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# INFRARED AND UV-VIS STUDIES OF COPPER(II) COMPLEXES OF 3,6-BIS((SALICYLIDENAMINO)ETHYL)-SULFANYLPYRIDAZINE

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**ABSTRACT.** Copper(II) complexes of a new multidentate ligand 3,6- bis((salicylidenamino)ethyl)-sulfanylpyridazine (SALESP) have been prepared and characterized by elemental analysis, infrared and ultraviolet-visible spectra. SALESP is a potentially hexadentate ligand and its reactions with copper (II) salts lead to the mononuclear complex Cu(SALESP) in the case of $Cu(OAc)_2$ with a four coordinate $CuN_2O_2$ geometry, and binuclear $Cu_2(SALESP)X_2$ when the counter ion was X (X = $Br^-$, $Cl^-$, $NO_3^-$). In the bromide binuclear compound, the ligand is tetradentate without participation of the pyridazine nitrogens, leading to square planar copper while for the chloro and the nitrato complexes, coordination via the pyridazine nitrogens occurs giving square pyramidal copper centers. Electronic spectra in dimethylformamide showed a solvatochromic shift due to the coordination of the solvent to the copper centers.

## INTRODUCTION

The ability of polynucleating ligands to hold two or more metal ions in close proximity is quite well known and very sophisticated systems are now available [1-9]. Recently, an appreciable amount of work on the copper complexes, with binucleating ligands containing pyridazine moiety, has been published and revealed the possibility for diazine to participate or not in coordination [10-16]. As part of our work on polynucleating ligands we present the details of synthesis and a structural study of $CuX_2$ complexes (X = $AcO^-$, $Br^-$, $Cl^-$, $NO_3^-$) with a new ligand SALESP (3,6-bis((salicylideneamino)-ethyl)sulfanylpyridazine), using infrared and electronic spectroscopy. This ligand produces mononuclear and homobinuclear copper complexes and compounds of this type are supported to have a diazine bridge in addition to an anionic $Br^-$, $Cl^-$ or $NO_3^-$ bridge [17, 18] with the SALESP acting as a tetradentate or an hexadentate ligand.

## EXPERIMENTAL

All the reactants and solvents were commercial products and were used without further purification. The elemental analysis, performed by the "Service Central de Microanalyse du CNRS", Vernaison France are given in Table 1. IR spectra were run on a Nicolet 5SXC FTIR spectrophotometer as polyethylene pellets, nujol mulls, or hexachlorobutadiene mulls. Electronic spectra were recorded on a Beckman DU-64 spectrophotometer. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker AM300 spectrometer in deuterated chloroform solution.

Table 1. Analytical data.

| Compound | % C | | % H | | % N | | % S | |
|---|---|---|---|---|---|---|---|---|
| | *Calc.* | *Found* | *Calc.* | *Found* | *Calc.* | *Found* | *Calc.* | *Found* |
| SALESP | 60.25 | 60.43 | 5.06 | 4.98 | 12.77 | 12.82 | 14.62 | 14.97 |
| A | 52.84 | 52.25 | 4.03 | 3.82 | 11.20 | 11.07 | 12.82 | 13.47 |
| B | 36.42 | 36.98 | 2.79 | 2.42 | 7.74 | 7.05 | 8.86 | 8.61 |
| C | 41.64 | 41.35 | 3.18 | 3.09 | 8.83 | 8.70 | 10.10 | 10.84 |
| D | 38.43 | 37.35 | 2.93 | 2.69 | 12.22 | 11.81 | 9.32 | 10.21 |

*3,6-bis((salicylidenamino)ethyl)sulfanylpyridazine (SALESP).* Sodium metal (4.75 g, 0.206 mol) was dissolved in degassed absolute ethanol (100 mL) under argon and the solution refluxed for 45 min. A solution of 2-aminoethanethiol hydrochloride ( 11.70 g, 0.103 mol) in 100 mL of degassed absolute ethanol was then added, whereupon a white solid (NaCl) separated immediately. The reaction mixture was stirred at 70 °C for 45 min and a solution of 3,6-dichloropyridazine (7.5 g, 0.05 mol) in degassed absolute ethanol (~100 mL) was added dropwise, while stirring, over a period of 1 h. The reaction mixture was then refluxed for 8 h and left at room temperature overnight. The white solid was filtered off and washed with 2 x 25 mL of ethanol. The ethanolic fractions were combined and immediately treated with an excess of salicylaldehyde. A yellow precipitate was obtained after about 5 min. Stirring was continued for 2 h and then the precipitate was filtered off and washed with several portions of ethanol and two portions of ether, and air-dried. Then it was crystallized in $CHCl_3$. Yield: 20.4 g, 93%; mp: 111 °.

