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Supramolecular compounds of azo dyes derived from 1-phenylazo-2-naphthol and their nickel and copper complexes

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Supramolecular compounds of azo dyes derived from 1-phenylazo-2-naphthol and their nickel and copper complexes

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In this study, experimental techniques including Raman, infrared and X-ray crystal diffraction, as well as quantum chemistry calculations, are used to investigate two new azo dyes supramolecular complexes: 1-phenylazo-2-naphthol (Sudan I) with nickel(II) ion and 1-(2,4-xylylazo)-2-naphthol (Sudan II) with copper(II) ion. The crystallographic structures have been solved for bis-1-(pheny-1-azo)-2-naphtholatenickel(II) and bis-1-(2,4-xylylazo)-2-naphtholatecopper(II) complexes, revealing the presence of supramolecular interactions, such as the centroid–centroid π -stacking interactions and CH $\cdots \pi$ hydrogen interactions. These weak intermolecular interactions appear to play an important role on the crystal structure stability for both compounds. Density functional theory calculations at B3LYP/6-311++G(d,p) level were performed in order to help understanding such molecular interactions and to assign the vibrational spectra. The experimental and theoretical data have allowed the analysis of the packing forces, revealing charge accumulation at key molecular regions.

Keywords: azo dyes; metal complexes; supramolecular chemistry; Raman spectroscopy

Introduction

Azo compounds belong to a very important class of chemicals receiving attention by the scientific media, as they are highly coloured and can be used as dyes and pigments, even in the food industry (1). The structures of the azo dyes are of specific interest to the dyes and pigments industries, as many of the materials commercially significant properties (solubility, habit, stability and even colours) are dependent on or are influenced by their solid-state structures (2). Recently, azo metal chelates have also attracted increasing attention due to their interesting electronic and geometrical features in connection with their application for molecular memory storage, nonlinear optical elements and printing systems (3-5). Another advantage for complexes involving azo dyes and transition metal ions is the possibility to obtain new compounds with biological activity (6, 7). Transition metals have also been used in the treatment of several diseases, as metal complexes which are capable of cleaving DNA under physiological conditions are of interest in the development of metal-based anticancer agents (8, 9). This is an impetus for inorganic chemists to develop innovative strategies for the preparation of more effective, target-specific and preferably non-covalently bound anticancer drugs (10, 11).

Crystallographic structures of azo dyes have been described in the literature (12-17), but most of the work focuses on the tautomeric equilibrium between azo and hydrazo forms, mainly for the azo dyes derived from 1-phenylazo-2-naphtol (Scheme 1) where the structural difference is on the substituent bonded to the phenyl or naphthol rings. However, the discussions about supramolecular interactions are rarely mentioned. The supramolecular packaging of this class of compounds is completely different when the functional groups are changed, and weak interactions of the π -stack type can be observed. Several inorganic synthesis (3-5, 18) have been carried out aiming to produce more intense dyes using transition metal ions; however, no crystallographic structures of such azo dyes derived from 1-phenylazo-2-naphthol have been described so far.

Supramolecular interactions of aromatic systems have attracted the attention of many researchers in recent years (19-23). The supramolecular arrangement of azo dyes are based on non-covalent supramolecular interactions, which keep packaged the whole system, and also has raised particular interest in this chemical system. Azo dyes derived from 1-phenylazo-2-naphthol system have two aromatic rings which are good candidates to generate interactions such

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Scheme 1. Tautomeric equilibrium between azo and hydrazo form for Sudan I ($R_1 = R_2 = H$) and Sudan II ($R_1 = R_2 = CH_3$).

as π -stacking and are responsible for different arrangements of the crystalline system (24). However, the formation of a metallic complex with azo dyes can provide other arrangements presenting no crystalline analogy with the isolated ligand; in this sense, there are few studies in literature reporting the supramolecular arrangement of metallic complexes involving azo dyes (2, 15, 25).

