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Investigation of the Tunable Magnetic Exchange Propagated through the 1,4-Benzenedicarboxythiolato Ligand in Copper(II) Binuclear Complexes

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Abstract

Five binuclear copper(II) complexes where the two metal ions are bridged through the dithioterephthalato dianion were prepared and their spectral and magnetic properties studied by both experimental and computational techniques. The varying degree of distortion, away from the ideal octahedral chromophore, induced by the terminal polyamine ligands plays a dominant role in the nature and magnitude of the spin exchange phenomenon occurring between the two metal ions.

Introduction

A vast number of copper(II) binuclear complexes involving a variety of bridging and terminal ligands have been prepared and studied in recent years [1]. These complexes, besides providing models for the study of biologically interesting compounds [2] (copper containing enzyme sites), offer a challenge for inorganic chemists to establish foundations for the molecular engineering of magnetic systems with properties forseeable both in nature and magnitude [3]. Accordingly, an exhaustive investigation of the effect of structural and bonding parameters of magnetic centers and bridging species, on the strength and nature of the magnetic interactions, is necessary as a first step. It has been verified experimentally [4] that the variation of both the terminal and bridging ligands in copper(II) molecular magnetic systems results in a considerable modification of the expressed spin exchange. This tuning of the magnetic exchange is attributed to the metal d-level splitting, which is markedly affected by the geometric changes around the magnetic centers. The effect is usually discussed in terms of the availability of the magnetic orbitals of symmetry and energy permitting the overlap with the bridging unit's LCAO-MOs.

Recently we have investigated by experimental and theoretical procedures the magnetic properties of a series of phthalato-bridged copper(II) dimers [5]. The observed versatile magnetic behaviour of these molecular magnetic systems prompted us to extend further our research programm to include the dithiophthalato analogues. The presence of a sulfur atom in the active bonding site of the thiolato ligand, combined with the flexibility of the thiocarboxylato group, regarding its twist with respect to the Ar–C bond, hint at the possibility of the occurrence of exceptional coordination numbers and magnetic center geometries in these complexes [6]. In this paper, we report the experimental results concerning the synthesis, structure and bonding of five new copper(II) binuclear complexes formulated as $[\mathrm{CuL}_n(\mu\text{-DTT})\mathrm{CuL}_n](\mathrm{ClO}_4)_2$, where L = ethylenediamine **1** ($n = 2$), propylenediamine **2** ($n = 2$), triethylenetetramine **3** ($n = 1$), 2,2′-bipyridyl **4** ($n = 2$) and 9,10-phenanthroline **5** ($n = 2$) and DTT = 1,4-benzenedicarboxythiolato(dithioterephthalato) ligand.

The tunable magnetic exchange propagated through the extended 1,4-benzenedicarboxythiolato bridging unit in some of these complexes (**1** and **4**) is also discussed on the grounds of both experimental and theoretical procedures.

Experimental and Theoretical

Preparation of Complexes

All complexes were prepared following the same general procedure. A solution of 2 mmol of copper(II) perchlorate in 20 ml EtOH was mixed with an ethanolic solution of 2 (or 4) mmol of the appropriate polyamine. To this mixture an ethanolic solution of the disodium salt of the dithioterephthalic acid prepared *in situ*, by mixing equimolar solutions of the acid and sodium hydroxide was added slowly

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TABLE I. Extended Hückel Parameters

Atom	H(ss)	ζ(s)	H(pp)	ζ(p)	H(dd)	ζ_1(d)	ζ_2(d)
Cu	−8.65	2.050	−5.13	1.325	−13.04	5.95*	2.30
S	−22.52	1.817	−11.96	1.817			
O	−28.34	2.275	−11.74	2.275			
N	−25.15	1.950	−12.80	1.950			
C	−22.15	1.625	−11.45	1.625			
H	−13.70	1.300					

*Contracted d functions have been used for copper, their coefficients being set equal to 0.5933 and 0.5744 respectively.

under continuous magnetic stirring. The reaction mixture was left at room temperature for a further 10–15 min after the completion of the addition. During this period the desired complexes are precipitated as microcrystalline solids, filtered off and washed successively with ethanol and ether before being dried over P_2O_5. All compounds gave satisfactory elemental analyses (see 'Supplementary Material').

