

Role of the CF₃ Attractive Group on the Electrochemical and Magnetic Properties of Copper(II) Dinuclear Compounds with Robson-type Binucleating Ligands

PASCAL LACROIX, OLIVIER KAHN

Laboratoire de Spectrochimie des Eléments de Transition, UA no. 420, Université de Paris-sud, 91405 Orsay, France

FRANÇOIS THEOBALD

Laboratoire de Chimie du Solide Cristallin, Université de Paris-sud, 91405 Orsay, France

JACQUES LEROY and CLAUDE WAKSELMAN

CNRS-CERCOA, 2 rue Henry Dunant, 94320 Thiais, France

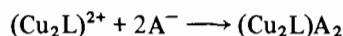
(Received June 1, 1987)

Abstract

From the recently described 2,6-diformyl-4-trifluoromethylphenol, we have synthesized the compounds $[\text{Cu}_2(\text{L}_{1,2}\text{CF}_3)](\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$. L_1CF_3 and L_2CF_3 are the 4-trifluoromethyl substituted Robson-type binucleating ligands with propylene and butylene lateral chains, respectively. The crystal structure of $[\text{Cu}_2(\text{L}_1\text{CF}_3)](\text{ClO}_4)_2$ has been solved. The compound crystallizes in the orthorhombic system, space group *Pbca*: $a = 9.537(4)$, $b = 18.072(10)$, $c = 34.340(11)$ Å, $Z = 8$. The structure consists of the expected copper(II) dinuclear entities, with the perchlorate groups making additional bridges of either side of the macrocycle. The molecular skeleton is significantly bent in a boat fashion. The electrochemical properties of those two 4-trifluoromethyl substituted compounds have been investigated and compared to those of the 4-methyl substituted compounds $[\text{Cu}_2(\text{L}_1\text{CH}_3)](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}_2(\text{L}_2\text{CH}_3)](\text{ClO}_4)_2$. The replacement of CH_3 by CF_3 shifts the first reduction wave by *ca.* 0.15 V and the second one by *ca.* 0.18 V. The magnetic properties of $[\text{Cu}_2(\text{L}_1\text{CF}_3)](\text{ClO}_4)_2$ and $[\text{Cu}_2(\text{L}_1\text{CH}_3)](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ have been compared. In spite of the modification of the redox properties, the singlet–triplet energy gaps J have been found equal within the experimental uncertainties ($J = -710(10) \text{ cm}^{-1}$).

Introduction

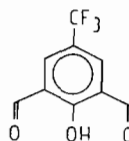
Recently, we decided to investigate a new class of inorganic compounds containing both exchange coupled polymetallic units and potentially electron-donor or electron-acceptor units [1]. More precisely, we attempted to synthesize systems of the type $(\text{Cu}_2\text{L})\text{A}_2$ according to the reaction



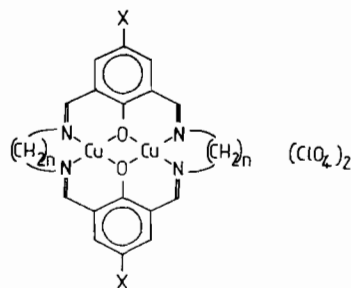
in which a partial electron transfer from A^- toward $(\text{Cu}_2\text{L})^{2+}$ takes place. Such a partial reduction of $(\text{Cu}_2\text{L})^{2+}$ by A^- is possible if the difference between the redox potentials of the two couples $(\text{Cu}_2\text{L})^{2+}/\text{Cu}_2\text{L}^+$ and A/A^- is inferior to a limit value estimated at 0.25 V by Wheland [2].

