

Vibrational study of the interaction of dinaphthalenic Ni(II) and Cu(II) azamacrocycle complexes methyl and phenyl substituted with different metal surfaces

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Abstract

The FT-IR and Raman spectra in the solid state, the reflection–absorption IR spectra (RAIRS) and the surface enhanced IR (SEIR) and surface enhanced Raman spectra (SERS) of the Ni(II) (*trans*-7,14-dimethyl-5,12,-diphenyl-1,4,8,11-tetra-aza-2,3-9,10-dinaphthyl-cyclotetradeca-5,7,12,14-tetraene) and Cu(II) (5,7,12,14-tetramethyl-1,4,8,11-tetra-aza-2,3-9,10-dinaphthyl-cyclotetradeca-5,7,12,14-tetraene) are reported. The RAIRS analysis and differences observed in the relative intensities of complexes deposited onto KBr and Cu surfaces suggest that the organisation of each macrocycle is different on both surfaces. SERS data allow to propose for both complexes an adsorbate–substrate interaction between the complex and the colloidal Ag surface. Complexes are oriented face-on to the surface being the number of Cu macrocycles oriented face-on to the surface larger than that of the Ni macrocycles. The organisation of the complexes on Au film is different to that found on Ag colloids and rather random. The phenyl groups avoid a better organisation of the Ni complex on the surface. SEIR data analysis of samples deposited on Au film suggests that the Ni complex is less organised than the Cu complex. The dynamic and energetic of the adsorbate–substrate interaction is interpreted by using a simple molecular model and INDO/1 calculations. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Porphyrins and naphthalocyanine compounds have been extensively investigated due to their interesting electrooptic properties and their application in the field of the solar energy conversion, laser electrophotography,

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photosensitisation, electrocatalysis and chemical sensing [1–3]. In the last 3 years we have used vibrational spectroscopy to study azamacrocycles and their metal complexes looking for the most appropriated molecular systems which efficiently interact with metal surfaces. For that purpose we have considered several combinations of structural variables such as changes in both the ring macrocycle and the π electronic size, as well as the number of the eventual metal co-ordinating nitrogen atoms. Our results allowed us to determine the effect that different metal surfaces have on their organisation, structure and orientation when adsorbed on a metal surface [4–10]. In this work a new variable consistent in the addition of substituent groups in an azomacrocyclic has been considered. Macrocycle complexes here considered are the Ni(II) (*trans*-7,14-dimethyl-5,12-diphenyl-1,4,8,11-tetra-aza-2,3-9,10-dinaphthyl-cyclotetradeca-5,7,12,14-tetraene) ($\text{NiN}_4\phi_2$) and Cu(II) (5,7,12,14-tetramethyl-1,4,8,11-tetra-aza-2,3-9,10-dinaphthyl-cyclotetradeca-5,7,12,14-tetraene) (CuN_4), see Fig. 1. To determine the influence that smooth copper, colloidal silver and gold island films have on the molecular structure, organisation and orientation of these complexes, we used infrared, reflection-absorption infrared (RAIRS), surface enhanced IR (SEIR), Raman

and surface enhanced Raman scattering (SERS) spectroscopies. In order to interpret the experimental results we performed a semiempirical INDO/1 calculation based on a molecular model for the adsorbate-substrate interaction.

2. Experimental

2.1. Materials

The synthesis and purification of the complexes have recently been described [11].

2.2. Preparation of the metal colloid and samples for SERS, RAIRS and SEIR

The silver colloid for the SERS measurements was prepared by following the method reported by Lee and Meisel by using citrate as reducing agent [12]. 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 microliters of the solutions were added to 500 μl of silver colloid. The liquid samples were placed into 1 mm optical path length capillaries, while the solid samples were placed in a brass holder.

Copper foils from Merck of 99.7% purity were used as smooth surfaces for the RAIRS 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} moles 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.

Gold island surfaces for the SERS and SEIRS experiments were obtained by sublimation of Au (10 nm thickness) onto a CaF_2 monocrystal. Samples dissolved in ethanol were dropped on the surface; then, the solvent was evaporated under vacuum. For the SEIR experiments the same sample was washed several times with ethanol and the spectrum was registered at each dilution.

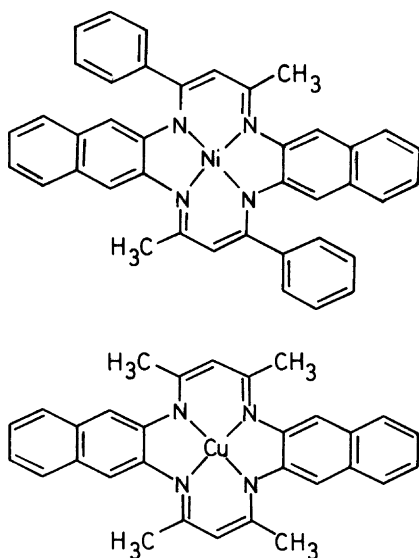


Fig. 1. Molecular structure of the Ni(II) and Cu(II) complexes.