*$Cu(C_{22}H_{20}N_4O_2S_2)$, (A).* A suspension of SALESP (1.754 g, 4 mmol) in methanol (100 mL) was heated until the dissolution of the ligand was complete. A solution of $Cu(OAc)_2.H_2O$ (0.798 g, 4 mmol) in methanol (50 mL) was added and the mixture was refluxed for 10 min. The color of the solution changed gradually from brown to green. Refluxing was continued for 10 h. Olive green crystals were formed which were filtered hot, washed with chloroform and dried under vacuum over $P_2O_5$; yield: 1.36 g, 68%.

*$[Cu_2(C_{22}H_{20}N_4O_2S_2)Br_2]$, (**B**).* The preparation was identical to that of $Cu(C_{22}H_{20}N_4O_2S_2)$ except that copper bromide (1.787 g of $CuBr_2$ ) was used in place of copper acetate and the molar ratio (ligand/metal) was 1: 2. The mixture was just refluxed for 2 h. The resulting crystals were dark green; yield: 1.83 g, 63%.

*$[Cu(C_{22}H_{20}N_4O_2S_2)Cl_2]$,(C).* The preparation was identical to that of $Cu(C_{22}H_{20}N_4O_2S_2)$ except that copper chloride (1.076 g of $CuCl_2$) was used in place of copper acetate and the molar ratio (ligand/metal) was 1:2. The mixture was just refluxed for 1 h. The resulting crystals were brown; yield: 1.42 g, 56%.

*$[Cu(C_{22}H_{20}N_4O_2S_2)(NO_3)_2]$ (**D**).* The preparation was the same as above, except that copper acetate was

substituted by copper nitrate (1.5 g of $Cu(NO_3)_2$) and the molar ratio (ligand/metal) was 1:2. The resulting crystals were greenish; yield: 1.98 g, 72%.

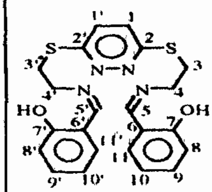
## RESULTS AND DISCUSSION

The basis of our synthetic route was to take advantage of the well-known condensation reaction of primary amine on formyl moiety. The reaction of salicylaldehyde with two equivalents of 3,6-bis((aminoethyl)sulfanyl)pyridazine in the absence of metal affords the di(Schiff base) SALESP in quantitative yield. The yellow solid obtained was stable in air and soluble in common organic solvents.

The $^1H$ and $^{13}C$ NMR spectra of the acyclic ligand have been recorded in $CDCl_3$ and the chemical shifts (ppm) are reported in Table 2.

Table 2. $^1H$ and $^{13}C$ NMR assignments for SALESP (δ in ppm from TMS, $CDCl_3$).

| $^1H$ | Assignment | $^{13}C$ | Assignment |
|---|---|---|---|
| 7.08 (s, 2H) | H1, H1' | 125.84 | C1, C1' |
| - | - | 161.10 | C2, C2' |
| 3.66 (t, 4H) | H3, H3' | 30.87 | C3, C3' |
| 4.01 (t, 4H) | H4, H4' | 58.20 | C4, C4' |
| 8.38 (s, 2H) | H5, H5' | 166.24 | C5, C5' |
| - | - | 118.61 | C6, C6' |
| - | - | 158.15 | C7, C7' |
| 6.95 (m, 2H) | H8, H8' | 116.99 | C8, C8' |
| 7.28 (m, 2H) | H9, H9' | 132.40 | C9, C9' |
| 6.85 (m, 2H) | H10, H10' | 118.61 | C10, C10' |
| 7.22 (m, 2H) | H11, H11' | 131.45 | C11, C11' |
| 13.15 (s, 2H) | OH | - | - |



In the $^1H$ NMR spectrum the low field signal corresponding to the phenolic OH is seen at 13.15 ppm while the signal for HC=N was found further downfield at 8.38 ppm. The aromatic signals for the disubstituted ring appeared as multiplets (6.90 - 7.30 ppm). Both S-$CH_2$ and N-$CH_2$ methylene hydrogens appeared as pairs of triplets at 3.66 ppm and 4.01 ppm, respectively. The signal which appeared as a singlet at 7.08 ppm was attributed to the hydrogens of the pyridazine ring.