A few years ago, we described the compound $[\text{Cu}_2(\text{L}_1\text{CH}_3)](\text{TCNQ})_2$ where $[\text{Cu}_2(\text{L}_1\text{CH}_3)]^{2+}$ is the dinuclear cation schematized below and reported first by Robson [3], and TCNQ is 7,7',8,8'-tetracyanoquinodimethane [1]. In this compound $[\text{Cu}_2(\text{L}_1\text{CH}_3)](\text{TCNQ})_2$, there is no partial reduction of the dinuclear cation by TCNQ^- owing to the too large difference between the redox potentials. Indeed, $[\text{Cu}_2(\text{L}_1\text{CH}_3)]^{2+}$ can be reduced in the mixed valence species $[\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}(\text{L}_1\text{CH}_3)]^+$ at -0.53 V (*versus* NHE) and in $[\text{Cu}^{\text{I}}_2(\text{L}_1\text{CH}_3)]$ at -0.91 V [4]. As for the $\text{TCNQ}/\text{TCNQ}^-$ couple, its redox potential is 0.36 V [5].

In this paper, we explore the various ways to make more reducible the copper(II) dinuclear cations with Robson-type ligands. One of the ways reported by Hendrickson *et al.*, [6, 7] consists of replacing the propylene lateral chains by butylene chains. Such a modification makes the copper(II) coordination spheres more flexible and allows a tetrahedral distortion favouring the $\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{I}}$ reduction. Another way consists of replacing the CH_3 substituent on the aromatic ring by a more electro-attractive substituent like CF_3 . This is feasible since our report [8] on the synthesis of



In the next section, we focus on the four compounds



- $n = 3$, $X = \text{CH}_3$ (1)
 $X = \text{CF}_3$ (2)
 $n = 4$, $X = \text{CH}_3$ (3)
 $X = \text{CF}_3$ (4)

We describe the crystal structure of 2, then we compare the electrochemical properties of 1–4. Finally, we compare the magnetic properties of 1 and 2 in order to get new insights on the relation between the exchange interaction in a $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ species and its redox properties.

Experimental

Syntheses

$[\text{Cu}_2(\text{L}_1\text{CH}_3)](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (1) was synthesized as previously described [3]. $[\text{Cu}_2(\text{L}_2\text{CH}_3)](\text{ClO}_4)_2$ (3) was prepared in a similar manner. The synthesis of 2,6-diformyl-4-trifluoromethylphenol has been very recently reported [8].

$[\text{Cu}_2(\text{L}_1\text{CF}_3)](\text{ClO}_4)_2$ (2) was prepared as follows. To a solution of 2,6-diformyl-4-trifluoromethylphenol (109 mg, 5×10^{-4} mol) and copper(II) perchlorate (185 mg, 5×10^{-4} mol) in 10 ml of dry acetonitrile was added dropwise a solution of 1,3-diaminopropane (37.1 mg, 5×10^{-4} mol) in 2 ml of dry methanol. After 10 min heating, the green solution was evaporated to dryness in vacuum. Recrystallization from hot water of the residue affords 2 as a green polycrystalline powder. Single crystals were obtained by slow diffusion (over a period of three days) of diethylether into a concentrated solution of 2 in acetonitrile. *Anal.* Calc. for $\text{C}_{24}\text{H}_{20}\text{N}_4\text{O}_{10}\text{Cl}_2\text{F}_6\text{Cu}_2$: C, 34.46; H, 2.41; N, 6.70; Cl, 8.48; F, 13.63. Found: C, 34.55; H, 2.60; N, 6.40; Cl, 8.68; F, 11.8%.

$[\text{Cu}_2(\text{L}_2\text{CF}_3)](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (4) was synthesized in a similar manner, except that the mixture was refluxed overnight under nitrogen before evaporation to dryness. *Anal.* Calc. for $\text{C}_{26}\text{H}_{32}\text{N}_4\text{O}_{14}\text{Cl}_2\text{F}_6\text{Cu}_2$: C, 33.35; H, 3.44; N, 5.98; Cl, 7.57. Found: C, 33.85; H, 3.46; N, 5.91; Cl, 7.51%.