Magnetic Measurements

Magnetic measurements were carried out on polycrystalline samples with a Faraday-type magnetometer equipped with a Cahn RG-HV electrobalance. The applied field was 0.625 T. Mercury tetrakis(thiocyanato)cobaltate(II) and the complex $[Ni(en)_2]S_2O_3$ were used as susceptibility standards. Corrections for diamagnetism of the complexes were calculated from Pascal's table [7]. The TIP per copper ion was assumed to be 60×10^{-6} cm^3 mol^{-1}.

EPR Measurements

EPR powder spectra were measured at room temperature and at 77 K on a JES-ME 3X spectrometer in the X-band at $\nu = 9.30$ GHz.

Optical Measurements

Reflectance spectra were measured in the region 200–800 nm on a Hitachi 365 spectrophotometer using Li_2CO_3 discs. Sr_2ZnTeO_6 and freshly sintered MgO were used as standards. Infrared spectra were recorded on a Perkin-Elmer 467 spectrophotometer (4000–250 cm^{-1}) using KBr pellets.

Computational Details

The Extended Hückel LCAO-MO formalism [8] at the SCCC level of approximation has been applied to model representation (Fig. 1) of the complexes, using the FORTICON8 computer program [9]. The basis set used for the calculations is presented in Table I.

Using the Hamiltonian matrix elements obtained from a separate calculation on the bridging ligand and the $Cu(NH_3)_2^{+2}$ fragment, a new calculation was performed on the hypothetical mono-nuclear non-charged complex, where NH_3 molecules are intended to account for the $-NH_2$ donor groups of the polyamines. The final Hamiltonian obtained from the application of the SCCC scheme on this model was then used, unperturbed, for the calculation on the model binuclear complex. A strictly octahedral environment was assumed around the copper ions, with the Cu–O, Cu–S and Cu–N bond lengths being the usual ones for Cu(II) complexes [10] (set equal to 2.57, 2.02 and 2.05 Å respectively). The structural parameters for the COS^- moiety were those of the thiobenzoic moiety in its Zn(II) complex [11].

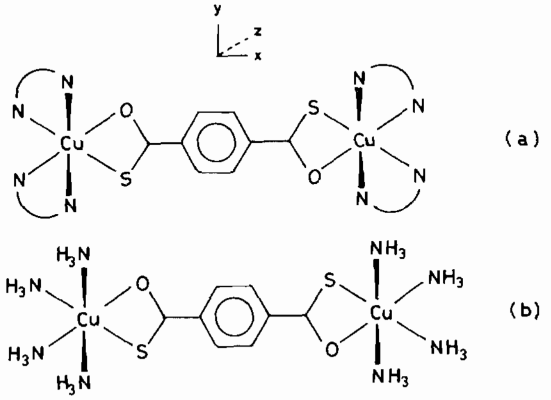

Fig. 1. Representative drawing of the complexes studied (a) and the model complex used in the EH calculations (b), along with the coordinate system used.

Results and Discussion

All complexes under investigation were microcrystalline solids, insoluble in most of the common organic and inorganic solvents. In most of them an intramolecular redox reaction very common to monothiocarboxylato copper(II) compounds [12, 13] is taking place slowly even in the solid state leading to the formation of Cu(I) impurities and the polymeric form of the bridging ligand disulfide*.

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*The product was identified on the basis of C and H elemental analysis IR ($\nu_{SS} = 900$ cm^{-1}) and MS data (*m/e* 588 = M^+, *m/e* 524 M − S_2, *m/e* 216 = $[COS]_2$, *m/e* 64 = $[S_2]$, *m/e* 34 = $[H_2S]$).

