Coordination Modes in a (Thiosemicarbazone)copper(II)/Oxalato System − Structures of $[\{Cu(L)\}_2(ox)]\cdot 2H_2O$, $[Cu(HL)(ox)(H_2O)]$, $[\{Cu(HL)\}_2(ox)][Cu(ox)_2]\cdot 2H_2O$ and $[\{Cu(HL)\}_2(ox)](NO_3)_2$ − Ferro- vs. Antiferromagnetic Behavior in Dinuclear Compounds

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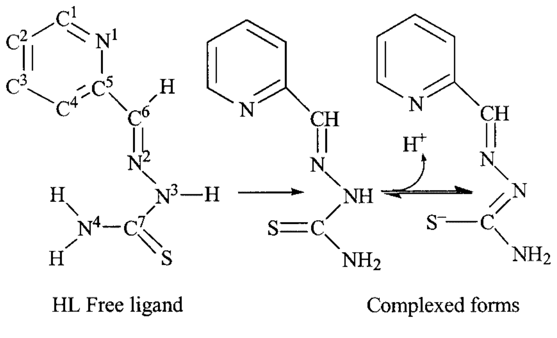
Complexes with the formula $[\{Cu(L)\}_2(ox)]\cdot 2H_2O$ (**1**), $[Cu(HL)(ox)(H_2O)]$ (**2**), $[\{Cu(HL)\}_2(ox)][Cu(ox)_2]\cdot 2H_2O$ (**3**) and $[\{Cu(HL)\}_2(ox)](NO_3)_2$ (**4**) (HL = $C_7H_8N_4S$, pyridine-2-carbaldehyde thiosemicarbazone) have been synthesized from $Cu(L)(NO_3)$ and oxalic acid while modulating the stoichiometries and the pH of the media. Single crystal X-ray diffraction studies show that the structures of **1** and **4** contain dinuclear entities with distorted square pyramidal copper(II) ions. The dinuclear complexes are centrosymmetric in **1** and non-centrosymmetric in **4**. The metal centers are coordinated to the NNS atoms from the tridentate thiosemicarbazone ligand and to two oxygen atoms from the oxalato coligand. The latter ligand exhibits tetradentate behavior and acts as a bridge between the copper(II) ions. The thiosemicarbazone ligand is either present in the anionic (**1**) or the neutral (**4**) form. Compound **2** is composed of monomeric species containing square pyramidal copper(II) ions that are coordinated to the thiosemicarbazone ligand, one water molecule and one monodentate oxalato coligand. It is important to note that the oxalato is highly twisted in this complex, the O(1)–C(8)–C(9)–O(3) dihedral angle between the carboxylate groups is 79.9(4)°. Compound **3** contains both the dinuclear cationic species, analogous to those described for compound **4**, and square planar (bisoxalato)copper(II) anions. Strong hydrogen bonds and π-π stacking are present in these complexes. Structural and spectroscopic results suggest the presence of relevant ligand-to-metal charge transfers in these compounds. The EPR spectra of **1**, **2** and **4** exhibit rhombic symmetry. Magnetic measurements on **1** and **4** show antiferromagnetic and ferromagnetic coupling, respectively. The susceptibility data were fitted to the Bleaney–Bowers equation for copper(II) dinuclear complexes. The J/k values obtained are −6.20 and +7.73 K for compounds **1** and **4**, respectively.

Introduction

Numerous studies on the copper(II) derivatives of pyridine-2-carbaldehyde thiosemicarbazone (HL = $C_7H_8N_4S$, see Scheme 1) have been conducted during the last thirty years, mainly with regard to the biological properties of these compounds.[1] Spectroscopic results suggested the existence of a planar $[Cu(L)(H_2O)]^+$ species in aqueous solution (or, more correctly, tetragonally elongated $[Cu(L)(H_2O)_3]^+$ species), with a log K value (K = formation constant) of 16.90.[2] This species exhibits two acid−base equilibria with proton dissociation constants $pK_{a1} = 2.40$ (the equilibrium between $[Cu(HL)(H_2O)_3]^{2+}$ and $[Cu(L)(H_2O)_3]^+$) and $pK_{a2} = 8.30$ (the equilibrium between $[Cu(L)(H_2O)_3]^+$ and $[Cu(L)(OH)(H_2O)_n]$).[3] The coordination of the ligand by the copper(II) ion is maintained even at pH values below 1.4. The high stability of the metal-ligand system allowed for the isolation of several com-



Scheme 1

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Table 1. Summary of crystallographic data and parameters for **1**, **2**, **3** and **4**

	1	**2**	**3**	**4**
Formula	$C_{16}H_{18}Cu_2N_8O_6S_2$	$C_9H_{11}CuN_4O_5S$	$C_{20}H_{24}Cu_3N_8O_{16}S_2$	$C_{16}H_{16}Cu_2N_{10}O_{10}S_2$
M	609.58	350.82	887.22	699.59
System	Triclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	*Ibca*
a/Å	6.1735(1)	11.068(2)	8.478(1)	13.053(2)
b/Å	9.6005(2)	10.148(2)	9.383(1)	12.998(2)
c/Å	10.4955(2)	12.020(2)	10.369(1)	28.835(4)
α/°	98.488(1)	90	68.543(2)	90
β/°	101.902(1)	112.303(3)	85.459(3)	90
γ/°	108.155(1)	90	80.115(3)	90
V/Å^3	563.16(2)	1248.9(3)	756.1(2)	4892.6(1)
Z	1	4	1	8
D_c/g cm^{-3}	1.797	1.866	1.949	1.900
μ/mm^{-1}	2.126	1.942	2.318	1.985
$F(000)$	616	712	894	1408
h,k,l range	±8, ±12, ±13	±13, (−10)−12, (−15)−14	(−7)−10, (−9)−11, ±12	(−16)−15, ±16, (−30)−36
θ range/°	2−28	2−26	2−26	2−26
GOF	1.035	1.021	0.996	0.996
R_1 (all data)	0.0383	0.0622	0.0599	0.1511
R_1 [$I > 2\sigma(I)$]	0.0336	0.0351	0.0366	0.0490
wR_2.(all data)	0.0926	0.0886	0.0898	0.1306
wR_2 [$I > 2\sigma(I)$]	0.0906	0.0780	0.0806	0.0919

pounds containing $[Cu(HL)]^{2+}$, as well as the $[Cu(L)]^{+}$, whose crystal structures have been characterized.[4] They exhibit a 1:1 metal/thiosemicarbazone stoichiometry, with the thiosemicarbazone acting as an NNS tridentate ligand. Magnetic studies on complexes with $[Cu(L)]^{+}$ fragments have also been carried out.[4f,4g,4j,4k] However, the magnetic behavior of derivatives containing the neutral ligand has not yet been studied. This is partly because monomeric compounds are formed with some of the ligands in an acidic medium. From this point of view, it would be important to find a ligand that is able to stabilize both the $[Cu(L)]^{+}$ and the acidic $[Cu(HL)]^{2+}$ species in dinuclear complexes. Therefore, the oxalato ligand, which is versatile and has a low pK_{a1} value and up to four chelating centers, could be used to study the influence of the neutral vs. anionic character of the ligand on the properties of these compounds.