Crystallographic Data Collection and Structure Determination

The crystal used was about 0.3 mm in its largest size. It was sealed in a Lindemann tube and mounted on an Enraf Nonius CAD 4 diffractometer. The cell dimensions were obtained from the least-square fit of 25 reflections in the range $12^\circ < \theta < 16^\circ$. Data collection was performed at room temperature with graphite-monochromated Mo $K\alpha$ radiation in the θ - 2θ scan mode up to $2\theta = 36^\circ$. 2437 reflections were collected; 1321 of them with $I > 2\sigma(I)$ were kept for further calculations. Intensity controls every other hour on two reflections (640 and 548) showed variations less than 10% after two days. Lorentz and polarization corrections were applied while absorption corrections were not considered necessary.

Copper atoms were located using MULTAN and the other atoms using SHELX. Some hydrogen atoms appeared on Fourier difference maps but the positions were fixed using AFIX instructions in SHELX. Weights were calculated according to $w = 0.9296 / [\sigma^2(F) + 0.008459F^2]$. Anisotropic temperature factors were introduced only for the copper atoms. The final R values were $R = 0.098$ and $R_w = 0.099$. Owing to the highly disordered character of the structure, it has not been possible to improve further the refinement. The atomic coordinates are given in Table I and the main bond lengths and bond angles in Table II.

TABLE I. Final Least-squares Atomic Coordinates for $[\text{Cu}_2(\text{L}_1\text{CF}_3)](\text{ClO}_4)_2^a$

	x/a	y/b	z/c
Cu(1)	0.8485(3)	0.1025(1)	0.1491(1)
Cu(2)	1.0692(3)	0.0004(2)	0.1129(1)
O(1)	0.9811(15)	0.0970(7)	0.1047(4)
O(2)	0.9513(15)	0.0095(7)	0.1600(4)
C(1)	1.0014(23)	0.1416(11)	0.0748(7)
C(2)	0.9224(25)	0.2118(12)	0.0742(7)
C(3)	0.9363(25)	0.2582(13)	0.0435(7)
C(4)	1.0122(27)	0.2407(13)	0.0116(7)
C(5)	1.0876(29)	0.1739(13)	0.0124(8)
C(6)	1.0827(25)	0.1266(12)	0.0434(7)
C(7)	1.0226(35)	0.2936(16)	-0.0248(9)
F(1)	0.9290(45)	0.3350(24)	-0.0258(12)
F(2)	1.1372(31)	0.3303(14)	-0.0220(8)
F(3)	1.0429(35)	0.2504(17)	-0.0563(9)
F(1B)	1.0155(48)	0.3633(23)	-0.0104(12)
F(2B)	1.1182(83)	0.2793(39)	-0.0471(21)
F(3B)	0.9058(47)	0.2874(24)	-0.0430(13)
C(11)	0.9711(22)	-0.0208(10)	0.1944(6)
C(12)	1.0668(24)	-0.0819(11)	0.2001(7)
C(13)	1.0900(25)	-0.1081(12)	0.2353(6)
C(14)	1.0284(29)	-0.0841(14)	0.2684(8)
C(15)	0.9233(28)	-0.0294(13)	0.2633(7)
C(16)	0.8988(25)	0.0025(12)	0.2274(7)

(continued)