2.3. Instrumental

2.3.1. Infrared spectra

The FT-IR spectra of KBr pellets in the region 4000–450 cm^{-1} were registered by using a Perkin-Elmer series 2000 apparatus. This spectrometer operates with a DTGS detector. Spectra were registered with the resolution of 4 cm^{-1} . Three hundred scans were accumulated. The FT-IR spectra in the region 600–200 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. RAIR spectra were recorded with a WeeMax variable angle accessory of Pike-Technologies mounted on the Perkin-Elmer optical bench. Different incident radiation angles, in the range 30–80° for samples deposited onto smooth copper surface were used. Transmission SEIR spectra were registered in a FT Bruker model IFS 66 spectrophotometer with a DTGS detector at room temperature. The spectral resolution was set at 8 cm^{-1} and 500 scans were registered for obtaining the final spectra.

2.3.2. Raman spectra

FT-Raman and FT-SERS spectra were obtained 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 50–100 mW in the case of the solid samples and 50–250 mW in the SERS. Up to 1000 scans were accumulated for the solid and solution samples.

3. Calculations

3.1. INDO/1 semiempirical calculation

For this calculation we have used a simple model in which the NiN_4 and CuN_4 structures without substituents interact with a smooth copper surface. The structure of the model compounds, Fig. 2, was optimised by using the semiempirical method INDO/1. In order to represent the adsorbate-smooth copper surface interaction, the metal surface was supposed to be a cluster composed by a minimum of five copper atoms representing a 001 face. Four of these atoms make a square and the fifth atom is located in the centre of the square at 2.55 Å from the corners, see Fig. 2. This distribution agrees quite well with experimental results [13] and it is similar to the metal surface characteristics of the model proposed by Lamoen et al. [14] for the computation of the structure, electronic and transport properties of perylenes monolayers adsorbed on the Au(111) surface. This surface model was also used in a similar study carried out for azabipiridyl [4], naphthalocyanine (Npc) and CuNpc macrocycles interacting with a copper surface [5].

The most relevant Wiberg index values for the isolated and the macrocycle-cluster interaction systems are displayed in Table 1. The stabilisation energy for the macrocycle-surface interaction models in Fig. 2 is –2078 and –2401 kJ/mol for the Cu and Ni complexes, respectively; the M–Cu distance is equal to 2.0 Å for both systems. These data and the corresponding Wiberg index values for the macrocycle ring suggest that the adsorbate-substrate interaction is

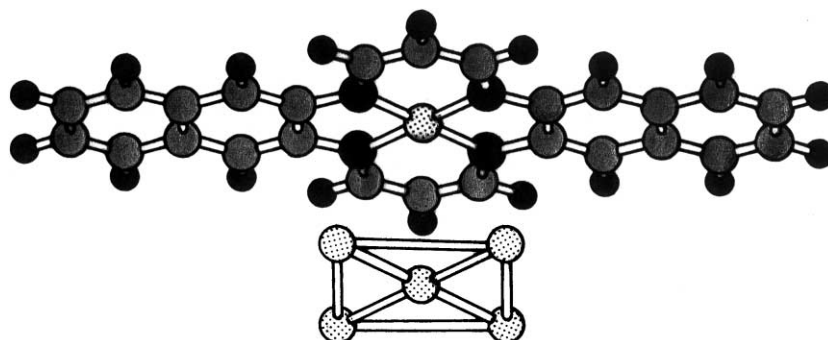


Fig. 2. Adsorbate-substrate interaction model for the RAIRS study.

Table 1
Most relevant Wiberg index values for different interactions

Cu–Cu _{surface}	0.252
Ni–Cu _{surface}	0.400
Cu–N on the surface	0.435
Cu–N free	0.387
Ni–N on the surface	0.286
Ni–N free	0.325

more significant in the case of the Ni complex. Since the Wiberg index values are not different for the rest of the macrocycle-copper surface systems in relation to the free macrocycles, it is possible to infer that a π electronic redistribution is produced by the interaction effect, mainly involving the co-ordination site of the adduct; the rest of the macrocycle is predicted to be structurally unaltered.

4. Results and discussion

4.1. Infrared

The spectral analysis and the IR band assignments were performed on the basis of several publications on macrocycles [3–9,15–28] and molecules whose structure is similar to the different fragments of the macrocycle such as phenanthroline derivatives [29–32] and Schiff bases and their metal complexes [33,34]. In this sense, we have also considered related ligands and complexes [35–37] as well as characteristic group frequencies [38–40]. In addition, we have attributed many of the bands by taking into account the spectral results shown below (Table 2).

