Synthesis, Structure, Spectroscopic and Magnetic Properties of Two Copper(II) Dimers containing Pyridine-2-carbaldehyde Thiosemicarbazonate (L), $[\{CuL(X)\}_2]$ (X = Cl or Br)†

Javier García-Tojal,[a] M. Karmele Urtiaga,[b] Roberto Cortés,[a] Luis Lezama,[a] M. Isabel Arriortua[b] and Teófilo Rojo*,[a]

[a] *Departamento de Química Inorgánica, Universidad del País Vasco, Aptdo. 644, 48080 Bilbao, Spain*
[b] *Departamento de Mineralogía-Petrología, Universidad del País Vasco, Aptdo. 644, 48080 Bilbao, Spain*

The compounds $[\{CuL(X)\}_2]$ (X = Cl **1** or Br **2**, HL = pyridine-2-carbaldehyde thiosemicarbazone) have been synthesised and structurally characterized. Both crystallize in the triclinic space group $P\bar{1}$. For compound **1**, a = 7.915(3), b = 8.262(5), c = 9.016(2) Å, α = 67.97(3), β = 92.26(2), γ = 71.33(4)°, Z = 2, R = 0.046, R' = 0.054. For **2**, a = 7.617(1), b = 8.451(3), c = 8.966(2) Å, α = 68.50(2), β = 95.94(1), γ = 71.73(2)°, Z = 2, $R = R'$ = 0.035. The copper(II) ions have square-pyramidal environments with the tridentate thiosemicarbazone ligands and the halide atoms in an equatorial position. The sulfur atom of the tridentate ligand acts as a bridging ligand occupying the apical position of the symmetric copper atom in the dimeric structure. Such a disposition of the sulfur bridges is very scarce. Q-Band ESR spectra of the two compounds show rhombic signals with g_1 = 2.183, g_2 = 2.053, g_3 = 2.033 for **1** and g_1 = 2.161, g_2 = 2.057, g_3 = 2.033 for **2**. Magnetic measurements on **1** and **2** show antiferromagnetic couplings between the copper(II) cations through the sulfur bridges. The exchange parameter is $J/k = -6.8$ K (-4.7 cm^{-1}). Magnetostructural correlations have been analysed by using extended Hückel molecular orbital calculations.

Thiosemicarbazones, in particular carbaldehyde ones, exhibit antitumour activity in their own right. Early mechanistic studies led to the postulation that the inhibition of ribonucleoside diphosphate reductase results in the antitumour activity.[1-3] In the last years some copper(II) complexes of N-heterocyclic carbaldehyde thiosemicarbazones have drawn attention[4,5] due to the fact that complexes of such compounds have significantly greater antitumour activity than the free thiosemicarbazone itself. Biochemical studies showed that the metal complexes enter cells to a greater extent, the copper(II) complex being subsequently reduced to the quite stable copper(I) species. The possibility of metal complexes being a useful source of drugs is just beginning to be explored. In particular, there is a need to understand how such compounds interact with cells so that mechanistic information may be accumulated to facilitate the rational design of new materials.

Particular attention has been paid to the role of metal chelation in the mechanism of action of these compounds, which has been hypothesized since the early work of French and his co-workers.[6-8] Among the important mechanistic conclusions emanating from the structural studies was that a *N,N,S*-tridentate ligand system is a common feature of all thiosemicarbazone compounds with carcinostatic potency. In particular, the copper complexes of pyridine-2-carbaldehyde thiosemicarbazone have shown to be stable in biological systems[1] and have *in vitro* cytotoxic effects against Ehrlich cells.[2,9] Also a second mechanism of interaction has been suggested involving the binding of the copper(II) drug to the nitrogen bases of DNA or RNA. The interest in copper(II) pyridine-2-carbaldehyde thiosemicarbazone (HL) complexes arises from the marked antitumour properties of the compound $[\{CuL(MeCO_2)\}_2]$,[10] only recently characterized as a dimer in the solid state by single-crystal X-ray crystallography.

On the other hand, the magnetic properties of these kinds of complexes have not been extensively studied. It is well known that these tridentate ligands result in planar copper(II) entities. The stacking of parallel planar copper(II) complexes through different halogeno and pseudohalogeno bridging atoms, with long apical distances, gives weak magnetic interactions due to the poor overlap of the magnetic orbitals sited in planes normal to the direction of the exchange propagation. However, to our knowledge no example of complexes having sulfur as the bridging ligand exists.

We have synthesised and characterized the $[\{CuL(X)\}_2]$ (X = Cl **1** or Br **2**) compounds in this paper in order to study their structural and magnetic properties, which can provide a chemical basis for the antitumour action. This study has been done with the aim of obtaining new pyridine-2-carbaldehyde copper(II) complexes which can potentially be used as antitumour agents.

