

New 1,3,4-Oxadiazolecopper(II) Derivatives Obtained from Thiosemicarbazone Complexes

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Pyridine-2-carbaldehyde thiosemicarbazone and pyridine-2-carbaldehyde 4*N*-methyl thiosemicarbazone ligands (HL_I and HL_Imm respectively) undergo an oxidative cyclization when treated with bromate or iodate, leading to 2-amino-5-pyridin-2-yl-1,3,4-oxadiazole and 2-methylamino-5-pyridin-2-yl-1,3,4-oxadiazole (HL_{II} and HL_{II}mm). This reaction occurs either with free ligands or when coordinated to copper(II). Some of the starting ([{Cu(L_Imm)(NO₃)₂}] (3), intermediate Cu(L_I)(IO₃)·(H₂O) (1), [{Cu(L_I)I₂}] (2), [{Cu(L_Imm)Br₂}] (4), and final compounds [{Cu(HL_{II})(H₂O)₃}₂](SO₄)₂ (5), [{Cu(HL_{II}mm)(H₂O)₂(SO₄)₂}]·2H₂O (6), (HL_{II}) (7), [HL_{II}mm]·3H₂O (8) have been isolated and characterized by elemental analyses, IR, UV-visible, NMR, and EPR spectroscopy. The structures of 2, 3, 4, 5, 6, and 8, solved by X-ray diffraction methods, contain dinuclear entities with either square-pyramidal (2, 3, 4) or octahedral (5, 6) copper(II) ions.

Structural and spectroscopic results suggest that ligand-to-metal charge transfer occurs in these compounds. The EPR spectra at 120 K exhibit rhombic (1, 3, 4), isotropic (2), and axial (5, 6) signals. Magnetic measurements show antiferromagnetic couplings for 2, 4, 5, and 6. The susceptibility data were fitted by the Bleaney–Bowers equation for copper(II) dimers. The obtained *J/k* values are –20.20, –8.85, –2.75, and –2.78 K for 2, 4, 5, and 6, respectively. However, ferromagnetic intradimeric interactions are present in 3 (*J/k* = +9.90 K) together with antiferromagnetic interdimer coupling (*z'J'/k* = –1.70 K). Magneto-structural studies show the influence of the non-thiosemicarbazone coligand in the magnetic behaviour of these complexes.

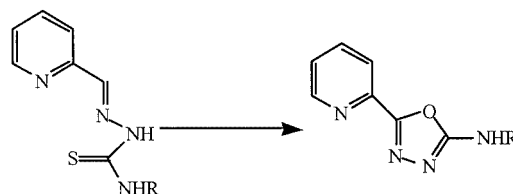
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Introduction

Several copper(II) complexes of *N*-heterocyclic carbaldehyde thiosemicarbazones are of interest because they show a greater carcinostatic activity than the free thiosemicarbazone.^[1–3] However, despite several proposals, the mechanism of their action in cells^[4–13] is unclear. A deeper knowledge of their reactivity is essential to understand their interactions with biological molecules.

Among the reactions involving thiosemicarbazones, some published mechanisms of the oxidative cyclization give rise to thiadiazoles, thiadiazolines, pyrazolones, 1,2,4-triazoline-5-thiones, and other compounds.^[14–16] Recently, we reported the oxidation of pyridine-2-carbaldehyde 4*N*-methyl-

thiosemicarbazonecopper(II) entities that led to the attainment of a copper(II) complex with the 2-methylamino-5-pyridin-2-yl-1,3,4-oxadiazole ligand, using potassium bromate as oxidant (see Scheme 1).^[17] The singularity of this reaction lies not only in the fact that 1,3,4-oxadiazoles are obtained from a non-acylated substrate for the first time, but in the novel process of desulfurization of thiosemicarbazones that implies this oxidative cyclization. The usual methods of preparing oxadiazoles consist of the cyclization of substrates such as acyl thiosemicarbazides^[18] or acyl thioureas^[19,20] with a variety of oxidants.



Scheme 1

We present here the synthesis and spectroscopic studies of 8 new compounds, [Cu(L_I)(IO₃)·(H₂O)] (1), [{Cu(L_I)I₂}] (2), [{Cu(L_Imm)(NO₃)₂}] (3), [{Cu(L_Imm)Br₂}] (4), [{Cu(HL_{II})(H₂O)₃}₂](SO₄)₂ (5), [{Cu(HL_{II}mm)(H₂O)₂-

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(SO₄)₂·2H₂O (**6**), (HL_{II}) (**7**), and (HL_{II}mm)·3H₂O (**8**) (HL_I = pyridine-2-carbaldehyde thiosemicarbazone, HL_Imm = pyridine-2-carbaldehyde 4*N*-methylthiosemicarbazone, HL_{II} = 2-amino-5-pyridin-2-yl-1,3,4-oxadiazole and HL_{II}mm = 2-methylamino-5-pyridin-2-yl-1,3,4-oxadiazole), together with the structural characterization of six of them and the magnetic properties of **2**, **3**, **4**, **5**, and **6**. These compounds are reactants, products or intermediates in the oxidative cyclization process. A mechanism is proposed for the reaction.

Results and Discussion

The Oxidation Process

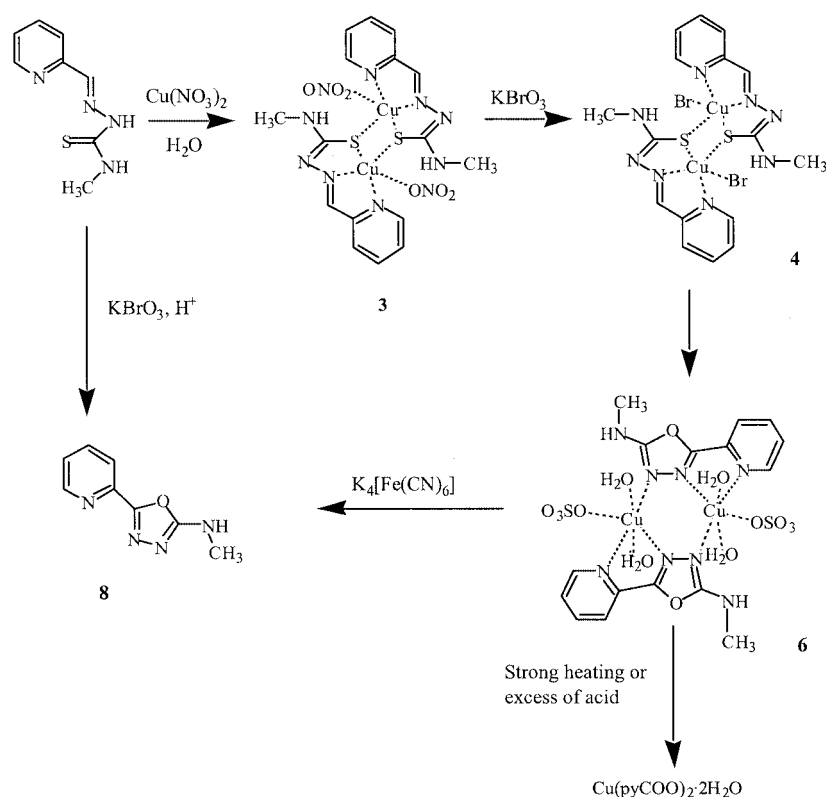
The reactions involved in the oxidative attack of bromate on HL_Imm derivatives are summarized in Scheme 2.