Assignment of $^{13}C$ signals was ascertained by DEPT experiment. In particular it can be seen that C10 and C10' were upfield by about 13 ppm with respect to the C11, C11', C9 and C9' signals. The presence of the imine group and the OH, substituent, respectively on the 1 and 2 positions of the aromatic ring could introduce electronic effect which may shield C6, C6', C7 and C7'. It can be noted that the signals of the pyridazine ring atoms indicate shielded carbon atoms. The C2 and C2' are more shielded than C1 and C1' according to their different magnetic environnements. C3, C3' C4 and C4' can be differenciated by their direct bordering atoms. C3 and C3' are downfield by about 28 ppm with respect to C4 and C4' signals.

*Infrared study.* The characteristic frequencies of the ligand and the copper complexes and their assignment are listed in Table 3. The ligand can potentially coordinate one Cu(II) cation with

Table 3. IR spectral data ($cm^{-1}$)[a].

| SALESP | A | B | C | D | Assignment |
|---|---|---|---|---|---|
| 1661=830x2 w, sh | | 1650=825x2 sh | | | overtone |
| 1636 vs | 1600 sh | 1594 sh | 1593 s | 1599 m | ν(C=N) |
| 1611 s | 1614 s | 1614 s | 1635 m | 1629 s | ν (C==N) ring |
| 1578 vs | 1572 sh | | | | νs (C==C) ring |
| 1528 vw | 1537 vs | 1537 m | 1547 m | 1556 m | ν (N==N) |
| 1497 m | | | | | δOH |
| | | | | 1489 sh | $\nu_4 NO_3^-$ |
| 1458 m | 1470 m | 1469 sh | 1473 s | 1466 s | δ($CH_2$) |
| 1444 vw | 1447 s | 1444 m | 1448 w | 1454 s | ν(C-C) ring |
| 1427 vw | | | 1429 w | 1422 | } δ ($CH_2$) |
| 1400 sh | 1400 sh | | 1398 m | | |
| 1389 m | 1385 m | 1388 m | | 1390 m | δ [ring] ; ω($CH_2$) |
| 1372 m | | | | | νOH---N |
| | 1350 m | 1350 sh | 1352 m | 1342 | } δ [ring] |
| 1332 m | 1329 m | 1316 m, b | | | |
| | | | | 1300m, sh | $\nu_1$ ($NO_3^-$) |
| 1295 vw, sh | | | | | τ($CH_2$) |
| 1281 s | 1283 sh | 1272 m | 1277 s | 1283 s | νa(C-N) |
| 1216 sh | 1222w, sh | 1216 w | 1225 w, sh | 1227 w | ω($CH_2$) |
| 1201 m | 1201 m | 1195 m | 1201 m | 1213 w | νa(C-N) |
| | | | 1183 w | 1183 sh | } ω ($CH_2$) |
| 1178 w, sh | | 1172 vw | 1161w | 1174 w | |
| 1149 vs | 1145 s | 1148 vs | 1141 m | 1157 m | νs(C-N) |
| 1115 m | 1127 sh, m | 1128 sh, m | 1128 sh, m | 1139 sh, m | ν(C-O) |
| 1072 m | 1072 w, sh | 1078 w | 1072 w | 1074 w | } γ ($CH_2$) |
| | 1050 sh | 1067w, sh | 1055 sh | 1044 sh | |
| 1028 w | 1030 w | 1039w, sh | 1036 w | 1039 sh | } δ [ring] |
| 1011 sh | | 1028 w | 1017 w, sh | | |
| | | | | 1024 m | ν2 ($NO_3^-$) |
| 1001 s | 1001 w | 1000 w | 1000 vw | 1000 w | ν(C-C) |
| 978 sh | 974 w | 978 w | 972 w | 972 w | } ω [(C-H)ring] |
| 964 m | | | | | |
| 950 w, sh | | | | | γOH |
| 938 w, sh | 941 sh | 922 w | 940 w, sh | 944 w, sh | } ω [(C-C)ring] |
| 885 s | 908 s | 906 m | 897 s | 902 m | |
| 866 s | 889 sh | 889 w | 874 m | 878 w | |
| 850 s | 847 m | 850 sh | 845 w | 845 m | |
| 831 s | 812 m | 825 s | 828 m | 804 m | |
| | | | | 800 w,sh | ν6 ($NO_3^-$) |
| 775 s | | | 789 sh | | [(C-H) ring] |
| 766 sh | | | 769 s | 765 s | } ν (S-C) |
| 752 vs | 752 vs | 750 vs | | | |
| 744 sh | 733 sh | 739 sh | | 739 sh | ρ($CH_2$) |

