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New Cu(II) and Zn(II) complexes of benzolamide with diethylenetriamine: synthesis, spectroscopy and X-ray structures

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Abstract

New benzolamide (H_2bz, 5-phenylsulfonamide-1,3,4-thiadiazole-2-sulfonamide) zinc(II) and copper(II) complexes with diethylenetriamine were synthesized and characterized. The crystal structures of the [M(Hbz)$_2$(dien)] (M = Cu(II), Zn(II); dien = diethylenetriamine) complexes were determined. The metal centre adopts a near regular square pyramidal geometry. The benzolamidate anion acts as a monodentate ligand through the thiadiazole N atom contiguous to the deprotonated sulfonamido group. Spectroscopic properties are in good agreement with the crystal structures. The EPR and electronic spectroscopic studies showed that the copper(II) species doped into the zinc(II) complex adopts a near square planar geometry. The energy and composition of the SOMO of [Cu(Hbz)$_2$(dien)] and of copper substituted [Zn(Hbz)$_2$(dien)] were studied.

Keywords: Divalent metals; Zinc; Copper; Benzolamide; Diethylenetriamine; Ternary complexes

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1. Introduction

There are many areas of considerable potential interest for sulfonamide coordination chemistry. Metal complexes of 2-sulfanilamidopyrimidine (sulfadiazine) have been used to prevent bacterial infections of burns, and many of these complexes have been structurally characterized [1,2]. A tungsten complex of the bis-sulfonamide of 2,6-bis(aminomethyl)-pyridine catalyses cleavage of N–N bonds and is therefore of interest as a model for fixation of nitrogen [3]. More recently, a chiral zinc-sulfonamide complex has been demonstrated to be a relevant catalyst in enantioselective cyclopropanations [4]. Moreover, aromatic and heteroaromatic sulfonamides are well known as inhibitors of carbonic anhydrase (CA) and they have been extremely useful in the study of molecular properties and of the catalytic mechanisms of zinc-containing carbonic anhydrases [5].

A part of our investigation is focused on the study of these heteroaromatic sulfonamides as ligands. Neutral sulfonamides are expected to be poor ligands because of the withdrawal of the electron density from the nitrogen atom onto the electronegative oxygen atoms. However, if the sulfonamide N atom bears a dissociable hydrogen atom, this same electron-withdrawing effect increases its acidity and in the deprotonated form sulfonamide anions are effective sigma-donor ligands. Our previous studies on the interaction of sulfonamides with metal ions (Zn(II), Co(II), Ni(II) and Cu(II)) have shown that these can bind in several ways and not only as unidentate anions through the sulfonamide N atom [6–11]. Recently, as a continuation of our investigation, we initiated the study of the coordination behaviour of benzolamide (H_2bz, 5-phenylsulfonamide-1,3,4-thiadiazole-2-sulfonamide). Benzolamide (Fig. 1) contains two dissociable protons and affords potentially chelating thiadiazole and sulfonamide N donor binding sites, hence different coordination possibilities can be expected.

We have reported ternary zinc and copper benzolamide complexes with amines (ammomia, diethylenetriamine (dien), dipropylenetriamine (dpt) and tris(2-benzimidazolyl-methylamine) (L)) [12,13]. In these complexes the coordination behaviour of the benzolamide was different. Thus, in Cu(bz)(NH_3)$_4$, Cu(bz)(dien)·H_2O and Cu(bz)(dpt)·H_2O the dideprotonated sulfonamide coordinates the metal ion through the N atom of the free sulfonamido

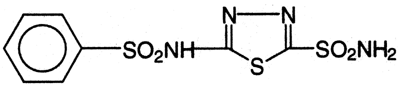

Fig. 1. Benzolamide.

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group, whereas in the polymer $\{[Zn_2(bz)_2(NH_3)_4] \cdot 2H_2O\}_\infty$ the dinegative benzolamide anion acts as a bridge, linking two metal centres through the N atom of the free sulfonamido group and the thiadiazole N closest to the substituted sulfonamido moiety. In the $[Zn(Hbz)L]ClO_4 \cdot H_2O$ compound the monodeprotonated benzolamide interacts via thiadiazole N contiguous to the substituted sulfonamido moiety [13]. In this paper, as a part of our continuing interest in the coordination behaviour of benzolamide, we report the synthesis, structure and spectroscopic properties of the new benzolamide $M(Hbz)_2(dien)$ (M = Cu(II) and Zn(II)) complexes in which the sulfonamide in its monodeprotonated form interacts through one of the thiadiazole N atoms.