Here we present the syntheses, crystal structures and spectroscopic features of the complexes $[\{Cu(L)\}_2(ox)]\cdot 2H_2O$ (**1**), $[Cu(HL)(ox)(H_2O)]$ (**2**), $[\{Cu(HL)\}_2(ox)][Cu(ox)_2]\cdot 2H_2O$ (**3**) and $[\{Cu(HL)\}_2(ox)](NO_3)_2$ (**4**). The magnetic behavior of compounds **1** and **4** is also discussed. Approximate molecular orbital calculations of the extended Hückel type have been carried out in order to understand the magnetic features in these systems.

Results and Discussion

Structural Analysis

The addition of potassium oxalate to an aqueous solution of $Cu(L)(NO_3)$ at pH = 4−8 yields compound **1**, which contains the anionic thiosemicarbazone ligand, irrespective of the ratio of the reactants. However, at very low pH values (close to 1), the amounts of the reactants play an important role. Thus, stoichiometric amounts of $Cu(L)(NO_3)$ and oxalic acid lead to the formation of compound **2**. In contrast, an excess of nitrate in the reaction medium yields **4**. A few crystals of **3** were isolated from an experiment designed to crystallize compound **2**. Unfortunately, we have not yet found a reproducible method of synthesizing this complex.

Single crystals suitable for X-ray data collection were obtained for the title complexes. Crystallographic details are given in Table 1.

The crystal structures of compounds **1** and **4** are formed by the $[Cu(L)]^{+}$ and $[Cu(HL)]^{2+}$ entities, respectively, linked through a bis-bidentate oxalato ligand, which leads to the dinuclear centrosymmetric $[\{Cu(L)\}_2(ox)]$ (**1**) and noncentrosymmetric $[\{Cu(HL)\}_2(ox)]^{2+}$ (**4**) species. Waters of crystallization are also present in the lattice of **1**. The nitrate counterions are also present in the lattice of **4**. The molecular structures of **1** and **4** are shown in Figure 1 and 2, respectively. Selected interatomic dimensions are given in Table 2. The copper(II) ions are five-coordinate with two nitrogen and one sulfur atoms from the thiosemicarbazone ligand [Cu−N(1), N(2), S: 2.044(2), 1.955(2), 2.2759(6) and 2.027(6), 1.956(5), 2.306(2) Å, for **1** and **4**, respectively] and one oxygen atom of the carboxylate [Cu−O(1): 1.966(2) and 1.943(4) Å, for **1** and **4**, respectively] in the basal position. The axial position is occupied by the oxygen atom belonging to the adjacent carboxylate group in the same oxalato ligand [Cu−O(2) 2.308(2) and 2.300(5) Å, for **1** and **4**, respectively]. The intramolecular Cu···Cu′ distances are 5.531(1) Å in **1**, and 5.320(2) Å in **4**. The distortions of the coordination polyhedra have been analyzed by means of the Addison's parameter from the limiting values correspond-

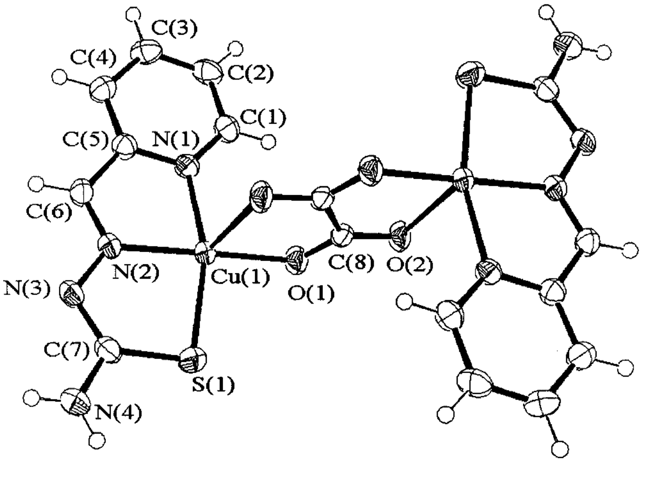

Figure 1. Molecular structure of **1** with thermal ellipsoids at the 50% probability level

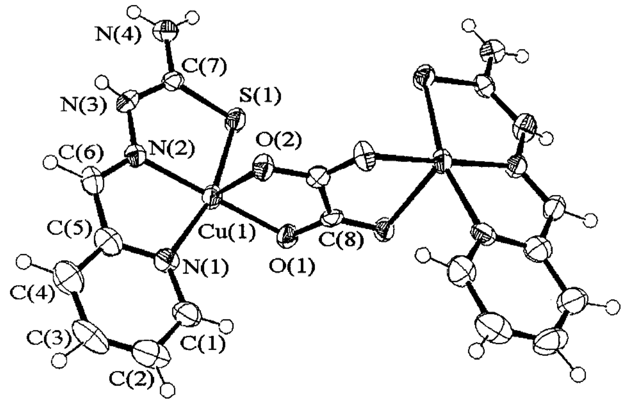

Figure 2. Molecular structure of **4** with thermal ellipsoids at the 50% probability level

ing to square pyramidal (SP, $\tau = 0$) and trigonal bipyramidal (TBP, $\tau = 1$) topologies.[5] The τ values obtained are 0.22 (**1**) and 0.26 (**4**), which indicate that the environment of the copper(II) ions is close to the SP topology. Note the different positions of the ligands in the dinuclear entities (*trans* and *cis* for **1** and **4**, respectively), which breaks the centrosymmetry in **4** and forms a C2 axis with respect to the oxalato ligand. The *cis* configuration of the dinuclear species is not usual in thiosemicarbazone derivatives.[6]

The crystal structure of complex **2** consists of [Cu(HL)(ox)(H_2O)] monomers, as represented in Figure 3. Several distances and angles are shown in Table 2. Each copper(II) ion is five-coordinate, with one sulfur and two nitrogen atoms of the thiosemicarbazone ligand [Cu−N(1), N(2), S: 2.027(3), 1.967(3), 2.281(1) Å] and an oxygen O(1) atom of the oxalato ligand [Cu−O(1): 1.933(2) Å] in the basal plane. The axial position is occupied by the oxygen atom belonging to a water molecule [Cu−O(5) 2.285(3) Å]. The distortion of the coordination polyhedron gives a value of $\tau = 0.18$, characteristic of a geometry close to SP topologies.