The oxidative cyclization proceeds smoothly with the addition of bromate to a dark green aqueous solution of complex **3** adjusted to pH ≈ 6. After filtering off compound **4** the colour of the solution gradually becomes lighter. At the same time, the pH decreases to 3–4 and an irritant gas evolves from the reaction mixture, and single crystals of **6** are obtained after two days. The reaction is faster when small amounts of acid are added with slight heating. Excess acid and too much heat have led to brown solutions from which crystals of bis(pyridinecarboxylate)copper(II) were

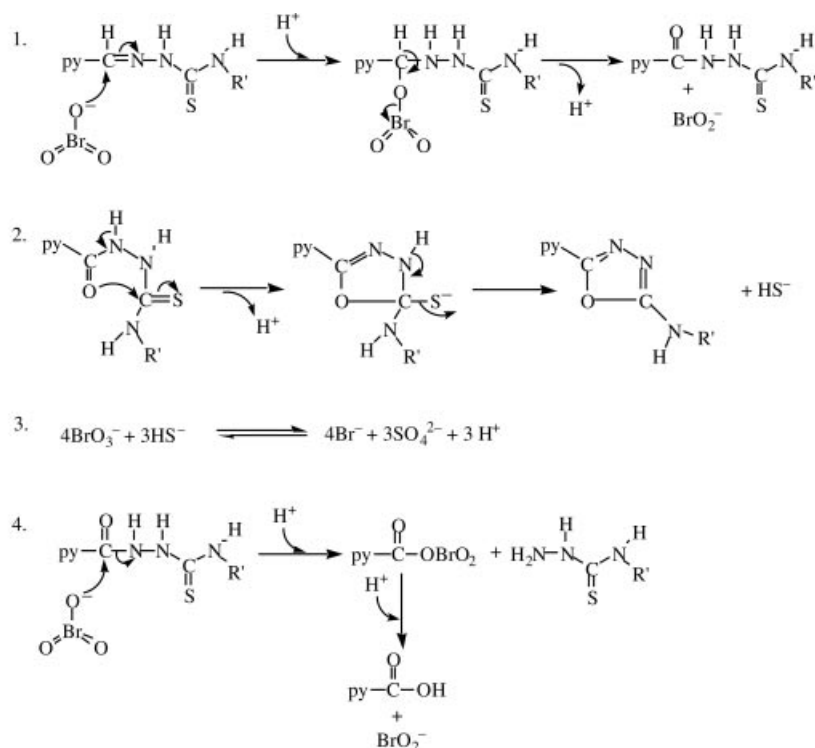
isolated.^[17] Ligand **8** can be removed from **6** by the addition of K₄[Fe(CN)₆]·3H₂O in ethanol. Furthermore, it can also be synthesized by direct oxidative cyclization of HL_Imm.

The oxidation of HL_I was developed in exactly the same way as for HL_Imm, and analogous compounds were identified. This procedure was also applied to a new ligand, HL_Idm (pyridine-2-carbaldehyde 4*N*,4'-*N*-dimethylthiosemicarbazone), prepared following a published method.^[21] However, no oxidation compounds could be isolated with either the thiosemicarbazone free ligand or the respective copper(II) complex as starting material, suggesting that steric effects can influence the oxidative cyclization.

The cyclization of the free ligands takes place either with bromate or iodate, requires pH ≈ 0–1 and yields similar results. For copper(II) complexes, oxidation with bromate occurs even at pH ≈ 6, but no evidence of oxidative cyclization of thiosemicarbazone–copper(II) compounds was detected using iodate at pH ≈ 6. This seems to accord with the reduction potentials: E° (BrO₃[−]/Br[−]) = 1.15 V, E° (IO₃[−]/I[−]) = 1.09 V. The reaction of a thiosemicarbazone–copper(II) complex with bromate yields different products from those obtained with iodate. In fact, bromato thiosemicarbazonecopper(II) derivatives cannot be isolated. The use of acidic media gives rise to mixtures of compounds in both cases. Several attempts using chlorate as oxidant did not produce evidence of oxidative cyclization. This is surprising given its reduction potential [E° (ClO₃[−]/Cl[−]) = 1.45 V at pH ≈ 0]; kinetic factors could account for this result.



Scheme 2



Scheme 3

From the experimental results we propose the two-step mechanism shown in Scheme 3 for the free ligand, and an analogous mechanism is proposed for the copper(II) complexes:

i) Formation of the Acylthiosemicarbazide

An initial nucleophilic attack of the bromate anion on the azomethinic carbon of the thiosemicarbazone ligand yields a new carbonyl group and bromite is released. The bromite can act as an oxidizing agent on other thiosemicarbazone ligands, giving rise to hypobromite ions. The successively reduced bromo derivatives from each oxidation step thus act as oxidants until the complete conversion of bromate into bromide.

Consequently, an acidic media should favor the beginning of the reaction, which is in good agreement with our experimental observations.

ii) Cyclization to 2-Amino-5-pyridin-2-yl-1,3,4-oxadiazole

In a second step, the acylthiosemicarbazide cyclizes to 2-amino-5-pyridin-2-yl-1,3,4-oxadiazole and, as a result, is desulfurized. This reorganization leads to a decrease in pH (in good agreement with experimental observations). The removal of the sulfur atom from the ligand, to give sulfate, could be due to concomitant inorganic processes such as those represented in reaction 3. Furthermore, the coupled reaction 3 shifts, to the right, reaction 2.

Further bromate attack on the acyclic carbon would cleave the acylthiosemicarbazide, in competition with step ii). As a result, pyridine-2-carboxylic acid and other second-

ary products would be obtained (Scheme 3, reaction 4), which is in good agreement with the experimental results.

Since most published oxidation reactions leading to oxadiazoles take acylated compounds as reactants,^[18–20] it seems highly probable that this intermediate is formed in a first step. Oxidative attacks similar to reaction 1 have been reported for the conversion of carbodiimide into urea using dimethyl sulfoxide as oxidant.^[22,23] Furthermore, bromate derivatives oxidize primary alcohols to esters,^[24] synthesize benzoxiodol-3-one starting from 2-iodobenzoic acid^[25] and oxidize a keto group in the preparation of benzoic acid from benzoin.^[26]

Conversely, cyclizations of open-chain compounds such as thioureas, thiosemicarbazides, semicarbazones or even thiosemicarbazones have been employed^[19,27,28] to prepare ring-type molecules. These processes are an alternative to conventional organic synthesis, usually proceeding quickly and in only one step. The method we present here, starting from easily prepared thiosemicarbazonecopper(II) complexes, allows the preparation of 2-amino-1,3,4-oxadiazoles as the only product and requires, in some cases, less than an hour.

Structural Analysis

Crystal Structures of the Thiosemicarbazone Derivatives

The molecular structure of compound **2** is shown in Figure 1. Selected distances and angles are given in Table 1. The crystal contains $[\text{Cu}(\text{L}_1)]$ entities, which stack through the sulfur atom of the thiosemicarbazone ligand to give the

centrosymmetric $[\{\text{Cu}(\text{L}_1)\text{I}\}]_2$ dimer. Each copper(II) ion has a distorted square-pyramidal topology ($\tau = 0.17$)^[29] and is surrounded by one sulfur and two nitrogen atoms of one thiosemicarbazone ligand and the iodo ligand in the basal plane. The axial position is occupied by the sulfur atom of the symmetric $[\text{Cu}(\text{L}_1)\text{I}]$ entity inside the dimer.

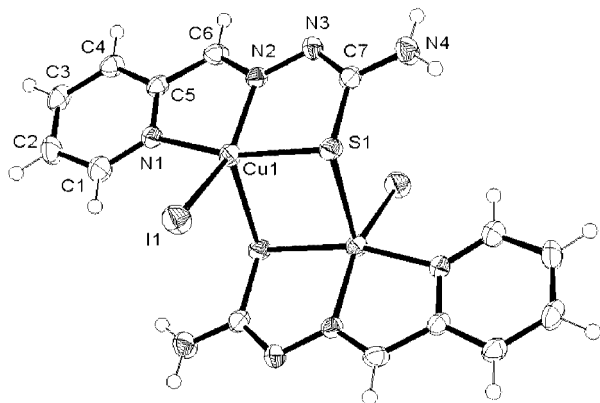


Figure 1. Molecular structure of **2** with thermal ellipsoids at 50% probability level

Table 1. Selected bond lengths [Å] and angles [°] for **2** and **4**

	2	4
Cu–N(1)	2.033(4)	2.034(4)
Cu–N(2)	1.997(4)	1.980(5)
Cu–S	2.271(1)	2.269(2)
Cu–X	2.6009(7)	2.3710(9)
Cu–S ⁱ	2.775(1)	2.833(2)
Cu [⋯] Cu ⁱ [a]	3.455(1)	3.577(2)
Cu [⋯] Cu ⁱⁱ	5.319(1)	4.932(2)
N(3)–C(7)	1.335(6)	1.331(7)
C(7)–S	1.749(5)	1.739(6)
S–Cu–N(1)	163.4(1)	163.8(2)
X–Cu–N(2)	152.9(1)	162.7(1)
Cu–S–Cu ⁱ	85.80(4)	88.3(1)
S–Cu–S ⁱ	94.20(4)	91.7(1)

[a] Symmetry transformations used to generate equivalent atoms: **2**: i = $-x + 1, -y + 1, -z + 1$; ii = $-x + 1, -y + 2, -z + 1$; **4**: i = $-x + 1, -y + 1, -z + 2$; ii = $-x + 1, -y, -z + 2$.