Table 3. Continued.

| SALESP | A | B | C | D | Assignment |
|---|---|---|---|---|---|
| 672 w | | 685 w | 683 vw | 673 vw | |
| | 667 vw, sh | 669 vw | 667 vw | 661 vw | |
| | 655 w | 644 w | | 644 vw | |
| 636 s | | | 639 w | 622 sh | |
| | 613 m | 611 m | | | |
| | | 600 sh | 596 m | 598 m | ring breathing |
| | | 580 w | 588 m | 580 sh | |
| 571 m | 575 m | 575 w | | 570 sh | |
| 553 w | 545 w | 545 w | 551 w | 546 w | |
| 516w | 535 w | 538 w | 525 m | 536 w | |
| | 493 w, b | 493 w | 490 sh | 493 m | |
| 469 m | 470 sh | 473 sh | 475 w | 480 w | γ [(C-C)ring] |
| 455 m | 458 m | 455 m | 455 m | 460 m | |
| | | | 447 m | 448 sh | |
| | | | | 396 mw | νa[(Cu-O)nitrate] |
| | | 410 sh | 412 w | 408 sh | |
| | 383 m | 384 m | 382 m | 378 mb | |
| | 370 sh | 360 sh | 370w, sh | 370 sh | ring |
| | | 355 sh | 355w, sh | 350 sh | |
| | 345 vw | 345 sh | | | |
| | 328 vw | 328 sh | 320 w | 323 w | |
| | | | | 341 m | νs[(Cu-O)nitrate] |
| | 305 w | 309 w | 312 m | 315 m | ν (Cu-O) |
| | | | 281 s | | νa (Cu-Cl) |
| | 268 w | | | 269 m, b | ν (Cu-N) |
| | | | 251 m | 250 m | ν[(Cu-N)pyridazine] |
| | | 240 m | | | νa (Cu-Br) |
| | | | 220 m | | νs (Cu-Cl) |
| | | 210 sh | | | νs (Cu-Br) |

[a]s, strong ; m, medium ; w, weak ; b, broad ; sh, shouldering ; vs, very strong.

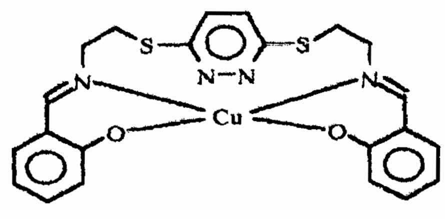
electroneutrality after deprotonation of the salicylaldehyde hydroxide groups (compound **A**). It can also coordinate one additional cation with external or internal counter ions (binucleating compounds **B, C** and **D**).

The infrared spectrum of the ligand SALESP was much as expected. Bond formation was revealed by absorptions in specific regions of the spectrum and the disappearance of certain bands that were observed in the spectra of the reactants. There are no bands which could be assigned to $NH_2$, SH or C=O of the unchanged reactants. The absence of the bands indicated the complete formation of azomethine linkage and the formation of the sulfanylpyridazine moiety. A broad and strong absorption centered at 1327 $cm^{-1}$ was present in the infrared spectrum. This pattern and the shifting of νC=N and νC-O toward lower frequencies compared to the common frequencies attributed to these vibrations in usual Schiff-bases [19-22] were indicative of the presence of strong intramolecular hydrogen bonding between the OH moiety and the imine nitrogen atom [23]. δOH and γOH were respectively located at 1497 $cm^{-1}$ and 950 $cm^{-1}$. The νC=N stretching frequency occured at 1636 $cm^{-1}$ in agreement with previous assignments. Upon complexation, this band shifted to low frequencies (1593-1600 $cm^{-1}$) attesting the participation of the imine nitrogen in the copper coordination sphere.