The crystal structure of compound **3** is made up of centrosymmetric $[\{Cu(HL)(ox)\}_2]^{2+}$ cationic entities and $[Cu(ox)_2]^{2-}$ bis(oxalato)copper(II) anions. A perspective view of the structure is shown in Figure 4. Selected distances and angles are given in Table 2. The Cu(1) and Cu(2) copper(II) ions exhibit square-pyramidal ($\tau = 0.09$) and square-planar geometries, respectively. Cu(1) is coordinated to one sulfur and two nitrogen atoms of the thiosemicarbazone ligand [Cu−N(1), N(2), S: 2.026(3), 1.952(3), 2.275(1) Å] and an oxygen O(1) atom of the oxalato ligand (Cu−O(1): 1.943(2) Å) in the basal plane. The axial position is occupied by the oxygen atom belonging to the adjacent carboxylate group in the same oxalato ligand [Cu−O(2): 2.261(2) Å]. The intramolecular Cu···Cu′ distance is 5.439(1) Å. The Cu(2) atoms in the bis(oxalato)copper(II) anions are bonded to the O(1S) and O(3S) atoms of each oxalato ligand with bond lengths of 1.937(2) and 1.941(2) Å, respectively. It is interesting to note that the Cu(2)−O(2) distance is 2.756(2) Å, and so the possibility of pseudocoordination must not be ruled out. This could give rise to the presence of chains in the structure, in which the bis(oxalato)copper(II) anions would act as a bridge between the $[\{Cu(HL)(ox)\}_2]^{2+}$ entities.

The thiosemicarbazone ligand exhibits high planarity, except in the cationic entities of **3**. The maximum deviation from the pyridine plane in **1**, **2**, **3** and **4**, corresponds to the S (0.21 Å), N(4) (0.23 Å), S (−0.86 Å) and N(4) (0.34 Å) atoms respectively. The copper(II) ions are above the plane formed by the thiosemicarbazone N(1)N(2)S set (0.22, 0.18, 0.23 and 0.13 Å in **1**, **2**, **3** and **4**, respectively). Both thiosemicarbazone molecules in the dinuclear entity are coplanar on **1** and **3** (dihedral angle ca. 0.0°), but in **4**, the angle formed by the two planes is 10.3°.

The oxalato ligand is planar in **1** and in the cationic $[\{Cu(HL)(ox)\}_2]^{2+}$ species of **3**. However, the O(1S)−C(1S)−C(2S)−O(2S) dihedral angle in the bis(oxalato)copper(II) anions in **3** is 9.6(4)°. The value of the analogous O(1)−C(8)−C(9)−O(3) and O(1)−C(8)−C(8)^{i}−O(1)^{i} angles in **2** and **4** are 79.9(4) and 2.5°, respectively. The highly twisted oxalate molecules, as those reported in **2** (e.g., O−C−C−O angles greater than 50°), are not very usual.[7] There are several possible explanations for this phenomenon. i) The O(2) atom points in the direction of the out-of-plane d_x orbitals (d_{xz} or d_{yz}) of the copper(II) ion. However, the Cu−O(2) distance is too long (2.916 Å). An Extended Hückel molecular orbital (EHMO) analysis[8] on the crystallographic coordinates of compound **2** has been carried out following a published method.[9] It gives no evidence of any significant overlap population between the Cu and O(2) atoms. ii) The existence of tangential π-π stacking between the pyridine and uncoordinated carboxylato moieties can also be considered, with a minimum atom···atom distance of 3.47 Å [O(3)···N(1)^{v}]. The angle between the pyridine and carboxylato planes is 5.3°. However, these interactions are probably weak due to the substantially offset π-stacked geometry. iii) Finally, very strong hydrogen bonds involving the O(3) and O(4) atoms are present in the crystal (see Table 2). These atoms belong to the uncoordinated carboxylate group in the oxalato ligands. The strength of these hydrogen bonds influences the

Table 2. Selected bond lengths (Å) and angles (°) for **1**, **2**, **3** and **4**; symmetry transformations used to generate equivalent atoms: **1**: *i*: $-x + 1, -y + 1, -z + 1$; *ii*: $x-1, y, z$; *iii*: $x + 1, y, z$; *iv*: $-x + 3, -y + 2, -z + 2$; *v*: $-x + 2, -y + 1, -z + 2$; *vi*: $-x + 1, -y + 2, -z + 1$; **2**: *i*: $-x + 1, -y + 1, -z$; *ii*: $x + 1/2, -y + 3/2, z + 1/2$; *iii*: $x, y-1, z$; *iv*: $-x + 1/2, y - 1/2, -z + 1/2$; *v*: $-x + 3/2, y + 1/2, -z + 1/2$; **3**: *i*: $-x, -y, -z + 1$;; *ii*: $-x + 1, -y, -z + 2$; *iii*: $x, y, z + 1$; *iv*: $-x, -y, -z + 2$; **4**: *i*: $x, -y, -z + 1/2$; *ii*: $-x, y, z - 1/2$; *iii*: $x - 1/2, y, -z + 1/2$; *iv*: $x - 1/2, -y, z$; *v*: $-x, -y + 1/2, z$

