



Effect of the counter-anion on the structural and magnetic properties of a copper(II) complex with 2-[(bis(2-pyridylmethyl)amino)methyl]-4-methyl-6-(methylthio)phenol

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ABSTRACT

A new 2-[(bis(2-pyridylmethyl)amino)methyl]-4-methyl-6-(methylthio)phenol copper^{II} perchlorate complex, $[\text{Cu}_2(\mu\text{-SL})_2](\text{ClO}_4)_2$ (**1**), was synthesized and magnetically and structurally characterized. The complex consists of two similar but not equivalent $[\text{Cu}_2(\mu\text{-SL})_2]^{2+}$ bimetallic cations designed as *P* and *Q*. Cation *P* has a square-base pyramidal cupric centre bonded to an approximately trigonal bipyramidal one, while cation *Q* has two equivalent square-base pyramidal copper centres, related by an inversion center. The cupric centres in both units are bridged by two phenolate oxygen atoms from two deprotonated HSL molecules, defining a central Cu_2O_2 core. Each Cu^{II} centre has a N_3O_2 coordination sphere. Magnetic studies done for (**1**) show an overall weak antiferromagnetic behavior. The best fit of the experimental data was obtained using a modified Bleaney–Bowers equation with $g_1 = g_2 = 2.05$, $J_P = -13.4 \text{ cm}^{-1}$ and $J_Q = +5.22 \text{ cm}^{-1}$ for *P* and *Q*, respectively. The properties of the new complex are compared to those reported for the hexafluorophosphate complex with the same ligand, in terms of the effect of the distortion caused by the use of a different anion.

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1. Introduction

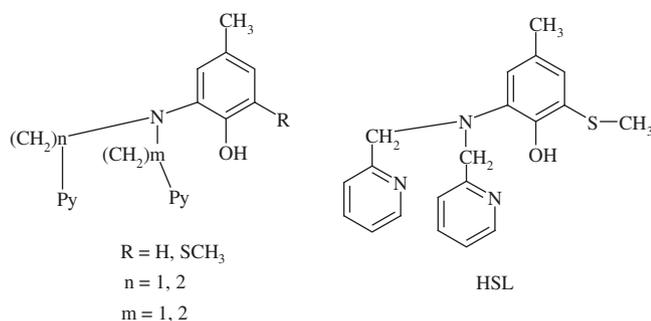
Tripodal aminophenol derivatives act as polydentate ligands giving rise to different mono- or polynuclear species, depending on the experimental conditions [1–13]. Dimeric copper(II) species bridged by one or two deprotonated phenoxo ligands have been reported by several authors, and the magnetic properties have been rationalized, taking into account the structural parameters and the coordination modes of the phenoxo group to the copper centres (axial or equatorial) [1,2,12,13]. Usually, the axial coordination mode has been observed for systems with the 5,5,6 sequence of the chelate rings, while for a ring sequence of 6,6,6, the equatorial position of the phenolate ligand is favored. The axial or equatorial preferences of the phenolate group have been attributed mainly to the steric effect imposed by the smaller rings [14–17].

In previous works [1] we have reported the structural and magnetic properties of dimeric copper(II) complexes with several tripodal pyridylalkylaminophenol ligands, with different length of each arm of the tripodal ligand (Scheme 1).

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Coordination modes observed in this type of bis(μ -phenoxo) bridged dimeric copper(II) complexes include equatorial–equatorial, axial–equatorial and mixed modes depending on the length of the arms. The geometries around the copper(II) centres vary from square base pyramidal to bipyramidal, and pseudo octahedral. From a magnetic point of view, the exchange interaction between the copper(II) centres also varies from moderate antiferromagnetic to weak ferromagnetic. In all these complexes the counteranion was hexafluorophosphate. Hexafluorophosphate, tetrafluoroborate and perchlorate anions are generally chosen as counterions due to experimental reasons, since these permit the isolation of single crystals suitable for X-ray diffraction structural studies, because of their potential to form crystalline solids with large complex cations. In this sense, they are expected to have no effect on the complex cation properties. Contrary to what is inferred, there exists strong evidence that changes in the counteranion may lead to very important modifications in the structure and properties of the obtained compounds [18–20]. For example, several nickel(II) complexes bridged by azido anions have been reported with different amine ligands. When 1,3-propanediamine and its 2,2′-dimethyl derivative are used, *trans* 1-D antiferromagnetic systems are always obtained [19] with ClO_4^- and PF_6^- ; while an antiferromagnetic dinuclear complex is obtained [18] with



Scheme 1. Tripodal pyridylalkylaminophenols used as ligands.