Experimental

Pyridine-2-carbaldehyde thiosemicarbazone (HL) was synthesised according to a published method.[11] Copper(II) chloride and bromide were obtained from Aldrich Chemical Co. All the complexes were dried under vacuum. Microanalyses were performed with a Perkin-Elmer analyzer. Infrared spectra were recorded in KBr pellets, in the 4000–400 cm^{-1} region, on a Nicolet 520 FTIR spectrophotometer, ESR spectra (at 298 K and Q band) on a Bruker ESP300 spectrometer, equipped with an Oxford continuous-flow cryostat and calibrated by the NMR probe to obtain the magnetic field (the frequency was measured with a Hewlett-Packard frequenciometer). Magnetic measurements were carried out on polycrystalline samples with a pendulum-type susceptometer/magnetometer (Manics DSM8) equipped with a helium continuous-flow cryostat

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: eV ≈ 1.60 × 10^{-19} J.

working in the 4.2–100 K range. The magnetic field was approximately 10 000 G (1 T). Diamagnetic corrections were estimated from Pascal's constants.

Preparation of the Copper Complexes.—Both [CuL(Cl)] **1** and [CuL(Br)] **2** were prepared by the same procedure. Ethanolic solutions of pyridine-2-carbaldehyde thiosemicarbazone (1 mmol) were added to a water solution (20 cm^3) containing 1 mmol of the respective copper(II) halides. The resulting dark green precipitates (yields about 80%) were filtered off, washed with water and dried over P_2O_5 for 24 h. Both precipitates were recrystallized from aqueous solutions to give, after evaporating for several days at room temperature, good quality dark green single crystals adequate for X-ray analysis. Elemental analyses were consistent with the stoichiometries $C_7H_7ClCuN_4S$ (Found: C, 29.75; H, 2.50; N, 19.65. Calc.: C, 30.20; H, 2.55; N, 20.15%) and $C_7H_7BrCuN_4S$ (Found: C, 25.85; H, 2.00; N, 17.20. Calc.: C, 26.05; H, 2.20; N, 17.35%) for **1** and **2** respectively.

Crystal-structure Determination.—Crystallographic details for compounds **1** and **2** are given in Table 1. Preliminary cell parameters were determined by rotation and Weissenberg photographs performed on a Weissenberg–Stoe 1971 camera. The crystals were sealed in glass capillaries and transferred to the goniometer head of an Enraf–Nonius CAD4 diffractometer. Unit-cell parameters were calculated from the setting angles of 25 carefully centred reflections obtained in the $10 < \theta < 24°$ range. Two reflections were chosen as intensity standards and measured every 3600 s of X-ray exposure time, and two orientation controls were measured every 250 reflections. No significant intensity decay was observed during the data collection. The data were measured using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) and an ω–2θ scan mode.

For compound **1**, 3308 unique reflections were measured ($1 \leqslant \theta \leqslant 28°$, $+h, \pm k, \pm l$). 2158 Reflections were assumed as observed applying the criterion $I \geqslant 2.5\sigma(I)$. For **2**, 3172 unique reflections were measured ($1 \leqslant \theta \leqslant 30°$, $+h, \pm k, \pm l$) and 1729 were considered as observed [$I \geqslant 2.5\sigma(I)$]. In both cases corrections were made for Lorentz and polarization effects. Empirical absorption corrections were made by using the DIFABS[12] program.

Structure analysis and refinement. Direct methods (MULTAN)[13] were employed to solve the structure of complex **1**. The structure of complex **2** is isostructural. They were then refined by the full-matrix least-squares method, using the SHELX 76[14] computer program. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = (\sigma^2|F_o| + p|F_o|^2)^{-1}$ (p 0.0035 **1** and 0.0004 **2**). Scattering factors and anomalous dispersion coefficients were taken from ref. 15. All non-hydrogen atoms were assigned anisotropic thermal parameters. The H-atom positions were determined from Fourier difference syntheses. The final R factors were 0.046 (R' = 0.054) for **1** and 0.035 (R' = 0.035) for **2**. Maximum and minimum peaks in the final difference syntheses were 1.75, −0.36 and 0.88, −0.43 e Å^{-3}, respectively. The final atomic positional parameters for the non-hydrogen atoms of **1** and **2** are listed in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Crystal Structures of [{CuL(X)}$_2$] (X = Cl *or* Br).—Crystals of both complexes **1** and **2** contain [CuL(X)] discrete planar entities which stack through the sulfur atom of the ligand to give centrosymmetric [{CuL(X)}$_2$] dimers. A perspective view of the dimer is shown in Fig. 1. Selected interatomic dimensions are given and compared in Table 3. The copper(II) ion is five-co-ordinate, with the two nitrogen and sulfur atoms of the ligand [Cu–N(1), –N(2), –S 2.034(4), 1.975(3), 2.278(1) for **1**

