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PAPER

Vapochromic Properties *vs.* Metal-Ion Coordination of β-Bispyrazolato–Copper(II) Coordination Polymers: a First-Principles Investigation.

Maurizio Casarin,[a] Daniel Forrer,[a,b] Luciano Pandolfo,[a] Claudio Pettinari,[c] and Andrea Vittadini*[a,b]

We investigate a series of monoadducts of the β-bispyrazolato–copper(II) 1D coordination polymer with plane-wave DFT-D calculations. We find that weak Lewis bases, such as H_2O and CH_3OH, prefer a symmetric bridging coordination to the Cu(II) ions, which in turn assume a highly distorted 4 + 2 octahedral configuration. Stronger Lewis bases, viz. NH_3 and pyridine, prefer instead to bind to a single

10 Cu(II) ion, which adopts a 5-fold coordination in a square-pyramidal environment. A semi-bridging coordination, corresponding to a 5 + 1 distorted octahedral Cu(II) environment, is finally predicted for molecules of intermediate Lewis basicity, such as CH_3CN. The soundness of these results is corroborated by the nice correlation found between the theoretical coordination number of the Cu(II) ions, the computed spin-down fundamental band gap, and the experimentally observed vapochromic effects.

15 ## Introduction

After the fundamental work of Hoskins and Robson,[1] the studies on coordination polymers (CPs) have been largely developed, being these compounds promising materials in different research and industrial fields, as gas storage, gas purification,
20 heterogeneous catalysis, etc.‡ Recently, metal-azolates (imidazolates, pyrazolates, tri and tetra-azolates) emerged as very promising CPs frameworks in crystal engineering and functional materials synthesis.[2-11] In this context, an interesting case is represented by bispyrazolato–copper(II) CPs, hereafter $Cu(pz)_2$,
25 which can be synthesized in two forms, named α and β. The former, which is the thermodynamically stable phase, is denser, has an intense green colour, and is characterized by a pseudo-tetrahedral coordination of the Cu ions.[12] The β form, instead, is beige and structurally different, as the Cu ions are in a square-
30 planar environment. The anisotropy of the coordination sphere of the metal ions gives to the β form a Lewis acidic character, so that it can react with vapours of small molecules such as H_2O, NH_3, CH_3OH, MeCN, and pyridine, giving rise to compounds of different colours (see Table 1).[13] XRD measurements indicate
35 that in the water adduct, which is pink and characterized by an orthorhombic *Cmcm* symmetry, water molecules symmetrically bridge the Cu ions. These turn out to be in a highly distorted octahedral environment, where the axial ligands, viz. the O atoms, are at a 2.913 Å distance, which is much longer than that
40 of the equatorial N atoms (2.037 Å), i.e., Cu ions have a 4 + 2 coordination number (c.n.). Theoretical investigations[14] revealed that the formation of the adducts is made possible by a low-energy transformation path where adjacent planes of polymer chains are mutually displaced, which opens channels where guest
45 molecules can be arranged. Furthermore, the guest water molecules are not only involved in the Cu···O···Cu interaction, but also in OH···π interactions with the pz rings of the

neighbouring chain. This in part explains the strong axial distortion of the Cu octahedral environment. No clear structural
50 information about the local coordination of the other guest molecules are available.

Table 1. Experimental properties of the investigated compounds (from Ref. [13]). Lattice constants in Å.

Cmpd	Composition	Colour	a	b	c	S.G.
1	$Cu(pz)_2 \cdot H_2O$	pink	16.96	6.24	7.28	*Cmcm*
2	$Cu(pz)_2 \cdot NH_3$	blue	17.06	6.33	7.24	*Cmcm*
3	$Cu(pz)_2 \cdot CH_3OH$	pink				n.a.
4	$Cu(pz)_2 \cdot pyridine$	blue	14.23	11.28	7.25	*Pmnm*
5	$Cu(pz)_2 \cdot CH_3CN$	pink	16.06	8.23	7.20	*Cmcm*

55 A further interesting aspect of β-$Cu(pz)_2$ that we intend to address in the present work concerns vapochromic properties. In fact, whereas sorption of some molecules such as H_2O, CH_3OH, and CH_3CN weakly affects the host colour, which turns from beige to pink, more spectacular changes are observed in the cases of NH_3
60 and pyridine, where an intense blue colour is instead obtained. This stimulated us to investigate the structural and electronic properties of this series of adducts.