2. Experimental

2.1. Materials

Benzolamide (H_2bz, 5-phenylsulfonamide-1,3,4-thiadiazole-2-sulfonamide) was provided by Professor C.T. Supuran (University of Florence, Italy). All reagents were of the highest grade commercially available and used without further purification.

2.2. Methods

IR spectra were recorded on a Perkin-Elmer 843 instrument. Samples were prepared using the KBr technique. Electronic spectra were registered on a Shimadzu UV 2101PC spectrophotometer. EPR spectra were carried out with a Bruker ER 200 D spectrometer. Magnetic susceptibility measurements at room temperature were taken with a fully automated AZTEC DSM8 pendulum-type susceptometer. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. Corrections for diamagnetism were estimated from Pascal's constants.

2.3. Synthesis

2.3.1. Cu(Hbz)$_2$(dien)

0.25 mmol of diethylenetriamine was added with continuous stirring to 40 ml of an ethanolic solution containing 0.25 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ and 0.5 mmol of benzolamide. Immediately, a little amount of a blue solid was formed. It was separated by filtration and the filtrate was left to stand at 4°C. After a few days prismatic blue crystals suitable for X-ray measurements were obtained. The crystals were filtered, washed with cooled ethanol and dried under vacuum. Yield 40%. *Anal*. Found: C, 29.45; H, 3.28; N, 19.23. Calc. for $C_{20}H_{27}CuN_{11}O_8S_6$: C, 29.83; H, 3.35; N, 19.14%.

2.3.2. Zn(Hbz)$_2$(dien)

The synthesis procedure is similar to that described above but $Zn(ClO_4)_2 \cdot 6H_2O$ was used and no solid was obtained after the addition of diethylenetriamine. After 3–4 days prismatic colourless crystals were obtained from the resulting solution at room temperature. Yield 30%. *Anal*. Found: C, 29.57; H, 3.31; N, 19.32. Calc. for $C_{20}H_{27}ZnN_{11}O_8S_6$: C, 29.76; H, 3.34; N, 19.10%.

2.3.3. Doped Zn,Cu(Hbz)(dien)

0.25 mmol of dien was added to 40 ml of an ethanolic solution containing 0.225 mmol of $Zn(ClO_4)_2 \cdot 6H_2O$ and 0.025 of $Cu(ClO_4)_2 \cdot 6H_2O$ under stirring. The solution turned dark blue and then 0.5 mmol of benzolamide was added. It was stirred for about half an hour and then was left to stand at room temperature. Slow evaporation of the solvent gives a violet precipitate. Yield 65%.

2.4. Crystal data and structure refinement

A well-shaped blue crystal of $[Cu(Hbz)_2(dien)]$ ($0.22 \times 0.25 \times 0.27$ mm) and a colourless crystal of $[Zn(Hbz)_2(dien)]$ ($0.17 \times 0.18 \times 0.18$ mm) were mounted on a Siemens P4 four circle diffractometer coupled to Mo Kα radiation. The unit cell dimensions were determined from the angular settings of 25 reflections with $1.88 < \theta < 22.5°$ for the Cu(II) compound and $1.87 < \theta < 22.5°$ for the Zn(II) complex. A total of 4376 and 4415 reflections were measured for $[Cu(Hbz)_2(dien)]$ and $[Zn(Hbz)_2(dien)]$, respectively, of which 4130 ($R_{int} = 0.0248$) and 4161 ($R_{int} = 0.0452$) were unique ($0 \leq h \leq 12$, $-12 \leq k \leq 11$, $-14 \leq l \leq 14$). Semi-empirical absorption corrections from ψ scans were applied for $[Zn(Hbz)_2(dien)]$ and no absorption corrections were applied for $[Cu(Hbz)_2(dien)]$. Each structure was solved by direct methods [14] and refined by full-matrix least-squared analysis on F^2. Largest peak and hole in the final difference map were $+0.767$ and -0.664 e Å^{-3} (Cu(II) compound) and 0.415 and -0.563 e Å^{-3} (Zn(II) complex). Other relevant parameters of crystal structure determination are collected in Table 1.