In the present study, we report the experimental and theoretical investigation using Raman, infrared spectroscopy and X-ray diffraction of bis-1-phenylazo-2-naphtholatenickel(II) and bis-1-(2,4-xylylazo)-2-naphtholatecopper(II) complexes, aiming to get insight on the main driving forces responsible for the supramolecular interactions in such compounds.

Experimental

Materials and experimental methods

All azo-compounds were purchased from Aldrich and used without any further treatment; the solvents used were spectroscopic grade. The synthesis of bis-1-(phenylazo)-2naphtholatenickel(II) was carried out by slow addition of 1 mmol of 1-phenyl-azo-2-naphthol dissolved in methanol 30 mL to 1 mmol of Na₂CO₃ under stirring and then to 1 mmol of nickel chloride hexahydrate dissolved in deionised water. The reaction was refluxed at 60°C for ca. 8 h, yielding an orange solid which was filtered and washed several times with cold deionised water; after drying it was isolated in 67% yielding. Good crystals for X-ray analysis were obtained from slow evaporation of a toluene solution in a test tube on the bench at room temperature. The procedure to obtain bis-1-(2,4-xylylazo)-2-naphtholatecopper(II) was similar: 1 mmol of 1-(2,4-xylylazo)-2-naphthol was solubilised in 30 mL of methanol and 1 mmol of Na₂CO₃ slowly added with stirring, followed by 1 mmol of CuCl₂. The resulting solution was refluxed for 8 h whereupon a red precipitate was isolated by filtration and washed with cold water to yield 68% of the desired product. The same procedure for obtaining good crystals for X-ray analysis described above was done for the copper complex. The melting points for both complexes were above 350°C, and the molecular formulae obtained by X-ray diffraction were C₃₂H₂₂NiN₄O₂ and C₃₆H₃₀CuN₄O₂.

Raman spectra were recorded in the solid phase using a LabRAM, Micro-Raman Spectrometer Jobin Yvon/Horiba

equipped with CCD detector thermoelectronically refrigerated $(-70^{\circ}C)$, 80 × objective having 0.75 numerical aperture, 1800 grooves/mm grating and 300 µm confocal aperture. The samples were excited by a 785.5-nm diode laser with 60 S exposition time and five accumulations for each spectral window. Infrared spectra were recorded in a Bomem FTIR MB102 spectrometer in the $1800-360 \text{ cm}^{-1}$ region, of the sample supported in a KBr pellet, with 4 cm^{-1} of spectral resolution, and 128 scans. Single-crystal X-ray data were collected using an Oxford Gemini A (Ultra Diffactometer Agilent, CA, USA) with μ (Cu K) ($\lambda = 3.959$ Å) at temperature 150K for Sudan I and Sudan II complexes. Data collection, reduction and cell refinement were performed by CrysAlis RED, Oxford diffraction Ltd (26), Version 1.171.32.38. The structures were determined and refined using SHELXL-97 (27). The empirical isotropic extinction parameter x was refined according to the method previously described by Larson (28), and a Multiscan absorption correction was applied (29). The structures were drawn by ORTEP-3 for Windows (30) and Mercury (31) programs.

Calculations

The structures for the metal complexes were fully optimised in gas phase at B3LYP (32, 33) level using the 6-311++G(d,p) (34) triple-zeta basis set with inclusion of diffuse and polarisation functions at heavy and hydrogen atoms (the optimised structures are shown in Figure S1 as Supplementary Material). All of the geometries were considered as neutral species with the multiplicities set to singlet for the nickel complex and doublet for the copper complex. The final geometries were characterised as minima on the potential energy surface through harmonic frequencies calculation (all frequencies found real). The infrared (IR) and Raman intensities were also calculated and the band spectra simulated by fitting a Lorentzian-type function (35), with parameters set to $10 \,\mathrm{cm}^{-1}$ for the average width of the peaks at half height and 2×10^{-6} mol cm⁻³ for sample concentration. The spectra for all species were then assigned according to the normal-mode analysis. Frequency scaling was not needed as the predicted values and the spectra profiles were in satisfactory agreement with experimental ones, allowing unambiguous band assign-