[B(C₆H₅)₄][−]. When the amine ligand is ethylenediamine, an antiferromagnetic dinuclear complex [18] was reported with PF₆[−] and a ferromagnetic dinuclear one with ClO₄[−] [20]. The obtained results are explained by the different sizes of the counteranion, which forces different kinds of packing in each case, resulting in changes in the structure, and therefore in the properties.

We have obtained a new dimeric copper(II) complex with the HSL² ligand using ClO₄[−] as the counteranion instead of PF₆[−], as reported earlier. This work described the structural and magnetic characterization of this new complex; a comparison is made with the properties of the one reported previously, with PF₆[−] as counteranion.

2. Experimental

All reagents were reagent grade and used without further purification, unless stated otherwise. Solvents were of HPLC quality and were used as received. Elemental analyses for C, H, and N were performed at CEPEDeq (University of Chile) on a Fison-Carlo Erba EA 1108 model analyzer. Copper was determined by atomic absorption spectroscopy. IR spectra were obtained as KBr pellets on a Bruker Vector 22 instrument. ¹H NMR spectra were recorded in CDCl₃ on a Bruker AMX-300 NMR spectrometer. Chemical shifts are reported as δ values downfield of an internal Me₄Si reference.

2.1. Syntheses

2.1.1. 2-[(Bis(2-pyridylmethyl)amino)methyl]-4-methyl-6-(methylthio)-phenol (HSL)

The ligand was synthesized by a Mannich reaction of 2-(methylthio)-p-cresol [21] with bis(2-pyridylmethyl) amine [22], paraformaldehyde, and 2-(methylthio)-p-cresol in 57% yield, as described previously [2]. ¹H NMR (CDCl₃) for HSL: δ 11.4 (1H, broad, OH), 8.58 (2H, d, pyridine α protons), 7.63 (2H, t), 7.36 (2H, d) and 7.16 (2H, t) (pyridine protons), 6.92 (1H, s), and 6.72 (1H, s) (phenylprotons), 3.86 (4H, s, CH₂Py), 3.75 (2H, s, CH₂Ph), 2.46 (3H, s, CH₃S), 2.26 (3H, s, CH₃Ph).

2.1.2. [Cu₂(μ-SL)₂](ClO₄)₂

CuCl₂ (0.27 g, 2 mmol) was added to a solution of the ligand HSL (2 mmol) and triethylamine (2 mmol) in methanol (10 mL), and the mixture was refluxed for 60 min. Excess tetra-*n*-butylammonium perchlorate was added to the solution, and the crystalline product precipitated immediately. Recrystallization from an acetonitrile–methanol mixture affords crystals suitable for X-ray structural studies.

IR (cm^{−1}, KBr pellets): 2920 (s, m), 2858 (s, w), 1609 (s, s), 1575 (s, w), 1457 (s, s), 1094 (s, vs), 860 (s, w), 802 (s, m), 768 (s, m), 623 (s, s).

UV–Vis (methanol): 485 nm (ε = 400 M^{−1}); 754 nm (ε = 200 M^{−1}).

Anal. Calc. for C₄₂H₄₄Cu₂Cl₂N₆O₁₀S₂: C, 47.78; H, 4.20; N, 7.96; Cu, 12.04. Found: C, 48.3; H, 4.18; N, 7.84; Cu, 12.35%.

2.1.3. Single-crystal X-ray diffraction

The crystal structure of [Cu₂(μ-SL)₂](ClO₄)₂ (**1**) at room temperature was determined by X-ray diffraction measurements on a prismatic 0.49 × 0.18 × 0.07 mm³ single crystal. Data collection was run on SMART CCD diffractometer, using ω-scans. Data reduction was done with SAINT [23], while the structure solution by direct methods, completion and refinement was conducted with SHELXL [24]. Empirical absorption corrections were applied using SADABS [25]. The hydrogen atoms positions were calculated after each cycle of refinement with SHELXL using a riding model for each structure, with C–H distance varying from 0.93 to 0.97 Å. U_{iso}(H) values were set equal to 1.2 U_{eq} of the parent carbon atom (1.9 U_{eq} for Methyl). During the final stages of the refinement it was clear there was disorder on the three non-equivalent uncoordinated charge balancing perchlorate anions. The perchlorate anions associated to Cl1 and Cl2 centres were modeled using two positions, labeled A and B, for the four oxygen atoms. They were then refined and finally held constant at 0.43/0.57(A/B) and 0.36/0.64(A/B) respectively. For the third perchlorate anion, associated to Cl3, the disorder was modeled using six positions for the four oxygen atoms, restricted to add 4. The occupancies were finally held constant at 0.85, 0.50, 0.84, 0.65, 0.48 and 0.68 for O10, O11, O12, O13, O14 and O15 respectively. Additional data collection and refinement details are given in Table 1.