TABLE I. (continued)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
C(17)	1.0658(32)	-0.1134(15)	0.3096(8)
F(4)	0.9876(52)	-0.1672(22)	0.3154(11)
F(5)	1.1921(36)	-0.1308(22)	0.3086(11)
F(6)	1.0232(46)	-0.0653(24)	0.3366(10)
F(4B)	1.0578(55)	-0.1928(24)	0.3030(13)
F(5B)	1.1791(43)	-0.0976(28)	0.3232(14)
F(6B)	0.9612(65)	-0.0996(32)	0.3309(13)
C(20)	0.8198(24)	0.2334(12)	0.1025(6)
N(1)	0.7682(19)	0.1973(9)	0.1329(5)
C(21)	0.6446(27)	0.2317(12)	0.1514(7)
C(22)	0.6378(28)	0.2163(13)	0.1933(7)
C(23)	0.6067(28)	0.1357(13)	0.2028(8)
N(2)	0.7415(19)	0.0916(9)	0.1967(5)
C(24)	0.7817(22)	0.0553(11)	0.2257(6)
C(30)	1.1326(27)	-0.1145(13)	0.1653(7)
N(3)	1.1412(21)	-0.0951(10)	0.1309(6)
C(31)	1.2172(34)	-0.1463(16)	0.1048(8)
C(32)	1.2281(46)	-0.1211(21)	0.0671(11)
C(33)	1.2827(0)	-0.0514(20)	0.0528(12)
N(4)	1.1691(26)	0.0067(13)	0.0658(7)
C(34)	1.1710(28)	0.0616(13)	0.0397(8)
Cl(1)	0.8025(8)	-0.3407(4)	0.3221(2)
O(3)	0.7271(28)	-0.3072(13)	0.2923(7)
O(4)	0.7512(23)	-0.4178(10)	0.3293(6)
O(5)	0.9472(21)	-0.3420(9)	0.3102(5)
O(6)	0.7915(24)	-0.3015(12)	0.3567(7)
Cl(2)	1.2397(9)	-0.0284(4)	0.4253(2)
O(7)	1.1222(44)	-0.0780(22)	0.4347(13)
O(8)	1.1933(26)	0.0289(14)	0.3986(8)
O(9)	1.3506(28)	-0.0687(13)	0.4139(8)
O(10)	1.2915(39)	0.0146(19)	0.4583(10)
O(7B)	0.7157(92)	-0.0966(44)	0.1041(24)
O(8B)	0.7006(69)	0.0090(40)	0.1163(22)
O(9B)	0.6574(54)	-0.0588(24)	0.0434(16)
O(10B)	0.8848(62)	-0.0302(31)	0.0604(17)

^ae.s.d.s in parentheses.TABLE II. Principal Distances (Å) and Angles (°) for [Cu₂(L₁CF₃)(ClO₄)₂]

Distances	
Cu(1)–O(1)	1.984(14)
Cu(1)–O(2)	1.981(13)
Cu(1)–N(1)	1.957(16)
Cu(1)–N(2)	1.937(17)
Cu(2)–O(1)	1.957(14)
Cu(2)–O(2)	1.979(14)
Cu(2)–N(3)	1.958(18)
Cu(2)–N(4)	1.878(24)
O(1)–C(1)	1.318(25)
O(2)–C(11)	1.314(24)
C(1)–C(2)	1.474(30)
C(2)–C(3)	1.355(33)
C(3)–C(4)	1.350(34)
C(4)–C(5)	1.406(35)
C(5)–C(6)	1.364(36)
C(6)–C(1)	1.357(33)
C(4)–C(7)	1.577(38)

TABLE II. (continued)

C(7)–F(1)	1.165(53)
C(7)–F(2)	1.282(43)
C(7)–F(3)	1.347(42)
C(7)–F(1B)	1.355(50)
C(7)–F(2B)	1.218(83)
C(7)–F(3B)	1.283(56)
C(11)–C(12)	1.446(29)
C(12)–C(13)	1.317(32)
C(13)–C(14)	1.350(35)
C(14)–C(15)	1.419(36)
C(15)–C(16)	1.380(33)
C(16)–C(11)	1.392(31)
C(14)–C(17)	1.550(37)
C(17)–F(4)	1.242(52)
C(17)–F(5)	1.246(46)
C(17)–F(6)	1.333(48)
C(17)–F(4B)	1.454(51)
C(17)–F(5B)	1.213(52)
C(17)–F(6B)	1.263(63)
C(2)–C(20)	1.432(33)
C(20)–N(1)	1.326(28)
N(1)–C(21)	1.477(30)
C(21)–C(22)	1.466(34)
C(22)–C(23)	1.521(34)
C(23)–N(2)	1.527(31)
N(2)–C(24)	1.253(26)
C(24)–C(16)	1.471(31)
C(12)–C(30)	1.474(34)
N(3)–C(30)	1.233(32)
C(31)–N(3)	1.477(35)
C(32)–C(31)	1.376(48)
C(33)–C(32)	1.448(52)
N(4)–C(33)	1.573(36)
C(34)–N(4)	1.337(34)
C(6)–C(34)	1.450(34)
Cl(1)–O(3)	1.388(26)
Cl(1)–O(4)	1.498(20)
Cl(1)–O(5)	1.440(21)
Cl(1)–O(6)	1.387(24)
Cl(2)–O(7)	1.471(42)
Cl(2)–O(8)	1.453(28)
Cl(2)–O(9)	1.344(27)
Cl(2)–O(10)	1.460(35)
Cl(2)–O(7B)	1.611
Cl(2)–O(8B)	1.623
Cl(2)–O(9B)	1.438
Cl(2)–O(10B)	1.468
N(1)–Cu(1)–O(1)	94.3(6)
O(1)–Cu(1)–O(2)	77.8(6)
N(2)–Cu(1)–O(2)	90.8(6)
N(2)–Cu(1)–N(1)	97.0(7)
O(1)–Cu(2)–O(2)	78.4(6)
N(3)–Cu(2)–O(2)	90.8(7)
N(3)–Cu(2)–N(4)	98.5(10)
N(4)–Cu(2)–O(1)	92.3(9)
Cu(1)–O(1)–Cu(2)	102.0(6)
Cu(1)–O(2)–Cu(2)	101.3(6)
Cu(1)–O(2)–C(11)	126.5(12)
Cu(1)–O(1)–C(1)	131.3(13)
Cu(2)–O(1)–C(1)	126.5(13)
Cu(2)–O(2)–C(11)	128.2(13)