Table 1 Summary of crystallographic data and parameters for [CuL(Cl)] **1** and [CuL(Br)] **2***

	1	**2**
Formula	$C_7H_7ClCuN_4S$	$C_7H_7BrCuN_4S$
M	278.2	322.5
Crystal size/mm	0.17 × 0.13 × 0.16	0.09 × 0.11 × 0.12
a/Å	7.915(3)	7.617(1)
b/Å	8.262(5)	8.451(3)
c/Å	9.016(2)	8.966(2)
α/°	67.97(3)	68.50(2)
β/°	92.26(2)	95.94(1)
γ/°	71.33(4)	71.73(2)
U/Å^3	509.2(4)	494.1(3)
D_m/g cm^{-3}	1.80(2)	2.16(1)
D_c/g cm^{-3}	1.82	2.17
μ/cm^{-1}	25.75	63.88
F(000)	278	314
h,k,l range	10, ± 11, ± 12	11, ± 11, ± 12
2θ Range (°)	2.0–56.0	2.0–60.0
Reflections collected	3308	3172
Observed reflections [$I \geqslant 2.5\sigma(I)$]	2158	1729
$R = (\Sigma\|\Delta F\|)/(\Sigma\|F_o\|)$	0.046	0.035
$R' = [\Sigma w(\|\Delta F\|)^2/\Sigma w\|F_o\|^2]^{\frac{1}{2}}$	0.054	0.035

* Details in common: triclinic, space group $P\bar{1}$ (no. 2); Z = 2; 149 parameters; unit-cell parameters and their e.s.d.s were derived by a least-squares fitting of the setting angles of 25 reflections in the range $10 \leqslant \theta \leqslant 24°$ for both compounds **1** and **2**.

Table 2 Fractional atomic coordinates for [CuL(X)]

	Compound **1** (X = Cl)			Compound **2** (X = Br)		
Atom	x	y	z	x	y	z
Cu	0.024 90(6)	0.164 34(6)	0.067 64(5)	0.030 39(8)	0.160 64(7)	0.066 71(6)
S	0.193 8(1)	0.042 5(1)	−0.090 2(1)	0.196 4(2)	0.038 9(2)	−0.088 0(1)
X	0.220 6(2)	−0.016 3(2)	0.303 0(1)	0.272 97(8)	−0.015 61(7)	0.322 50(6)
N(1)	−0.156 8(4)	0.336 0(4)	0.147 3(4)	−0.154 9(5)	0.330 5(5)	0.139 8(4)
N(2)	−0.088 8(4)	0.382 4(4)	−0.141 9(4)	−0.090 4(5)	0.379 0(5)	−0.149 2(4)
N(3)	−0.038 9(5)	0.395 0(4)	−0.287 4(4)	−0.041 7(6)	0.391 6(5)	−0.294 5(4)
N(4)	0.156 2(6)	0.235 4(5)	−0.406 9(4)	0.160 7(7)	0.235 3(6)	−0.405 7(5)
C(1)	−0.190 7(6)	0.302 6(6)	0.296 7(5)	−0.189 6(8)	0.299 4(7)	0.288 4(6)
C(2)	−0.323 3(7)	0.433 2(7)	0.331 8(6)	−0.319 1(8)	0.431 2(8)	0.321 1(6)
C(3)	−0.423 6(6)	0.603 4(6)	0.208 9(6)	−0.417 0(8)	0.602 0(7)	0.194 5(7)
C(4)	−0.391 0(6)	0.637 7(6)	0.052 1(5)	−0.385 3(7)	0.638 1(6)	0.037 9(6)
C(5)	−0.256 5(5)	0.500 7(5)	0.025 3(4)	−0.254 2(6)	0.498 8(6)	0.015 9(6)
C(6)	−0.213 8(5)	0.523 2(5)	−0.135 6(4)	−0.213 9(7)	0.521 2(6)	−0.145 0(5)
C(7)	0.091 9(6)	0.240 2(5)	−0.273 8(4)	0.093 9(7)	0.236 4(6)	−0.274 4(5)

Table 3 Selected bond distances (Å) and angles (°) for $[\{CuL(X)\}_2]$ (X = Cl or Br)