2.1.4. Magnetic susceptibility

The ZFC and FC magnetic susceptibility measurements at variable temperature, in the range of 2.0–291 K, were performed on a microcrystalline sample using a Cryogenics SX600 SQUID magnetometer at 0.02 and 0.25 kOe. Diamagnetic corrections (estimated from Pascal constants) [26] and sample holder contributions were taken into account. The fit was performed minimizing the agreement factor $R = [\sum(\chi_M T_{\text{obs}} - \chi_M T_{\text{calc}})^2 / \sum(\chi_M T_{\text{obs}})^2]^{1/2}$.

3. Results and discussion

3.1. Synthesis

The complex was obtained straight forward by reaction of the ligand with CuCl₂ in a 1 to 1 M ratio in the presence of triethylamine as

Table 1
Crystal data and structure refinement details for (**1**).

Complex	1
Formula weight	1054.97
Crystal system	monoclinic
Space group	P2 ₁ /n
a (Å)	13.1509(14)
b (Å)	13.3134(14)
c (Å)	21.806(2)
α (°)	74.191(2)
β (°)	86.641(2)
γ (°)	66.190(2)
V (Å ³)	3355.1(6)
Z (Z')	6(3)
δ (g cm ^{−3})	1.566
μ (mm ^{−1})	1.228
F(000)	1626.0
θ (°)	3.40–50.36
Index ranges	−15 ≤ h ≤ 15 −15 ≤ k ≤ 15 −26 ≤ l ≤ 26
N _{tot} , N _{uniq} (R _{int}), N _{obs}	21262, 11908 (0.0482), 7640
Refinement parameters	961
Goodness-of-fit (GOF) on F ²	1.029
R ₁ , wR ₂ (obs)	0.0679, 0.1415
R ₁ , wR ₂ (all)	0.1101, 0.1609
Maximum and minimum Δρ	0.909 and −0.845