TABLE II. Reflectance and Electron Paramagnetic Resonance Spectral Data

Complex	UV–Vis absorption bands[a] (cm^{-1})			EPR g values		
	$\pi \rightarrow \pi^*$	CT	d → d	g_1 (or $g_\perp$)	g_2 (or $g_\parallel$)	g_3
1	38760 32780sh	29500	16300–18360	2.06	2.20	
2	40490 36110 32260sh	30300	11130–14280	2.03	2.11	2.19
3	38170 31450sh	29670	13160–16630	2.07	2.27	
4	39220 32680	28900–26000	12050–14320		2.12	
5	39200 32470	29760	14830–17850	2.02	2.11	2.16

[a] sh indicates a shoulder of a main band.

Therefore, all measurements were carried out on freshly prepared samples of the compounds. The more relevant spectral data of the solid compounds are summarized in Table II.

The salient feature of the IR spectra of the compounds is the presence of two broad bands at *ca.* 1580 and 1455 cm^{-1} which are attributed to the asymmetric and symmetric stretching vibrations of the COS moieties of the dithioterephthalato bridging ligand. The assignment of these vibrations has been based on the comparison of the IR spectra of the terephthalato and dithioterephthalato acids and their disodium salts. The two aforementioned bands are separated by 265 cm^{-1} in the case of the free acid and 87 cm^{-1} in the case of its disodium salt. The differences obtained for the complexes under study lie in a rather small margin around 130 cm^{-1}. This observation reveals that the bonding mode of the bridging unit in the compounds studied is intermediate between those of the free acid (unidentate through-sulfur bonding) and the disodium salt (extensive electron density delocalization on the COS groups). Following a well-established criterion [14] for the bonding mode of the thiocarboxylato group, it is evident that the dithioterephthalato ligand is coordinated in an aniso bidentate fashion towards the metal ions in all the studied complexes. The characteristic absorption of the perchlorate anions was detected in the region 1090–1160 cm^{-1} as a strong broad band with a single maximum, indicating that the ClO_4 anions are counteranions and do not participate in the metal coordination sphere [15].

The electronic reflectance spectra of the complexes (depicted schematically in Fig. 2) are indicative of distorted octahedral copper(II) environments [16]. The distortion is of varying degree, being more pronounced in **3** and **4**, where the carbon skeleton of the corresponding amine while undergoing structural rearrangements, removes the similarity of the terminal nitrogen atoms toward the central metal ion. Therefore, the local symmetry of the chromophore is lowered and practically all d–d excitations are allowed. As a consequence, strong and broad bands are detected in the region 12000–16000 cm^{-1}. For the rest of the complexes, a low intensity band is observed in the region 11000–18000 cm^{-1}, indicative of a rather limited distortion, probably a rhombic elongation of the chromophore.

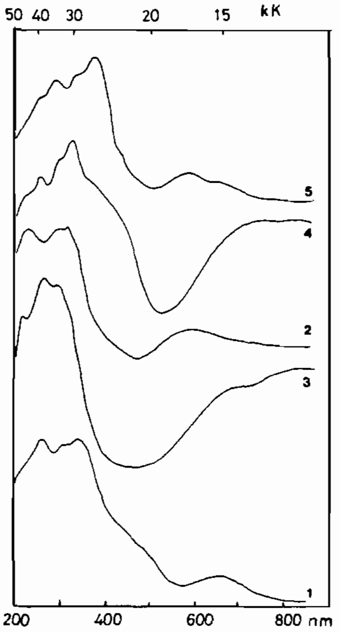

Fig. 2. Electronic reflectance spectra of the studied complexes in the region 900–200 nm.