	1[a]	**2**	**3**[b] [c] [d]	**4**[e]
Cu−N(1)	2.044(2)	2.027(3)	2.026(3)	2.027(6)
Cu−N(2)	1.955(2)	1.967(3)	1.952(3)	1.956(5)
Cu−O(1)	1.966(2)	1.933(2)	1.943(2)	1.943(4)
Cu−O(2)[a]/O(5)	2.308(2)	2.286(3)	2.261(2)	2.300(5)
Cu−S	2.2759(6)	2.281(1)	2.275(1)	2.306(2)
N(2)−C(6)	1.284(3)	1.278(4)	1.280(4)	1.279(8)
N(2)−N(3)	1.366(3)	1.360(4)	1.361(4)	1.365(7)
N(3)−C(7)	1.332(3)	1.352(4)	1.361(4)	1.355(8)
C(7)−S	1.743(2)	1.703(3)	1.704(4)	1.711(7)
N(4)−C(7)	1.336(3)	1.317(5)	1.310(5)	1.319(8)
N(1)−Cu−N(2)	80.79(8)	80.1(1)	80.2(1)	80.2(2)
S−Cu−N(1)	161.61(6)	162.71(8)	161.53(9)	163.8(2)
N(2)−Cu−O(1)	174.80(7)	173.7(1)	167.2(1)	179.5(2)
N(2)−Cu−O(2)[a]/O(5)	106.30(7)	85.9(1)	112.9(1)	100.9(2)
N(4)−C(7)−N(3)	116.1(2)	116.0(3)	116.9(3)	117.4(6)
N(4)−C(7)−S	119.2(2)	122.2(3)	122.1(3)	121.2(6)
Selected oxalate bonds				
O(1)[b]−C(8)/O(3)−C(9)	1.273(3)	1.273(4)/1.267(4)	1.266(4)	1.266(8)
O(2)[e]−C(8)/O(4)−C(9)	1.232(3)	1.238(4)/1.225(4)	1.244(4)	1.243(8)
C(8)−C(8)[a,b]/C(9)	1.565(4)	1.524(4)	1.559(7)	1.56(1)
Shortest Cu···Cu distances				
Intramolecular	5.531(1)^{i}		5.438(1)^{i}	5.320(2)^{i}
Intermolecular	6.174(1)^{ii,iii}	5.695(1)^{i}	4.583(1)[c] 5.153(1)[d]	3.697(2)^{v}

Hydrogen bonding contacts A−H···B

Compound	D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	<(DHA)
1	N(4)−H(4A)···N(3)^{iv}	0.86(3)	2.19(3)	3.044(3)	172(4)
	N(4)−H(4B)···O(1S)^{v}	0.86(3)	2.31(3)	2.983(3)	135(4)
2	O(5)−H(5A)···O(2)^{ii}	0.84(4)	1.93(4)	2.757(4)	166(4)
	N(3)−H(3A)···O(3)^{iii}	0.77(4)	1.90(4)	2.662(4)	173(4)
	N(4)−H(4A)···O(4)^{iii}	0.70(4)	2.09(5)	2.790(5)	172(5)
	N(4)−H(4C)···O(2)^{iv}	0.83(5)	2.35(5)	3.063(5)	145(4)
	O(5)−H(5B)···O(3)^{v}	0.70(5)	2.02(5)	2.706(4)	166(6)
3	N(4)−H(4B)···O(2S)^{ii}	0.78(4)	2.02(4)	2.798(5)	171(4)
	N(3)−H(3A)···O(4S)^{iii}	0.85(4)	1.91(4)	2.727(4)	163(4)
4	N(3)−H(3B)···O(2X)^{ii}	0.86	1.96	2.78(2)	159.0
	N(3)−H(3B)···O(2Y)^{ii}	0.86	1.98	2.77(3)	151.4
	N(4)−H(4A)···O(1S)^{iii}	0.86	2.08	2.797(8)	140.6
	N(4)−H(4B)···O(2)^{iv}	0.86	2.07	2.890(7)	159.9

[a] In the case of compound **1**, O(2) and C(8) atoms related to the symmetry operation *i*. [b] In the case of compound **3**, O(1) and C(8) atoms related to the symmetry operation *i*. [c] In the case of compound **3**, Cu(1)···Cu(2) distance in the asymmetric unit. [d] In the case of compound **3**, Cu(1)···Cu(1)^{iv}. [e] In the case of compound **4**, O(2) related to the symmetry operation *i*.

D···A intermolecular distances and the C(8)−O(2), C(9)−O(3), C(9)−O(4) bond lengths. This fact suggests that the hydrogen bonds are mostly responsible for the twisting of the oxalato ligand. On the other hand, for all these complexes, the longest C−O bonds in the coligands involve the oxygen atoms that are linked to the metal ions.

As in the case mentioned above, the lattice of these compounds contain several hydrogen bonds involving the N(3), N(4) and the oxygen atoms of the oxalato coligands (see Table 2).

The shortest distances between the planes of the pyridine and thiosemicarbazone fragments in different molecules are 3.28 [C(2)···N(2)^{ii}], 3.32 [C(1)···N(3)^{v}], 3.34 [C(5)···N(4)^{iv}] and 3.32 Å [N(4)···C(5)^{iv}] for **1**, **2**, **3** and **4**, respectively. This suggests the existence of π-π interactions of the slipped packing type,[10] as represented in Figure 5. Some structural parameters have been evaluated,[11,12] and the results are shown in Table 3. The coordination of a metal ion to the nitrogen heteroatom in heterocyclic molecules enhances the electron-withdrawing effect as a result of its positive charge, such that the stability of the π-π interaction increases.[13,14]

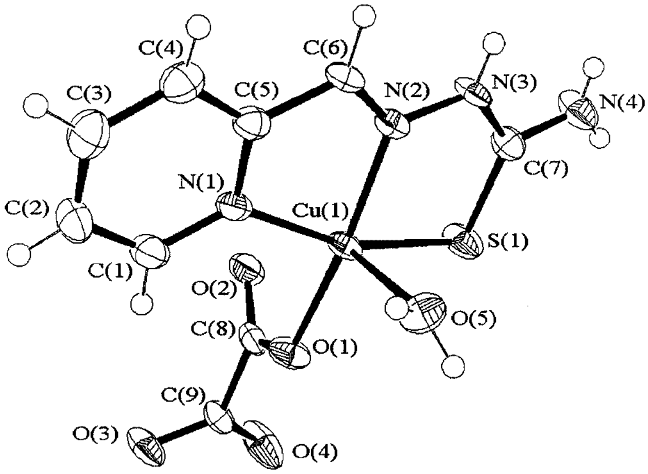

Figure 3. Molecular structure of **2** with thermal ellipsoids at the 50% probability level

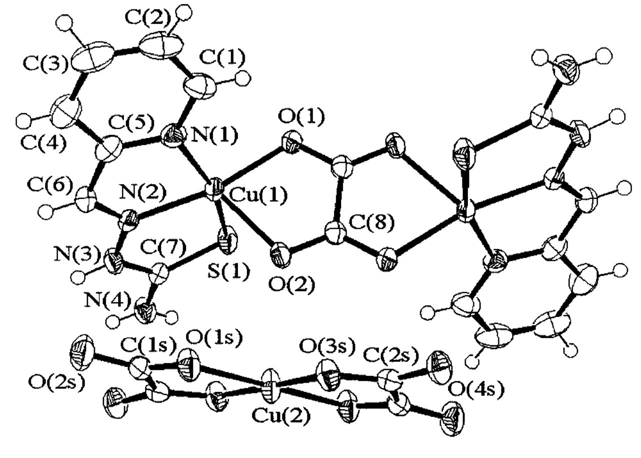

Figure 4. Molecular structure of **3** with thermal ellipsoids at the 50% probability level