	X			X	
	Cl	Br		Cl	Br
Metal co-ordination sphere					
Cu–N(1)	2.034(4)	2.023(4)	Cu–N(2)	1.975(3)	1.987(3)
Cu–X	2.240(2)	2.405(1)	Cu–S	2.278(1)	2.275(2)
Cu–S^I	2.760(2)	2.743(2)	Cu···Cu^I	3.486(2)	3.474(1)
Cu···Cu^{II}	5.089(1)	5.266(1)			
N(1)–Cu–N(2)	80.6(1)	80.7(2)	S–Cu–N(1)	163.8(1)	163.4(1)
S–Cu–N(2)	83.2(1)	82.8(1)	X–Cu–N(1)	97.9(1)	98.2(1)
X–Cu–N(2)	157.5(1)	151.3(1)	X–Cu–S	96.9(1)	96.7(1)
S–Cu–S^I	93.0(1)	92.9(1)	Cu–S–Cu^I	87.0(1)	87.1(1)
Average values in the thiosemicarbazone ligands					
C–C	1.398(7)	1.396(8)	C–N	1.302(6)	1.326(7)
C–S	1.756(3)	1.748(4)	N–N	1.361(8)	1.367(6)
C–C–C	120.0(5)	119.7(5)	C–C–N	119.7(4)	119.2(5)
C–N–C	118.9(4)	117.6(4)	C–N–N	115.6(3)	115.2(4)

I $-x, -y, -z$; II $1 - x, -y, 1 - z$.

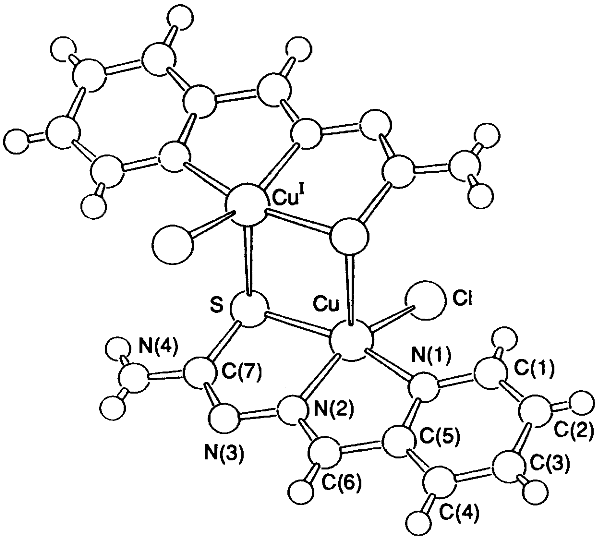


Fig. 1 Perspective view of the $[\{CuL(Cl)\}_2]$ dimer showing the atom numbering

and 2.023(4), 1.987(3), 2.275(2) Å for **2**] and the halide atom [Cu–X 2.240(2) and 2.405(1) Å for **1** and **2** respectively] occupying the basal position, while the axial position is occupied by the sulfur atom [Cu–S^I (I $-x, -y, -z$) 2.760(2) for **1** and 2.743(2) Å for **2**] of the symmetric planar copper entity inside the dimer. Copper(II) dimers with this type of bridging are very scarce. The distortions of the co-ordination polyhedra from the extreme square-pyramidal (*SPY*) and trigonal-bipyramidal (*TBPY*) topologies have been analysed by using the Muetterties and Guggenberger[16] model. The values of the distortion $\Delta \approx 0.70$ obtained clearly indicate that the environment of both copper atoms is close to the *SPY* topology.

The copper atoms sit above the basal planes (0.2 Å), toward the apical ligand. The most significant differences between the chloride and bromide structures are observed in the Cu–X_{basal} distance, which is 0.165 Å larger for the bromide compound. The bridging angles Cu–S–Cu^I are very similar in the two compounds, 87.0(1) (Cl) and 87.1(1)° (Br). The intradimeric Cu···Cu^I distances are 3.486(2) and 3.474(1) Å for **1** and **2**, respectively. The shorter interdimeric copper distance Cu···Cu^{II} for the chloride compound is 5.089(1) Å, while for the bromide it is 5.266(1) Å.

In both complexes the pyridine-2-carbaldehyde thiosemicarbazone ligands may be considered as rigid and quasi-planar. The average C–C and C–N bond distances in the ligand are 1.398(7), 1.302(6) Å, and 1.396(8), 1.326(7) Å for compounds **1** and **2**, respectively, in good agreement with values in the literature for this ligand.[17,18]

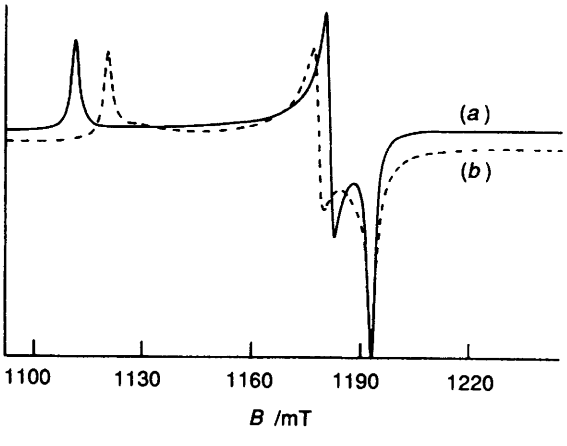


Fig. 2 Q-Band ESR spectra of polycrystalline samples of (*a*) $[\{CuL(Cl)\}_2]$ and (*b*) $[\{CuL(Br)\}_2]$

Infrared Spectroscopy.—Metal complexes of the pyridine-2-carbaldehyde thiosemicarbazone ligand show three bands in the 3450–3150 cm^{-1} region, which are assigned to the $\nu(NH_2)$ and ν(NH) stretching vibrations. The ν(C=N) vibration mode is shifted from 1612 cm^{-1} for the free thiosemicarbazone to 1600 cm^{-1} for the copper complexes, indicating the co-ordination of the nitrogen of the azomethine.