The EPR spectra of the compounds under study are essential in the effort to gain information about the local copper(II) geometries adopted by the complexes. The general feature of the recorded spectra is that they are indicative of a singlet ground state [17] and they remain unaltered at low temperatures (Spectra were recorded at room temperature and at 77 K, the spectra presented in Fig. 3 were obtained at 77 K). For **1** and **3**, the spectra recorded are axial, with a $g_\perp$ value of about 2.06 and $g_\parallel$ higher than 2.20. A small rhombic component may also be present but is unresolved by the recording technique used. For **2** and **5**, the spectra obtained are rhombic with a g value smaller than 2.04. This is an indication [16b] of a substantial degree of participation of the $|z^2\rangle$ orbital in the ground states of these complexes. Such a participation would be readily explained in terms of the

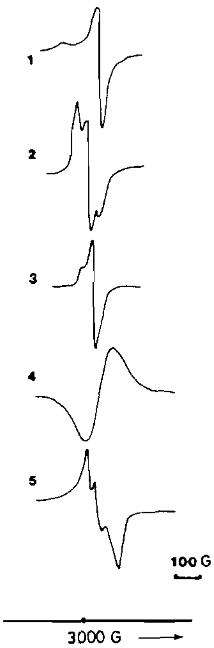

Fig. 3. Electron paramagnetic resonance spectra of the complexes in the solid state.

distorted octahedral chromophore structure of the complexes. Furthermore, grounds are now provided on which to argue for a *cis*-octahedral distortion in the aforementioned compounds. Finally, for **4**, the isotropic spectrum obtained accounts for the possibility of the occurrence of two nearly equivalent structures around the two copper ions such as the bicapped square pyramidal and *cis*-octahedral ones. As a consequence of the co-existence of two structures, the EPR signal emerges as an overlap of two different signals, not distinctly different so that the impression given is that of an isotropic spectrum. This experimental observation is in accord with the observed broad bands in the reflectance spectrum of the complex. The broadening must be attributed to the overlap of the transitions originating from the two different CuOSN$_4$ chromophores.

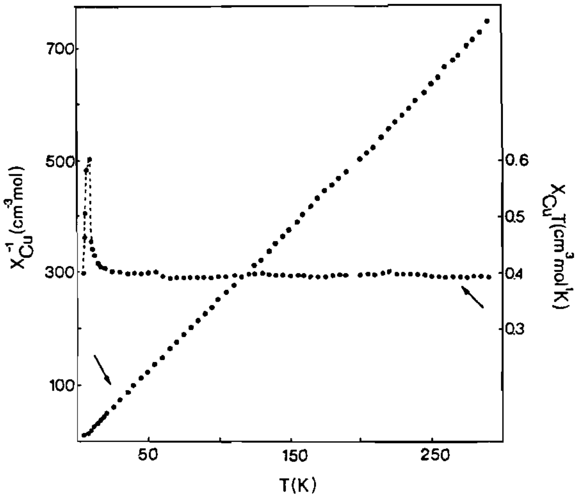

Fig. 4. Temperature dependence of the $\chi_{\mathrm{Cu}}T$ product and the inverse χ_{Cu} for **1**.

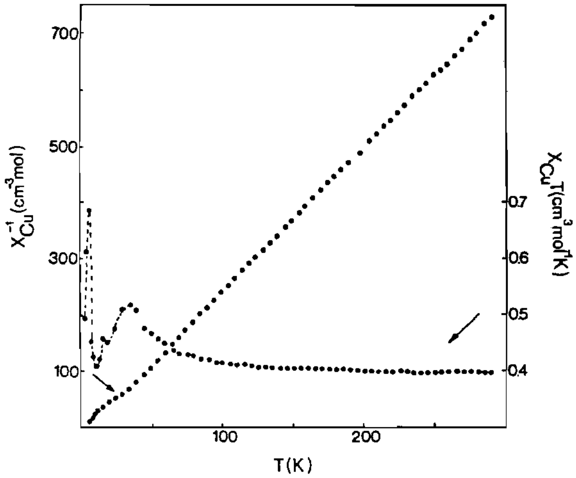

Fig. 5. Temperature dependence of the $\chi_{\mathrm{Cu}}T$ product and the inverse χ_{Cu} for **4**.