IR spectra of the complexes (1800–500 cm^{-1}) are shown in Fig. 3. The spectral pattern of both complexes is different, but frequencies are very similar; this suggests that the structure of the macrocycles is not much different. The higher absorption intensity in the 1650–1550 cm^{-1} region in the case of the Ni complex, is probably due to the presence of the phenyl groups, while the small frequency shifts can be attributed to the different effect of the cation in each complex.

From these IR spectra and data obtained from the literature, we have attributed bands of both spectra as follows: bands at 1625 and 1519 cm^{-1} for the Ni complex and at 1626 and 1518 cm^{-1} for the Cu

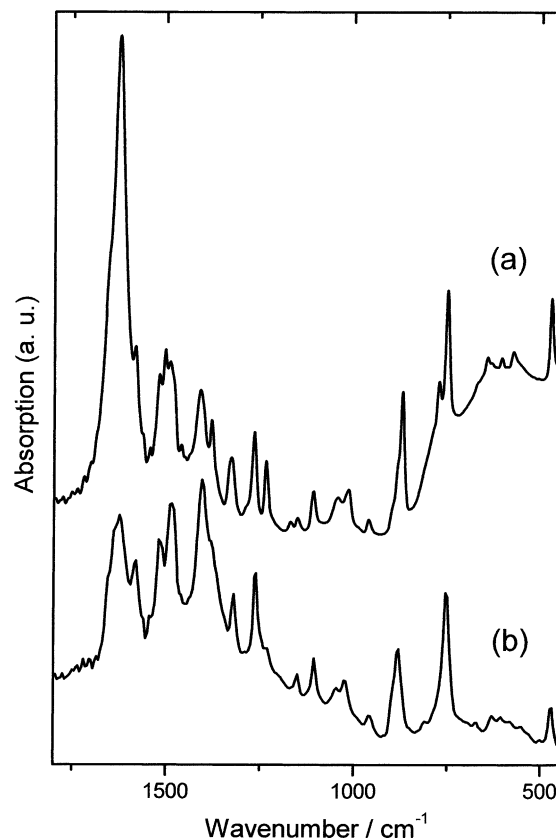


Fig. 3. FT-IR spectra of: (a) $\text{NiN}_4\phi_2$; (b) CuN_4 in KBr in the 1800–450 cm^{-1} range.

complex were assigned to νCN and νCC modes, normally coupled. Bands observed only in the spectrum of the Ni compound at 1504 and 1460 cm^{-1} should correspond to νCC of the phenyl groups since they are not observed in the IR of the Cu complex. Bands sensitive to the metal variation around 1491 and 1326 cm^{-1} are assigned to a νCN mode of the pyrrole moiety. Bands at 1409 and 1379 cm^{-1} in $\text{NiN}_4\phi_2$ and at 1404 and 1380 cm^{-1} in CuN_4 are assigned to a coupled vibration of the methyl and naphthyl fragments. Bands in both complexes near 1265 cm^{-1} are assigned to δCH modes (Table 2). The δCH modes of both naphthyl and phenyl residues are expected in the 1200–1050 cm^{-1} spectral region. These vibrations do not undergo a significant change in frequency in both complexes indicating that they correspond to C–H moieties far from the co-ordination site, since they are not influenced by vibrations of this site.

Table 2
Infrared IR, Raman and SERS frequencies (cm^{-1}) of $\text{NiN}_4\phi_2$ and CuN_4