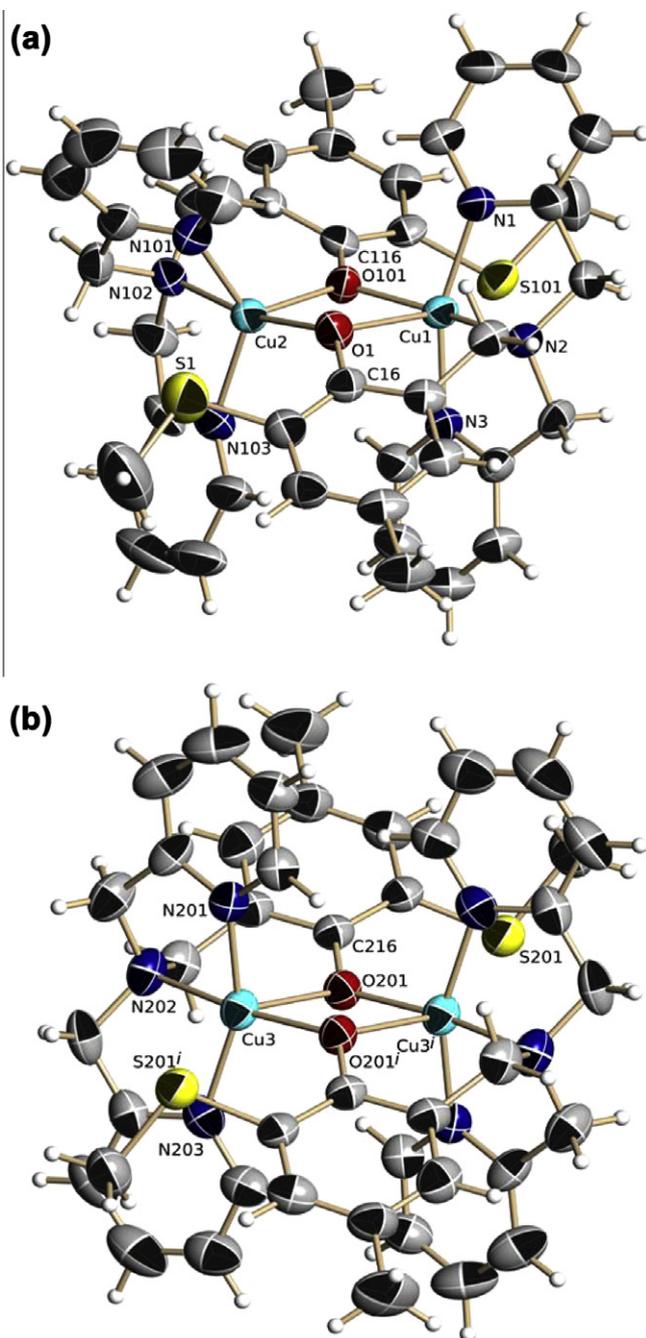


Fig. 1. Molecular structure diagram for cations *P* (a) and *Q* (b) within the asymmetric unit of **1**, including partial numbering scheme. Displacement ellipsoids at the 33% level of probability.

a base; the crystalline product was precipitated after addition of excess tetra-*n*-butylammonium perchlorate.

3.2. Structural description

The crystal structure determined for **(1)** shows two similar, but not equivalent $[\text{Cu}_2(\mu\text{-SL})_2]^{2+}$ bimetallic cations. One of them, containing Cu1 and Cu2, is pseudo-centrosymmetric, while the other, containing Cu3 and Cu3ⁱ (ⁱ: 2 - *x*, 1 - *y*, -*z*), is strictly centrosymmetric. We will refer in the following as cation *P* to the first, and cation *Q* to the second. Both units are depicted in Fig. 1a and b respectively. The asymmetric unit of the compound contains one and a half cationic $[\text{Cu}_2(\mu\text{-SL})_2]^{2+}$ units, and three uncoordinated counter balancing perchlorate anions.

It is important to note that according to the crystal structure there are two *P* cations for each *Q* cation within the unit cell. In both cations, the cupric centres are bridged by two phenolate oxygen from two deprotonated HSL molecules, defining a central Cu_2O_2 core, while the three remaining nitrogen atoms complete the coordination sphere of each cupric centre, leading to pentacoordination. Therefore, each copper(II) centre has a N_3O_2 environment. However, their coordination geometry differs slightly; while Cu1 and Cu3 could be well described as a slightly distorted square-base pyramids, with τ values of 0.11 and 0.20 respectively [27], the geometry around Cu2 is rather intermediate between a square-base pyramid and trigonal bipyramid, with τ equal to 0.57. In summary, cation *P* has a square-base pyramidal cupric centre (Cu1) bonded to an approximately trigonal bipyramidal one (Cu2), while cation *Q* has two square-base pyramidal centres (Cu3 and Cu3ⁱ). The structural parameters of cation *Q* are very similar to those observed for the copper ions in the complex with the same ligand reported earlier, $[\text{Cu}_2\text{L}_2](\text{PF}_6)_2$, using hexafluorophosphate as the counterion instead of perchlorate [2]. It is interesting to note that for each cupric centre there exists a sulfur atom from the SCH_3 substituent on one of the arms in HSL ligand, which is correctly placed in the proper direction to complete an octahedral environment. However, the rather long copper-sulfur distances, 2.812(2) Å (Cu1···S101), 3.137(2) Å (Cu2···S1) and 2.929(2) Å (Cu3···S201ⁱ), suggest this is probably the result of the steric demands of the ligand, precluding to qualify the coordination geometry as octahedral. A reasonable alternative description would be as *pseudo* or distorted octahedrons.

In contrast to what was observed for *Q*, with a strictly planar Cu_2O_2 core (because of the inversion centre), unit *P* presents a central core; which is not strictly planar, with deviations to the least-squares plane of -0.067(1) Å, -0.076(1) Å, 0.066(1) Å and 0.076(1) Å for Cu1, Cu2, O1 and O101, respectively.

Both units display rather distorted central Cu_2O_2 parallelograms, with short distances of 1.941(4) Å (Cu1–O101), 1.919(4) Å (Cu2–O1) and 1.931(3) Å (Cu3–O201ⁱ) and long ones of 2.432(4) Å (Cu1–O1), 2.140(3) Å (Cu2–O101) and 2.352(4) Å (Cu3–O201). The corresponding angles are 93.7(2)° (Cu2–O1–Cu1), 102.9(2)° (Cu1–O101–Cu2) for *P*, and 98.2(2)° (Cu3ⁱ–O201–Cu3) for *Q* (ⁱ = 2 - *x*, 1 - *y*, -*z*). The copper to copper distance is 3.194(1) Å for *P* and 3.245(1) Å for *Q*.