Computational Details

Density functional (DF) calculations have been performed by
65 using the PWSCF code of the Quantum-ESPRESSO package.[15] The Perdew–Burke–Ernzerhof[16] (PBE) exchange-correlation functional and Vanderbilt ultrasoft pseudopotentials[17] have been adopted. Van der Waals forces which stick together the 1D polymer chains have been kept into account by using the
70 dispersion-corrected DFT-D2 approach by Grimme.[18, 19] A total of 11, 6, 5, 4, and 1 valence electrons have been explicitly considered for Cu, O, N, C, and H, respectively. The smooth part

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of the wave function has been expanded in plane waves, with a 30 Ry kinetic energy cutoff, while for the augmented electron density charge a 250 Ry has been chosen. Integration over the Brillouin zone has been done using a $1 \times 2 \times 4$ Monkhorst–Pack mesh in the full orthorhombic unit cells. The internal coordinates and (when needed) the lattice constants have been fully optimized with a BFGS algorithm. Finite basis-set effects have been corrected following the procedure by Bernasconi et al.[20] All the compounds have been assumed to be in an antiferromagnetic (AFM) state, which has been shown to be favoured for $Cu(pz)_2$ systems.[14] The described approach has been shown to be adequate to predict the structural and electronic properties of $Cu(pz)_2$ systems in Ref. 14.

Results and Discussion

The systems investigated in the present study include the adducts formed by β-$Cu(pz)_2$ with H_2O, CH_3OH, NH_3, CH_3CN, and C_6H_5N, whose experimental properties are reported in Table 1.

We start by examining the case of the NH_3 adduct, which was investigated with several calculations. We first performed a complete structural optimization using an orthorhombic cell with four Cu ions, constraining the NH_3 molecule in a symmetric bridging coordination (indicated as 2a in Table 2) similar to the one observed for the already investigated H_2O adduct 1,[13, 14] see Figs. 1a and 1b. The obtained parameters (see Tables 1 and 2) are however less accurate than those obtained for 1, especially for b, which is underestimated by ~10%. In a second calculation, we relaxed the constraint on the NH_3 position, obtaining a very different local coordination, where the NH_3 lone pair is specifically directed towards one of the two Cu ions which originally shared it in the previously assumed structure (see Fig. 1c). This, on one hand, further worsens the agreement between the experimental and the theoretical parameters (see Tables 1 and 2), but, on the other, provides a significant stabilization to the system (–0.17 eV/molecule). We emphasize that in the case of 1 no similar tendency towards symmetry breaking is found. Therefore, we infer that the *Cmcm* symmetry observed experimentally for 2 is actually due to an average of less symmetric 2b-type structures. This is difficult to model by first principles with a supercell of reasonable size. We also point out that whereas the experimental lattice parameters of 1 and 2 are quite similar, large differences are instead present in the theoretical parameters, particularly along the "soft" a and b directions. On this basis, it seems that an unbiased and safe way to compare the stability of the asymmetric *vs*. the symmetric structures would be adopting the experimental lattice constants for both structures. Such calculations confirm that the asymmetric arrangement of NH_3 as in the 2b model is favoured by 0.11 eV/molecule.

Table 2. Theoretical structural properties of the investigated compounds (see Fig. 1). Lattice constants and distances are in Å. For all the compounds but 3, distances are taken from calculations using the experimental cell constants (see text).

Cmpd	a	b	c	Cu-N	Cu1-X	Cu2-X	c.n.
1	15.94	6.08	7.37	2.01	2.90	2.90	4+2
2a	16.68	5.70	7.30	2.02	2.94	2.94	4+2
2b	16.63	5.64	7.50	2.03	3.41	2.29	5
3	16.15	6.31	7.48	2.02	2.81	2.81	4+2
4	13.63	11.06	7.54	2.04	3.68	2.47	5
5	15.93	7.93	7.16	2.02	2.81	2.43	5+1

The NH_3-host interaction is evaluated by computing the energy difference:

$$\Delta E = E[Cu(pz)_2 \cdot NH_3] – E[Cu(pz)_2] – E[NH_3], \qquad (1)$$

where $E[Cu(pz)_2 \cdot NH_3]$ is the total energy of the compound, $E[Cu(pz)_2]$ is the total energy of the host frozen to the structure of the adduct, and $E[NH_3]$ is the total energy of the free molecule. This yields $\Delta E = 0.74$ eV for the stable structure, which is close to the 0.71 eV computed for 1.[14]