$\text{NiN}_4\phi_2$				CuN_4				Assignment
IR	Raman	SERS ^a	SERS ^b	IR	Raman	SERS ^a	SERS ^b	
1625 s	1626 vw	1629 m		1626 s	1602 w	1635 m		νCN , νCC , $\nu\text{CC}\phi$
	1609 w		1610 s				1614 s	
1584 sh	1583 s	1591 m	1581 sh	1581 mw	1581w		1580 m	νCC , $\nu\text{CC}\phi$
1544 sh		1548 m		1543 sh		1552 w		νCC , $\nu\text{CC}\phi$
1519 w	1519 ms	1519 w	1515 w	1518 md	1519 w	1518 m	1517 m	νCC , νCN
1504 w								$\nu\text{CC}\phi$
1491 w	1480 s	1479 w	1478 vvw	1488 m	1480 m	1482 m	1480 w	νCC , νCN
1460 sh	1452 ms	1452 w	1451 mw					$\nu\text{CC}\phi$
1409 m		1427 vvw		1404 ms	1402 s	1418 w	1403 w	δCH_3 , ν_{naph}
1379 mw	1373 vs	1375 ms	1376 s	1380 w	1374 w	1393 ms	1375 s	δCH_3 , ν_{naph}
1326 m	1346 m	1349 vw		1321 m	1347 w	1351 vw	1349 w	δCH_3 , νCN
1265 ms	1268 s	1272 ms	1271 w	1262 s	1272 m	1275 ms	1272 ms	δCH , νCN
1234 m	1229 w	1234 w	1235 w				1234 m	δCH
1168 w	1199 w	1175 w						$\delta\text{CH}\phi$, νCC
1150 w	1146 wm	1146 vvw	1163 w	1151 mw	1159 wb		1155 w	δCH
1107 mw	1103 vw			1105 m		1103 w		δCH
1043 w				1046 w	1044 vvw		1054 w	ρCH_3 , δCH
1014 w	1017 ms	1023 m	1022 mw	1023 mw	1021 ms	1022 m	1021 m	δCH
961 w	961 vw	957 m	959 vw	958 w		949 md	962 w	ρCH_3 , δCH
870 s			886 vw	882 s			886 bv	$\rho\text{CH}\phi$
			827 vw			832 w	828 w	ρCH
						804 wm		
773 w								$\rho\text{CH}\phi$
750 m	758 ms	763 m	762 ms	753 s	755 m		764 m	ρCH
644 w	643 w	636 w	635 m	630 w			635 w	macr. def.
606 mw	603 w	603 m	603 m	607 mw	601 w	601 m	603 m	ρCH , macr. def.
577 w				577 w				macr. def.
				552 w		547 vw		$\text{N}-\text{CCH}_3-\text{C}$ def.
473 m	471 vw	470 s	469 m	475 wm		470 m	469 m	macr. def.
	444 vw	442 w		443 mw	444 m			Ring def.
409 w	385 m		388 vw	420 w			388 vw	macr. def.
347 m	343 m	343 w		342 m	342 w	343 m		macr. def.
	319 vvw		322 w	302 w		315 vw	322 w	metal sens.
				291 mw				νCuN
				272 mw				νCuN
				242 md				metal sens.
		227 vs		226 s		225 vs		Ag-citrate
227 w		218 m				217 wb		macr. def.
205 mw				206 w				macr. def.

Relative intensity (abbreviations); vs, very strong; s, strong; m, medium; w, weak; vw, very weak; vvw, very very weak; b, broad; d, double; sh, shoulder; ϕ , phenyl ring; def., deformation; macr., macrocycle; sens., sensitive; naph, naphthalene ring.

^a SERS in colloidal silver.

^b SERS on Au film.

On the contrary, the δCH naphthyl modes observed at 1014 cm^{-1} in Ni and at 1023 cm^{-1} , may correspond to C–H moieties closer to the metal co-ordination site, as they display a large frequency variation due to the steric effect caused by the different structural

characteristics of the methyl and phenyl substituents and the different metals in each complex.

Out-of-plane C–H bending of naphthyl and phenyl groups are expected in the region below 1000 cm^{-1} , while below 750 cm^{-1} deformation ring vibrations

are expected. In particular, bands at 644, 577 and 409 cm^{-1} in Ni and at 630, 552 and 420 cm^{-1} in the Cu complex, which show similar spectral pattern, are interesting because the difference in energy allow us to infer that the corresponding modes is close related to the co-ordination site. That is not the case for bands at 606, 473 and 347 cm^{-1} in Ni and at 607, 475 and 342 cm^{-1} in the Cu complex, so that these vibrations could correspond to ring modes far from the co-ordination site. Bands below 230 cm^{-1} are mainly due macrocycle deformations.

4.2. RAIRS

RAIRS is a technique which can be used to infer the organisation of adsorbed molecules on a surface in a first approximation. Thus, RAIRS spectra of $\text{NiN}_4\phi_2$ and CuN_4 complexes were registered in order to obtain more information about the molecular organisation on smooth copper. 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. On the contrary, a solid film with a well defined molecular organisation will produce IR spectra with different relative intensities for in-plane and out-of-plane modes. This is due to the fact that, even if unpolarised IR light is employed, the perpendicular component of the electromagnetic field on the surface is larger than the parallel one. In fact, for molecules arranged face-on to the surface out-of-plane modes are supposed to be enhanced in the spectrum [15].

Complexes were deposited onto a smooth copper surface and onto a KBr monocrystal. The spectra of both complexes were compared with the corresponding spectrum of each complex dispersed in KBr. No substantial frequency differences between them were observed, pointing out that the surface does not markedly influence the corresponding complex structure.