The band appearing at 1550 cm^{-1} has been identified as the contribution of the $\delta(NH_2)$ deformation mode of the thioamide group. According to the literature,[19] this band undergoes an increase in energy, but a decrease in intensity owing to deprotonation of the ligand, upon co-ordination. The ν(C=S) band which appears at 825 cm^{-1} for the free thiosemicarbazone is absent for the copper complexes, due to the change of C=S to $C-S^-$.

Electron Spin Resonance and Magnetic Behaviour.—The Q-band ESR spectra of polycrystalline samples of compounds **1** and **2** have been recorded at room temperature (Fig. 2). Both spectra show rhombic symmetries for the *g* tensor in the $\Delta M_s = \pm 1$ region. For compound **1** $g_1 = 2.183$, $g_2 = 2.053$,

Table 4 Dinuclear copper(II) compounds formed by edge-sharing square pyramids

Compound	Bridging atom	Short distance/Å	Long distance/Å	Bridging angle/°	J/cm^{-1}	Ref.
$[\{Cu(terpy)(NCO)\}_2][PF_6]_2$	N				+1.8	24
$[\{Cu(terpy)(N_3)\}_2][PF_6]_2$	N	1.954	2.469	96.3	< −0.5	24
$[\{Cu(terpy)Cl\}_2][PF_6]_2$	Cl	2.218	2.723	89.76	−2.95	22
$[\{Cu(terpy)Br\}_2][PF_6]_2$	Br	2.36	2.83	88.6	−3.65	23
$[\{Cu(bpy)(N_3)_2\}_2][ClO_4]_2$	N	1.97	1.99	100.5	+105 ± 20*	25
$[Cu_2(tmen)_2(N_3)(OH)][ClO_4]_2$	N, O	1.915	2.015	95.7, 102.5	> +200*	26
$[\{CuL(Cl)\}_2]$	S	2.278	2.760	87.0	−4.70	This work
$[\{CuL(Br)\}_2]$	S	2.275	2.743	87.1	−4.70	This work

Abbreviations: terpy = 2,2′:6′,2″-terpyridine; bpy = 4-*tert*-butylpyridine; tmen = *N,N,N′,N′*-tetramethylethylenediamine.

* The presence of two short distances enhances the exchange interactions because the bridging and magnetic planes are the same.

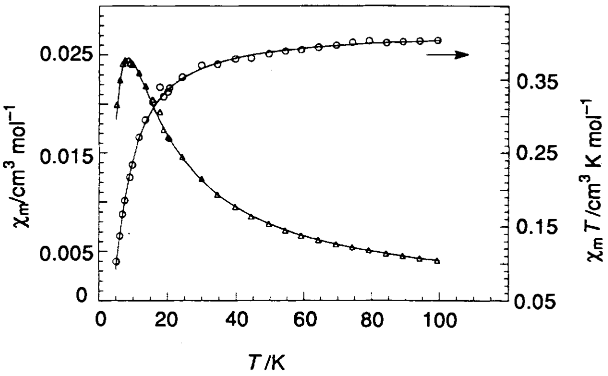


Fig. 3 Thermal variation of the molar susceptibility and χ_mT for $[\{CuL(Cl)\}_2]$

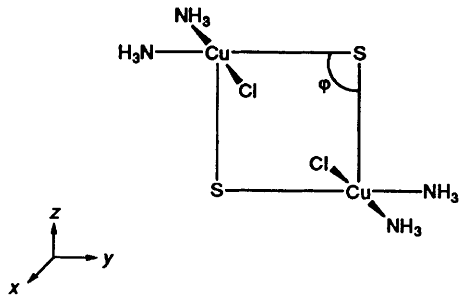
g_3 = 2.033; for **2** g_1 = 2.161, g_2 = 2.057, g_3 = 2.033. The minor g value is lower than that observed for square-pyramidal geometries in copper(II) ions. This can be explained in part by the distortion towards the trigonal-bipyramidal geometry and above all by the *cis* distortion in the basal plane of the square pyramid (rhombic basal plane).[20] No 'half-field' transitions have been observed for the compounds.

