine, part of the macrocycle and the complexes, the geometrical parameters indicate clearly the double and single bonds C-C (1.44 Å), C=N (1.32 Å), N-N (1.45 Å), while the angles are slightly bigger than in systems with sp^2 hybridization (132°). Concerning the coordination site, the calculated Cu-N bonds distances are about 2.0 Å; the phenanthroline and hydrazine NCuN angles are about 87°. We have performed only the calculation for the copper complex since the differences in structure between the complexes are minor; our experience point out that geometrical parameter changes up to 12% do not make difference in the calculated frequencies. The potential constants were determined in a Modified General Valence Force Field (MGVFF). Valence force constants are more

Table 4

Calculated frequencies (cm^{-1}) for a molecular model of the Cu(II) bis(phenylhydrazine)-1,10-phenanthroline complex, assuming a C_{2v} symmetry group

A_1	A_2	B_1	B_2
3064.6	3098.2	3064.6	3098.2
3057.9	955.2	3058.4	950.8
3049.4	939.8	3056.5	794.8
3047.7	777.7	3048.7	769.8
3014.0	351.7	3021.3	352.2
1792.4	128.4	1808.3	139.8
1640.2		1696.5	
1598.8		1584.8	
1465.3		1542.0	
1431.1		1504.3	
1362.1		1432.1	
1354.4		1346.1	
1336.3		1306.6	
1288.3		1245.3	
1255.9		1177.8	
1220.2		1170.3	
1163.4		968.7	
1112.1		914.0	
1031.6		771.0	
891.4		720.5	
746.0		671.8	
635.9		599.8	
535.6		551.7	
425.8		450.3	
396.5		397.1	
354.4		283.0	
224.5		241.4	
179.3			

transferable between similar structure than are Urey–Bradley force constants, specially for aromatic molecules where interactions between non-adjacent internal coordinates have to be included [30]. In fact, as was pointed out by Scherer and Overend [31] in the case of highly conjugated systems, the stretch–stretch interactions concerning the CC bonds in position *meta* and *para* should be considered important. The values of the internal force constants were transferred from analogous ligands and metal complexes [16,32–35] such as polyamine, phthalocyanine, porphyrin, 1,10-phenanthroline and porphyrinate metal complexes. The effects of the diagonal force constants (F) and those concerning the different types of interaction force constants (f) were examined systematically in trial and error calculations. The final force constants, which fit the observed frequencies, are listed in Table 3. Calculated frequencies are listed in Table 4. For aromatic $F(\text{CC})$, confident values should be higher than those reported with single CC bonds, so we have used values between 5 and 6.5 m dyn/Å, which can be

adjusted to fit the well-characterized frequency assigned to this normal mode. For ring bendings, it is observed that, in general, force constants involving the metal atom are smaller than the remaining ones. Initially, we have used in our calculations averaged values of those reported in the literature, [16,32–35].

3.5. IRRAS

Slight differences between the spectra of the copper complex dispersed in KBr and deposited onto the KBr monocrystal and the smooth copper surface were observed, see Fig. 5. The appearance of new bands at about 670 and 1050 cm^{-1} could be due to partial structural changes of the complex on both surfaces, while the general trends to shift to lower energy of all bands in the whole spectrum of the complex onto the surfaces is associated to a different crystallization rather than to a surface effect. So that, it can be inferred that there is no surface effect onto the structure of the complex. In order to infer about the organization and