4.2.1. $\text{NiN}_4\phi_2$

For the sake of brevity we show in Fig. 4a the RAIRS spectrum scanned at 70° only for the $\text{NiN}_4\phi_2$ complex adsorbed on a smooth Cu surface. The RAIRS spectra were analysed in the 1400–700 cm^{-1} region, since the bands corresponding to in-plane and out-of-plane C–H deformations, which are very important for understanding the adsorbate orientation, usually appear in

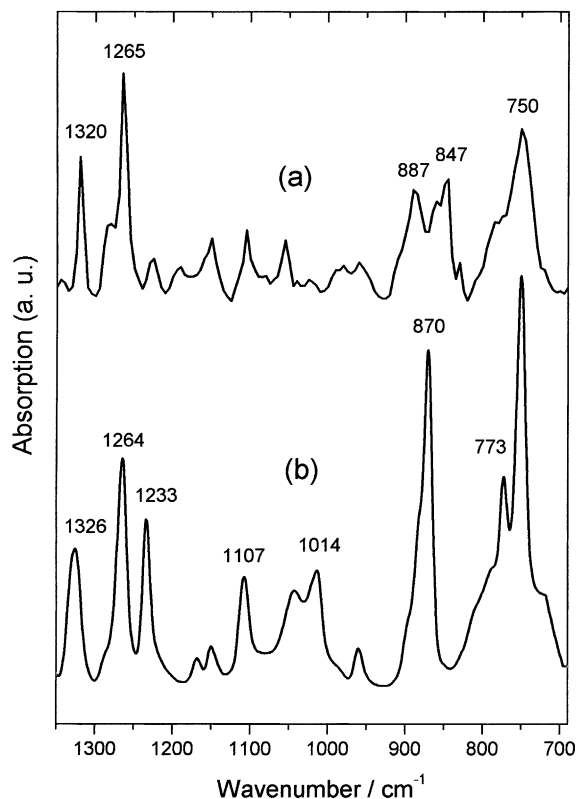


Fig. 4. Reflection-absorption IR spectra of $\text{NiN}_4\phi_2$ adsorbed on smooth Cu surface at 70° of the incident IR radiation (a); IR spectrum of the same complex in KBr (b). These spectra were baseline corrected for a better comparison.

this region. This spectrum is compared to that of the same complex in KBr (Fig. 4b). By taking the band at 1265 cm^{-1} as a reference, an intensity decrease of the absorption bands appearing at 1233 cm^{-1} and those falling in the 1200–1000 cm^{-1} region is observed. Since they may correspond to δCH motions of the naphthalene fragment of the macrocycle, we deduced a parallel orientation of these groups with respect to the metal surface.

Below 1000 cm^{-1} intense bands are observed at 887, 847 and 750 cm^{-1} in the RAIRS spectrum attributed to the ρCH motions of the naphthyl moiety, which are intensified due to their perpendicular orientation supposing a parallel orientation of these residues with respect to the surface. In contrast, the band at 870 and 773 cm^{-1} , are markedly decreased in the RAIRS. These are assigned to phenyl ρCH motions since they

are only observed in the Ni complex, thus their intensity decrease in the RAIRS suggests a perpendicular position of phenyl rings in the macrocycle complex, as we will also confirm from the analysis of SERS and SEIR spectra.

4.2.2. CuN_4

The RAIRS spectra registered for this complex follow a similar behaviour as compared to the Ni complex. The bands appearing in the 1200–1000 cm^{-1} region are relatively weakened, thus meaning that the naphthyl moiety adopts a parallel orientation on the surface. However, bands below 1000 cm^{-1} display a rather random intensity variation at different angles. This result suggests that these modes are highly coupled to other vibrational modes, thus avoiding to infer about the molecular organisation onto the surface.

4.3. SERS

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 [41]. Thus, SERS intensities would provide valuable information about the molecular orientation adopted by the adsorbate 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 C_2 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 polarisability derivative tensor α_{zz} will be the most intense at the surface plasmon resonance frequency and to the red of that frequency.

Figs. 5 and 6 display the Raman spectra of the solid and SERS in colloidal silver and on a Au film for both complexes.

4.3.1. $NiN_4\phi_2$

The SERS spectrum of this complex on Ag colloid in Fig. 5b displays a marked enhancement of bands at 471, 602 and 640 cm^{-1} . These bands are tentatively assigned to out-of-plane modes of the naphthyl moieties. In addition, bands attributed to in-plane