Based on the results insofar discussed, one may readily deduce that within the six coordinate scheme adopted by copper in the discussed complexes, several structural modifications may occur leading to substantially discrete electronic properties. This is not at all surprising since it is a well-known fact that the d^9 electronic configuration makes Cu^{2+} subject to Jahn–Teller distortion phenomena. It is therefore, of interest to investigate the effect of different local environments on the propagation of magnetic exchange phenomena through such an exceptionally large bridging ligand provided by the dithioterephthalato dianion. Unfortunately, due to the intramolecular redox reaction, taking place even in the solid state, it was impossible to obtain all complexes free of copper(I) impurities. As a result, only two complexes, namely **1** and **4** were free of Cu(I) impurity at the time of the magnetic measurements, therefore, results concerning low temperature magnetic measurements are presented and discussed only for these complexes. The results of the study are presented schematically in Figs. 4 and 5. An extremely sharp decrease of the susceptibility is observed, for both complexes, at very low temperatures, owing to antiferromagnetic coupling between neighbouring binuclear units ($J' = -0.8$ and -2.9 cm^{-1} respectively). The analysis of the magnetic data proceeded down to 18 and 25 K for **1** and **4** respectively and the resulting J values were -0.8 and $+18.3$ cm^{-1}. The $\chi_{\mathrm{Cu}}T$ product remains essentially constant in the region 25–290 K, while a sharp increase is observed in its value at lower temperatures. The sharp

TABLE III. Symmetry, Energy and Partitioning of the One Electron Levels in the region of the frontier MOs of a Binuclear Complex Possessing a Local Octahedral Copper(II) Symmetry[a]

MO	Energy (eV)	Cu	S	O	N(NH3)	C(Ph)
$18b_g$	−3.6467	0	1	1	0	91
$15a_u$	−6.3248	0	6	7	0	60
$24a_g$	−7.2605	0	6	10	0	52
$14a_u$	−8.1960	0	1	0	0	99
$17b_g$	−8.4423	0	22	23	0	14
$13a_u$	−9.4993	0	21	22	0	38
$22b_u$	−10.3182	16	61	3	9	9
$23a_g$	−10.4415	22	58	3	13	4
$22a_g$	−10.5056	29	7	40	9	13
$21b_u$	−10.7237	40	7	30	15	8
$21a_g$	−11.3179	30	14	16	18	17
$20b_u$	−11.3749	36	6	20	19	16
$16b_g$	−11.6710	2	51	44	0	3
$12a_u$	−11.7059	2	45	52	0	0
$15b_g$	−11.8297	39	6	22	7	13
$11a_u$	−12.1353	42	7	26	8	14
$14b_g$	−12.3297	7	8	19	0	61
$20a_g$	−12.3846	47	7	0	27	12
$19b_u$	−12.4736	54	3	1	38	2
$13b_g$	−12.8608	11	3	10	68	6
$10a_u$	−12.8698	14	4	7	68	3
$12b_g$	−12.8790	1	1	1	3	98
$9a_u$	−12.9276	88	2	1	4	2
$11b_g$	−12.9746	85	1	5	5	3
$8a_u$	−12.9780	84	2	3	6	3
$10b_g$	−13.0021	87	0	2	2	6

[a] The dashed line separates the occupied from the virtual levels.