The molecular structure of complex **3** has been described elsewhere^[17] (see Figure 2).

Compound **4** consists of $[\text{Cu}(\text{L}_1\text{mm})\text{Br}]$ entities linked through the sulfur atom of the thiosemicarbazone ligand, leading to dinuclear centrosymmetric $[\{\text{Cu}(\text{L}_1\text{mm})\text{Br}\}]_2$ species. A perspective view of the dimer is shown in Figure 3, and selected bond lengths and angles are given in Table 1. Each copper(II) ion is 5-coordinate, with two nitrogens and the sulfur atom of the ligand and the bromo ligand at the basal positions, while the axial position is occupied by the sulfur atom of the symmetric thiosemicarbazone-copper(II) entity. The calculated τ factor^[29] is 0.02, which indicates that the copper(II) ions have close to the square-pyramidal topology.

Both thiosemicarbazones (HL_1 and HL_1mm) can be considered as rigid and quasi-planar in these compounds. Con-

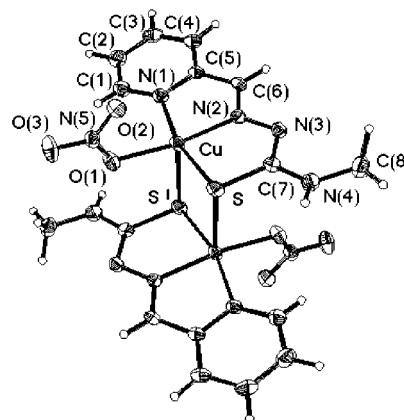


Figure 2. Molecular structure of **3** with thermal ellipsoids at 50% probability level

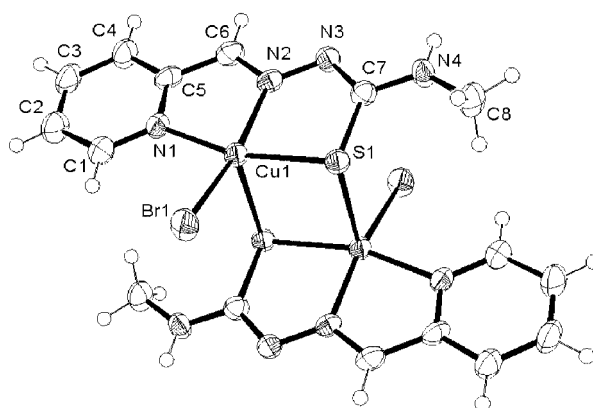


Figure 3. Molecular structure of **4** with thermal ellipsoids at 50% probability level

sidering the basal plane as that defined by the N(1)N(2)S donor set, the Cu and Sⁱ atoms lie at 0.012 and 2.689 Å above it for **2**, 0.090 and 2.832 Å in complex **3**, and at 0.051 and 2.870 Å in complex **4**. The coligands [I, O(1), and Br for **2**, **3**, and **4** respectively] sit 1.158, 0.162, and 0.598 Å below the mentioned plane.

It is worth mentioning the presence of chains of dimers that stack along the y axis at distances that suggest the occurrence of π – π interactions. Thus, the minimum distances found are 3.32 Å [C(7)⋯C(3)ⁱⁱ] in **2**, 3.38 Å [N(2)⋯C(5)ⁱⁱ] in **3**, and 3.44 Å [N(3)⋯C(1)ⁱⁱ] in complex **4**. In addition, π – π interactions occur along the z axis in compound **3**, with a minimum distance of 3.35 Å [C(3)⋯C(6)^{iv}, iv = $-x, -y + 1, -z$]. The dimers are also interconnected by intermolecular hydrogen contacts (see Supporting Information, and also the footnote on the first page of this article).

Both thiosemicarbazones undergo conformational changes upon coordination. N(1) and N(2) are *anti* with respect to the C(5)–C(6) bond and atoms N(2) and S are *anti* with respect to the N(3)–C(7) linkage in the free ligands.^[30,31] In both cases, they become *syn* after chelation. Furthermore, C(8) and S are *syn* in the free ligand as in **4**; but they are *anti* in complex **3**. This could be due to the steric hindrance induced by the size of the nitrato ligand.

Table 2. Selected structural differences between copper(II) complexes containing neutral and anionic HL_I or HL_Imm (Å, °) for **2**, **3**, and **4**

Compound	N(2)–N(3)–C(7)	S–C(7)–N(3)	S–C(7)–N(4)	Cu...N(3)	N(2)...C(7)
2	111.2(4)	124.9(4)	118.4(4)	2.99	2.23
3	111.5(2)	124.9(2)	116.8(2)	2.96	2.22
4	112.1(5)	124.6(5)	119.0(4)	2.96	2.22
HL range	116–118	121–122	121–123	2.89–2.90	2.28–2.32
L [–] range	109–114	123–127	117–119	2.94–3.00	2.22–2.23

All C–C and C–N lengths are similar in the free and coordinated ligands except for those corresponding to the N(3)–C(7) and C(7)–S bonds, which are 1.358(4) and 1.698(3) Å and 1.369(2) and 1.649(2) Å for HL_I and HL_Imm, respectively.^[30,31] The N(3)–C(7) and C(7)–S bond lengths decrease and increase, respectively, upon coordination, which has been related to the respective gain and loss in double-bond character upon complexation. The results summarized in Table 2 show that the selected parameters for **2**, **3**, and **4** are in good agreement with those expected for compounds containing HL_I or HL_Imm in anionic form.^[32]

As can be seen, complexes **2**, **3** and **4** are made up of [Cu(L)X] units connected through the thioamide sulfur atom, giving rise to {Cu₂(μ-SL)₂} dimeric entities similar to other copper(II) derivatives of pyridine-2-carbaldehyde thiosemicarbazone.^[33,34] A significant difference between compound **2** and the analogous chloro and bromo derivatives^[34] is the short deviation of the copper(II) ion with respect to the basal plane in **2** (0.012 Å) compared with those for [{Cu(L_I)Cl}₂] and [{Cu(L_I)Br}₂] (around 0.2 Å).

Crystal Structures of the Oxadiazole Derivatives

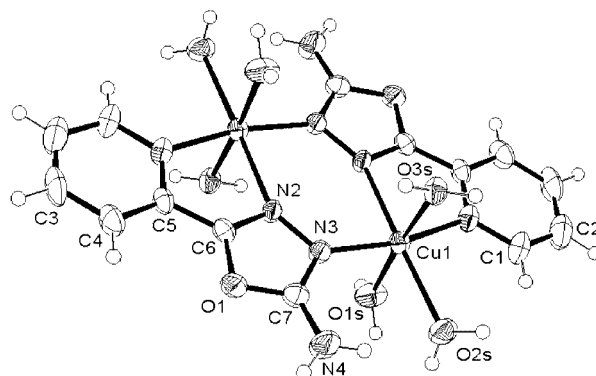
A perspective view of the structure of complex **5** is shown in Figure 4. Selected interatomic dimensions are given in Table 3. The crystal structure consists of cationic dimeric [{Cu(HL_{II})(H₂O)₃}₂]⁴⁺ entities and sulfate groups as counterions. Each copper(II) ion adopts a tetragonally distorted octahedral “4+2” geometry, being bonded to the oxygen atoms of three water molecules and to three nitrogen atoms: two belonging to one of the oxadiazoles and one to the ligand of the symmetric entity in the dimer, which acts as a bridge between the two metal ions. The high thermal parameters in the sulfate ions cause disorder in some of the oxygen atom positions.

The molecular structure of **6** has been described previously;^[17] the dimeric structure is shown in Figure 5.

In relation to the plane formed by the N(1)N(2)N(3) chelating set in **5** and **6**, the copper(II) atoms lie at 0.172 and 0.351 Å, respectively. In addition, the O(2S) and O(4) atoms are displaced by 0.159 and 0.866 Å, respectively, above the NNN plane.

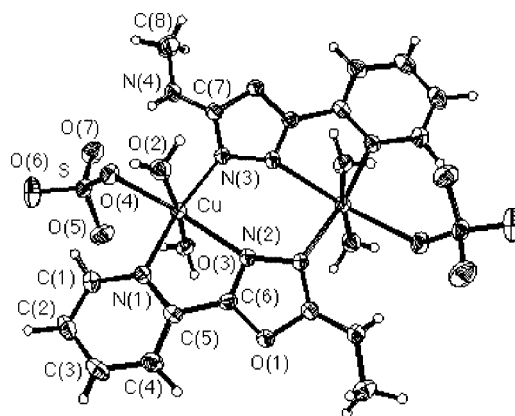
The structure of **8**^[17] consists of (HL_{II}mm) neutral units and three water molecules of crystallization which stabilizes the crystal lattice through a network of hydrogen bonds.