Figure 1. (Colour online) Thermal ellipsoid representation of (a) $C_{36}H_{30}NiN_4O_2$ and (b) $C_{36}H_{30}CuN_4O_2$ showing the atom labelling scheme. The thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms are drawn to an arbitrary scale.

ments. In order to analyse the intermolecular interactions in the solid state, the unit cell containing four repeating molecular units were partially optimised with only hydrogen positions set freely for optimisation. The molecular electrostatic potentials (MEP) (36, 37) for the distinct complexes were generated using the CUBEGEN utility available in the Gaussian 09 package. The MEP was mapped onto 0.02 e/bohr^3 electron density surface. All calculations were carried out with Gaussian 09 (38) program as installed in the computers of the Núcleo de Estudos em Química Computacional.

Results and discussion

X-ray diffraction measurements for the coordination complexes

Figure 1(a) shows the thermal ellipsoid representation of the new structure for Sudan I nickel complex; this nickel complex was crystallised in the triclinic system, space

group P - 1 with four molecules in the unit cell. The repeating unit of this structure occurs along its vertices and the centre of the unit cell, clearly showing the existence of an inversion centre. The crystallographic structure presents a central unit of the complex pointing to other four units, each one at the corners of a parallelogram, which also presents the nickel atoms exactly over the axis of the same parallelogram (Figure 2(a)), whereas the supramolecular arrangement can be seen along the b axis, according to Figure 2(b). The crystallographic refinements are listed in the Table 1 and the bond lengths and bond angles are shown in Table S1 as Supplementary Materials. The structure described here shows bond angles of 172.82° for the dihedral C11N1N2C1 (Figure 1(a)) and -147.37° for the C12C11N1N2. For the free ligand, these angles are close to 180° indicating a planar structure⁽³⁵⁾. The centroid-Ni-centroid (ring naphthol or ring phenyl) angle is 180.0° which affects the overall crystallographic arrangement by creating one adjacent plane in relation to



Figure 2. (Colour online) (a) Bi-dimensional arrangements parallel to the *ac* plane for the $C_{36}H_{30}NiN_4O_2$ (Symmetry Code i: 1 - x, 1 - y, 1 - z), (b) arrangements parallel to the *ab* plane and (c) electrostatic and π -stacking interaction parallel to the *ab* plane.

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Table 1. Main crystallographic parameters of the structure refinement for C₃₆H₃₀NiN₄O₂ and C₃₆H₃₀CuN₄O₂ complexes.

Compound	Complex nickel Sudan I	Complex cooper Sudan II	
Formula	C ₃₂ H ₂₂ NiN ₄ O ₂	$C_{36}H_{30}CuN_4O_2$	
Formula weight $(g \text{ mol}^{-1})$	553.23	61,418	
Temperature (K)	149.95(10)	150.00(10)	
Crystal system	Monoclinic	Monoclinic	
Space group	$P2_1/n$	$P2_1/n$	
a(A)	17.1357(6)	10.7157(2)	
$b(\dot{A})$	3.95810(10)	11.9298(2)	
c (Å)	17.2578(7)	11.7645(2)	
β	98.064(3)	105.802	
$V(\text{\AA})^3$	1158.93(7)	1447.09(4)	
Z	2	2	
Crystal size (mm)	$0.49 \times 0.08 \times 0.04$	$0.76 \times 0.24 \times 0.11$	
$\theta P \alpha \nu \gamma \varepsilon (\text{deg})$	2.58-66.33	1.79-29.52	
$d_{\rm calc} ({\rm gcm^{-1}})$	1.585	1.410	
$\mu(Mo K\alpha) (mm^{-1})$	0.879	0.796	
Transmission factors (min/max)	0.916/0.961	0.794/0.917	
Reflections measured/unique	19132/2042	67620/4064	
R _{int}	0.0742	0.0564	
Observed reflections $[F_{\alpha}^2 > 2\sigma(F_{\alpha}^2)]$	1699	3459	
No. of parameters refined	178	196	
$[F_{0} > 2\sigma(F_{0})]$	0.0699	0.0346	
$wR[F_{0}^{2} > 2\sigma(F_{0})^{2}]$	0.2106	0.0987	
S	1.120	1.0987	
RMS peak	0.177	0.072	