2.5. EHMO calculations

All calculations were performed using the Package of Programs for Molecular Orbital Analysis by Mealli and Proserpio [15] based on CDNT (atom Cartesian coordinate calculations), ICON (extended Hückel method with the weighted *Hij* formula) and FMO (fragment molecular orbital), including the drawing program CACAO (computer aided composition of atomic orbitals).

The extended Hückel parameters are as follows. *Hij*: Cu 4s, −11.40 eV; Cu 4p, −6.06 eV; Cu 3d, −14.00 eV; Zn 4s, −12.41 eV; Zn 4p, −6.53 eV; N 2s, −26.00 eV; N 2p, −13.40 eV; S 3s, −20.00 eV; S 3p, −13.30 eV; O 2s, −32.30 eV; O 2p, −14.80 eV; C 2s, −21.40 eV; C 2p, −11.40 eV; H 1s, −13.60 eV. Orbital exponents (contraction coefficients in double-ξ expansion given in parentheses): Cu 4s, 4p, 2.200; Cu 3d, 5.950 (0.5933), 2.300 (0.5744); Zn 4s, 2.010; Zn 4p, 1.700; N 2s, 2p, 1.950; S 3s, 3p, 1.817; O 2s, 2p, 2.275; C 2s, 2p, 1.625; H 1s, 1.300.

Table 1
Crystal data and structure refinement

	$[Cu(Hbz)_2(dien)]$	$[Zn(Hbz)_2(dien)]$
Formula	$C_{20}H_{27}CuN_{11}O_8S_6$	$C_{20}H_{27}ZnN_{11}O_8S_6$
Formula weight	805.43	806.25
Symmetry, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a (Å)	11.284(2)	11.256(5)
b (Å)	11.790(2)	11.827(5)
c (Å)	13.359(2)	13.405(2)
α (°)	103.582(10)	102.82(3)
β (°)	100.939(13)	101.58(4)
γ (°)	105.225(13)	105.41(3)
U (Å^3)	1606.0(4)	1612.2(12)
Z	2	2
D_c (g cm^{-3})	1.666	1.663
$F(000)$, μ (cm^{-1})	826, 11.33	828, 12.13
Refined parameters	415	416
GOF	1.077	0.973
R ($I > 2\sigma(I)$) [a]	$R_1 = 0.0489$, $wR_2 = 0.1310$	$R_1 = 0.0600$, $wR_2 = 0.1401$
R (all data)	$R_1 = 0.0748$, $wR_2 = 0.1531$	$R_1 = 0.1137$, $wR_2 = 0.17524$

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R_w = [\Sigma w(F_c^2)/\Sigma wF_o^4]^{1/2}$.

3. Results and discussion

3.1. Synthesis of the complexes

The ternary complexes $[M(Hbz)_2(dien)]$ were obtained by reaction of the metal salt, the triamine and benzolamide in a molar ratio 1:1:2. The ratio of reagents is important to obtain the compounds described here since the addition of an equimolecular amount of triamine and benzolamide leads to the formation of the previously reported $[M(bz)(dien)] \cdot H_2O$ compounds in which the benzolamide is present in its dideprotonated form [12].

3.2. Description of the crystal structures

A drawing of $[Cu(Hbz)_2(dien)]$ including the atomic numbering scheme is shown in Fig. 2. Interatomic distances and angles relevant to the coordination sphere for the $[Cu(Hbz)_2(dien)]$ and $[Zn(Hbz)_2(dien)]$ complexes are given in Table 2.