Magnetic susceptibility measurements for both compounds have been performed within the temperature range 4.2–100 K. Fig. 3 shows the thermal variation of the molar susceptibility (χ_m), together with the plot of χ_mT *vs.* T for the chloride compound. The results from the bromide are essentially the same, within the experimental error margins. The measurements show Curie–Weiss behaviour at temperatures larger than 25 K, the Weiss temperature being −4.8 K. The Curie constant is approximately 0.42 cm^3 K mol^{-1}. The χ_m value rapidly increases with decreasing temperature, reaching a maximum of 0.025 cm^3 mol^{-1} at 8 K after which it rapidly decreases. The χ_mT value continuously decreases on decreasing the temperature. These variations are indicative of antiferromagnetic interactions for both compounds. The identical magnetic behaviour, within the experimental uncertainties, of both compounds is in accordance with the practically equal parameters, apical distances and bridging angles, in the Cu_2S_2 bridging units.

The magnetic behaviour may be described by using the Bleaney–Bowers equation for two copper atoms,[21] derived from the Heisenberg isotropic spin Hamiltonian ($H = -2J\hat{S}_1\hat{S}_2$), for two coupled $S = \frac{1}{2}$ ions, equation (1) where $N_\alpha = 60 \times 10^{-6}$

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

cm^3 mol^{-1} per copper(II) ion. The best least-squares fit (solid line in Fig. 3) is obtained from the parameter $J/k = -6.8$ K (-4.7 cm^{-1}) and when g is fixed at 2.09 as obtained from the ESR measurements.



Scheme 1

Table 4 compiles different examples of copper(II) dinuclear compounds with topologies consisting of edge-sharing square pyramids.[22–26] As can be seen, the magnetic exchange constant of the present compounds is significantly higher than those obtained for compounds with halide[22,23] or pseudo-halide[24] bridging ligands which have long–short bridging distances. In the case of two short bridging distances the exchange coupling can be significantly greater because the exchange propagation direction is in the same plane as that of the magnetic orbitals.[25,26]

Molecular Orbital Calculations.—It is well known that the interaction between two $S = \frac{1}{2}$ metal atoms in a dimer leads to two molecular states: a spin singlet ($S = 0$) and a triplet ($S = 1$), separated by $2J$. The interaction will be antiferromagnetic ($J < 0$) if $S = 0$ is the ground state. On the contrary, if $S = 1$ the interaction will be ferromagnetic ($J > 0$). The singlet–triplet energy gap $2J$ may be expressed as the sum of the antiferromagnetic and ferromagnetic contributions[27] in the form $J = J_{AF} + J_F$. Whereas ferromagnetic contributions are usually small, antiferromagnetic ones can be considered as proportional to the square of the gap between the molecular orbitals constructed from the magnetic orbitals[28] ($J_{AF} \propto \Delta^2$). Extended-Hückel molecular orbital (EHMO) calculations can be employed to evaluate such interactions.

In copper(II) dimers where the metal environment is an elongated square pyramid the interactions through halide or pseudo-halide bridging ligands have been shown to be weak.[22–24] The geometry is unfavourable to transmit the exchange interaction because the magnetic orbitals ($x^2 - y^2$) are essentially localized in the basal planes, which are normal to the direction of exchange propagation. However, the effect of other bridging ligands, such as sulfur, has not yet been analysed. The EHMO calculations performed in this work have been, by means of the CACAO[29] program, on an idealized dimer as shown in Scheme 1, with the four NH_3 molecules as terminal ligands. The apical distance has been considered equal to 2.75 Å.

For a copper(II) dimer with one unpaired electron on each metal atom two molecular orbitals are generated from the magnetic orbitals of the two copper atoms. In this case, the

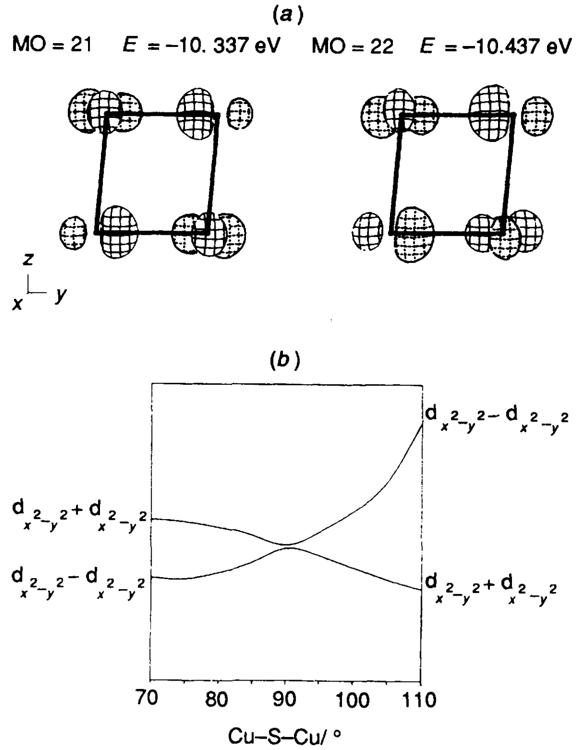


Fig. 4 (*a*) Molecular orbitals formed by the symmetric and antisymmetric combinations of the $d_{x^2-y^2}$ magnetic orbitals. (*b*) Walsh diagram for the two combinations of magnetic orbitals upon variation of the bridging angle

highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) combinations have $d_{x^2-y^2}$ as their main contribution, corresponding to their symmetric and antisymmetric combinations [see Fig. 4(*a*)]. The square of the energy gap between these combinations will be proportional to the antiferromagnetic interaction in the compound. The Walsh diagram for these significant orbitals when the bridging angle (φ) varies from 70 to 110° is shown in Fig. 4(*b*). The variation of the square of the energy gaps as a function of the bridging angles is shown in Fig. 5(*a*). As can be seen, J diminishes for bridging angles ranging from 70 to 90° and then increases up to a bridging angle of 110°. The variation of J_{AF} as a function of the apical Cu–S distance has also been considered [Fig. 5(*b*)]. The exchange coupling increases significantly with decreasing distance, as could be expected.

The influence of different atoms (N, O, S, Cl, Br) acting as bridging ligands on the magnitude of the square of the energy gaps in such compounds has also been evaluated. Fig. 5(*c*) shows that the sulfur atom is the most favourable in the magnitude of antiferromagnetic interactions. Comparing these results with the data shown in Table 4, it can be observed that the theoretical trends are in good agreement with the experimental values obtained for the exchange parameter. The interactions increase in the sequence O < N < Cl < Br < S.

Conclusion

Two new copper(II) compounds with the pyridine-2-carbaldehyde thiosemicarbazone ligand have been synthesised. In both cases the crystal structure reveals dimeric molecules with the sulfur atom of the tridentate ligand acting as a bridge between the copper ions. This type of bridging is very unusual. The ESR measurements show rhombic signals for both compounds. The g values obtained are indicative of the existence of distortions in the square-pyramidal topologies. Magnetic susceptibility data indicate antiferromagnetic interactions through the sulfur ligands. The J value obtained is significantly larger than those corresponding to similar dimers with halides or pseudo-halides as bridging ligands. The EHMO calculations allow us to establish that the factors controlling the magnitude of the antiferromagnetic contribution are the apical C–S distance, together with the bridging angle. Significant variations favouring the sulfur bridges with respect to other bridging atoms (N, O, Cl, Br) have also been observed.

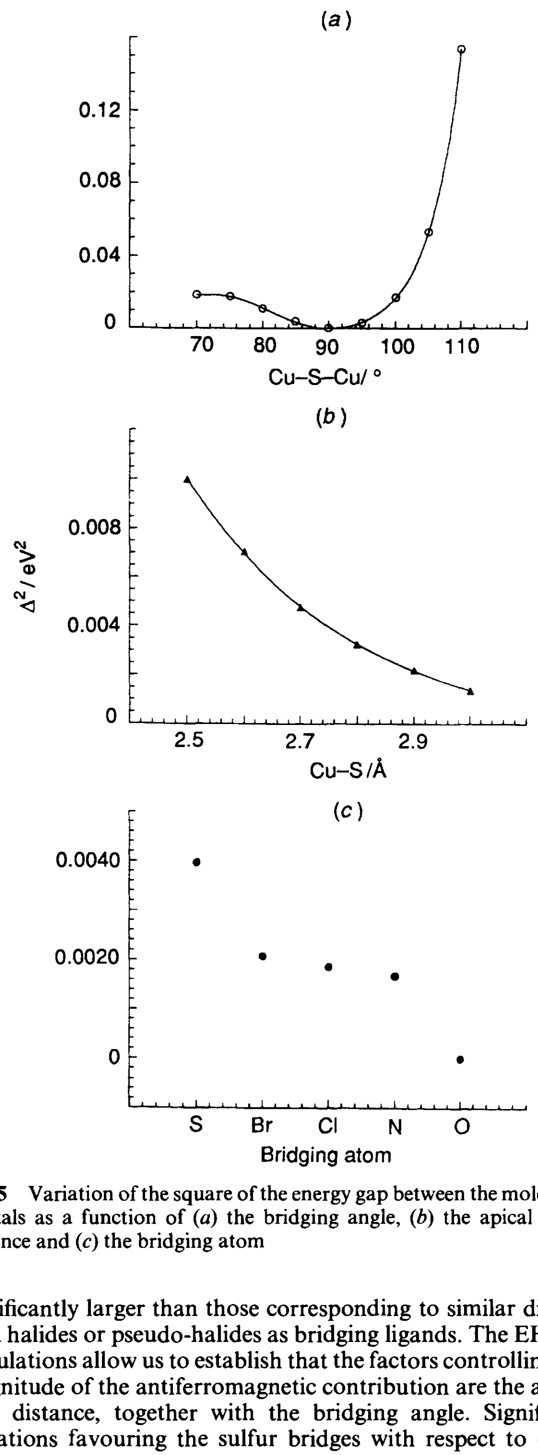


Fig. 5 Variation of the square of the energy gap between the molecular orbitals as a function of (*a*) the bridging angle, (*b*) the apical Cu–S distance and (*c*) the bridging atom