Finally, it is relevant to note that the phenolate group, which is highly planar, it is not coplanar with the central Cu_2O_2 plane. In fact, the phenolate groups lie at opposite sides of the central plane. The angle defined by the central Cu_2O_2 plane and the O–C vector is 27.6° (O1–C16) and 16.9° (O101–C116) for *P* and 31.4° for *Q*. Besides, the phenolate moiety is rotated in relation to the Cu_2O_2 core by 33.4° (O1) and 23.4° (O101) for *P* and 34.9° for *Q*. These structural parameters have been reported to influence the magnetic coupling between the cupric centres in binuclear copper complexes bridged by phenolate groups [28]. Table 2 shows a summary of the most relevant bond distances and angles as determined from the X-ray diffraction.

Mono-, bi- and trinuclear copper complexes have been described for the HSL ligand [1,2]. In all these complexes the ligand also behaves as a tetracoordinating moiety with a N_3O donor set. The coordination geometry of the metal center in the mononuclear complex, $[\text{Cu}(\text{HSL})\text{Cl}]\text{PF}_6$ has been described as slightly distorted square pyramidal with the apical position occupied by the hydroxyl group of the phenol. In this mononuclear complex the ligand is protonated, contrary to the results observed for the reported complex, and for other similar systems in which the ligand is deprotonated. As already mentioned, the structural parameters for the reported dimeric centrosymmetric complex $[\text{Cu}_2(\text{SL})_2](\text{PF}_6)_2$ [2] are very similar to those found for unit *Q*. The axial position is occupied by the phenoxo group, while another phenoxo group

Table 2
Selected bond distances (Å) and bond angles (°) for (1).

Cu1–O1	2.432(4)	Cu2–O1	1.919(4)
Cu1–O101	1.941(4)	Cu2–O101	2.140(3)
Cu1–N1	2.008(5)	Cu2–N101	2.024(5)
Cu1–N2	2.025(4)	Cu2–N102	2.006(4)
Cu1–N3	1.993(5)	Cu2–N103	2.071(5)
Cu1···S101	2.812(2)	Cu2···S1	3.137(2)
Cu1···Cu2	3.194(1)		
Cu3–O201	2.352(4)	Cu3201 ⁱ	1.931(3)
Cu3–N201	2.023(5)	Cu3–N202	2.033(4)
Cu3–N203	1.986(5)	Cu3···S201 ⁱ	2.929(2)
Cu3···Cu3 ⁱ	3.245(1)		
O101–Cu1–N1	97.7(2)	O1–Cu2–N101	93.74(2)
O101–Cu1–N2	167.3(2)	O1–Cu2–N102	167.8(2)
O101–Cu1–N3	98.9(2)	O1–Cu2–N103	109.7(2)
N1–Cu1–N2	82.3(2)	N101–Cu2–N102	80.6(2)
N1–Cu1–N3	160.7(2)	N101–Cu2–N103	133.6(2)
N2–Cu1–N3	83.7(2)	N102–Cu2–N103	81.7(2)
N1–Cu1–O1	100.8(2)	N101–Cu2–O101	121.3(2)
N2–Cu1–O1	90.4(2)	N102–Cu2–O101	88.5(2)
N3–Cu1–O1	92.4(2)	N103–Cu2–O101	100.7(2)
O1–Cu2–O101	85.2(2)	O101–Cu1–O1	77.1(1)
O1–Cu2–S1	69.0(1)	N101–Cu2–S1	72.1(1)
N102–Cu2–S1	118.6(1)	N103–Cu2–S1	79.6(2)
O101–Cu2–S1	152.3(1)		
O201 ⁱ –Cu3–N201	102.6(2)	O201 ⁱ –Cu3–N202	171.3(2)
O201 ⁱ –Cu3–N203	93.5(2)	N203–Cu3–N201	159.2(2)
N201–Cu3–N202	82.3(2)	N203–Cu3–N202	83.5(2)
O201 ⁱ –Cu3–O201	81.8(2)	N201–Cu3–O201	94.2(2)
N203–Cu3–O201	101.2(2)	N202–Cu3–O201	90.8(2)
Cu2–O1–Cu1	93.7(2)	Cu1–O101–Cu2	102.9(2)
Cu3 ⁱ –O201–Cu3	98.2(2)		