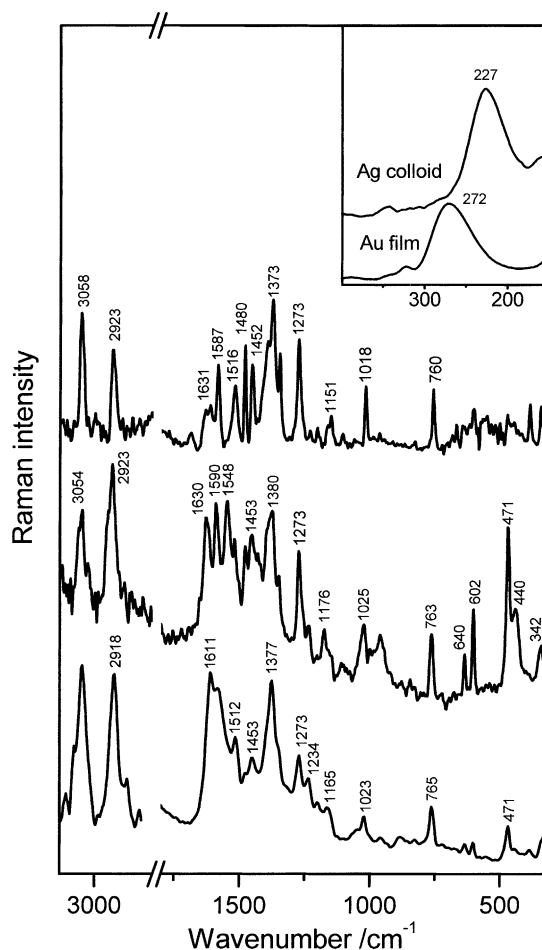


Fig. 5. Raman spectrum of $NiN_4\phi_2$: (a) in the solid; (b) SERS in colloidal silver; (c) SERS on Au film. Asterisks represents bands due to ethanol. The inset figure corresponds to the b and c ones amplified in the 100–400 cm^{-1} region.

vibrations of the naphthyl moiety at 1273, 1380, 1480 and 1514 cm^{-1} undergo a relative intensity decrease. All the above results suggest that the coordination plane of the complex is face-on oriented on the metal. On the other hand, the observation of an enhancement in bands at 1176 and 1237 cm^{-1} , attributed to in-plane δCH phenyl modes and at 1453, 1548, 1590 and 1630 cm^{-1} attributable to the νCC of the phenyl substituents or to modes in which this group is involved, suggests the perpendicular orientation of these groups with respect to the metal. This orientation is connected to the existence of a relatively intense band at 3054 cm^{-1} due to νCH modes of

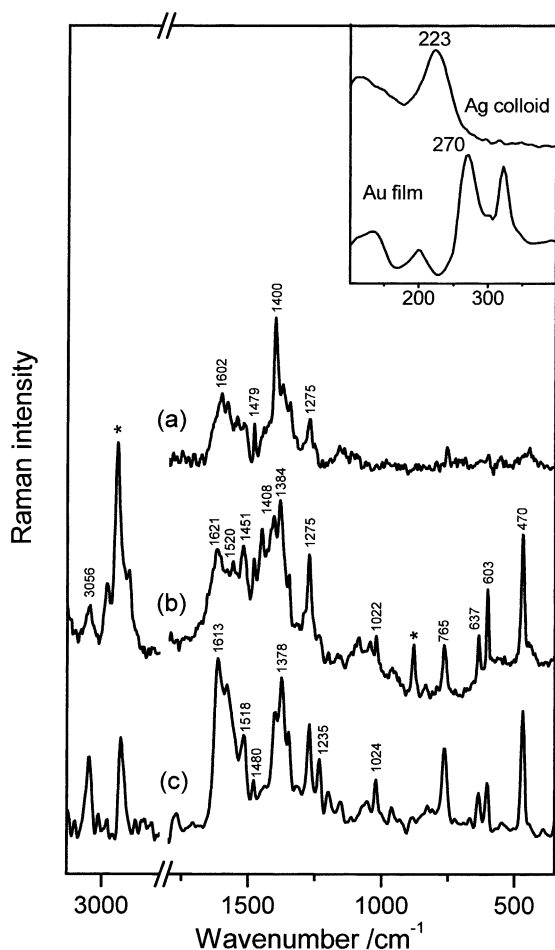


Fig. 6. Raman spectrum of CuN_4 : (a) in the solid; (b) SERS in colloidal silver; (c) SERS on Au film. Asterisks represents bands due to ethanol. The inset figure corresponds to the b and c ones amplified in the $100\text{--}400\text{ cm}^{-1}$ region.

phenyl group. The frequency shifts observed for some bands indicate the existence of an interaction between the complex and the metal surface. This is corroborated by the presence of an intense band at 227 cm^{-1} , that we tentatively assign to $\nu_{\text{Ag-N}}$ motions.

The SERS spectrum registered on Au film (Fig. 5c) is different to that obtained on Ag colloid. The out-of-plane bands of the naphthyl group in the $400\text{--}700\text{ cm}^{-1}$ region are weaker, while the naphthyl in-plane δCH bands at 1023 and 1165 cm^{-1} and the naphthyl ν_{CC} modes appearing at 1377 , 1512 and 1611 cm^{-1} , increase their intensities markedly. This increase is also extensive to the ν_{CH} modes at

3054 cm^{-1} . All these results indicate that the organisation of the Ni complex on Au changes with respect to that found on Ag colloids. In fact, on Au film it is not possible to conclude about a parallel or perpendicular orientation of the complex on the metal.