In synthesis, our calculations show that replacing H_2O by NH_3 lowers the local symmetry at the Cu ions, which change their c.n. from 4 + 2 to 5. On this basis we performed our subsequent calculations with no constraints, allowing the structure to evolve towards the asymmetric/symmetric minimum. As in the case of the methanol adduct 3 there are no experimental structural data available, all our considerations are referred to the theoretically optimized structure (see Table 2). Similarly to H_2O, CH_3OH prefers a *symmetric* bridging configuration, and is arranged with its symmetry plane placed parallel to the (001) plane of the compound (see Fig. 1d). This molecular orientation increases the intermolecular repulsions along the a axis, which is thus slightly elongated with respect to the value computed for 1. The Cu···O distances are significantly shorter for 3 than for 1, which is easily explained by the absence of an absorbate-polymer interaction comparable to the OH···π interaction between H_2O and the pz rings. In contrast to that, methanol molecules interacting through the O atoms with neighbouring polymer chains are mutually involved in weak CH···O interactions, giving rise to van der Waals chains parallel to the $Cu(pz)_2$ ones (see Fig. 2).

The case of 4 is rather similar to 2: the pyridine molecules are bonded to only one ion, which in turn adopts a 5 c.n. (see Fig. 1e). Surprisingly, however, the agreement between the theoretical and the experimental lattice constants (Tables 1 and 2) is significantly better than in 2. Possibly, this difference is indicative of higher structural order.

The last compound we discuss here is the CH_3CN adduct 5. While the theoretical lattice constants of this system are in good agreement with the theoretical ones (see Tables 1 and 2), we find that, when compared to the other compounds, 5 exhibits a structural peculiarity: even though the guest molecule adopts an asymmetric bonding configuration (similarly to the cases of 2 and 4), it still interacts with *two* Cu ions, as in 1 and 3, thus adopting a semi-bridging geometry. From the ions viewpoint, this brings to a "5 + 1" distorted octahedral coordination (see Fig. 1f), with the longer Cu···X distance similar to the cases of 1 and 3 (see Table 2). Overall, it seems that the local coordination of 5 is closer to the situation in 1 and 3, that in 2 and 4. This is confirmed by the

very low energy gain provided by the 5 +1 coordination mode vs. the symmetric 4 + 2 (0.03 eV/molecule), and by the average angle formed between the equatorial and the axial ligands, which is a gauge of the displacement of the central ion from the equatorial ligand plane, and is 97.4° for **2**, 93.8° for **4** and only 91.6° for **5**.

If we now examine all the compounds together, it seems that a rationale for the structural differences (viz., the c.n. of the metal ions) can be given on the basis of the Lewis basicity of the incorporated guest molecules: molecules with a low Lewis basicity (H_2O and CH_3OH) prefer to interact electrostatically with two Cu(II) ions, whereas molecules with a high Lewis basicity (NH_3 and pyridine) prefer a chemical interaction with a single Cu(II) ion. CH_3CN is somewhat in a borderline situation, being more basic than H_2O and CH_3OH, but significantly less basic than pyridine and NH_3.[21] [§] This is in tune with the expected behaviour of complexes of simple σ-donor ligands.

It is now interesting to compare the experimentally observed colours of the examined compounds (see Table 1) with the c.n. of the Cu ions as predicted by our calculations (see Table 2). Apparently all the pink compounds are associated to a distorted octahedral configuration, whereas all the blue compounds are associated to a square-pyramidal coordination. To obtain further insight into this matter, we looked at the local density of states (LDOS) of a single Cu ion (see Fig. 3). In general, and as expected for a d^9 ion, these curves are characterized by a series of peaks close in energy, which correspond to the filled d levels, and to a single well-separated state of the minority spin, which corresponds to the empty d spin orbital. As the electron spin is conserved in optical transition, the colour of the compounds must be in relation with the d-d transitions corresponding to the spin-down gaps of Fig. 3.[#] For all the compounds characterized by a distorted octahedral configuration the values of these gaps

correspond to absorptions in the blue (**1**) or in the green (**3** and **5**). In contrast to that, compounds with square pyramidal coordination have gaps corresponding to adsorption in the red-brown (**2**) or in the yellow-brown (**4**). Overall, if we also keep in mind that electronic transitions in an octahedral field are symmetry-forbidden, the above described theoretical findings are in nice agreement with the experimentally observed vapochromic effects. It is also interesting to note that in the case where NH_3 were in a symmetric bridging configuration, the band gap of **2** would be higher and the compound would appear of a pink colour, similarly to **1**, at odds with the experiment. This provides further support to our prediction of a square-pyramidal coordination in **2** (and **4**).