These kinds of interactions have also been observed in other thiosemicarbazone systems.[15]

Complexation induces conformational changes in the ligand. Atoms N(1) and N(2) are *anti* with respect to the C(5)−C(6) bond in the free ligand,[16] however, they are *syn* after chelation. Furthermore, the N(2) and S atoms are *anti* with respect to the N(3)−C(7) bond in the neutral ligand[16] and the pyridinium $(H_2L)Cl{\cdot}H_2O$ cationic derivative.[17] However, in the metal complexes, they adopt a *syn* geometry. The C−C and C−N distances are similar to those found in the free ligand and its cationic form, with the exception of the N(3)−C(7) and C(7)−S bond lengths in compound **1**. These bond lengths are significantly different from those observed in the free ligand: 1.358(4) and 1.698(3) Å, respectively. This fact suggests that the double-bond character of the N(3)−C(7) bond in the thiosemicarbazone anionic ligand increases, and that of the C(7)−S bond decreases. However, the bond lengths in the complexed neutral thiosemicarbazone ligands are not different from those in the free ligand. These results are related to the thione vs. thiolate character of the ligand in the neutral or anionic forms, respectively, suggesting the presence of appreciable metal-to-ligand π-back donation in the neutral thiosemicarbazone, due to an increase in the π-acceptor character of the sulfur atom of the ligand. The bond lengths are often in the range of experimental error. Other structural parameters, such as some bond angles and non-contact distances are more appropriate for the evaluation of the anionic vs. neutral character of the ligand on complexation.[18] The results summarized in Table 4 show that the distances and angles for the title complexes are in good agreement with those expected for compounds containing the pyridine-2-carbaldehyde thiosemicarbazone ligand in the anionic (**1**) and neutral (**2**, **3**, **4**) forms.

Table 3. 1: N(1), C(1), C(2), C(3), C(4), C(5) ring in compound **1**; 2: C(6), N(2), N(3), C(7), S, N(4) set in compound **1**, N(3) is considered to be the "centroid"; 3: N(1), C(1), C(2), C(3), C(4), C(5) ring in compound **2**; 4: C(6), N(2), N(3), C(7), S, N(4) in compound **2**, N(3) is considered to be the "centroid"; 5: N(1), C(1), C(2), C(3), C(4), C(5) ring in compound **3**; 6: C(6), N(2), N(3), C(7), S, N(4) in compound **3**, N(4) is considered to be the "centroid"; 7: C(6), N(2), N(3), C(7), S, N(4) in compound **4**, N(4) is considered to be the "centroid"; 8: N(1), C(1), C(2), C(3), C(4), C(5) ring in compound **4**; DC: distance (Å) between the centroids of the sets *i* and *j*; ANG: angle (°) between the least-squares planes; DZ: distance (Å) between the "centroid" of *j* plane and the least-squares plane of *i* ring; DZ′: distance (Å) between the centroid of *i* ring and the least-squares plane of *j*; DXY: distance (Å) between the "centroids" of *i* and *j* projected onto the least-squares plane of *i*; DXY′: distance (Å) between the "centroids" of *i* and *j* projected onto the least-squares plane of *j*; DS: distance (Å) from the centroid of *i* to the nearest hydrogen atom of *j* plane

i	*j*	DC	ANG	DZ	DXY	DZ′	DXY′	DS
1	2^{ii}	3.31	8.13	3.22	0.63	3.16	0.94	3.86
1	1^{vi}	3.79	0.00	3.49	1.32	3.49	1.32	3.67
3	4^{i}	3.34	3.97	3.32	0.45	3.25	0.45	3.34
3	4^{v}	3.89	6.63	2.98	2.48	3.41	1.96	3.63
5	6^{iv}	3.26	11.39	3.21	0.48	3.11	1.00	3.23
7	8^{iv}	3.32	11.96	3.28	0.29	3.24	0.66	4.01
7	8^{v}	3.37	8.35	3.33	0.63	3.27	0.90	3.92

Spectroscopic Studies

The unambiguous assignment of the IR absorption bands in these compounds is made difficult by the highly delocalized thiosemicarbazone system and the oxalato coligands, which give rise to many infrared absorptions. One of the relevant features in some of the complexes is the presence of bands in the 2900−2300 cm^{-1} region which can be assigned to the ν(OH) and ν(NH) vibrations, which are shifted to lower energies as a result of the strong hydrogen bonds. This is in good agreement with the structural results.[19,20] The bands at 1646, 1347 and 800 cm^{-1} in **1** are assigned to the ν_{as}(COO), ν_s(COO) and ν(OCO) absorptions of the oxalato ligand, respectively.[21] Compound **2** shows absorptions at 1644, 1573, 1382, 1339, 830 and 805 cm^{-1} for both the coordinated and uncoordinated carboxylate groups. The complexity of the spectrum of compound **3** only allows for the identification of the bands at 1655, 1640, 1392 and 803 cm^{-1}, which correspond to the oxalato ligands. The same absorptions are found in **4** at