The oxadiazole ligands in these compounds contain two aromatic rings (pyridinic and oxadiazolic) whose planes are at 7.1, 6.3, and 7.4° with respect to each other (for, **5**, **6**,

Figure 4. Molecular structure of the dimeric cationic entity of **5** with thermal ellipsoids at 50% probability levelTable 3. Selected bond lengths [Å] and angles [°] for **5**

Cu–N(1)	2.053(3)	C(5)–C(6)–N(2)	125.8(3)
Cu–N(2) ⁱ	2.377(3)	N(1)–Cu–N(2) ⁱ	76.7(1)
Cu–N(3)	2.009(3)	N(1)–Cu–N(3)	167.6(1)
Cu–O(1S)	1.967(3)	N(1)–Cu–O(1S)	90.1(1)
Cu–O(2S)	2.357(3)	N(1)–Cu–O(2S)	99.0(1)
Cu–O(3S)	1.980(2)	N(1)–Cu–O(3S)	88.8(1)
Cu...Cu ⁱ [a]	4.481(2)	N(3)–Cu–O(1S)	90.3(1)
Cu...Cu ⁱⁱ	7.460(1)		

[a] Symmetry transformations used to generate equivalent atoms: i = –x + 1, –y, –z + 1; ii = –x + 1, –y, –z.

Figure 5. Molecular structure of the dimeric complex **6** with thermal ellipsoids at 50% probability level

and **8**, respectively), indicating that complexation induces a higher planarity in the oxadiazole ligands. These values are in good agreement with those observed for [Cu(HL_{II}–

$\text{mm})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ and $[\text{Cu}(\text{HL}_{\text{I}}\text{mm})(\text{oxalate})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (1.8 and 0.3° , respectively).^[35]

The bond lengths in these complexes are quite similar to those of the free ligand. However, the C(5)–C(6)–N(2) angle decreases upon coordination^[17] (see Table 3). The N(3) and C(8) atoms are *syn* with respect to the C(7)–N(4) bond in the structure of $\text{HL}_{\text{I}}\text{mm}$ whereas in complex **6** they show an *anti* conformation. Taking into account that the above-mentioned $[\text{Cu}(\text{HL}_{\text{I}}\text{mm})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ and $[\text{Cu}(\text{HL}_{\text{I}}\text{mm})(\text{oxalate})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ complexes also display the *syn* conformation, this conformational change could be attributed to steric hindrance induced by the sulfato group.^[35]

Several hydrogen bonds involving the water molecules and sulfate anions help stabilize the lattice in complexes **5** and **6**, leading to a sheet-like structure (see Supporting Information). The sheets are connected by π – π stacking interactions with a shortest interplanar atom...atom separation of C(4)···C(6)^v (3.45 Å, $v = -x + 2, -y, -z + 1$) and N(3)···C(3)^{vii} (3.378 Å, $\text{vii} = x - 1, y, z$) for **5** and **6**, respectively. A peculiar view of the packing in complex **6** with alternating layers of dimers parallel to the $(-1, 3, 0)$ and $(-3, -9, 1)$ planes is shown in Figure 6.

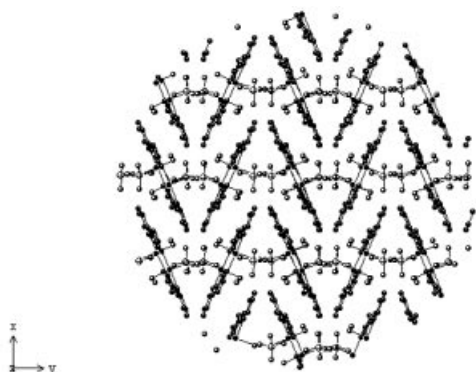


Figure 6. Arrow-like perspective of complex **6**

Analysis of the molecular packing of **8** suggests the lattice is stabilized by several hydrogen bonds, involving mainly the N(1), N(3) and N(4) atoms of the ligand and the lattice water (see Supporting Information). Pseudo-chains of coplanar molecules parallel to the $(2, 6, -4)$ plane alternate with other chains of molecules parallel to the $(-2, 6, 4)$ plane along the y axis (Figure 7). Each column is made up of sets of three molecules interconnected by π – π interactions (minimum distances 3.330 and 3.269 Å for C(6)···C(7)^v and C(7)···N(1)ⁱⁱⁱ, respectively). In addition, the molecules belonging to each column are linked through another hydrogen bond, which involves the N(4) and N(1) atoms.

Spectroscopic Studies

The IR spectrum of complex **1** exhibits absorptions at 808 and 735 cm^{-1} which can be assigned to the ν_1 and ν_3 vibrations of the halato group. Complex **3** shows strong bands at 1517, 1234, and 1023 cm^{-1} assignable to the ν_5 ,

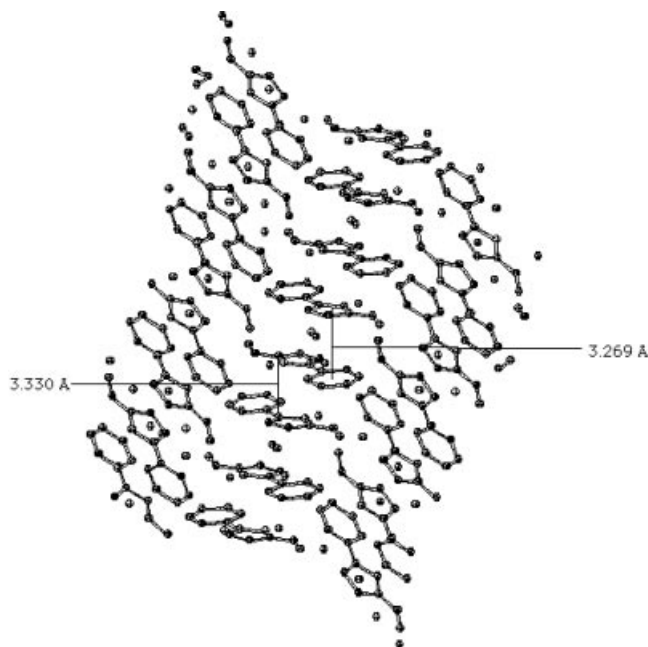


Figure 7. Pseudo-chains formed by the stackings of molecules in **8**

ν_1 , and ν_2 modes of the monodentate nitrato ligand,^[36] in good agreement with the structural results.

For **5** and **6** the 1300 – 900 cm^{-1} region displays many absorptions due to the coexistence of the oxadiazole and sulfate ligands, hampering definitive assignments. Nevertheless, the bands at 1095, 1065, and 640 cm^{-1} for complex **5** could be assigned to the ν_3 and ν_4 modes of the T_d sulfate. Conversely, **6** shows absorptions at: 1108(ν_3), 1050 (ν_3), 968 (ν_1), 645 (ν_4), 617 (ν_4), and 455 cm^{-1} that can be attributed to a monodentate-coordinated sulfate with C_{3v} symmetry.

The diffuse reflectance spectra of the thiosemicarbazone complexes are characterized by bands in the 210–245, 260–295, 380–415, and 460–500 nm regions, corresponding to intraligand ($\pi \rightarrow \pi^*$), ($n \rightarrow \pi^*$), LMCT $\text{S} \rightarrow \text{Cu}^{\text{II}}$, and $\text{X} \rightarrow \text{Cu}^{\text{II}}$ ($\text{X} = \text{N}, \text{O}, \text{Br}, \text{I}$), respectively^[37–39] (see Table 4). The bands observed in solid samples in the 575–740 nm region are characteristic of d→d transitions for compounds exhibiting a square-pyramidal geometry with a $d_{x^2-y^2}$ ground state. A shoulder observed at 895 and 979 nm in the spectra of the nitrato and iodo derivatives is attributed to the distortion towards trigonal bipyramidal topology.