Symmetry labels ⁱ: 2 – x, 1 – y, –z.

from a second copper ion occupies the fourth basal position to form an unsymmetrically bridged Cu₂O₂ core. Taki et al. [7] reported the X-ray structure of a dimeric copper(II) complex with an analogous ligand having a 4-tert-butyl substituent on the phenol ring instead of a methyl, L¹H = (2-methylthio-4-tert-butyl-6-[[bis(pyridin-2-ylmethyl)amino]methyl] phenol). The complex, [Cu^{II}₂(L¹⁻)₂](PF₆)(ClO₄), consisted of two non-equivalent five-coordinated copper(II) ions having square pyramidal geometry with a N₃O₂ donor set ($\tau = 0.06$ and 0.04 for the two copper ions). In this compound, the pyridine nitrogen atom acts as the axial ligand for one copper ion, whereas the phenolate oxygen atom serves as the axial ligand for the second copper ion. Thus, one phenolate oxygen is the equatorial ligand for both copper ions, while the other phenolate oxygen acts as the equatorial ligand for one of them, and as the axial ligand for the second one, bridging the copper atoms in a equatorial–axial fashion, as in the Q unit of the reported complex.

3.3. Magnetic susceptibility characterization

The thermal dependence of the magnetic susceptibility for (1), at applied fields of 0.02 and 0.25 kOe, was obtained in a temperature range of 2.5–291 K. A complete reversibility between ZFC and FC measurements and no field dependence of the magnetic susceptibility was observed.

Fig. 2 shows the χ_{MT} (T) plot at 0.25 kOe. At 291 K the value of χ_{MT} is 1.59 cm³ mol⁻¹ K, which is very close to the expected value for four non-interacting copper(II) centres (1.50 cm³ mol⁻¹ K). This value remains almost invariant till approximately 70 K. From this temperature the value of χ_{MT} decreases markedly reaching a value of 0.69 cm³ mol⁻¹ K at 2.5 K. This behavior can be associated with antiferromagnetic interactions between the copper(II) centres at temperatures lower than 70 K. It is important to note, that the value of 0.69 cm³ mol⁻¹ K obtained at 2.5 K, does not correspond to a

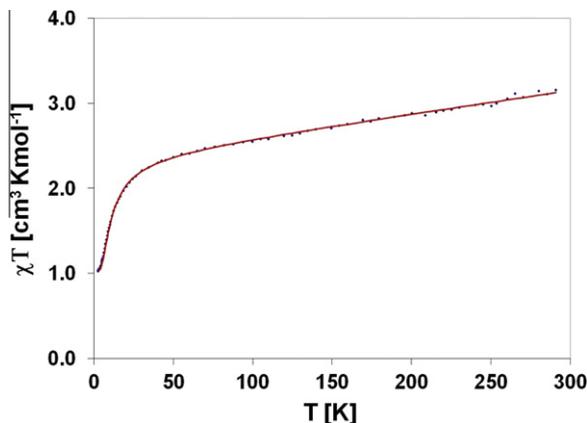


Fig. 2. Plot of the χ_{MT} product vs. T for of [Cu₂(μ-SL)₂](ClO₄)₂ (1). The solid line shows the best fit of the data.

completely compensated spin value as expected for an antiferromagnetic ground state with $S = 0$ and, it is lower than the value of 0.75 cm³ mol⁻¹ K expected for two uncoupled copper(II) ions.

Since two similar but not equivalent [Cu₂(μ-SL)₂]²⁺ bimetallic cations (P and Q) are present in the crystal structure, in a 2 to 1 ratio, the variable temperature susceptibility data were fitted using the following expression:

$$\chi_{MT} = 2\chi_{MP} + \chi_{MQ} \quad (1)$$

where χ_{MP} and χ_{MQ} correspond to the contribution of cations P and Q to the total magnetic susceptibility. The magnetic susceptibility contributions were modeled by the Bleaney–Bowers expression, using the isotropic exchange Hamiltonian ($H = -JS_1S_2$) for the two interacting $S = 1/2$ centres [29],

$$\chi_{Mi} = \frac{2Ng^2\beta^2}{k_B T} \left[\frac{1}{3 + \exp(-J_i/k_B T)} \right] \quad (2)$$