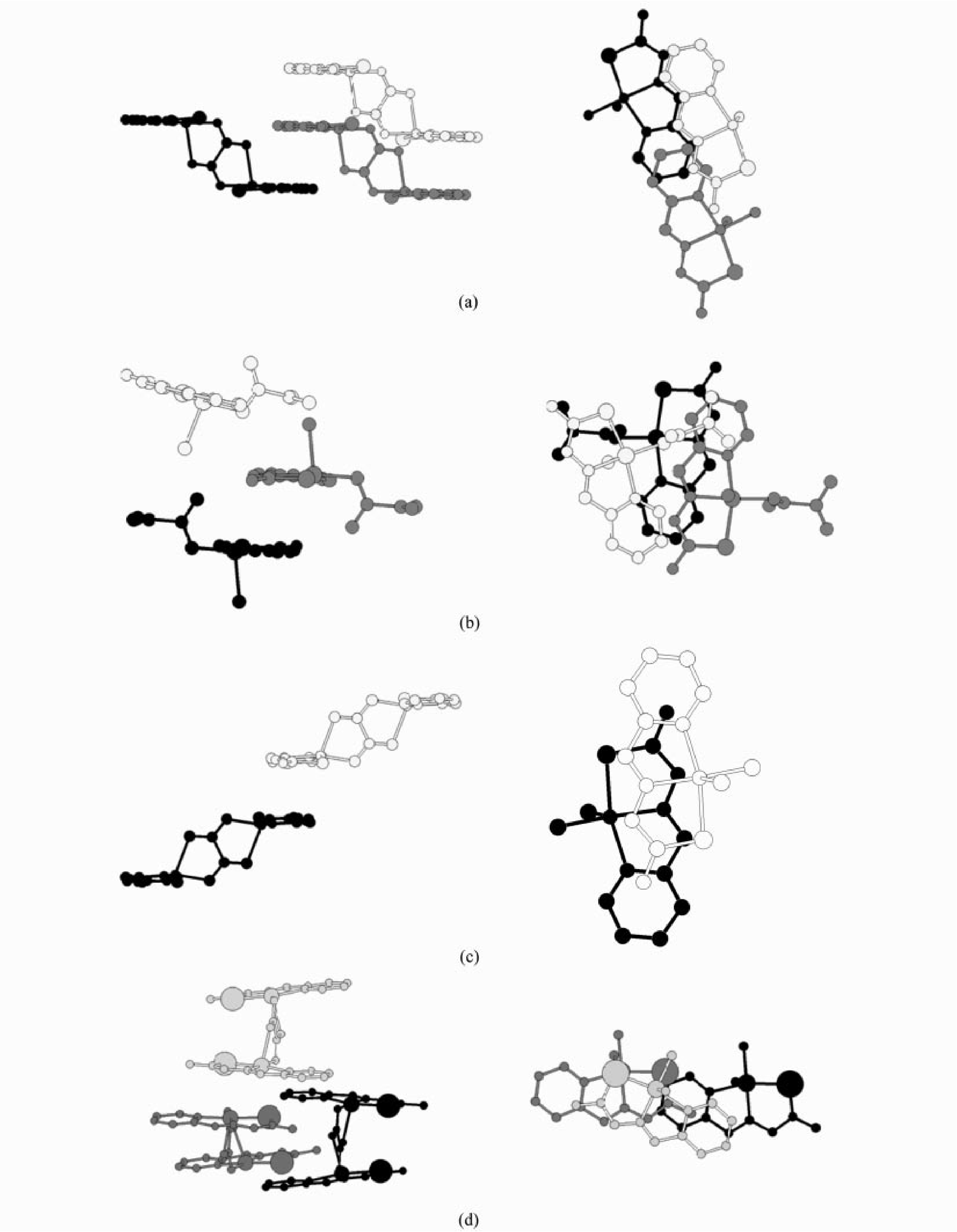

Figure 5. Details of π-π stacking for (a) **1**, (b) **2**, (c) **3** and (d) **4**; drawings (a) and (c) on the right represent monomeric fragments for clarity

Table 4. Selected structural differences between copper(II) complexes containing neutral (HL) and anionic (L^-) pyridine-2-carbaldehyde thiosemicarbazone ligand (Å) and (°)

Compound	N(2)−N(3)−C(7)	S−C(7)−N(3)	S−C(7)−N(4)	Cu···N(3)	N(2)···C(7)
1	112.0(2)	124.7(2)	119.2(2)	2.94	2.24
2	117.0(3)	121.7(3)	122.4(3)	2.89	2.31
3	116.7(3)	121.0(3)	122.1(3)	2.89	2.32
4	117.6(6)	121.3(5)	121.2(6)	2.89	2.32
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

1654, 1302 and 797 cm^{-1}. Furthermore, compound **4** shows bands at 1383 and 820 cm^{-1} that can be assigned to the ν_3 and ν_2 vibration modes of the nitrate counterion.

The reflectance spectra of the title compounds show bands in the 210−230, 275−290, 360−430 and 630−950 nm regions. These are assigned to ($\pi \rightarrow \pi^*$) pyridine, ($n \rightarrow \pi^*$) pyridine, ($n \rightarrow \pi^*$) thiosemicarbazone, LMCT N/O/S → d and d → d transitions, respectively.[22,23]

The absorption band observed in the 360−380 nm region is assigned to a S → Cu^{II} charge transfer transition. This band is shifted to lower energies in compound **1**. The decrease in energy for the complexes containing the ligand in the anionic form may be due to a decrease in the strength of the π-interactions between the copper and sulfur atoms, and hence results in a C−S bond with greater thiolate behavior.[4e,4h,4j] The absorptions between 420−430 nm can be assigned to LMCT O/N → Cu^{II} transitions, as was observed in other related compounds.[24]

The maxima observed in the 630−665 nm region are characteristic of d → d transitions for square pyramidal copper(II) complexes with a $d_{x^2-y^2}$ ground state. These bands show unresolved shoulders obscured by the tails above 700 nm, which can be due to the distortion of the coordination polyhedra in these compounds to trigonal-bipyramidal geometry. In this sense, the higher the distortion, the greater the wavelength. This is in accordance with the Addison's parameters calculated in the crystallographic section.

The X-band EPR spectra of complexes **1**, **2** and **4** at room temp. are shown in Figure 6. All the spectra exhibit rhombic signals. The obtained *g* values are given in Table 5. These values are similar to those observed for other pyridine-2-carbaldehyde thiosemicarbazone derivatives containing copper(II) ions with distorted square pyramidal topologies, with a $d_{x^2-y^2}$ ground state.[4b,4d−4k]

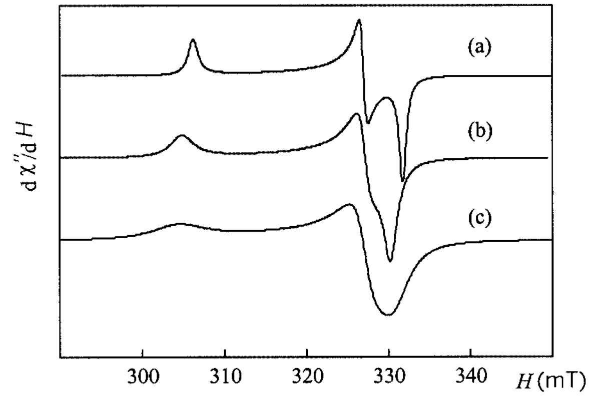

Figure 6. X-band EPR spectra of (a) **1**, (b) **2** and (c) **4** in the solid state at room temp.

Table 5. Experimental EPR parameters

Compound	Temperature	g_1	g_2	g_3
1	room temp.[a]	2.200	2.062	2.032
2	room temp.[a]	2.211	2.061	2.041
4	room temp.	2.212	2.062	2.044
	4 K	2.230	2.063	2.025

[a] No variation in the *g*-values from room temperature to 4 K.