The metal ion is pentacoordinated by five N atoms, the structure being best described as a regular square pyramid. The three N atoms (N(5), N(6) and N(7)) of the dien ligand occupy equatorial positions. The remaining two M(II) square pyramidal coordination sites are occupied by two benzolamidate anions that interact through the thiadiazole N atom contiguous to the deprotonated sulfonamido group (N(3), N(9)). The Cu–N(dien) bond distances are in the narrow range from 2.014(5) to 2.035(5) Å and the Zn–N(dien) lengths range from 2.082(7) to 2.202(7) Å. As expected from the ionic radii of the divalent metal ions, the average of these Zn–N bond distances is considerably longer than those involving Cu. Both MN_5 chromophores are essentially square pyramidal but with significant differences in the local molecular stereochemistry. In particular, in the Zn complex the Zn–N(6) (2.202(7) Å) is the longest bond distance while in the Cu compound the Cu–N(6) (2.035(5) Å) distance is one of the shorter distances. Moreover, the equatorial Cu–N(thiadiazole) (Cu–N(3), 2.070(5) Å) is markedly shorter than the axial Cu–N(thiadiazole) distance (Cu–N(9), 2.233(5) Å) but the equatorial Zn–N(thiadiazole) (Zn–N(3), 2.188(7) Å) is longer than the axial Zn–N(thiadiazole) distance (Zn–N(9), 2.042(7) Å). The equatorial Cu–N(thiadiazole) is found to be comparable to the corresponding bond in Cu(II) complexes with related sulfonamides [7,9] and the equatorial Zn–N(thiadiazole) is comparable to the same distance in the $[Zn(Hbz)L]ClO_4 \cdot H_2O$ compound (L = tris(2-benzimidazolyl-methylamine)) [13]. The axial Cu–N(thiadiazole) length is ca. 0.23 Å shorter than that of the $Cu(Hacm)_2(en)_2$ complex (H_2acm = acetazolamide, en = ethylenediamine) [8]. The

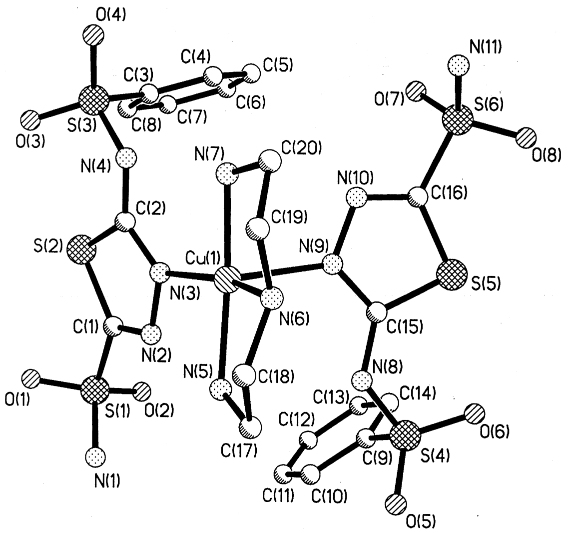

Fig. 2. Drawing of the $[Cu(Hbz)_2(dien)]$ complex.

Table 2
Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses

$[Cu(Hbz)_2(dien)]$		$[Zn(Hbz)_2(dien)]$	
Cu(1)–N(5)	2.014(5)	Zn(1)–N(5)	2.093(7)
Cu(1)–N(6)	2.035(5)	Zn(1)–N(6)	2.202(7)
Cu(1)–N(9)	2.233(5)	Zn(1)–N(9)	2.045(7)
Cu(1)–N(7)	2.017(5)	Zn(1)–N(7)	2.082(8)
Cu(1)–N(3)	2.070(5)	Zn(1)–N(3)	2.188(7)
N(5)–Cu(1)–N(7)	163.4(2)	N(7)–Zn(1)–N(5)	149.8(3)
N(5)–Cu(1)–N(6)	82.8(2)	N(5)–Zn(1)–N(6)	80.1(3)
N(7)–Cu(1)–N(6)	83.8(2)	N(7)–Zn(1)–N(6)	80.2(3)
N(5)–Cu(1)–N(3)	90.8(2)	N(5)–Zn(1)–N(3)	88.7(3)
N(5)–Cu(1)–N(9)	100.8(2)	N(9)–Zn(1)–N(5)	109.2(3)
N(6)–Cu(1)–N(9)	94.6(2)	N(9)–Zn(1)–N(6)	99.5(3)
N(6)–Cu(1)–N(3)	162.3(2)	N(3)–Zn(1)–N(6)	153.4(3)
N(7)–Cu(1)–N(3)	99.2(2)	N(7)–Zn(1)–N(3)	98.9(3)
N(7)–Cu(1)–N(9)	90.8(2)	N(9)–Zn(1)–N(7)	96.5(3)
N(3)–Cu(1)–N(9)	102.8(2)	N(3)–Zn(1)–N(9)	107.0(3)

Cu–N(dien) bond distances are similar to those in other Cu(II) complexes with dien [16–19].