The UV–visible spectra of complexes **3** and **4** in aqueous solution are very similar (see Table 4) and differ significantly from their respective solid spectra, especially in the LMCT region, as also occurs with the spectra of complexes **1** and **2** in solution. This strongly suggests that $[\text{Cu}(\text{L}_{\text{I}}\text{mm})(\text{H}_2\text{O})_3]^+$ and $[\text{Cu}(\text{L}_{\text{I}})(\text{H}_2\text{O})_3]^+$, respectively, are present in aqueous solution. The band at 225 nm in the spectrum of complex **2** [and the analogous $\text{Cu}(\text{L}_{\text{I}}\text{mm})\text{I}$] is also present in aqueous solutions of KI, being attributed to charge-transfer bands between the iodide ion and the solvent molecules.

The UV–visible spectra of the oxadiazole complexes **5** and **6** show absorptions in the 220–230, 260–285, and

Table 4. UV-visible spectroscopic data [λ (nm), ϵ ($\text{M}^{-1}\cdot\text{cm}^{-1}$)]

1 ^[a]	224, 277, 380(sh), $\approx$ 409(sh), 600(sh), 742(sh)
1 ^[b]	280(14600), 315(10750), 382(9600), 629(170)
2 ^[a]	230, 267, 407, 467(sh), 650, 979(sh)
2 ^[b]	225(27600), 281(16600), 317(12500), 383(11250), 628(190)
3 ^[a]	237, 274, 412, 468(sh), 597, 895(sh)
3 ^[b]	244(sh,8100), 287(11600), 328(11900), 384(10800), 624(160)
4 ^[a]	277(sh), 405, 473(sh), 595, 717(sh,b)
4 ^[b]	244(sh, 8300), 287(11700), 330(11900), 385(10700), 624(160)
5 ^[a]	223, 285, 339(sh), 368(sh), 705(b), 1118(b)
5 ^[b]	252(sh, 5300), 291(11700), 749(20)
6 ^[a]	225, 269, 339(sh), 401(sh), 482(sh), 698, 1166
6 ^[b]	297(13600), 765(20)
7 ^[c]	296 (21300)
7 ^[d]	203(18000), 293(31100)
8 ^[c]	300 (11100)
8 ^[d]	204 (23500), 298 (40800)

[a] In solid. [b] In water solution ($6\cdot 10^{-5}$ M). [c] In ethanolic solution ($6\cdot 10^{-5}$ M). [d] In methanolic solution ($6\cdot 10^{-5}$ M).

330–500 nm regions which can be attributed to intraligand $\pi\rightarrow\pi^*$, $n\rightarrow\pi^*$ and LMCT $\text{N/O}\rightarrow\text{Cu}^{\text{II}}$ transitions, respectively.^[35] A very broad absorption at around 700 nm and a less intense shoulder in the 1100–1170 nm range are also observed, which are consistent with a copper(II) chromophore with a tetragonally distorted octahedral geometry.^[40] These bands could be assigned to the ${}^2\text{E}_g\leftarrow{}^2\text{B}_{1g}$ and ${}^2\text{A}_{1g}\leftarrow{}^2\text{B}_{1g}$ transitions, respectively – in good agreement with the results reported for analogous triazole systems.^[41] The solution spectra of complexes **5** and **6** are similar to those of the $[\text{Cu}(\text{HL}_{\text{I,II}}\text{mm})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ complex. Furthermore, a study involving the latter has shown that some LMCT bands shift to higher energies in solution, overlapping with the intraligand absorptions.^[35]

The g tensors for the powder X-band EPR spectra of the title complexes are shown in Table 5. The spectra of compounds **1**, **3**, and **4** are characteristic of a $d_{x^2-y^2}$ ground state for square-pyramidal copper(II) chromophores,^[42] similar to those reported for other copper(II) thiosemicarbazone complexes.^[33,34,43] Compound **2** exhibits a broad (≈ 200 G peak-to-peak) isotropic signal at room temperature in the $g = 2.074$ region. Upon lowering the temperature to 120 K the signal intensity increases but its shape does not change. The X-band EPR spectra of complexes **5** and **6**

Table 5. Experimental EPR parameters

Complex	g_1	g_2	g_3
1 ^[a]	2.178	2.047	2.032
2 ^[a]	$g_{\text{iso}} = 2.074$		
3 ^[b]	$g_{\parallel} = 2.181$	$g_{\perp} = 2.043$	
3 ^[c]	2.186	2.049	2.025
4 ^[b]	$g_{\parallel} = 2.149$	$g_{\perp} = 2.038$	
4 ^[c]	2.152	2.043	2.031
5 ^[a]	$g_{\parallel} = 2.363$	$g_{\perp} = 2.077$	
6 ^[a]	$g_{\parallel} = 2.294$	$g_{\perp} = 2.082$	

[a] No variation in the g values from room temperature to 120 K. [b] At room temperature. [c] At 120 K.

consist of an axial signal whose g values accord with a copper(II) ion in an elongated octahedral geometry.

Magnetic Behaviour

Plots of the molar susceptibility (χ_m), together with the $\chi_m T$ vs. T curves for compounds **2**, **3**, **4**, **5**, and **6** are given in Figures 8, 9, 10, 11, and 12, some of which show a shoulder around 60 K that is characteristic of O_2 . The magnetic measurements all obey the Curie–Weiss law above 50 K. The Weiss temperatures are -9.46 (**2**), $+2.87$ (**3**), -5.75 (**4**), -1.76 (**5**), and -1.26 K (**6**). The C_m experimental values range from 0.40 to 0.44 $\text{cm}^3\cdot\text{K}\cdot\text{mol}^{-1}$ and the calculated μ_{eff} values at room temperature are 1.8 BM for

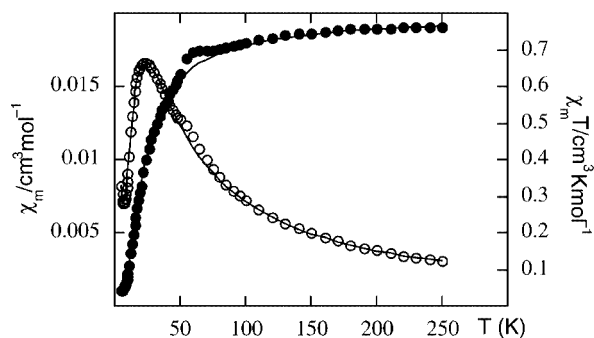


Figure 8. Thermal variation of the molar susceptibility (open circles) and $\chi_m T$ (black circles) for **2**. Solid lines represent the best fit

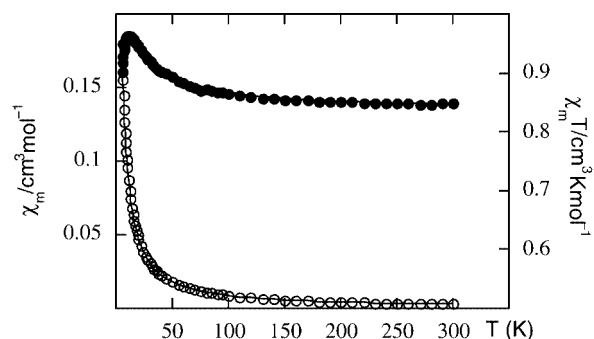


Figure 9. Thermal variation of the molar susceptibility (open circles) and $\chi_m T$ (black circles) for **3**. Solid lines represent the best fit

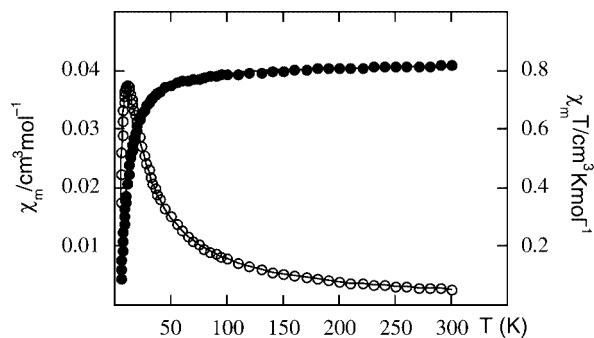


Figure 10. Thermal variation of the molar susceptibility (open circles) and $\chi_m T$ (black circles) for **4**. Solid lines represent the best fit

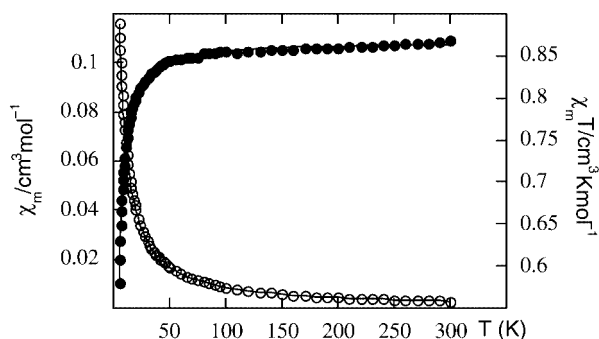


Figure 11. Thermal variation of the molar susceptibility (open circles) and $\chi_m T$ (black circles) for **5**. Solid lines represent the best fit