Magnetic Behavior

The plots of the molar susceptibility (χ_m) vs. *T*, together with the $\chi_m T$ vs. *T* curves, for compounds **1** and **4** are given in Figure 7 and 8. In all the cases, the magnetic measurements obey the Curie−Weiss law at temperatures higher than 50 K. The Weiss temperatures are −3.47 (**1**) and +3.27 K (**4**). The C_m experimental values are 0.41 (**1**) and 0.42 $cm^3{\cdot}K{\cdot}mol^{-1}$ (**4**), and the calculated μ_{eff} values at room temperature are 1.80 (**1**) and 1.84 BM (**4**). For compound **1**, the χ_m value increases with decreasing temperature, reaching a maximum at 7.0 K (0.026 $cm^3{\cdot}K{\cdot}mol^{-1}$), and the $\chi_m T$ value continuously decreases when the temperature is lowered, indicating the presence of antiferromagnetic interactions. However, compound **4** does not exhibit a maximum in the plot of χ_m vs. *T*, and the $\chi_m T$ value increases on

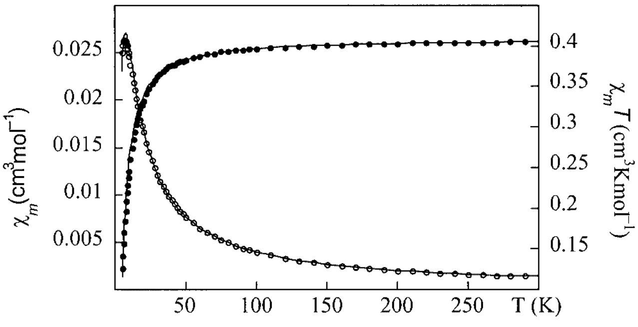

Figure 7. Thermal variation of the molar susceptibility (○○) and $\chi_m T$ (●●) for **1**; solid lines represent the best fit

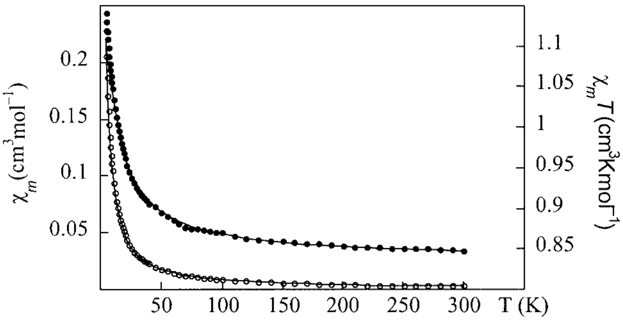

Figure 8. Thermal variation of the molar susceptibility (○○) and $\chi_m T$ (●●) for **4**. Solid lines represent the best fit

lowering the temperature, which is characteristic of ferromagnetic behavior.

Considering the dinuclear nature of these complexes, the susceptibility data was fitted to the expression derived from the Heisenberg isotropic spin Hamiltonian ($H = -2J\, S_1 S_2$), for two coupled $S = 1/2$ ions, given by Bleaney−Bowers for copper(II) dinuclear compounds[25]:

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

where $N\alpha$ = temperature independent contribution, N is Avogadro's number, β = Bohr magneton, and k = Boltzmann constant. The best least-squares fit (solid line in Figures 7 and 8) is obtained from the parameters J/k = −6.20 K (−4.30 cm^{-1}, taking into account 3% paramagnetic impurities) and +7.73 K (+5.37 cm^{-1}). The g values are 2.089 and 2.112 for complexes **1** and **4**, respectively. These g values are in good agreement with those obtained from EPR (2.098 (**1**) and 2.106 (**4**)). Taking into account the structural features, the existence of magnetic interactions between the different species was considered. However, an improvement in the fit was not observed.

The small values of the magnetic interactions suggest that the exchange propagation direction is in a different plane from that formed by the magnetic $d_{x^2-y^2}$ orbitals. These results agree with the presence of exchange coupling through the oxalato ligand. It must be pointed out that, in spite of the weak magnetic exchange in **4**, this is the strongest ferromagnetic interaction observed in oxalato-bridged copper(II) dinuclear complexes.[26]

It has been proposed[27] that the antiferromagnetic contribution to the magnetic exchange constant J for a dinuclear system with two unpaired electrons is proportional to the square of the energy difference (Δ^2) between the two molecular orbitals constructed from the $d_{x^2-y^2}$ magnetic orbitals. EHMO calculations using the crystallographic coordinates have been carried out to give a qualitative explanation for the magnetic behavior of these complexes. The Δ values are 0.016 and 0.021 eV for **1** and **4**, respectively. These results do not show a qualitative agreement between the gap of the two $d_{x^2-y^2}$ magnetic orbitals involved and the values of the exchange constant. There are at least three possibilities that can be proposed to explain such a disagreement. i) The limitations of the EHMO calculations do not allow us to give a perfect sequence for very similar J values in the pyridine-2-carbaldehyde (thiosemicarbazone)-copper(II) system.[4k] However, a good qualitative accordance is usually obtained for different J values, as those described here. ii) The crystal structure of **4** shows Cu···S^{v} distances of 3.184(2) Å, which relate copper(II) ions at 3.697(2) Å. The contraction of the cell at low temperatures decreases the Cu···S^{v} distance. However, as mentioned before, the fit of the curves when considering interactions between different species, was not improved. iii) The non-centrosymmetric nature exhibited by compound **4** could be responsible for the decrease in the antiferromagnetic contribution, which is not reflected in the magnitude of Δ^2, giving rise to the ferromagnetic behavior of this compound.[28]

Conclusion

The control of the experimental conditions in the pyridine-2-carbaldehyde (thiosemicarbazone)copper(II)/oxalato system results in the formation of a rich variety of compounds. In particular, both the amount of reagents and the pH of the medium play an important role in the syntheses of the complexes. As a result either monomeric (**2**) or dinuclear entities (**1** and **4**) can be obtained. The formation of one-dimensional systems is possible , as can be seen by the structure of compound **3**, but up to date, we have not been able to find a reproducible synthetic method to obtain this compound. These results can be used as structural models to predict the possible interactions between the $[Cu(L)(H_2O)_3]^+$ entities and carboxylate-containing biomolecules present in physiological medium.

Magnetic susceptibility data indicate the presence of weak antiferromagnetic and ferromagnetic interactions in **1** and **4**, respectively. The noncentrosymmetric structure of **4** seems to be responsible for the difference in sign of the magnetic properties observed, relative to compound **1** (centrosymmetric). These results demonstrate that the μ-oxalato (thiosemicarbazone)copper(II) systems are appropriate for tunable exchange interactions.