This expression was used assuming that, although both binuclear copper units [Cu₂(μ-SL)₂]²⁺ present the same coordination sphere (CuN₃O₂), the different distortions in each binuclear units should produce different exchange interactions and therefore different magnetic exchange constants. Phuengphai et al. [30] also used an expression with two different J values (one for each dinuclear unit present in the compound) to fit the experimental magnetic data of a Cu^{II} coordination compound containing two different phosphato-bridged dinuclear units, [Cu₂(phen)₂(μ-H₂PO₄-O,O')₂(H₂PO₄)₂][Cu₂(phen)₂(μ-H₂PO₄-O,O')(μ-H₂PO₄-O)(μ-HPO₄-O)]₂(H₂O)₉ (phen = 1,10-phenanthroline). The best fit of the experimental data was obtained from Eq. (2) (Fig. 2) using $g_1 = g_2 = 2.05$, $J_P = -13.4$ cm⁻¹ and $J_Q = 5.22$ cm⁻¹ with $R = 7.5 \times 10^{-5}$. These results show that the magnetic exchange between the copper(II) centres within the cationic species P and Q is rather weak.

Literature data show that the magnetic behavior of bis(μ-phenoxo)dicopper(II) complexes is modulated mainly by the bridging angle Cu–O(Ph)–Cu [31,32]. Usually, bis(μ-phenoxo)dicopper(II) complexes exhibit moderate to strong antiferromagnetic spin coupling between copper(II) ions, with bridging angles greater than 97°, while weak antiferromagnetic or ferromagnetic exchange interactions, which is scarce in this type of compounds, is rationalized in terms of different structural parameters [28,33–36]. In the case of pentacoordinated Cu^{II} ions the most frequently found geometries are square pyramid or trigonal bipyramid. The magnetic orbitals (i.e., the orbitals that contain the unpaired electrons) are $d_{x^2-y^2}$ and d_{z^2} , respectively. The magnetic interaction may occur in an equatorial–equatorial, axial–axial or equatorial–axial

arrangement, depending on the magnetic orbitals involved, resulting in a rather strong (first two arrangements) or a weak magnetic exchange (last arrangement) [33–36].

The magnitude of the magnetic exchange interactions between copper(II) ions in binuclear complexes is dependent upon the orbital ground-state configuration of the copper(II) ions. Strong magnetic exchange interactions require both good σ -bonding orientation of the magnetic orbitals, and good superexchange pathways provided by the bridging atom orbitals.

In compound (**1**) cation *Q* is characterized by a centrosymmetric unit formed by two copper(II) ions with a slightly distorted square pyramid geometry ($\tau = 0.21$) and Cu–O(Ph)–Cu angles of 98.2° , and an *axial-equatorial* coordination mode of the phenolate ions to the Cu^{II} ions. If we take into account the relevance of the Cu–O(Ph)–Cu angle in the observed magnetic behavior, it can be anticipated that the planar *Q* cation should be characterized by an antiferromagnetic interaction (Cu–O–Cu angle = 98.2°). However, the *axial-equatorial* coordination mode of both phenoxo ligands produces unfavorable overlap between the magnetic orbitals, canceling the antiferromagnetic interaction and leading to an overall weak ferromagnetic exchange. Therefore, cation *Q* can be related with $J_Q = +5.22 \text{ cm}^{-1}$. The reported *J* value for the analogous complex with hexafluorophosphate as counteranion, $[\text{Cu}_2\text{SL}_2](\text{PF}_6)_2$, is $+3.4 \text{ cm}^{-1}$.

On the other hand, cation *P* has two copper centres; Cu1 exhibits square pyramid geometry ($\tau = 0.11$) while Cu2 presents an approximately trigonal bipyramid geometry ($\tau = 0.57$). Both copper ions are bridged by two phenoxo groups in *axial-axial* and *equatorial-equatorial* coordination modes having Cu–O(Ph)–Cu bond angles of 94.05° and 102.85° , respectively. This configuration of the phenoxo bridges would favor antiferromagnetic exchange between the copper ions. Nevertheless, the non-planarity of the Cu₂O₂ moiety (hinge distortion = 7.13°) together with the out of plane shift of the phenyl ring (27.6° and 16.9°), and the rotation of the phenyl ring respect to the Cu₂O₂ plane (33.4° and 23.4°) reduce the magnetic interaction [28] resulting in a low magnetic exchange constant, *J*, of -13.4 cm^{-1} . It is possible to conclude that the geometry distortions around the Cu₂O₂ core result in a poor orbital overlap through the phenoxo bridges, despite being *axial-axial* or *equatorial-equatorial*.