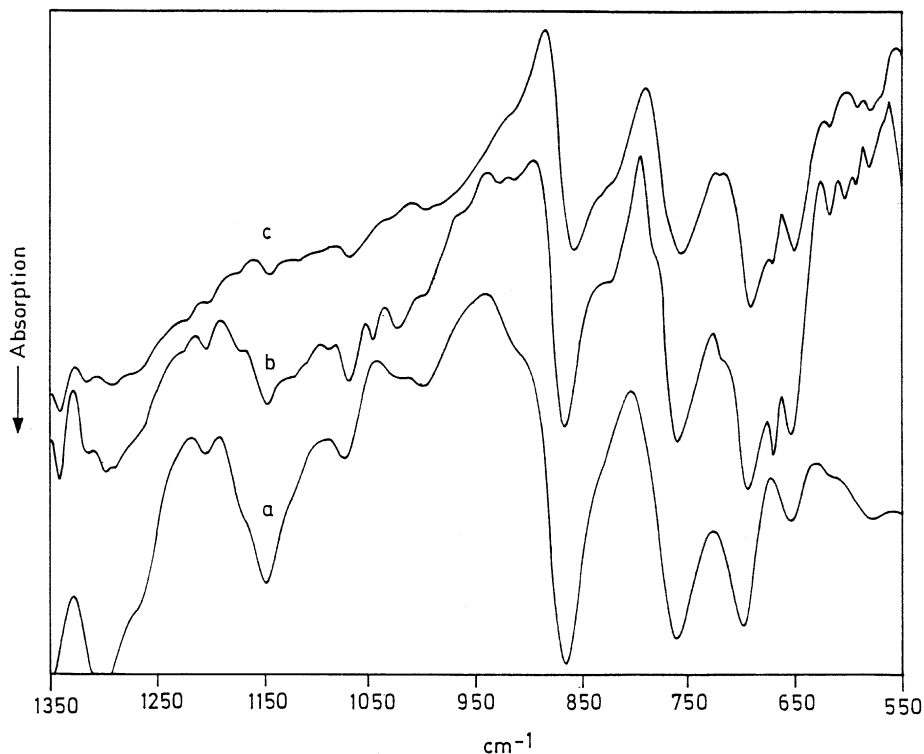


Fig. 5. Infrared spectrum of bis(phenylhydrazine)-1,10-phenanthroline Cu(II) complex: (a) dispersed in KBr; (b) deposited onto a KBr monocrystal; and (c) deposited onto a smooth copper surface.

the orientation of the different molecular fragments of the macrocycle complex onto the surface we have performed the IRRAS measurements in the range of 80–30° of the incident IR radiation angle, see Fig. 6.

According to Perry and Somorjai [36], the incident radiation angle of 90° corresponds to a beam parallel to the surface. For a KBr pellet, a random orientation of crystallites exists in the solid, and the electric field of the IR radiation, perpendicular to the pellet, will excite both in-plane and out-of-plane modes of the macrocycle. A solid film with a well-defined molecular organization could produce IR spectra with

different relative intensities for in-plane and out-of-plane modes. Therefore, molecules arranged face-on to the smooth copper surface would strongly absorb the incident IR radiation normal to the surface through its plane molecular modes [37].

The intensity ratios between the CH in-plane deformation bands at 1149 and 1208 cm^{-1} increases when passing from 80 to 30° which suggests that they belong to different and perpendicular aromatic groups. The ratio between intensities of the out-of-plane CH vibrations at 865 and 764 cm^{-1} , and 865 cm^{-1} and 692 cm^{-1} increases from 80 to 30° which confirms