the naphthol ring and to the phenyl rings (Figure 2(c)). The solid-state arrangement displays supramolecular interactions of the π -stacking type between the two adjacent rings of the naphthol group (Figure 2(c)). The distance between the two centroids from the naphthol groups (opposite rings) is 3.852 (2) Å, whereas the centroid–centroid distance of the adjacent rings is 3.958(2) Å (not shown in Figure 2(c)). These distances suggest an arrangement which is maintained by supramolecular π -stacking interactions observed between the centroids of the naphthol groups, being notably important for the packaging of this crystalline system. Such packing in columns of π -stacking molecules extends in the same direction of the *b*-axis.

In order to probe the molecular arrangement of the unit cell, the electrostatic potential surface was generated for the solid-state structure including four repeating units. Figure S2 in the Supplementary Material shows the MEP along the packaging of this supramolecular crystal lattice, whose colour scale ranges from red (negative MEP) to blue (positive MEP). The nickel atom seems to experience a purely electrostatic interaction with the oxygen atoms of the layers above and below. The interplanar Ni–O distance was 3.188 Å (Figure 2(c)) and is smaller than the one measured between adjacent rings (3.958 Å, π -stacking). It is straightforward to note that the oxygen atoms are much more polarised than other parts of the molecule suggesting an electrostatic interaction with the metal atom.

Figure 1(b) shows the thermal ellipsoid representation of the new structure for Sudan II copper complex; this complex was crystallised in the monoclinic system, space group $P2_1/n$ with two molecules in the unit cell. The repeating unit of this structure occurs with the metal located in the axis b of the unit cell extending over the ac plane (Figure 3(a)) and the supramolecular packaging along *ab* plane (Figure 3(b)). Conventional interactions such as π -stacking type were not found, although this compound contains several centroids. However, it is strongly suggestive that the interaction that keeps the packaging of this supramolecular system is based on the CH interaction present in the naphthol rings with adjacent centroids present in the phenyl groups (CH··· π interaction - Figure 3(c)). The distance between the CH β groups from the naphthol ring to the adjacent centroid of the phenyl ring is 3.399 Å, as shown in Figure 3(c). It is also important to note that the angle between the naphthol centroids and the CH group of the phenyl ring is 155.86°, which is significantly smaller than the optimal value of 180°, decreasing the interaction strength. The structure described here shows bond angles of 176.50° for C11N2N1C5 and -76.71° C12C11N1N2 dihedral. This clearly shows that the phenyl ring is almost perpendicular to NN bond mainly due to the steric hindrance of methyl at ortho position. The MEP for the cooper complex monoclinic system is shown in Figure S3 in the Supplementary Material; the result suggests that in the gas phase, the phenyl ring is the molecular region of the complex presenting a higher charge density, whereas the hydrogen from the naphthol ring has been characterised as positive centre, suggesting a non-classical CH $\cdots \pi$



Figure 3. (Colour online) (a) Bi-dimensional arrangements parallel to the *ab* plane for the $C_{36}H_{30}CuN_4O_2$ (Symmetry Code i: 1 - x, 1 - y, 1 - z), (b) arrangements parallel to the *bc* plane and (c) interactions of the type CH··· π in the *bc* plane.

interaction directed to the phenyl ring centroid as the major feature responsible for the supramolecular packaging of this system.