Conclusions

We performed DFT-D calculations on a series of monoadducts of the β-bis-pyrazolate-copper(II) 1D polymer. We found that guest molecules with a weak Lewis basicity adopt either a bridging or a semibridging coordination, as already demonstrated for the H_2O adduct. In contrast to that, stronger Lewis bases such as NH_3 and pyridine prefer a terminal coordination, which switches the Cu(II) ion environment from a highly distorted octahedral to a square-pyramidal one. This shrinks the fundamental band gap of the minority spin, and explains the experimentally observed vapochromic effects.

Acknowlegement

Notes and references

[a] Dipartimento di Scienze Chimiche, Universita` di Padova, via Marzolo 1, I-35131 Padova, Italy.
[b] Istituto CNR per l'Energetica e le Interfasi (CNR-IENI), via Marzolo 1, I-35131 Padova, Italy.; Fax: +39 049 8275235; Tel: +39 049 8275161; E-mail: andrea.vittadini@unipd.it
[c] Scuola di Farmacia, University of Camerino, Via S. Agostino, 1, I-62032 Camerino (MC), Italy.

‡ For recent accounts on CPs see the Special Issues of: *Chemical Society Reviews,* 2009, **38**, 1201-1508 and *Chemical Reviews,* 2012, **112**, 673-1268, as well as Ref [22].

§ This is also consistent with the spectrochemical series,[23] which is largely influenced by the Lewis basicity of the ligands, and provides an alternative way of explaining the herein described results.

We note that the spin-down gap of the five-fold coordinated ions is narrower the more the ion is displaced from the equatorial ligand plane (see above), as expected on the basis of simple crystal-field theory arguments.

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Figure Captions

Fig. 1 Ball and sticks representations of the structures of: (a) **1**. (b) **2** in a hypothetical, symmetric geometry **2a**. (c) 2 in its stable geometry **2b** (d) **3**. (e) **4**. (g) **5**. Relevant weak interactions are shown as dotted lines. The orthorhombic cells contains another polymer chain which is hidden for clarity.

Fig. 2. Sketch of a van der Waals chain formed by CH_3OH molecules, and extending along the *c* direction in **3**. Note that molecules are also alternatively coordinated through the O atom to two parallel and adjacent polymer chains, which ideally run above and below the plane of the page.