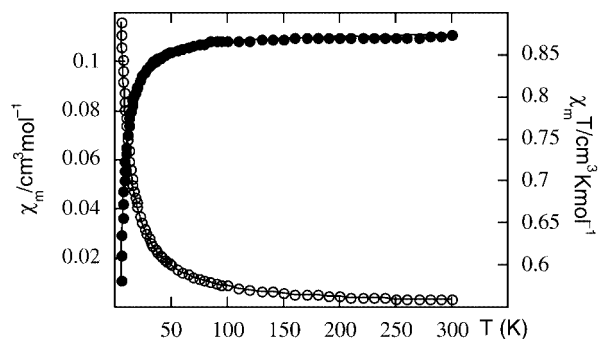


Figure 12. Thermal variation of the molar susceptibility (open circles) and $\chi_m T$ (black circles) for **6**. Solid lines represent the best fit

all compounds. The χ_m values increase with decreasing temperature for most complexes, reaching a maximum at 22.0 (0.008 cm³·mol^{−1}, **2**), 11.0 (0.019 cm³·mol^{−1}, **4**), 3.3 K (0.058 cm³·mol^{−1}, theoretical values arising from the fit in **5**) and 3.4 K (0.058 cm³·mol^{−1}, theoretical values arising from the fit in **6**). The $\chi_m T$ value continuously decreases on lowering the temperature, indicating the presence of antiferromagnetic interactions. However, compound **3** does not exhibit a maximum in the χ_m vs. T plot and $\chi_m T$ increases on lowering the temperature, which is characteristic of ferromagnetic behaviour.

Taking into account the dimeric nature of these complexes, we fitted the susceptibility data with the Bleaney–Bowers expression for copper(II) dinuclear compounds,^[44] derived from the Heisenberg isotropic spin Hamiltonian ($H = -2J \cdot S_1 S_2$), for two coupled $S = 1/2$ ions:

$$\chi = \frac{Ng^2\beta^2}{kT} \left(\frac{2}{3 + \exp(-2J/kT)} \right) + N\alpha \quad (1)$$

where $N\alpha$ = a temperature independent contribution, N is the Avogadro constant, β = Bohr magneton, and k = the Boltzmann constant. The best least-squares fit (solid line in Figures 8–12) is obtained with $J/k = -20.20$ K (−14.03 cm^{−1}, taking into account 5% paramagnetic impurities in **2**), −8.85 K (−6.14 cm^{−1}, **4**), −2.75 K (−1.91 cm^{−1}, **5**),

and −2.78 K (−1.93 cm^{−1}, **6**). For **3**, the influence of intermolecular interactions must be considered in the fit treated in the molecular field approximation, and the values obtained are $J/k = +9.90$ K and $z'J' = -1.70$ K (+6.88 and −1.18 cm^{−1}, respectively). The g -values of 2.06, 2.11, 2.10, 2.15, and 2.16 for **2**, **3**, **4**, **5**, and **6**, respectively, are in good agreement with those obtained from EPR, 2.07 (**2**), 2.09 (**3**), 2.08 (**4**), 2.17 (**5**), and 2.15 (**6**). Taking into account the structural features, the existence of interdimeric magnetic interactions in these compounds should be considered. However, the fit was improved only for **3**, due to the opposite sign of the ferromagnetic intradimer vs. antiferromagnetic interdimer interactions. The data are given in Table 6 together with a summary of the J values for all copper(II) dinuclear derivatives of HL₁ and HL₁mm described to date.

The strength of the magnetic interactions in the **2**, **3**, and **4** thiosemicarbazone derivatives suggests that the exchange propagation direction is in a different plane to that formed by the magnetic $d_{x^2-y^2}$ orbitals. These results agree well with the existence of an intradimer exchange coupling in the Cu₂S₂ units. However, the relatively intense antiferromagnetic coupling in **2** and the ferromagnetic interactions in **3** have not been observed before in the pyridine-2-carbaldehyde thiosemicarbazone–copper(II) system. Ferromagnetic interactions in other thiosemicarbazone–copper(II) systems have been referenced,^[45] but, as far as we are aware, no magneto-structural studies have been carried out.

The results suggest that the nature of the coligands in the basal plane influences in the magnetic behaviour. Here, O-donor coligands show the smallest antiferromagnetic contributions to the J values. It has been established that the less electronegative is the donor atom in the basal plane the stronger the induced antiferromagnetic coupling is, due to a greater hybridization of the $d_{x^2-y^2}$ metal orbital towards the bridge.^[46,47] Figure 13 shows a good accordance between the average J values and Pauling's electronegativity of the compounds in Table 6.

Conversely, the relationship between J and other structural parameters is not evident even for a given X-donor set. Several concomitant factors could be involved in the values of the exchange coupling constants for these compounds, such as the Cu⋯Cu intradimer distance, SP vs. BPT distortions around the copper(II) ion, deviation of the metal ion from the basal plane, deviation of the coligand from the basal plane, Cu–X apical distances, N(2)–Cu–S–Cu'/N(1)–Cu–O(1)–Cu' dihedral angles which give a measurement of the shift of the [Cu(L)X] entities constituting the dimer, the influence of the thiosemicarbazone and coligands.

A qualitative study of the relationship between the magnetic exchange constant J and the square of the energy difference (Δ^2) between the two magnetic orbitals involved^[48] required an extended Hückel molecular orbitals (EHMO) analysis.^[49] Such EHMO calculations, using the crystallographic coordinates of the compounds following a procedure previously described,^[50] gave a Δ^2 for **3** that is at least ten times smaller than those obtained for antiferro-

Table 6. Comparison of the J , Δ^2 , and selected structural parameters for pyridine-2-carbaldehyde thiosemicarbazonecopper(II) dinuclear complexes

Compounds, [donor atom of the basal coligand]	Bridging atom (X')	Cu...Cu' / Cu-X' (Å)	Cu-X...Cu' angle (°)	J (cm ⁻¹)	Δ^2 (eV) ² ·10 ³
[{Cu(L _I mm)(NO ₃) ₂ } ₂] [O]	S	3.4482(2) / 2.7659(6)	85.83(2)	+6.88	0.12
[{Cu(L _I)(NO ₂) ₂ } ₂] ^[71] [O]	S	3.554(1) / 2.918(2)	85.5(1)	-3.40	1.09
[{Cu(L _I)Cl} ₂] ₂ ^[34] [Cl]	S	3.486(2) / 2.760(2)	87.01(4)	-4.70	11.45
[{Cu(L _I)Br} ₂] ₂ ^[34] [Br]	S	3.474(1) / 2.743(2)	87.12(5)	-4.70	17.42
[{Cu(L _I mm)Br} ₂] ₂ [Br]	S	3.577(2) / 2.832(2)	88.31	-6.14	3.72
[{Cu(L _I)I} ₂] ₂ [I]	S	3.455(1) / 2.775(1)	85.80(4)	-14.03	15.62
[{Cu(L _I)(NCS) ₂ } ₂] ^[33] [N]	S	3.450(3) / 2.754(5) ^[a]	85.9(1) ^[a]	-5.09	45.80
[{Cu(L _I)(NCO) ₂ } ₂] ^[33] [N]	S ^[b]	[b]	[b]	-4.24	[b]
[{Cu(L _I)(N ₃) ₂ } ₂] ^[33] [N]	S ^[b]	[b]	[b]	-2.93	[b]
[{Cu(L _I)(HCOO) ₂ } ₂] ^[71] [O]	S	3.503(2) / 2.820(2)	86.34(5)	-2.80	1.68
[{Cu(L _I)(CH ₃ COO) ₂ } ₂] ^[61,72]	O	3.442(1) / 2.427(2)	103.5(1)	-3.10	1.60
[{Cu(L _I)(CH ₃ CH ₂ COO) ₂ } ₂] ^[71] [O]	O	3.460(2) / 2.387(2)	105.35(9)	-3.30	1.85

^[a] Average value. ^[b] Crystal data not available.