Molecular modelling based on DFT calculation was used to predict structural and spectroscopic properties for the nickel and copper complexes. The B3LYP/6-31++G (d,p)-optimised geometries for the two complexes are depicted in Figure S1 as Supplementary Material, with the main structural parameters quoted in Tables S1 and S2. Both complexes show square planar geometry around the metal with O1NiO1i, O1CuO1i, N1NiN1i and N2CuN2i angles equal to 180°, which is in good agreement with the experimental data. Overall, there are no significant differences between the experimental data from X-ray diffraction and those calculated for isolated molecule, which suggests that intermolecular forces are not much pronounced. Experimentally, the Ni(II) complex presents O1NiN1 angles equal to 90.01° and for the copper complex the O1CuN2 angle is 89.58°. Regarding the O-Ni bond, the experimental value is 1.843(3) Å, slightly shorter than the O-Cu distance, of 1.877(17) Å. The nickel complex presents the N-Ni bond equal to 1.911(3) Å, which is also slightly shorter than the N-Cu bond 1.918(12) Å.

Spectroscopic analysis

Table 2 shows the main vibrational wavenumbers and assignments of the IR and Raman spectra for both compounds. The observed and calculated IR spectra can be seen in Figures S4 and S5 in Supplementary Material. Although having different metal centres and structural differences on the phenyl rings, both complexes present similar IR spectra. The IR spectra present bands at 565, 471 and 456 cm⁻¹ for the nickel complex which are assigned according to the normal mode analysis as $v_s(NiO)$. The band at 502 cm⁻¹ has been assigned to $v_s(NiN)$. In the low wavenumber region, the copper complex presents bands at 563, 494 and 454 cm⁻¹, due to the symmetric $v_s(CuO)$, whereas the band at 506 cm⁻¹ refers to the $v_s(CuN)$ mode. Generally, such bands are difficult to attribute due to their

Table 2. Experimental main vibrational wavenumbers (in cm^{-1}) for bis-1-phenylazo-2-naphtholatenickel(II) and bis-1-(2,4-xylylazo)-2-naphtholatecopper (II).