Fig. 3 Local density of states of a single Cu ion of the investigated compounds (see Fig. 1). Positive/negative values indicate spin up/spin down states, while filled/empty areas indicate occupied/unoccupied states. Values of the spin-down gaps are also indicated.
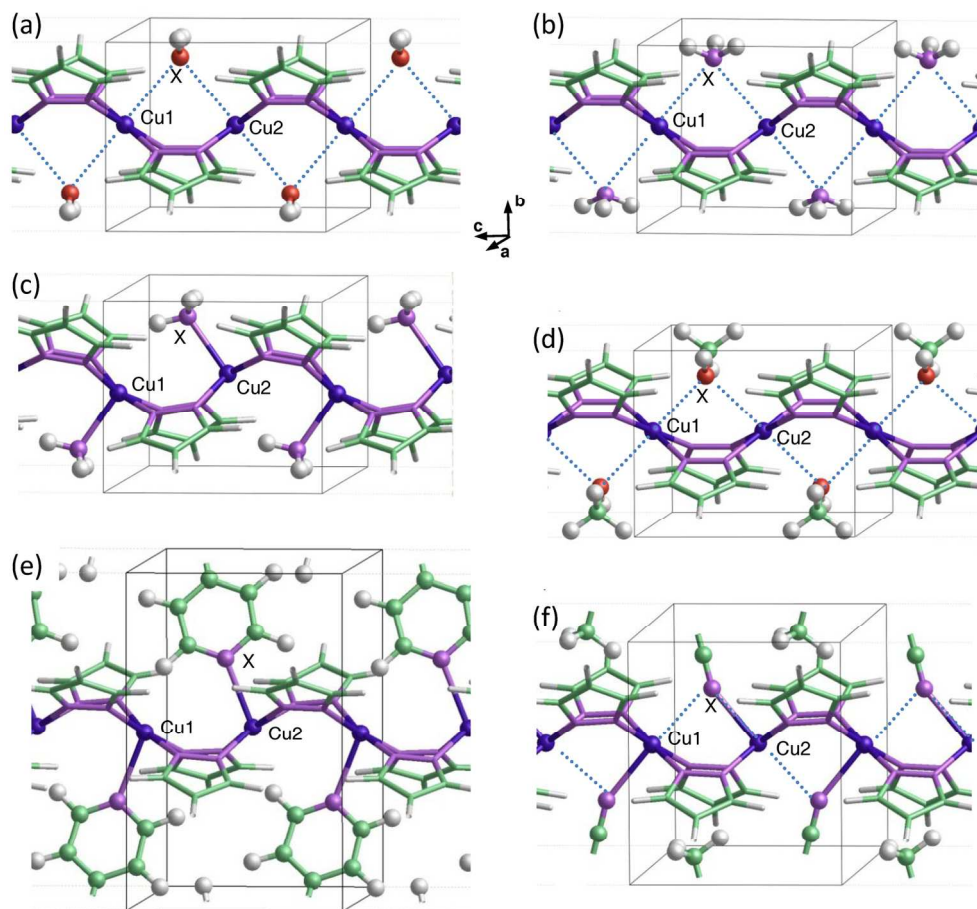
Figure 1. Ball and sticks representations of the structures of: (a) 1. (b) 2 in a hypothetical, symmetric geometry 2a. (c) 2 in its stable geometry 2b (d) 3. (e) 4. (g) 5. Relevant weak interactions are shown as dotted lines. The orthorhombic cells contains another polymer chain which is hidden for clarity.
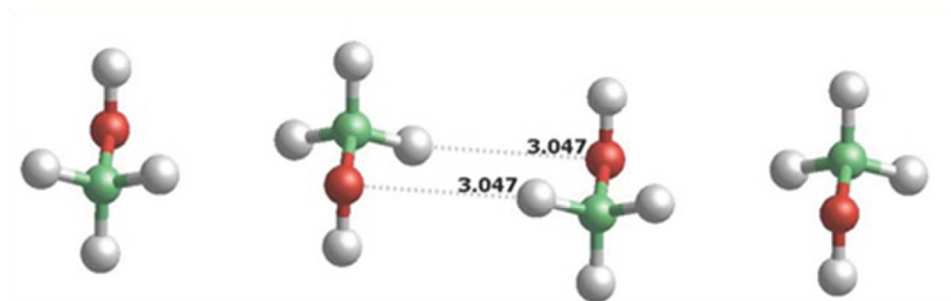160x153mm (300 x 300 DPI)