Acknowledgements

This work has been carried out with the financial support of the Universidad del Pais Vasco/Euskal Herriko Unibertsitatea (UPV 130.310.EB017/92) and the Ministerio de Educación y Ciencia (DGICYT grant) which we gratefully acknowledge. J. G.-T. thanks the Basque Government/Eusko Jaurlaritza for his Doctoral Fellowship.

References

1 L. A. Saryan, E. Ankel, C. Krishnamurti, D. H. Petering and H. Elford, *J. Med. Chem.*, 1979, **22**, 1218.

2 W. E. Entholine, J. Knigth, H. Whelan and D. H. Petering, *Mol. Pharmacol.*, 1977, **13**, 89.

3 E. C. Moore, K. C. Agrawal and A. C. Sartorelli, *Proc. Am. Assoc. Cancer Res.*, 1975, **16**, 639.

4 G. R. Gale, in *Antineoplastic and Immunosuppressive Agents Part II*, eds. A. C. Sartorelli and D. G. Johns, Springer, Berlin, 1975, pp. 829–840.

5 D. H. Petering and H. G. Petering, in *Antineoplastic and Immunosuppressive Agents Part II*, eds. A. C. Sartorelli and D. G. Johns, Springer, Berlin, 1975, pp. 841–849.

6 F. A. French, A. E. Lewis, A. H. Sheena and E. J. Blanz, jun., *Fed. Proc., Fed. Am. Soc. Biol.*, 1965, **24**, 402.

7 F. A. French and E. J. Blanz, jun., *Cancer Res.*, 1966, **26**, 1638.

8 E. J. Blanz, jun., F. A. French, J. R. DoAmaral and D. A. French, *J. Med. Chem.*, 1970, **13**, 1124.

9 W. E. Entholine, J. Knigth, H. Whelan and D. H. Petering, *J. Med. Chem.*, 1976, **19**, 339.

10 W. E. Antholine, B. Kalyanaraman and D. H. Petering, *Environ. Health Perspect.*, 1985, **64**, 19.

11 F. E. Anderson, C. J. Duca and J. V. Scudi, *J. Am. Chem. Soc.*, 1951, **73**, 4967.

12 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

13 P. Main, L. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq and M. M. Woolfson, MULTAN 84, A System of Computer Programs for Crystal Structure Determination from X-Ray Diffraction Data, Universities of York and Louvain, 1988.

14 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.

15 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, p. 99.

16 E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, 1974, **96**, 1748.

17 E. W. Ainscough, A. M. Brodie, J. D. Ranford and J. M. Waters, *J. Chem. Soc., Dalton Trans.*, 1991, 1737.

18 E. W. Ainscough, A. M. Brodie, J. D. Ranford and J. M. Waters, *J. Chem. Soc., Dalton Trans.*, 1991, 2125.

19 M. C. Jain, R. K. Sharma and P. C. Jain, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1229.

20 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 1970, **5**, 143.

21 B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, 1952, **214**, 451.

22 T. Rojo, M. I. Arriortua, J. Ruiz, J. Darriet, G. Villeneuve and D. Beltrán, *J. Chem. Soc., Dalton Trans.*, 1987, 285.

23 T. Rojo, M. I. Arriortua, J. L. Mesa, R. Cortés, G. Villeneuve and D. Beltrán, *Inorg. Chim. Acta*, 1987, **134**, 59.

24 R. Cortés, M. K. Urtiaga, L. Lezama, J. I. R. Larramendi, M. I. Arriortua and T. Rojo, *J. Chem. Soc., Dalton Trans.*, 1993, 3685.

25 S. Sikorav, I. Bkouche-Waksman and O. Kahn, *Inorg. Chem.*, 1984, **23**, 490.

26 O. Kahn, S. Sikorav, J. Gouteron, S. Jeanin and Y. Jeanin, *Inorg. Chem.*, 1983, **22**, 2877.

27 J. G. Girerd, Y. Journaux and O. Kahn, *Mol. Phys.*, 1977, **34**, 1063.

28 O. Kahn, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 834.

29 C. Mealli and D. M. Proserpio, Computer Aided Composition of Atomic Orbitals (CACAO Program), PC version, July 1992; see also *J. Chem. Educ.*, 1990, **67**, 399.

Received 11*th April* 1994; *Paper* 4/02137A