Experimental Section

Preparation of the Complexes: Thiosemicarbazide, pyridine-2-carbaldehyde, oxalic, nitric and trifluoroacetic acids, potassium oxalate, sodium nitrate and copper(II) nitrate were purchased from Fluka, Merck and Prolabo and used as received. Published methods with small modifications were used to synthesize HL[29] and $Cu(L)(NO_3)$.[4b,30]

$[\{Cu(L)\}_2(ox)]\cdot 2H_2O$ (1): An aqueous solution of potassium oxalate (0.092 g, 0.5 mmol) was added to a solution of $Cu(L)(NO_3)$ (0.30 g, 1 mmol) in water (40 mL). The pH was adjusted to 6 by adding NaOH (5 M). The reaction mixture was stirred for 3 h, then filtered, washed and dried. The yield was 0.21 g (70%). Dark-green crystals were obtained by the slow reaction of aqueous solutions of **1** and potassium oxalate in a diffusion device. $C_{16}H_{18}Cu_2N_8O_6S_2$ (609.58): calcd. C 31.5, H 3.0, N 18.4, S 10.5; found C 31.3, H

3.0, N 18.0, S 10.3. Molar conductivity of $5\cdot10^{-4}$ M solutions in dimethylformamide at 25 °C: $\Lambda_M = 5.2\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$. Selected IR bands (KBr): $\tilde{\nu}$ = 3568 m, 3438 m, 3385 m, 3104 m, 1646 br. vs, 1604 s, 1559 m, 1481 m, 1448 s, 1428 br. s, 1347 w, 1324 m, 1297 s,sh, 1229 m, 1172 s, 1155 s, 880 m, 800 m, 779 m, 626 m, 410 w cm^{-1}. UV-Vis: λ_{max} (reflectance spectrum on solid sample) λ = ca. 800 (vb,sh), 646 (b), 422 (sh), 378, 277, 227 nm.

[Cu(HL)(ox)(H_2O)] (2): Oxalic acid (0.63 g, 5 mmol) was dissolved in water (15 mL), and was allowed to react with an aqueous solution of Cu(L)(NO_3) (0.30 g, 1 mmol). The pH was adjusted to 1 by adding nitric acid. After 3 h of constant stirring, the blue solid was filtered, washed and dried. Yield 0.24 g (around 70%). This complex was also prepared from aqueous solutions of **1** and oxalic acid in a diffusion device, both solutions were acidified with several drops of trifluoroacetic acid. After two weeks, greenish-blue crystals suitable for X-ray studies were collected. $C_9H_{11}CuN_4O_5S$ (350.82): calcd. C 30.8, H 3.2, N 16.0, S 9.1; found C 30.5, H 2.8, N 16.2, S 8.8. Molar conductivity of $5\cdot10^{-4}$ M solutions in dimethylformamide at 25 °C: $\Lambda_M = 69.0\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$. Selected IR bands (KBr): $\tilde{\nu}$ = 3354 m, 3231 w, 2864 w (br.), 2696 w, 1644 s, 1614 m, 1573 vs, 1473 s, 1448 m, 1382 w, 1339 m, 1298 vs (sh), 1273 s, 1226 m, 1182 m, 1109 m, 921 m (sh), 830 w, 804 w, 778 sh, 769 s, 653 m (sh), 623 w, 489 w, 414 w cm^{-1}. UV-Vis, λ_{max} (reflectance spectrum on solid sample) = ca. 720 (sh), 630 (b), 360, 287, ca. 220 nm. Deep-blue good quality crystals of [{Cu(HL)}$_2$(ox)][Cu(ox)$_2$]·2H_2O (**3**) co-crystallized, together with those of **2**. All the attempts to synthesize this compound separately were unsuccessful. Selected IR bands (KBr): $\tilde{\nu}$ = 3433 m, 3345 m, 3160 m, 1655 vs, 1638 vs, 1624 vs, 1613 vs,sh, 1582 s, 1392 m, 1299 m, 1254 m, 1226 m, 1178 s, 803 w, 778 s, 738 w, 694 w, 617 w, 490 w, 410 w cm^{-1}.

[{Cu(HL)}$_2$(ox)$_{0.5}$]·(NO_3)$_2$ (4): Aqueous solutions of oxalic acid (0.092 g, 0.5 mmol), sodium nitrate (0.42 g, 5 mmol) and Cu(L)(NO_3) (0.30 g, 1 mmol) were mixed with vigorous stirring. The pH of the resulting mixture was adjusted to about 1 by the addition of nitric acid. Four hours later, a turquoise-blue precipitate appeared. This was filtered, washed and dried. The yield was 0.24 g (around 70%). This complex can be also synthesized from an aqueous suspension of **1** by adding nitric acid (final pH $\approx$ 1). Finally, crystals of this compound were collected by slow evaporation of the mother liquors of **2**. $C_{16}H_{16}Cu_2N_{10}O_{10}S_2$ (699.59): calcd. C 27.5, H 2.3, N 20.0, S 9.2; found C 27.3, H 2.2, N 19.9, S 9.2. Molar conductivity of $5\cdot10^{-4}$ M solutions in dimethylformamide at 25 °C: $\Lambda_M = 133.2\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$. Selected IR bands (KBr): $\tilde{\nu}$ = 3294 m, 3138 m, 1654 vs, 1624 s, 1616 s, 1586 s, 1474 m, 1434 s, 1383 s, 1339 s, 1302 s, 1280 s, 1224 s, 1178 m, 1163 m, 1019 w, 921 w, 879 w, 820 w, 797 w, 771 m, 742 m, 651 m, 623 w, 415 w cm^{-1}. UV-Vis, λ_{max} (reflectance spectrum on solid sample) = ca. 950 (vb, sh), 663 (vb), 428 (sh), 367 (sh), 283, ca. 214 nm.

Physical Measurements: Microanalyses were performed with a LECO CHNS−932 analyzer. Conductivity measurements were made by a CRISON 522 conductimeter. Infrared spectra were obtained with samples prepared as KBr pellets in the 400−4000 cm^{-1} region on a Nicolett Impact 410 FTIR spectrophotometer. Reflectance spectra were recorded on a Cary 2415 spectrometer in the range 200−2000 nm. For UV-visible solution measurements, a Varian UV-VIS-NIR spectrophotometer was employed in the range 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 performed in the temperature 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.[31] Direct methods (SHELXS-97)[32] were employed to solve the structures and were then refined by full-matrix least-squares methods, using the SHELXL-97 computer program.[33] 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.[34] Refinements were made on F_o^2 for all reflections. The high thermal parameters in the nitrate ions of compound **4** are the cause of the disorder in some of the oxygen atom positions. CCDC−194996 (**1**), −194997 (**2**), −194998 (**3**) and −194999 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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