4.3.2. CuN_4

The SERS spectrum on Ag colloid (Fig. 6b) indicates that the complex adopts a face-on orientation on the metal as deduced also for the Ni complex; this is inferred from the intensification of the naphthyl out-of-plane bands at 471 , 602 and 637 cm^{-1} . The close position of these bands in relation to the Ni complex indicates a similar structure of the macrocycle when adsorbed on Ag, irrespective of the nature of the coordination metal. This result is also similar to that obtained by us for azabipyridil macrocycle complexes [42]. The absence of phenyl groups in the Cu complex explains the fact that the spectrum shows a marked difference in the $1450\text{--}1650\text{ cm}^{-1}$ region, where the corresponding in-plane bands appear. This orientation also accounts for the relative intensity decrease of the ν_{CH} band at 3056 cm^{-1} . In fact this band in the Cu complex corresponds to the ν_{CH} modes of the naphthyl moieties which are oriented parallel to the metal surface. The interaction of the macrocycle with the Ag surface is also deduced from the frequency shifts of some bands mainly those corresponding to the pyrrole moieties, which are the fragment through which the macrocycle-surface interaction takes place. The presence of the band at 224 cm^{-1} corroborates this interaction.

On Au film (Fig. 6c) a marked intensification of the in-plane modes of the $1500\text{--}1650\text{ cm}^{-1}$ region is also observed along with a relative increase of the band at 3056 cm^{-1} . However, we observe prominent bands at 470 , 603 and 637 cm^{-1} , which suggests the existence of face-on oriented macrocycles. The simultaneous observation of both out-of-plane and in-plane intense modes on the Au film is probably an effect of the existence of a random orientation of the molecules on this metal.

4.3.3. Comparison between SERS of Ni and Cu complexes on Ag and Au surfaces

The molecular organisation degree can be inferred from an intensity ratio of in an out-of-plane modes; in the case of the Ni complex adsorbed on Au film

(Fig. 5c) the 1611/471 ratio resulted higher than the 1613/470 ratio calculated for the Cu complex on the same surface (Fig. 6c). This is interpreted in terms that most of the Cu macrocycles are oriented face-on to the Au. This fact is attributed to the existence of phenyl groups in the Ni complex, which probably avoid in a large extent the organisation of the macrocycles on the metal surface. According to this interpretation, it is confirmed that the complexes are better organised on the Ag surface, since the ratios between in-plane and out-of-plane modes is maintained for both complexes (Figs. 5b and 6b). This idea is confirmed in a previous work where we have observed spectral differences when using different metallic surfaces [43].

We believe that a different adsorbate organisation must be expected on Ag colloid and on Au film, as a diffusion of the molecule from the bulk to the interface occurs in the first case. This process implies a solubilisation of the compound in the aqueous medium, then a diffusion of the molecule to reach the surface and finally its adsorption. This adsorption mechanism should give rise to a better organisation of the adsorbate on the metal surface since the diffusion step controls the deposition rate. On the contrary, in the case of the Au island film, the compound is directly deposited on the metal surface and practically constrained to adopt simultaneously the best orientation for all the molecules. Under such conditions is more probable that the adsorbate adopts a disordered orientation in the Au film. These effects strongly depend on the nature of the adsorbate. We have demonstrated that the organisation is also possible on Au film, but in the case of macrocycles with an extended π -electron system [10,42,43].

4.4. SEIR

SEIR spectra of the complexes deposited on a Au film are displayed in Fig. 7 together to those of the complexes deposited on neat CaF₂. In the Ni complex (Fig. 7a–c) the most important feature is the remarkable intensity decrease of the band at 1611 cm⁻¹, which undergoes a strong up shift to 1629 cm⁻¹. The rest of bands remains more or less at the same frequency and height with the exception of that at 1482 cm⁻¹, which shifts downward. In the case of the Cu complex (Fig. 7d–f) a marked decrease of bands at 1404, 1515, 1581 and 1624 cm⁻¹ is also noted, the last