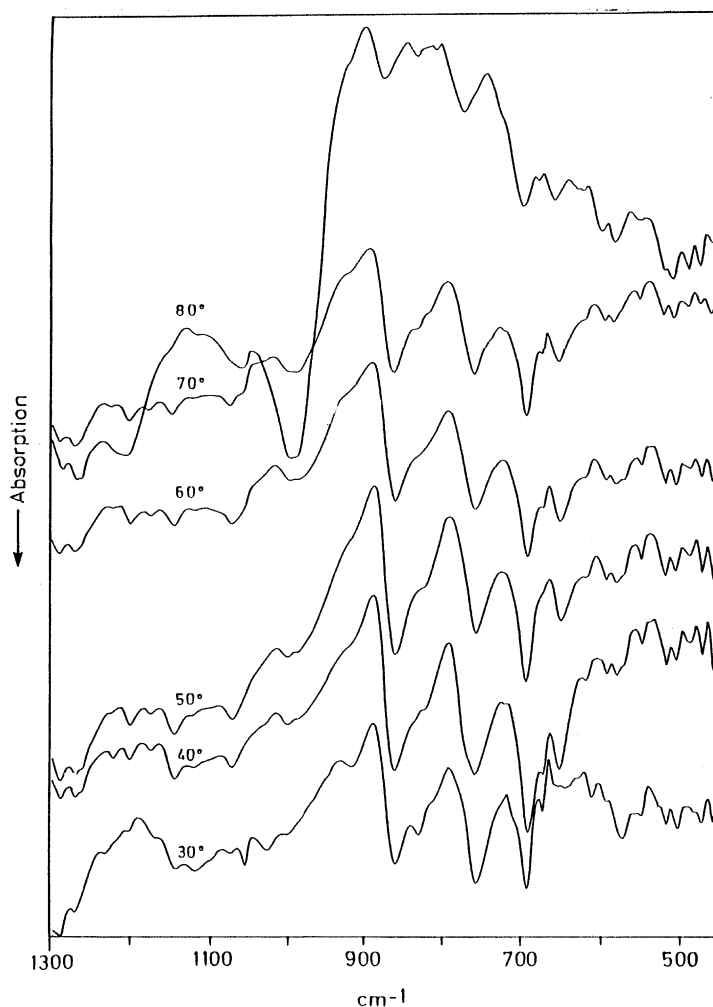


Fig. 6. Infrared reflection-absorption spectrum of bis(phenylhydrazine)-1,10-phenanthroline Cu(II) complex at different incident radiation angles.

the idea that these vibrations belong to different molecular fragments. A rather constant value is calculated for the ratio 764/692 which suggests that both modes belong to the same fragment. The ratio between the band at 764 cm^{-1} and the other out-of-plane CH mode at 654 cm^{-1} is rather constant which indicates that they belong to the same aromatic ring. At this stage of the discussion, it is difficult to assign to which of the aromatic fragments belong any of these bands. This situation prevents to infer about an eventual preferential organization and orientation of the molecule onto the surface.

3.6. SERS spectra

No surface enhanced Raman spectra were obtained. According to the SERS selection rules, the spectral profile of the adsorbate is strongly dependent on the orientation of the main molecular axes with respect to the surface [38]. Thus, SERS intensities would provide valuable information about the molecular orientation that the adsorbate adopts once adsorbed on the metal surface. For this reason, symmetry assignments are central to the discussion of molecular orientation of adsorbed species on the surface of colloidal Ag particles. If the molecules are oriented face-on the metal surface, with the nitrogen atoms face to the silver atoms, the main axis of the molecule and the normal to the surface are parallel; thus, the most symmetric vibrational modes, that derive their intensity from the zz component of the polarizability derivative tensor, α_{zz} will be the most intense at the surface plasmon resonance frequency and to the red of that frequency. Thus, the fact that we have not observed Raman enhancement by surface effect suggest that there is no adsorbate–substrate interaction and that the molecules are randomly oriented and organized on the surface. The electronic π system of macrocycles is not sterically available to interact with the metal surface, which is due to the non-planar structural characteristics of the coordination site and the stereochemistry of the phenyl substituents.

4. Conclusions

Infrared spectra indicate that the metal coordination imposes structural modifications of the macrocycle

ring and important electronic energy redistributions mainly around the coordination site. The metal coordination involves only the phenantroline and hydrazine nitrogen atoms. The normal coordinate analysis has produced a set of force constants which interpret quite well the experimental assignment. Reflection–absorption experiments have demonstrated to be useful to discriminate normal modes of different fragments of the macrocycles. IRRAS data of the copper complex onto the smooth copper allow us to conclude that the non-planar structure of the coordination site and the presence of phenyl groups disposed nearly perpendicular to the rest of the molecule sterically hindrance any interaction of the π electronic system with the smooth copper surface. These structural characteristics also are responsible of the fact that we have not observed SERS spectra.

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