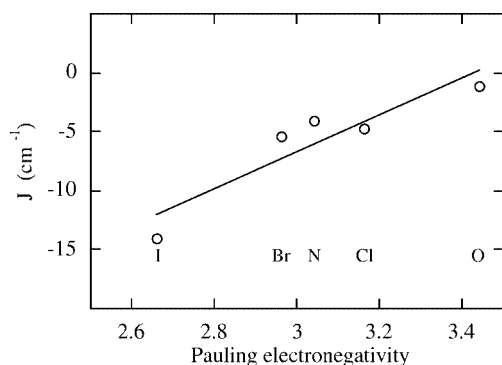


Figure 13. Plot of the average values of J (cm⁻¹) vs. the Pauling's electronegativities. The electronegativities are 3.44, 3.16, 3.04, 2.96, and 2.66 for O⁻, Cl⁻, N⁻, Br⁻, and I⁻ donors, respectively

magnetic derivatives in good accordance with its ferromagnetic behaviour. Unfortunately, the limitations of the EHMO calculations did not allow us to determine a perfect sequence for the J values. The most important disagreement involves Δ^2 for [{Cu(L_I)(NCS)}₂] and [{Cu(L_I)I}₂], but can be explained by taking into account that [{Cu(L_I)(NCS)}₂] is the only noncentrosymmetric compound in Table 6. Thus, it has been proposed that lowering the symmetry gives rise to a decrease in the antiferromagnetic contribution which is not reflected in the magnitude of Δ^2 .^[51,52]

The small values obtained for the magnetic exchange constant in **5** and **6** contrast with those reported for similar dimeric compounds containing copper(II) ions bridged through analogous diazole and triazole ligands.^[41,53–56] This is consistent with the value of Δ gap in the EHMO analysis (0.099 eV for **5**), which is smaller than those reported for pyrazolate bridged compounds.^[57,58] Such behaviour can be explained considering that the d_{z^2} orbitals lie in the O(4)–Cu–N(2) direction for compounds **5** and **6**, which involves the longest bond lengths and points to the oxadiazole bridges. The magnetic $d_{x^2-y^2}$ orbitals, however, are perpendicular to the exchange propagation direction.

Conclusion

HL_I and HL_Imm react with potassium bromate or iodate in an oxidative cyclization process that involves the elimination of sulfur and the attainment of the respective HL_{II} and HL_{II}mm ligands. This reaction also occurs when the copper(II) derivatives of these thiosemicarbazone ligands are used as reactants. The oxadiazole–copper(II) complexes so-formed maintain the dimeric nature of their thiosemicarbazonecopper(II) precursors. The planarity of the ligands gives rise to π – π stacking interactions that, along with the hydrogen bonding, stabilize the crystal packing. Weak anti-ferromagnetic intradimeric interactions are present in both thiosemicarbazone and oxadiazole–copper(II) systems. However, the nitrato derivative **3** shows ferromagnetic behaviour. The relative scarcity of pyridine-2-carbaldehyde thiosemicarbazone–copper(II) compounds, as well as the limitations of the semiempirical calculations developed, prevents good quantitative results. However, the influence of the electronegativity of the non-thiosemicarbazone basal donor atom seems to be clear.

Experimental Section

Materials: Thiosemicarbazides, pyridine-2-carbaldehyde, copper(II) sulfate pentahydrate, copper(II) nitrate trihydrate, potassium bromate and iodate, sodium bromide, potassium iodide, and potassium ferrocyanide trihydrate were purchased from commercial sources and used as received. Published methods with small modifications were used to synthesize HL_I,^[59] HL_Imm,^[31,60] Cu(L_I)(NO₃)₂,^[61] and [{Cu(L_Imm)(NO₃)₂}₂].^[17] All operations should be carried out in a fume cupboard.

Preparation of the Complexes

Synthesis of 1, 2, 5, and 7: Compound **1** was synthesized by the addition of solid potassium iodate (0.85 g, 4 mmol) to an aqueous solution of Cu(L_I)(NO₃)₂ (0.30 g, 1 mmol) with continuous stirring. The pH of the reaction mixture was adjusted to 6.0 by addition of aqueous NaOH. A few minutes later, an abundant green precipitate appeared which was filtered off and dried (yield 0.30 g, 70%).

$\text{C}_7\text{H}_9\text{CuIN}_4\text{O}_4\text{S}$ (435.69): calcd. C 19.3, H 2.1, N 13.2, S 7.8; found C 19.3, H 2.1, N 12.9, S 7.4. The molar conductivity of $5 \cdot 10^{-4}$ M solutions in water (dimethylformamide) at 25 °C is $\Lambda_{\text{M}} = 97.4$ (immediate reaction to give **2**) $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Selected IR bands (cm^{-1} , KBr): 3498 m, 3438 m, 3365 m, 3296 m, 3170 m, 1640 s, 1606 s, 1484 m, 1448 m, 1436 m, 1383 w, 1322 m, 1222 m, 1162 s,sh, 708 m, 781 s, 735 s.

Attempts to recrystallize **1** in water furnished good-quality crystals of a new thiosemicarbazonatocopper(II) derivative that was identified as **2** (0.05 g, 16% yield). $\text{C}_7\text{H}_7\text{CuIN}_4\text{S}$ (369.67): calcd. C 22.7, H 1.9, N 15.2, S 8.1; found. C 22.3, H 1.9, N 15.3, S 7.6. The molar conductivity of $5 \cdot 10^{-4}$ M solutions in water (dimethylformamide) at 25 °C is $\Lambda_{\text{M}} = 123$ (31.3) $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Selected IR bands (cm^{-1} , KBr): 3423 s, 3279 m, 3135 m, 1625 s, 1600 s, 1480 s, 1446 vs, 1436 vs, 1226 m, 1166 s, 1155 m,sh, 909 m, 875 w, 778 m, 622 m, 469 m,b, 420 m.^[62]

Aqueous solutions of $\text{Cu}(\text{L}_1)(\text{NO}_3)$ (0.30 g, 1 mmol) and potassium bromate (0.17 g, 1 mmol) were mixed with stirring. The pH of the reaction mixture was adjusted to 6 by addition of aqueous 5 M NaOH and maintained with stirring overnight at room temperature. A small amount of precipitate appeared, which was filtered off and washed with water and acetone. The product was identified as the $[\{\text{Cu}(\text{L}_1)(\text{Br})\}_2]$ complex.^[34] Bright green crystals of **5** were then obtained from the mother liquor after one week at room temperature (0.22 g, 58% yield). $\text{C}_{24}\text{H}_{24}\text{Cu}_2\text{N}_8\text{O}_{16}\text{S}_2$ (751.6): calcd. C 24.6, H 3.6, N 14.4, S 8.2; found. C 24.6, H 3.6, N 14.3, S 8.2. The molar conductivity of $5 \cdot 10^{-4}$ M solutions in water (dimethylformamide) at 25 °C is $\Lambda_{\text{M}} = 227$ (32.6) $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Selected IR bands (cm^{-1} , KBr): 3381 m,b, 3077 m,b, 1684 s, 1577 m, 1518 m, 1493 m, 1441 m, 1350 m,sh, 1143 s,b, 1133 s, 1100–1000 s, 789 m, 751 m, 734 m, 619 m,b.

The HL_{II} ligand (**7**) was removed from complex **5** by the addition of $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ ^[17] (yield: 0.06 g, 45%). $\text{C}_8\text{H}_{14}\text{N}_4\text{O}_4$ (230.23): calcd. C 51.8, H 3.7, N 34.5; found. C 51.9, H 3.8, N 34.1. Selected IR bands (cm^{-1} , KBr): 3288 s, 3115 s, 1649 vs, 1588 vs,sh, 1562 s, 1460 vs, 1448 m, 1321 m, 1285 m, 1251 w, 1092 s, 1052 s, 1042 s, 786 m, 773 m, 742 s, 686 s, 620 m, 410 m. ^1H NMR (400 MHz; $[\text{D}_6]\text{DMSO}$, ppm): $\delta = 8.63$ (dt, $^3J = 5$ and 1.4 Hz, 1 H, H^1), 7.95 (d, $^3J = 2$ Hz, 1 H, H^4), 7.92 (m, 1 H, H^3), 7.47 (m, 1 H, H^2), 7.38 (s, 2 H, NH_2).