maxima which are present at temperatures slightly lower than 10 K, suggest a phase transition to a magnetically ordered state, with all the binuclear units in the triplet state ($S = 1$) and are followed by a dramatic decrease, while approaching the liquid He temperature. This drop of the value of the $\chi_{Cu}T$ product strongly suggests an antiferromagnetic three dimensional ordering of the binuclear units [18]. The very weak antiferromagnetic coupling in **1** is expected due to the large separation of the two magnetic centers (*ca.* 12 Å), but the rather strong ferromagnetic interaction in **4** is unexpected if not related to the spectroscopically derived evidence about the molecular structure of the complex. This ferromagnetic interaction may only be intepreted in terms of accidental orthogonality [19] of the two magnetic centers. Such an accidental orthogonality occurs when seemingly similar magnetic centers adopt different geometric arrangements, so that the two magnetic orbitals do not transform in a similar way. This is probably achieved, in the present case, by means of a bicapped square pyramidal and *cis*-octahedral environments around the two copper ions respectively.

TABLE IV. Symmetry, Energy and Type of the Calculated Electronic Transitions of a Binuclear Complex Possessing a Local Octahedral Geometry around Each Copper(II) Ion

Transition	Symmetry	Energy (cm^{-1})	Type
$12a_u \rightarrow 15a_u$	A_g	43403	$\pi \rightarrow \pi^*$
$12b_g \rightarrow 17b_g$	A_g	37786	
$14b_g \rightarrow 17b_g$	A_g	31356	
$12a_u \rightarrow 14a_u$	A_g	31356	
$18a_g \rightarrow 23a_g$	A_g	25707	L → M CT
$8a_u \rightarrow 14a_u$	A_g	38579	M → L CT
$9a_u \rightarrow 14a_u$	A_g	38173	
$21a_g \rightarrow 24a_g$	A_g	36855	
$10b_g \rightarrow 17b_g$	A_g	36779	
$11b_g \rightarrow 17b_u$	A_g	36577	
$11a_u \rightarrow 14a_u$	A_g	31785	
$8a_u \rightarrow 13a_u$	A_g	28059	
$9a_u \rightarrow 13a_u$	A_g	27652	
$15b_g \rightarrow 17b_g$	A_g	27322	
$19b_u \rightarrow 22b_u$	A_g	17385	d → d
$20a_g \rightarrow 23a_g$	A_g	15673	
$20a_g \rightarrow 22a_g$	A_g	15156	
$19b_u \rightarrow 21b_u$	A_g	14115	
$20b_u \rightarrow 22b_u$	A_g	8523	
$8a_u \rightarrow 22b_u$	B_g	21453	
$11b_g \rightarrow 22b_u$	A_u	21426	
$9a_u \rightarrow 22b_u$	B_g	21047	
$8a_u \rightarrow 23a_g$	A_u	20460	
$11b_g \rightarrow 23a_g$	B_g	20432	
$9a_u \rightarrow 22a_g$	A_u	19536	
$8a_u \rightarrow 21b_u$	B_g	18183	
$11b_g \rightarrow 21b_u$	A_u	18156	
$9a_u \rightarrow 21b_u$	B_g	17777	
$19b_u \rightarrow 23a_g$	B_u	16391	
$19b_u \rightarrow 22a_g$	B_u	15874	
$11a_u \rightarrow 22b_u$	B_g	14657	
$11a_u \rightarrow 23a_g$	A_u	13662	
$20a_g \rightarrow 21b_u$	B_u	13397	
$15b_g \rightarrow 22b_u$	A_u	12192	
$11a_u \rightarrow 21b_u$	B_g	11386	
$15b_g \rightarrow 23a_g$	B_g	11198	
$15b_g \rightarrow 22a_g$	B_g	10680	

In order to investigate as thoroughly as possible the electronic structure as well as to understand the mechanism governing the nature and magnitude of spin exchange of the studied complexes, a computational study of a model complex possessing a strict octahedral copper(II) environment was undertaken by using the EH approximation which has been proven to be more than adequate for the description of analogous systems [5, 19].