Infrared		Raman			
Nickel complex	Copper complex	Assignments	Nickel complex	Cooper complex	Assignments
1618 m	1614 m	$\nu_{\rm s} \rm CC$ naphthol	1588 w	1600 w	$\nu_{s}CC + \delta CH$
1595 w	1595 w	$\nu_{\rm s} CC$ naphthol	1543 w	1550 w	$v_{s}CC + \delta CH + v_{s}CN$
1548 m	1548 m	$v_{\rm s} CC + \delta CH$ naphthol	1499 w	1506 w	$\nu_{s}CO + \delta CH + \nu_{s}NN$
1500 vs	1502 vs	$\nu_{s}CC + \delta CH + \nu_{s}CC + \nu_{s}CN$		1483 w	$\delta CH + \nu_s CC + \nu_s NN$
1463 w	1477 w	$\nu_{\rm s} \rm CO + \delta \rm CH + \nu_{\rm s} \rm CN$	1463 w	1443 w	$\nu_{s}CO + \delta CH + \nu_{s}CN$
	1377 w	$\nu_{s}CO + \delta CH_{3} + \nu_{s}CN + \nu_{s}CC$	1360 vs	1357 vs	$\delta CH + \nu_s CO + \nu_s CC$
1404 w	1406 w	$\nu_{s}CO + \delta CH + \nu_{s}CN + \nu_{s}CC$	1302 w	1301 w	v _s CC
1369 vs	1359 vs	$v_{s}CC + \delta CH + v_{s}CN$	1250 w	1241 w	$\nu_{\rm s} \rm CC + \delta \rm CH$
1321 m		$\nu_{s}CC + \delta CH + \nu_{s}CN$	1199 m	1205 w	$\nu_{\rm s} \rm CC + \delta \rm CH$
1304 m	1307 m	$\nu_{s}CO + \delta CH + \nu_{s}CC$	1166 m		$\nu_{\rm s} \rm CC + \delta \rm CH$
1257 w	1255 w	$\nu_{\rm s} \rm CC + \delta \rm CH$ naphthol	1095 w	1099 w	$\nu_{\rm s} \rm CC + \delta \rm CH$
1214 w	1215 w	$\nu_{\rm s} \rm CC + \delta \rm CH$	996 w	998 w	$\nu_{\rm s} \rm CC + \delta \rm CH$
1187 m	1183 m	$\nu_{\rm s} {\rm CC} + \delta {\rm CH}$	906 w	908 w	ωCH
1147 m	1149 m	$\nu_{\rm s} \rm CC + \delta \rm CH$	738 w		ωCH
1103 w	1097 w	$\nu_{\rm s} \rm CC + \delta \rm CH$ naphthol		580 w	δССС
1028 w	1034 w	δCH/δCH ₃	561 w	556 w	ωCH/νCuN
1000 m	995 m	δССС	530 w	533 w	δССС
958 w	948 w	δСН	523 vs		δССС
909 w	909 w	$\nu_{s}CuN + \nu_{s}CC + \omega CH$	510 w		$\omega CH + \nu NiN$
862 w	872 w	ωCH	493 w		$\nu_{s}CC + \nu_{s}CN + \nu_{s}CN$
734 vs	760/719 vs	ωCH naphthol	427 vs	431 w	ωCH
695 vs	699 w	ωCH naphthol	389 m	375 w	ωCH
565 w	563 w	$\nu_{\rm s}{\rm NiO} + \nu_{\rm s}{\rm CC}/\nu_{\rm s}{\rm CuO}$	297 m		ωCH
502 w	506 w	v _s NiN/v _s CuN	263 w	280 w	δNiN/δCuN
471 w	494 w	$\nu_{\rm s}{\rm NiO}/\nu_{\rm s}{\rm CuO} + \nu_{\rm s}{\rm CC}$	228 m	234 w	$\delta NiO + \omega CH/\nu_s CuO$
456 w	454 w	v _s NiO/v _s CuO	200 m	199 w	δNiO/δCuO

Note: vs, very strong, w, weak and m, medium.

relatively low intensities, being a combination of several vibrational modes such as $\nu_s(CC)$, $\omega(CH)$ and $\delta_s(CH)$, all of them related to the organic skeleton. Another interesting aspect of these spectra is the split of the vibrational modes into two distinct moieties of the molecules, namely the phenyl ring and the naphthol ring. Both complexes show bands at 1500 cm^{-1} as the most intense ones, assigned as a coupled mode $[(\nu_s(CN) + \nu_s(CC) + \nu(C=O) + \delta_s(CH)];$ the bands at $1369/1359 \text{ cm}^{-1}$ are also assigned to a mixture of vibrational mode [$(\nu_s(CN) + \nu_s(CC) + \delta_s(CH)]$, and the bands at 734/760 cm⁻¹ are assigned to the $\omega_{\rm s}$ (CH) from the naphthol group for the nickel/copper. The band at 695 cm⁻¹ for the nickel complex is also assigned to the $\omega_s(CH)$ mode from the naphthol group as an intense band, whereas for the copper complex the same vibrational mode can be seen at 699 cm^{-1} as a weak band. Most of the medium intensity bands, such as those found at 1618/1614, 1548/1548, 1304/1307, 1147/1149 and 1000/995 cm⁻¹, are assigned as the symmetric $\nu(CC)$ modes, containing a contribution from the $\delta_s(CH)$ angular deformation. Two other IR bands are also important: at 1377 cm^{-1} for the copper complex, assigned as the $[\nu_s(CN) + \nu_s(CC) + \nu(C=O) + \delta_s(CH_3)]$ coupled vibrational mode, and at 1321 cm⁻¹, of medium intensity, for the nickel complex, assigned to the $[\nu_{s}(CN) + \nu_{s}(CC) + \delta_{s}(CH)]$ mode.