Although magnetostructural correlations for dinuclear bis(phenoxo)-bridged Cu^{II} complexes show a large dependence of the coupling on the bridging Cu–O–Cu angle, the *J* value in non planar systems also is dependent on the following structural parameters (i) large out-of-plane shifts for the phenoxo group (τ angle), which reduce the antiferromagnetic term; (ii) large hinge distortions (i.e., Cu–O–Cu–O) cancel the antiferromagnetic contributions, and can lead to ferromagnetic coupling at small Cu–O–Cu angles; (iii) a *syn* conformation of the phenoxo groups favors the antiferromagnetic contribution; (iv) for small τ angles, the rotation of the phenyl rings with respect to the Cu₂O₂ framework results in an increase of the antiferromagnetic interaction.

The reported analogous diphenoxocopper(II) complexes with the tripodal ligands HL = 2-[(bis(2-pyridylmethyl)amino)methyl]-4-methylphenol and HSL with hexafluorophosphate counteranions, $[\text{Cu}_2\text{L}_2](\text{PF}_6)_2$ and $[\text{Cu}_2(\text{SL})_2](\text{PF}_6)_2$, present centrosymmetrical square base pyramidal Cu^{II} centres, bridged in *axial-equatorial* fashion by two phenoxo groups, with a *J* values of -16.7 and $+3.4 \text{ cm}^{-1}$, respectively. The low values obtained for the coupling constants were rationalized in terms of a poor overlap between the magnetic orbitals, due to the *axial-equatorial* phenoxo bridging mode observed in these complexes. The difference in sign of the *J* values was related to the magnitude of the bridging angle Cu–O–Cu and the planarity of the phenyl ring in relation to the Cu₂O₂ plane. For $[\text{Cu}_2\text{L}_2](\text{PF}_6)_2$, the value of the angle is 98.5° , while for $[\text{Cu}_2(\text{SL})_2](\text{PF}_6)_2$ is 97.5° , the first presenting weak antiferromagnetism. Also,

the phenyl group of the phenoxo moiety for $[\text{Cu}_2\text{L}_2](\text{PF}_6)_2$ is out of the Cu₂O₂ plane, with the angle between the plane and the O–C vector of 21.7° , while for $[\text{Cu}_2(\text{SL})_2](\text{PF}_6)_2$ is 51.6° . Thus the more planar system, corresponding to $[\text{Cu}_2(\text{L})_2](\text{PF}_6)_2$, presents an antiferromagnetic exchange interaction.

In the case of $[\text{Cu}_2(\mu\text{-SL})_2](\text{ClO}_4)_2$ (**1**) reported in this work, cation *P* is also formed by two square base pyramidal Cu^{II} centres bridged in *axial-equatorial* fashion by two phenoxo groups with a more distorted geometry for the Cu^{II} ions, resulting in a non centrosymmetric Cu₂O₂ moiety. The angles between the Cu₂O₂ plane and O1–C16 and O101–C116 vectors correspond to 27.6° and 16.9° respectively. The second magnetic exchange constant of -13.9 cm^{-1} can be ascribed to the exchange interaction through the more planar phenoxo bridge with a Cu–O–Cu angle of 102.85° present in cation *P*, while the less planar with the more accurate Cu–O–Cu angle of 94.5° , would be less effective mediating the magnetic exchange.

4. Conclusions

A new Cu^{II} complex has been prepared with the tripodal ligand 2-[(bis(2-pyridylmethyl)amino)methyl]-4-methyl-6-(methylthio)phenol and perchlorate as the anion. The structural and magnetic properties analyzed, comparing these with the ones of previously reported complex, obtained with hexafluorophosphate as the counterion. For this species the *axial-equatorial* bridging mode of the two phenolate bridges explains the weak ferromagnetic interaction between the copper centres, while complex (**1**) consists of two similar but not equivalent dinuclear copper^{II} units, *P* and *Q*, being *Q* structurally and magnetically very similar to the reported one, while *P* is asymmetric and accounts for the overall weak antiferromagnetic behavior observed in this complex. Apparently, the size and shape of the counteranion influence the coordination and bridging mode of the ligand, resulting in important structural changes and hence modifying the magnetic properties of the obtained complex.

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Appendix A. Supplementary material

CCDC 896774 contains the supplementary crystallographic data for $[\text{Cu}_2(\mu\text{-SL})_2](\text{ClO}_4)_2$ (**1**). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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