The valence electron energy levels of the model complex are presented in Table III, along with their partitioning over the molecule. The computed electronic excitations, based on the eigenvalues of these energy levels, are presented in Table IV. A very good agreement is observed between the computed and the experimental spectra as far as the π–π^* and CT transitions are concerned. The d–d transitions that are computed account for a strictly octahedral complex and do not reflect any observed spectral features, apart from the fact that the transitions are expected to lie within a rather large margin. As it is expected, small structural changes within the chromophore would give rise, not only to differences in the positions of the observed maxima, but would result in a rather complicated spectrum, since nearly all the d–d transitions would be practically symmetry allowed.

Owing to the enormous number of atoms and basis functions present in the systems studied, *ab initio* calculations are impracticable while the severe approximations introduced by the EH do not allow for the deduction of irrefutible numerical results [20] regarding the nature of the spin exchange phenomenon propagated through the DTT^{2-} bridge. We therefore discuss this phenomenon in a qualitative manner, based on the electron distribution in the Frontier MOs of the model used for the calculations. A contour plot [21] of the two SOMOs of the model complex is shown in Fig. 6, where dotted lines present negative charge densities. Since the complex is centrosymmetric, only one magnetic orbital need be presented in the plot. The diffuseness of the sulfur atomic functions relative to those of oxygen is quite evident, the most striking observation though being that of the localization of the electron population within the metal ion and the two donor atoms of the thiocarboxylato ligand. Such a polarization of the electron population has been predicted to enhance the antiferromagnetic coupling in complexes where the two metal centers are not so far away from one another [22]. However, at very large distances, such as in the present case, the two chromophores do not interact in a direct way, therefore, the localization of the lone electron density on the atoms of the bonding site of the bridge may lead to intramolecular ferromagnetic coupling. To achieve this goal one only needs to remove the centrosymmetric character of the complexes by means of a small structural modification. Such a modification was the aftereffect of the coordination of a polyfunctional bulky amine like bipyridyl, which has proven to possess the possibility of rotating its two heterocyclic rings around the single C–C′ bond [23].

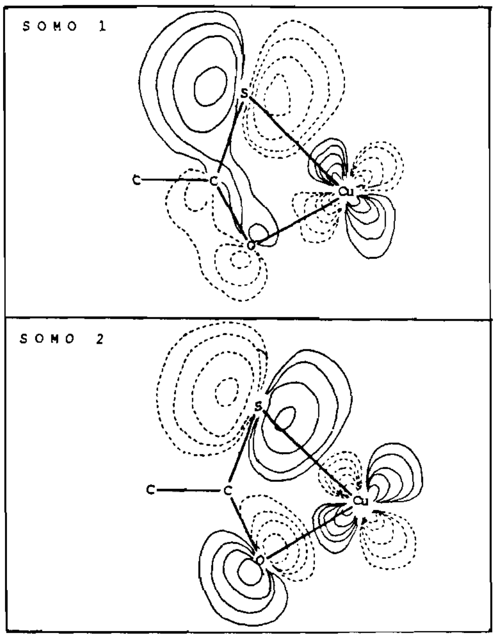

Fig. 6. Contour plots of the two SOMOs of a binuclear copper(II) complex having a local octahedral geometry. The outer contour represents an electron density of $[0.0156 \text{ e Bohr}^{-3}]^{1/2}$, while each inner one is scaled by a factor of 2. Negative density lobes are represented by dashed lines, while positive ones are indicated by solid lines.

In conclusion, it could be stated that unexpected ferromagnetic coupling may occur between copper(II) ions at extremely large distances, taking advantage of the flexibility of the thiocarboxylato group and the diffuse character of the sulfur atomic orbitals, in connection with the ability of specific terminal ligands such as bulky polyamines to create distorted chromophores with varying degree and type of distortion.

Supplementary Material

Tables of analytical data for the complexes and calculated and experimental magnetic data for complexes **1** and **4** (5 pages) are available on request from the authors.

Acknowledgement

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