The observed Raman spectra can be seen in Figure 4 and the calculated spectra are shown in Figure S6 in Supplementary Material. In the low wavenumber region, the vibrational modes are related to the metal–ligand bonds; for the nickel complex the band at 263 cm^{-1} is assigned to the $\delta(\text{NiN})$ mode, the band at 228 cm^{-1} to the



Figure 4. Experimental Raman spectra (a) for bis-1-(phenylazo)-2-naphtholatenickel(II) and (b) for bis-1-(2,4-xylylazo)-2-naphtholatecopper(II).

 $[\delta(\text{NiO}) + \omega(\text{CH})]$ and the band at 200 cm⁻¹ to $\delta(\text{NiO})$. For the copper complex, the same bands are observed at 280 cm^{-1} , assigned to the $\delta(\text{CuN})$ mode, at 234 cm^{-1} as δ (CuO) and at 199 cm⁻¹ as δ (CuO). The band at $510 \,\mathrm{cm}^{-1}$ can be attributed to the $[\nu_{\rm s}({\rm NiN}) + \omega({\rm CH})]$ mode; this band is observed in the nickel complex spectrum but it is not present for the copper complex. Several medium and weak intensity bands with contribution of the symmetric $v_{s}(CC)$ mode and angular deformation $\delta(CH)$ can also be noted, as for instance the ones at 1543/1550, 1250/1241, 1199/1205, 1095/1099 and $996/998 \text{ cm}^{-1}$ for the nickel/copper complexes, respectively. The nickel complex spectrum presents three bands with medium intensity in the region around 1360 cm⁻¹, assigned as $[\delta(CH) + \nu_s(C=O) + \nu_s(CC)]$ coupled mode. Less important bands, which can be used to characterise the ligands, are the ones at $520 \,\mathrm{cm}^{-1}$, assigned to δ (CCC), and at 427 cm⁻¹, assigned to ω (CH). Previous assignments are consistent with structures observed in the solid state (Figure 1) and can be further used for characterisation of azo dyes complexes in which crystal diffractions are not available.

Conclusions

Nickel and copper coordination compounds containing azo dyes ligands (Sudan I and Sudan II) were prepared and fully characterised by means of X-ray, vibrational spectra and quantum mechanics calculations. Both complexes present square planar geometry around the metal and the solid-state supramolecular structures are maintaining by π -stacking (Ni complex) and unconventional CH··· π (Cu complex) interactions. In addition to the crystal structures, the spectroscopic data were provided and the vibrational fingerprints assigned with the aid of normal mode analysis. We noted that the weak intermolecular interactions observed in the solid state do not twist the molecular geometries significantly, with the predicted vibrational spectra for isolated molecules in gas phase found in satisfactory agreement with observed ones. Moreover, we claim that these data might be useful for characterisation of structure of other coordination compounds derived from Sudan series.

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Supplementary material

Figure S1 shows the optimised geometries for both compounds at B3LYP/6-311++G(d,p) theory level, and Figures S2 and S3 shows the molecular electrostatic potentials (MEP) from total SCF density for the nickel complex and cooper complex, respectively, calculated at B3LYP/6-311++G(d,p) theory level. The Figure S4 and S5 show the experimental and theoretical infrared spectra for both compounds, and Figure S6 shows the calculated Raman spectra at B3LYP/6-311++G(d,p) level for nickel and copper complex, respectively. Tables S1 and S2 display the structural parameters obtained from X-ray diffraction and calculated at B3LYP/6-311++G(d,p) level. Cambridge Crystallographic Data Centre (CCDC) 882018 and 882019 contains the supplementary crystallographic data for Sudan I complex nickel and Sudan II complex copper. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk or from the CCDC, 12 Union Road, Cambridge CB2 IEZ, UK [Fax: (internet.) 1 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

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Supramolecular compounds of azo dyes derived from 1-phenylazo-2-naphthol and their nickel and copper complexes

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