Figure 2. Sketch of a van der Waals chain formed by CH3OH molecules, and extending along the c direction in 3. Note that molecules are also alternatively coordinated through the O atom to two parallel and adjacent polymer chains, which ideally run above and below the plane of the page.
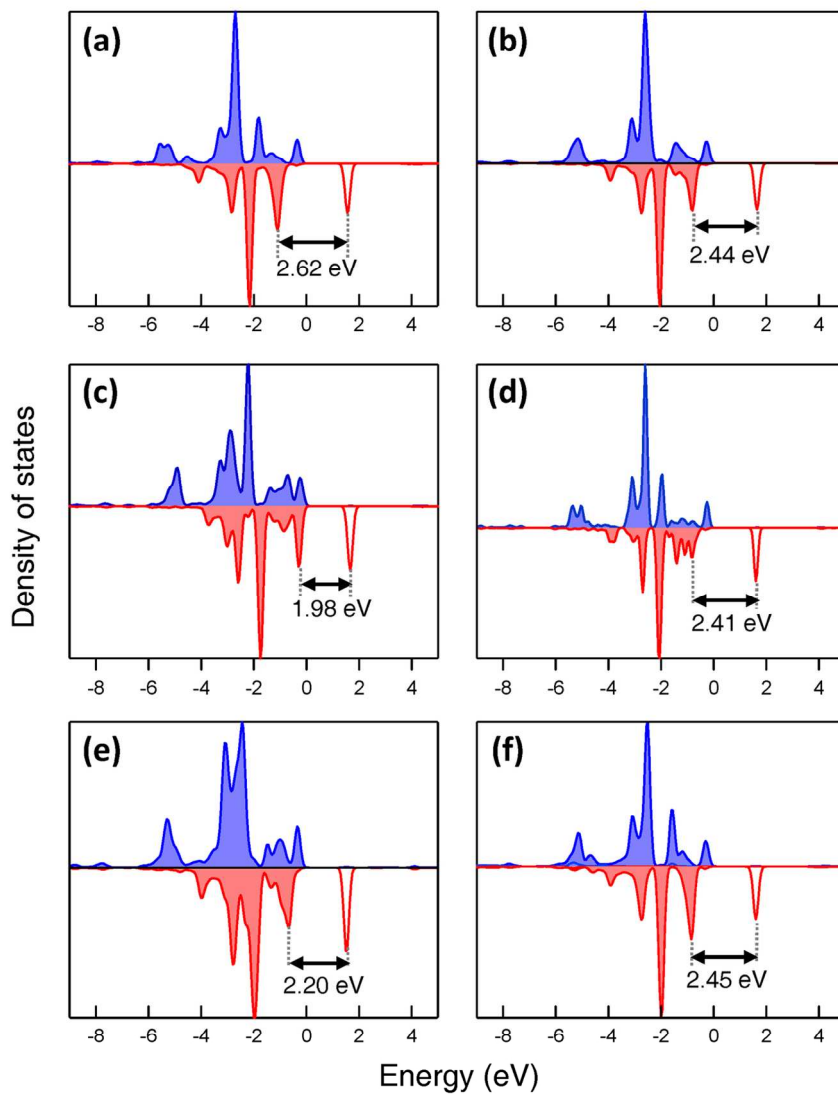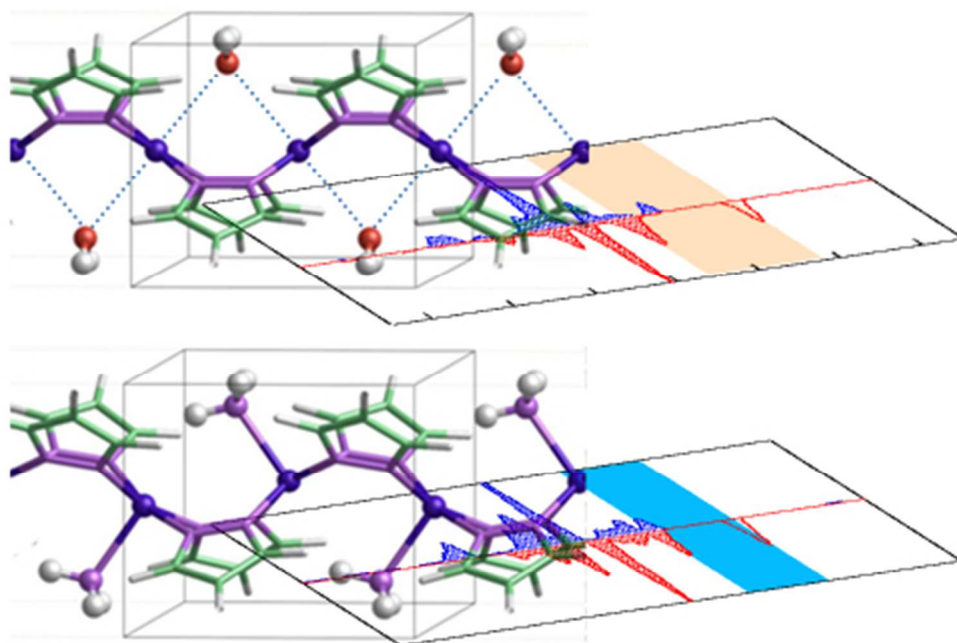40x12mm (300 x 300 DPI)

Figure 3. Local density of states of a single Cu ion of the investigated compounds (see Fig. 1). Positive/negative values indicate spin up/spin down states, while filled/empty areas indicate occupied/unoccupied states. Values of the spin-down gaps are also indicated.
126x162mm (300 x 300 DPI)

Vapochromic properties of Cu(II) coordination polymers are explained on the basis of first principles calculations.
129x91mm (96 x 96 DPI)