The N=N stretching vibration of the symmetrical azo group of pyridazine is forbidden in infrared. In the unsymmetrical compounds it appeared in the region 1500-1600 $cm^{-1}$ [25] and is characterized as a very weak band at 1528 $cm^{-1}$ in the spectrum of the ligand and as medium to very strong band (between 1537 and 1556 $cm^{-1}$) in the spectra of the complexes. The characteristic band of the C-OH group of the salicylaldehyde, lowered by the hydrogen bonding, was observed at 1115 $cm^{-1}$ in the spectrum of the ligand SALESP. Upon coordination, and after deprotonation νC-O is shifted to high frequencies giving the bands of medium intensity located at 1127, 1128, 1128 and 1139 $cm^{-1}$, respectively, in the spectra of A, B, C and D. All the spectra of the complexes exhibited bands at 305-345 $cm^{-1}$ and 268 $cm^{-1}$, assigned to Cu-O and Cu-N stretching vibrations.

We can therefore conclude that the ligand was at least tetradentate by the oxygen and the nitrogen of the pendant moieties. As it would be expected, the $CH_2$ in-plane and out-of-plane bending frequencies remained practically unaltered upon coordination and the same holded for the in-plane ring vibration and the ring breathing vibrations.

While compounds **B**, **C** and **D** were clearly binuclear, compound **A** was a mononuclear derivative: all attemps to have binucleating complex with copper acetate were unsuccessfull. No band of the acetate group was observed in the spectrum of **A**. The appearance of νN=N (i.r. forbidden in symmetrical pyridazine complexes) as a very strong band at 1537 $cm^{-1}$ revealed an unsymmetrical pyridazine moiety. A slight participation of one pyridazine nitrogen to the coordination with copper should be normally weakened by the Jahn-Teller effect [26]. But the presence of only two broad bands (νCu-O and νCu-N) in the low frequencies region and the absence of a band attributable to νCu-N (pyridazine) suggested a square planar environment for the copper (Figure 1).



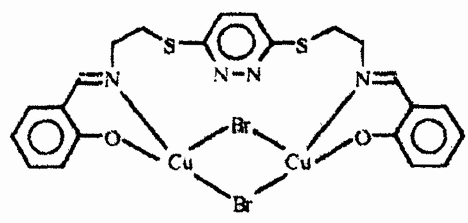




Figure 1. Suggested structure for Cu(SALESP), (**A**).
Figure 2. Suggested structure for $Cu_2$(SALESP)$Br_2$, (**B**).

The ir spectra of **A** and **B** were very similar; in both spectra the band assigned to νN=N was located at 1537 $cm^{-1}$ suggesting the same behaviour of the N=N moiety of the pyridazine. In the low frequencies region νCu-O appeared as a weak and broad band at 309 $cm^{-1}$ and νCu-N is probably obscured by the broad and medium absorption due to *νas*$CuBr_2$ and *νs*$CuBr_2$ located at 240 $cm^{-1}$ and 210 $cm^{-1}$ respectively. The number of bands in this region was in conformity with a square planar environment for each copper and it may be remarked here that this also confirms the conclusion arrived at regarding the copper environment through electronic spectral study (see below). The suggested structure is given in Figure 2.

For compound **C** one could note the lift of νN=N to 1547 $cm^{-1}$ suggesting a participation of the pyridazine nitrogen to the copper coordination. This is confirmed in infrared by the appearance of a

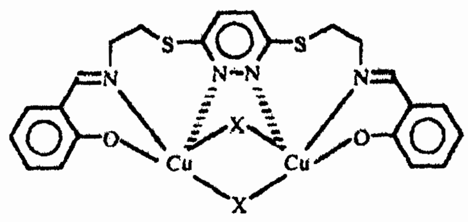


Figure 3. Suggested structure for $Cu_2(SALESP)X_2$; where $X = Cl^-$ for **C** and $X = NO_3^-$ for **D**.

new band of medium intensity which did not exist in the spectra of **A** and **B** and are located at 251 $cm^{-1}$. The Cu-N (azomethine) vibration is obscured by the strong absorption occuring at 281 $cm^{-1}$ and attributed to the Cu-Cl antisymmetric stretching. The band of medium intensity located at 220 $cm^{-1}$ are not present in the spectra of the other compounds; it can be assigned to the symmetric stretching νsCu-Cl. These low frequency values compared to those of terminal Cu-Cl stretching bands [27] were consistent with the presence of bridging chlorine atoms.