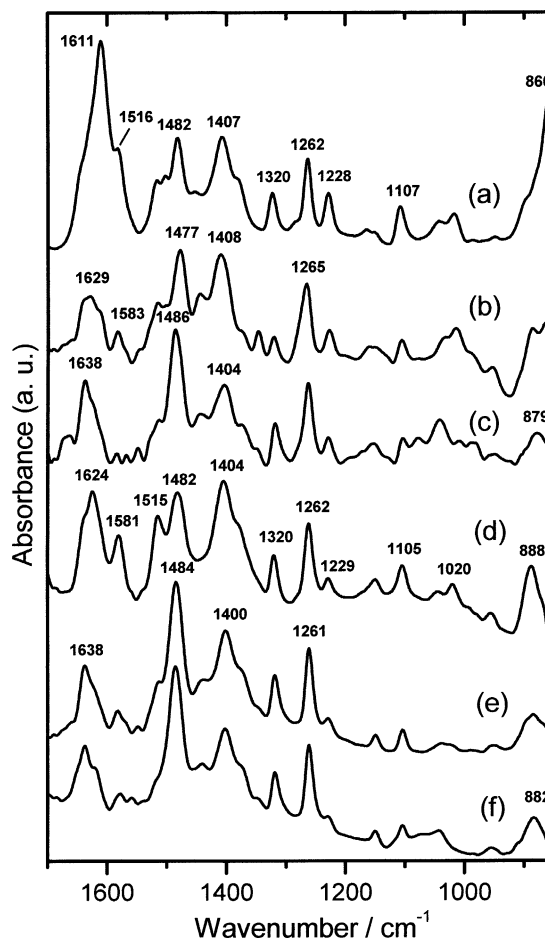


Fig. 7. (a) Infrared spectrum of Ni₄φ₂ deposited on CaF₂; (b and c) SEIRA spectra of Ni₄φ₂ on Au film before and after washing with ethanol, respectively. (d) Infrared spectrum of CuN₄ deposited on CaF₂; (e) and (f) SEIRA spectra of CuN₄ on Au film before and after washing with ethanol, respectively.

appearing at a higher frequency (1638 cm⁻¹). However, the other bands remains at more or less the same position and relative height. The intensity decrease of bands at 1228/1229, 1107/1105 and 860 cm⁻¹ observed in the SEIR spectra of both complexes is again related to the parallel orientation of naphthyl groups in relation to the metal surface.

It is interesting the effect of the dilution with ethanol on the above SEIR sample. This effect is more important in the case of the Ni complex: a relative decrease is observed for the 1408 cm⁻¹ band, which downward shifts to 1404 cm⁻¹, whilst the band at

1629 cm^{-1} shifts to 1638 cm^{-1} , and that at 1583 cm^{-1} almost disappear. In contrast, the SEIR of Cu complex does not undergo a significant change except for the band at 1580 cm^{-1} .

The different behaviour of both complexes as concerns the SEIR spectra before and after washing the sample with ethanol reflects again the fact that the Ni complex is less organised on the Au in relation to the Cu one, as we also deduced from the SERS spectra. The dilution lead to the removing of those molecules that are physisorbed onto the metal, i.e. that are weakly linked to the surface, remaining attached only the chemically adsorbed ones. The lower organisation of the Ni complex is attributed to the presence of a phenyl group in the ligand. In the case of the Cu complex the amount of chemisorbed adsorbates is significantly higher, as deduced from the similar SEIR spectra before and after washing the sample. Hence there is a good agreement between SERS and SEIR results.

The profile of the SEIR spectra obtained for both complexes after washing is very similar (Fig. 7c and f), thus indicating a similar structure of both complexes on the Au film. The small changes observed between the IR spectra of solid films and the SEIR are indicative of a low organisation degree in the Au film, since the molecules seem to be randomly orientated as in the case of the solid film. Nevertheless, the interaction of the metal with the macrocycles is demonstrated by the shifts that undergo the bands appearing above 1400 cm^{-1} and mainly those falling above 1600 cm^{-1} . This is consistent with an interaction of the macrocycles with the metal via the tetra-aza moiety, directly linked to the metal cation.

5. Conclusions

The RAIRS analysis and differences observed in the relative intensities of complexes deposited onto KBr and Cu surfaces suggest that the organisation of each macrocycle is different on both surfaces; the structure of each complex is not markedly influenced by surface effect and the phenyl substituent groups in the Ni complex are oriented perpendicular to the co-ordination site. SERS data allow to propose for both complexes an adsorbate–substrate interaction between the complex and the colloidal Ag surface. From this study

it is deduced that the co-ordination plane of the complexes is oriented face-on to the surface and the number of Cu macrocycles oriented face-on to the surface is larger than that of the Ni macrocycles. The organisation of the complexes on Au film is different to that found on Ag colloids and rather random. Complexes are better organised on the Ag surface. Phenyl groups hindrance a better organisation of the Ni complex on the surface. SEIR data analysis of samples deposited on Au film also suggests that the Ni complex is less organised than the Cu complex. The spectra of the chemisorbed molecules corresponding to the first layer of both complexes are very similar suggesting a similar structure on the Au surface. The INDO/1 semiempirical calculation performed for non-substituted macrocycles predicts a weak adsorbate–metal interaction occurring at 2.0 Å distance, thus confirming the steric effect of the substituents.

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