The in-plane angular distortions described by the ratio τ represent a percentage trigonal distortion of a square pyramidal geometry (1 for perfect trigonal bipyramidal, 0 for perfect square pyramidal). The calculated τ value from bond angles of 0.02 for the Cu(II) compound and of 0.06 for the Zn(II) complex clearly indicates a quasi regular pyramidal geometry [20]. For the two structures the major changes in the angles subtended at the metal centre are found in N(5)–M–N(7) and N(6)–M–N(3) which expand from 149.8(3) and 153.4(3)° [Zn(Hbz)$_2$(dien)] to 163.4(2) and 162.3(2)° [Cu(Hbz)$_2$(dien)]. The *cis* equatorial N–M–N bond angles differ from 90° owing to the presence of a chelate ring that produces rhombic in-plane effects [21].

In the copper compound the atoms that constitute the equatorial plane deviate 0.050 Å from planarity and those of the zinc complex deviate 0.006 Å. The copper atom is displaced 0.2543 Å from the equatorial plane towards the apical position and the zinc ion is situated at 0.4876 Å from this plane.

It is also interesting to note that the copper compound presents a square pyramidal geometry since of the dien complexes structurally characterized, very few contain dien and a monodentate ligand [17] and these adopt six-coordinate tetragonally elongated octahedral geometries, with both ligands located equatorially and anions weakly bound axially [17]. Square pyramidal geometries are found only in copper dien complexes with bidentate ligands [22]. This geometry is also exhibited by Cu(II) compounds with pentamethyldiethylenetriamine and a monodentate ligand, but in these cases a third ligand (either solvent or anion) binds in the axial position [23–25].

The uninegative benzolamidate anions behave as monodentate ligand through the thiadiazole N atom (N(3), N(9)) contiguous to the deprotonated sulfonamido group. This coordination behaviour is also exhibited by the monodeprotonated benzolamide in the [Zn(Hbz)L]ClO$_4$·H$_2$O compound (L = tris(2-benzimidazolyl-methylamine)) [13]. In these complexes the coordination mode of the benzolamide is determined by the fact that the deprotonation takes place on the substituted sulfonamido moiety. This makes the thiadiazole N closest to this sulfonamido group the best donor atom. However, it differs from that found in [Cu(bz)(NH$_3$)$_4$] [12] where the dideprotonated benzolamide acting as monodentate ligand binds the metal ion through the free sulfonamide N atom. Although it is difficult to rationalize the coordination behaviour of benzolamide, our investigation of its coordination properties has demonstrated that in the monodeprotonated form it behaves as a monodentate ligand coordinating the metal through the thiadiazole N atom closest to the substituted sulfonamido group. When dideprotonated it shows a more variable coordination behaviour, acting as a bridge through the thiadiazole and free sulfonamido N atoms [13] or as monodentate via free sulfonamido N atom [12].

It is interesting to compare the coordination behaviour of benzolamide and the structurally related acetazolamide (H$_2$acm, 5-acetamido-1,3,4-thiadiazole-2-sulfonamide) when both are monodeprotonated. Although both sulfonamides offer the same donor sites, a N thiadiazole atom and a N sulfonamido, the coordination behaviour of acetazolamide in the previously reported [Cu(Hacm)(dien)]·H$_2$O and [Cu(Hacm)(dpt)]·H$_2$O compounds [26] contrasts with that of benzolamide. Acetazolamide in these complexes acts as a monodentate ligand through the N sulfonamido atom.

3.3. IR spectra

In Table 3 are collected the most significant IR data for the complexes reported here. For comparison the IR data for related compounds are also included.

The modifications of the characteristic bands of the benzolamide ligand give some information about its coordination and/or its deprotonation. It is found that the changes in the asymmetric and symmetric stretching modes of the SO$_2$ group afford some evidence of the deprotonated nature of the benzolamide. When monodeprotonated, two bands are associated with each vibration, whereas when dideprotonated, one band for each vibration is observed. These bands show some splitting in the [Zn(Hbz)$_2$(dien)] complex that probably arises from hydrogen bonding or crystal packing effects. Moreover, it is noteworthy that in all the complexes, the ν(C=N) vibration is strongly modified. Since the changes occur in the complexes where the benzolamide is monodeprotonated and in the complexes where the benzolamide is

Table 3
IR selected bands (cm^{-1}) [a]