We can therefore suggest a square pyramidal environment around copper, the apical position being occupied by the N (pyridazine) (Figure 3)

As for compound **C**, the νN=N lifted to 1556 $cm^{-1}$, and in the spectrum of compound **D**, and νCu-N (pyridazine) was pointed as a band of medium intensity at 250 $cm^{-1}$. This was indicative of the participation of the N pyridazine nitrogen to the coordination.

Assignments of the nitrate absorptions are based upon the possible symmetry types $D_{3h}$ (free nitrate) and $C_{2v}$, or $C_s$ (coordinated monodentate, chelating or bridging nitrate). Eventhough it was rather difficult to differentiate these structures, ir spectroscopy is still useful in distinguishing between monodentate and bidentate nitrate [27-30].

Comparison of the spectra of the nitrate complex with that of the halide complexes allowed us to isolate absorption bands arising from the nitrate group. The nitrate stretching vibration ($\nu_4$, $\nu_2$ and $\nu_1$) occured as strong bands at 1409, 1300, and 1024 $cm^{-1}$ in the hexachlorobutadiene mull spectrum of **D**. $\nu_6$ was located at 800 $cm^{-1}$ as a shoulder and $\nu_3$ and $\nu_5$ were probably obscured by the out-of-plane $CH_2$ bending and the νC-S stretching.

All these features are consitent with an only bidentate nitrate group. The replacement of the smaller chlorine bridge with a bidentate nitrate bridge will normally increase the metal-metal separation but this had no effect on the pyridazine nitrogen interaction with copper as we noted that Cu-N (pyridazine) was found at the same frequencies (250 $cm^{-1}$) in the two compounds. According to this similarity, it is reasonable to suggest that **C** and **D** have similar structures involving the pyridazine nitrogen coordinationion with copper.

*Electronic spectra.* Details of the electronic spectra of **B**, **C** and **D** in dimethylformamide (DMF) were listed in Table 4. Compound **A** was not soluble in common solvents.

With regard to band position and intensity, the spectra were rather similar to those of Schiff base complexes derived from reaction of a number of ketones and salicylaldehyde with amine [31, 32]. The electronic absorption spectra of all complexes are characterized by strong doublet at around 275 and 375 nm resulting from transition within the ligand and/or from the metal to ligand charge transfer (MLCT) transition [33].

Table 4. Electronic spectra in DMF solutions at room temperature.

| Compound | d-d, MLCT (nm) | | | |
|---|---|---|---|---|
| B | - | 752 vw, 592 vw sh | 375 s | 276.5 vs |
| C | 940 m | 700 m | 372.5 s | 275 vs |
| D | 930 m | 655 m | 374 s | 275 vs |

v, very strong; s, strong; m, moderate; w, weak; sh, shoulder.

In the spectrum of **B**, the MLCT band tails in the visible region and tends to obscure the very weak d-d transitions located at 592 nm and 752 nm. The energies and the very low intensities of these d-d transitions compared favorably with similar binuclear square planar copper chelates [34, 35] or distorted octahedral systems with two weak apical coordination (Jahn-Teller effect) of solvent molecules. In **B**, we do not have a regular square planar copper since there are several different ligating atoms and this tends to decrease the crystal field splitting for the square planar complexes which frequently absorb at fairly high energies with a lower energy band at 15000 $cm^{-1}$ (666 nm).

The UV-Vis spectra of compounds **C** and **D** were almost similar and showed that, beside the presence of MLCT bands two broad bands of moderate intensity located at around 650-700 nm and 930-940 nm also occured. These shifts in the wavelength values compared to **B** were presumably due to a different behaviour of the copper in these compounds and were indicative of a structural difference as well in the coordinating sites as in stereochemistry around copper. It has been suggested [36-38] that d-d transitions around 900 nm and 600 nm were consistent with a square pyramidal Cu(II) environment or a pseudo-octahedral one with weak axial interaction with a solvent molecule. The spectra showed similarities with the spectrum of $[Cu_2(MIP)(OH)Cl_3H_2O]\cdot H_2O$ with MIP = 1,4-di(1'-methyl-2'-imidazolyl)-phthlazine in which we founded a $CuN_2OCl_2$ environment with transitions at 11800 $cm^{-1}$ (847 nm) and 14900 cm (671 nm) [39]. The shift to lower energies in **C** are presumably due to the weak coordination of a DMF molecule in the apical position.

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