Ligand **7** can also be prepared by oxidative cyclization of HL_1 in the absence of copper(II) as follows: solid potassium bromate (0.5 g, 3 mmol) was added to a suspension of the thiosemicarbazone in water (0.54 g, 3 mmol) acidified with H_2SO_4 to pH = 0–1. After a few minutes, the reaction mixture turned orange and a brown solid appeared. The suspension was filtered off and a solution of NaOH (5 M) was slowly added to the resulting clear solution to reach a pH ≈ 5 at 0 °C. After a further few minutes ligand **7** appeared as a white product which was washed with water and recrystallized from ethanol (yield 0.31 g, 45%).

Synthesis of 3, 4, 6, and 8: The oxidative cyclization procedure for HL_{I} mm is analogous to that described above for HL_1 . The synthesis and characterization of complex **3** has been reported in the literature.^[17]

Aqueous solutions of **3** (0.32 g, 0.5 mmol) and potassium bromate (0.17 g, 1 mmol) were allowed to react at pH 6 overnight. A green precipitate appeared that was filtered off, washed with water and acetone and dried. The product was identified as complex **4** (yield 0.03 g, 10%). $\text{C}_{16}\text{H}_{18}\text{Br}_2\text{Cu}_2\text{N}_8\text{S}_2$ (673.4): calcd. C 28.6, H 2.7, N 16.6, S 9.5; found. C 29.0, H 3.0, N 16.9, S 9.1. The molar conduc-

tivity of $5 \cdot 10^{-4}$ M solutions in water (dimethylformamide) at 25 °C is $\Lambda_{\text{M}} = 118.2$ (10) $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Selected IR bands (cm^{-1} , KBr): 3219 m, 1593 s, 1570 m, 1534 s, 1472 s, 1357 vs,b, 1304 s, 1281 s, 1227 s, 1183 m, 1119 m, 1042 s, 898 w, 883 w, 862 w, 777 w, 607 m.^[63]

After filtering complex **4**, the mother liquor was allowed to stand at room temperature, and after two days crystals of the complex **6** were obtained.^[17]

The HL_{I} mm ligand (**8**) can be obtained by analogous procedures to those described for **7**.^[17,64–66]

Physical Measurements: Microanalyses were performed with a LECO CHNS-932 analyser. Conductivity measurements were made by a CRISON 522 conductimeter. Infrared spectra were obtained in the 400–4000 cm^{-1} region on a Nicolett Impact 410 FTIR spectrophotometer with samples prepared as KBr pellets. Reflectance spectra were carried out on a Cary 2415 spectrometer in the 200–2000 nm range. For UV-visible solution measurements, a Varian UV-VIS-NIR spectrophotometer was employed (200–900 nm). X-band EPR spectra were recorded on a Bruker EMX spectrometer, equipped with a standard Oxford continuous flow cryostat. Magnetic measurements of powdered samples were carried out in the range 5–300 K using a Quantum Design MPMS-7 Squid magnetometer. Diamagnetic corrections were estimated from Pascal tables.

X-ray Crystallographic Studies: Crystal data collections were carried out on a Bruker Smart CCD area detector equipped with a single crystal diffractometer. Absorption corrections were made using the SADABS program.^[67] Direct methods (SHELXS-97)^[68] were employed to solve the structures and then were refined by full-matrix least-squares method, using SHELXL-97.^[69] All non-hydrogen atoms were assigned anisotropic thermal parameters. Hydrogen positions were determined by difference Fourier syntheses and introduced in calculations with a riding model. The scattering factors and anomalous dispersion coefficients were taken from International Tables of X-ray Crystallography.^[70] Refinements were made on F_o^2 for all reflections. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. The deposition numbers are CCDC-199599, -199600, and -199601 for compounds **2**, **4**, and **5**, respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk]. Crystallographic details for the crystal structures of compounds **2**, **4**, and **5** are shown in Table 7.

Supporting Information

Supporting information for this article (Hydrogen bond parameters ($\text{\AA}$, °) for the six crystal structures) is available from the WWW under <http://www.wiley-vch.de/home/eurjic> or from the author.

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Table 7. Summary of crystallographic data and parameters for the 2, 4, and 5

	2	4	5
Formula	C ₇ H ₇ CuIN ₄ S	C ₁₆ H ₁₈ Br ₂ Cu ₂ N ₈ S ₂	C ₁₄ H ₂₄ Cu ₂ N ₈ O ₁₆ S ₂
M	369.67	673.4	751.6
System	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	7.7994(2)	8.1165(6)	8.6438(4)
<i>b</i> /Å	8.5440(2)	8.2597(7)	16.9146(7)
<i>c</i> /Å	9.1997(2)	9.4001(8)	8.9918(4)
α /°	111.977(1)	66.291(1)	—
β /°	98.218(1)	80.284(2)	92.999(1)
γ /°	107.940(1)	71.364(2)	—
<i>U</i> /Å ³	517.17(2)	546.15(8)	1312.9(1)
<i>Z</i>	2	1	2
<i>D</i> _c /g cm ^{−3}	2.374	2.047	1.901
μ /mm ^{−1}	5.261	5.818	1.870
<i>F</i> (000)	350	330	764
2 θ Range (°)	2–28	2–28	2–28
GOF	1.050	1.012	1.048
<i>R</i> ₁ (all data)	0.0475	0.0726	0.0621
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0393	0.0522	0.0397
<i>wR</i> ₂ (all data)	0.1101	0.1749	0.0904
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.1053	0.1483	0.0802

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- [62] Compound **2** can be also obtained by addition of potassium iodide (0.166 g, 1 mmol) to an aqueous solution of Cu(L₁)(NO₃) (0.30 g, 1 mmol) (yield 0.34 g, 93%).
- [63] Compound **4** can be also prepared by mixing aqueous solutions of **3** (0.32 g, 0.5 mmol) and sodium bromide (0.1 g, 1 mmol) (yield 0.30 g, around 90%). Dark green crystals of **4** were obtained by slow reaction of **3** and sodium bromide in a diffusion device.
- [64] The use of iodate as oxidizing agent in the cyclization of HL₁mm and HL₁ gave the same results. However, the formation of iodine in the reaction forced us to make more separations to obtain the pure compounds and as a result the yield decreased.
- [65] An analogous procedure carried out on complex **3** with iodate as oxidant yielded the [Cu(L₁mm)(IO₃)] complex (yield 0.39 g, 90%) C₈H₉CuIN₄O₃S (431.7): calcd. C 22.2, H 2.3, N 12.9, S 7.4; found C, 22.2, H 2.3, N 12.9, S 7.2. The molar conductivity of 5·10⁻⁴ M solutions in water (dimethylformamide) at 25 °C is $\Lambda_M = 73$ (50) $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Selected IR bands (cm⁻¹, KBr): 3220 m, 2979 w, 1597 s, 1572 s, 1538 vs, 1477 vs, 1355 vs, 1308 m, 1288 vs, 1225 s, 1180 s, 1178 m, 1116 s, 1097 m, 1038 m, 811 vs, 779 s, 751 vs, 732 vs, 720 vs, 608 m, 489 m. UV-visible bands in water, λ_{max} [nm] (ϵ , M⁻¹·cm⁻¹): 287 (13000), 328 (13200), 385 (12000), 622 (170). EPR in the room temp.-to-120 K range (X-band, solid sample): $g_1 = 2.195$, $g_2 = 2.054$ and $g_3 = 2.030$. Likewise, the complex analogous to **2** was also synthesized and identified as [Cu(L₁mm)I] (yield 0.33 g, 85%). C₈H₉CuIN₄S (383.7): calcd. C 25.0, H 2.4, N 14.6, S 8.3; found C 25.0, H 2.4, N 14.8, S 7.8. The molar conductivity of 5·10⁻⁴ M solutions in water (dimethylformamide) at 25 °C is $\Lambda_M = 110$ (41) $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Selected IR bands (cm⁻¹, KBr): 3216 m, 3021 w, 2973 w, 1593 s, 1568 s, 1534 vs, 1472 s, 1354 vs, 1307 s, 1283 vs, 1225 s, 1178 s, 1118 s, 1099 m, 1039 s, 770 s, 603 w. UV-visible bands in water, λ_{max} [nm] (ϵ , M⁻¹·cm⁻¹): 224 (25200), 287 (12300), 329 (12400), 386 (11250), 622 (150). EPR in the room temp.-to-120 K range (X-band, solid sample): $g_{\parallel} = 2.121$ and $g_{\perp} = 2.038$.
- [66] Furthermore, complexes **5** and **6** were also prepared by adding CuSO₄·5H₂O to the acid, orange oxidizing solution of bromate and **7** or **8**, respectively, before the addition of NaOH.
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