Compound	$\nu(C{=}N)_{ring}$	$\nu(SO_2)_{asym}$	$\nu(SO_2)_{sym}$	ν(S–N)
Benzolamide(H$_2$bz)	1580–1570d, 1500	1360, 1320	1180, 1140	940, 910
[Cu(Hbz)$_2$(dien)]	1460	1360,1270	1180, 1150	940, 920
[Zn(Hbz)$_2$(dien)]	1480–1465d	1360–1350d, 1280–1260d	1170, 1140	930, 915
Cu(bz)(deta)(H$_2$O) [b]	1430	1275	1140	970, 950
Cu(bz)(dpt)(H$_2$O) [b]	1430	1300–1280d	1140–1130d	950–940d
[Zn(Hbz)L]ClO$_4$·H$_2$O [c]	1475	1356,1275	1160, 110	920

[a] d doublet.

[b] From Ref. [12].

[c] From Ref. [13].

dideprotonated, this fact could be attributed to the modifications that take place on the thiadiazole π-system upon deprotonation of the substituted sulfonamido group.

3.4. Magnetic susceptibility, electronic and EPR spectra

The [Cu(Hbz)$_2$(dien)] compound exhibits a normal value of magnetic moment for an orbitally non-degenerate ground state, 1.76 BM.

The solid electronic spectrum of [Cu(Hbz)$_2$(dien)] is in agreement with the crystallographic data. It presents a single broad ligand field absorption with a maximum at 630 nm as expected for copper(II) complexes having a square pyramidal geometry [27].

At room temperature the solid-state EPR spectrum of [Cu(Hbz)$_2$(dien)] is axial with the parallel component poorly resolved. The calculated EPR parameters are $g_\parallel \approx 2.30$ and $g_\perp = 2.13$. The EPR of the copper doped into its zinc counterpart is also axial in nature. The low-field region shows the quartet hyperfine structure from Cu ($I = 3/2$). The ground state parameters extracted from the experimental spectrum by simulation [28] are $g_\parallel = 2.21$, $g_\perp = 2.05$ and $A_\parallel = 191 \times 10^{-4}$ cm^{-1}. This $A_\parallel$ value of the complex diluted in the isomorphous zinc lattice is larger than the values expected for a five-coordinated geometry. It is well known that Cu(II) square planar and octahedral complexes with tetragonal elongation lead to a large parallel Cu hyperfine coupling. Further, the quotient $g_\parallel / A_\parallel$ lies in the range 105–135 cm, supporting a square planar geometry [29]. So, it seems that the Cu(II) assumes a stereochemistry much more close to that of a planar CuN$_4$ chromophore [30]. This change in the geometry is supported by the mull spectrum of the copper(II) complex doped in the corresponding zinc complex that exhibits a shift from 630 nm in the pure copper to 575 nm.

In acetonitrile the EPR spectrum of the [Cu(Hbz)$_2$(dien)] displayed axial anisotropy with some rhombic perturbation. The EPR features obtained from simulation are $g_\parallel \approx 2.29$, $g_\perp = 2.13$ and $A_\parallel = 185 \times 10^{-4}$ cm^{-1}. They are indicative of a square planar based structure. The UV–Vis spectrum shows a d–d band at ca. 600 nm ($\varepsilon = 130$ mol^{-1} cm^{-1}) which agrees well with a square planar arrangement around the copper ion. Apart from the d–d transition, the spectrum displays an intense absorption at 300 nm ($\varepsilon = 29120$ mol^{-1} cm^{-1}) and a less intense absorption at 245 nm ($\varepsilon = 16990$ mol^{-1} cm^{-1}) associated with ligand π–π* transitions. Both EPR and electronic spectra indicate that the geometry of the copper ion in solution is, like in the doped compound, nearer to square planar with weak apical interactions.

3.5. Extended Hückel molecular orbitals calculations

The crystal structures of the isomorphous [Cu(Hbz)$_2$(dien)] and [Zn(Hbz)$_2$(dien)] complexes have shown that both compounds present some differences in their local molecular stereochemistry. The most significant differences are found in the M–N(9) (2.233(5) (Cu) and 2.045(7) Å (Zn)), in the M–N(6) (2.035(5) (Cu) and 2.202(7) Å (Zn)) bond lengths and in the *trans* angles N(5)–M–N(7) and N(6)–M–N(3), which expand from 149.8(3) and 153.4(3)° [Zn(Hbz)$_2$(dien)] to 163.4(2) and 162.3(2)° [Cu(Hbz)$_2$(dien)]. Moreover, the [Cu(Hbz)$_2$(dien)] complex presents electronic properties (see Section 3.4) different to those of the copper doped compound that suggests that when the Cu(II) substitutes the Zn(II) ion does not adopt the geometry observed in the pure copper compound. In order to understand how these structural differences can affect the energy and composition of the relevant molecular orbitals of the complexes we have undertaken extended Hückel molecular orbital (EHMO) calculations by means of the CACAO program [15]. These calculations have been performed using the crystallographic coordinates derived from the crystal structures of the [Cu(Hbz)$_2$(dien)] compound and [Zn(Hbz)$_2$(dien)] in which the Zn(II) has been replaced by Cu(II) as a 'model' of the copper doped compound.

The SOMO of the [Cu(Hbz)$_2$(dien)] presents an energy of −11.049 eV (Fig. 3). The contribution of metal d orbitals to the SOMO is 39% ($d_{x^2-y^2}$ (28%), d_{xz} (8%), d_{xy} (2%) and d_{z^2} (1%)). The atomic orbitals of the ligands that participate in SOMO formation are the three N atoms of the dien (N(5), px 12%, py 2%; N(6), py 18%; N(7), px 10%, pz 3%) and one N thiadiazole atom (N(3), py 9%) from one of the benzolamidate ligands.

When these calculations are performed on the 'model' copper doped compound, a SOMO with an energy of −11.649 eV is obtained (Fig. 4). The overall contribution of the copper d atomic orbitals to this MO is 34% ($d_{x^2-y^2}$ (25%), d_{xz} (7%) d_{xy} (1%) and d_{yz} (1%)), although the ligand orbitals involved are the same as in Cu(Hbz)$_2$(dien) their contribution is slightly different (N(5), px 12%; N(6), py 21%; N(7), px 7%, pz 5%; N(3), py 9%).

The electronic and EPR spectra of the [Cu(Hbz)$_2$(dien)] and of the copper doped compound suggest a change of geometry for the Cu(II) ion when it replaces the Zn(II) ion in the [Zn(Hbz)$_2$(dien)] complex. The EHMO calculations have

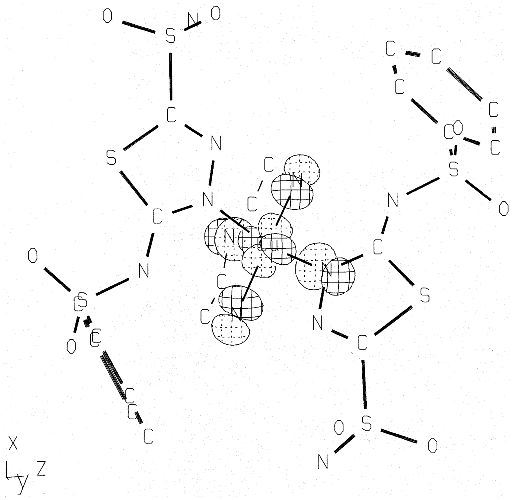

Fig. 3. SOMO of the [Cu(Hbz)$_2$(dien)] complex.

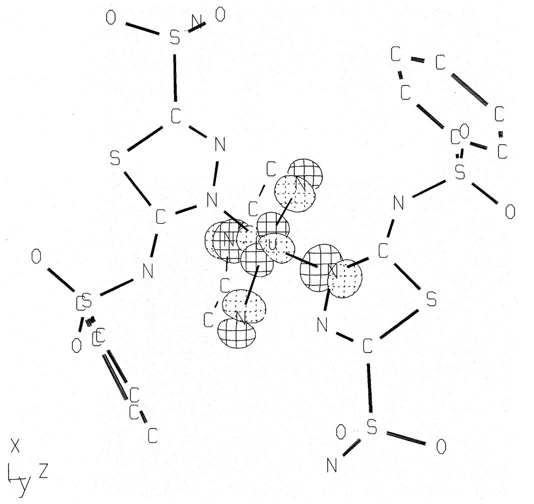

Fig. 4. SOMO of the copper substituted [Zn(Hbz)$_2$(dien)] complex.

shown that the energy difference between the SOMOs of both compounds, 0.6 eV (ca. 5000 cm^{-1}), could explain the variances found in their electronic properties.

Supplementary data

Supplementary crystallographic data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) on request, deposition numbers CCDC 132907/CCDC 132908.

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