(continued)

Crystal data: $C_{24}H_{20}N_4O_{10}Cl_2F_6Cu$; $M = 836.206$. Orthorhombic system; space group $Pbca$: $a = 9.537(4)$, $b = 18.072(10)$, $c = 34.340(11)$ Å, $V = 5917(8)$ Å³, $Z = 8$.

Electrochemistry

All measurements were performed under argon in DMF with tetraethylammonium perchlorate as a supporting electrolyte (0.1 M/l). A DACFAMOV electrochemistry system was used. Cyclic voltammetry was made in a cell containing a platinum working electrode, an auxiliary electrode and a saturated calomel electrode. The ferrocene/ferricinium⁺ couple was utilized as an internal reference [9].

Magnetic Measurements

These were carried out on powder samples of 1 and 2 with a Faraday-type magnetometer equipped with a He continuous-flow cryostat. HgCo(SCN)₄ was used as a susceptibility standard. Diamagnetic corrections were estimated as -334×10^{-6} cm³ mol⁻¹ for 1 and -328×10^{-6} cm³ mol⁻¹ for 2.

Discussion

Description of the Structure of 2

Two perspective views of the structure of 2 with the labeling scheme of the atoms are shown in Fig. 1. As expected, the structure consists of copper(II) dinuclear entities with the phenolic oxygen atoms of the macrocycle as bridges. The perchlorate groups make additional bridges between the copper atoms of a same molecule, of either side of the plane of the macrocycle. Each copper atom has the 4 + 2 coordination with two nitrogen and two oxygen atoms in the basal plane and two oxygen atoms belonging to perchlorate groups occupying the apical positions with Cu–O apical bond lengths varying from 2.48 to 3.01 Å. Surprisingly, the molecular skeleton is far from being rigorously planar. To see that, it is convenient to consider the mean planes Π_1 calculated from Cu(1), Cu(2), N(1), N(2), N(3), N(4), and Π_2 and Π_3 calculated from the carbon atoms of the aromatic rings C(1) to C(6) and C(11) to C(16), respectively. The deviations of Cu(1), Cu(2), N(1), N(2), N(3) and N(4) from Π_1 are less than 0.03(1) Å but the bridging oxygen atoms O(1) and O(2) are displaced from the same side of Π_1 by 0.12(1) Å. Moreover, Π_1 and Π_2 make an angle of 21(1)° and Π_1 and Π_3 an angle of 4(1)°.

The structure is highly disordered. The disorder concerns the CF₃ groups, the perchlorate groups and perhaps also the propylene lateral chains. Concerning the CF₃ groups, they were found to occupy two positions resulting from a rotation around the C–(F₃) bond with occupancy factors of 0.62 and

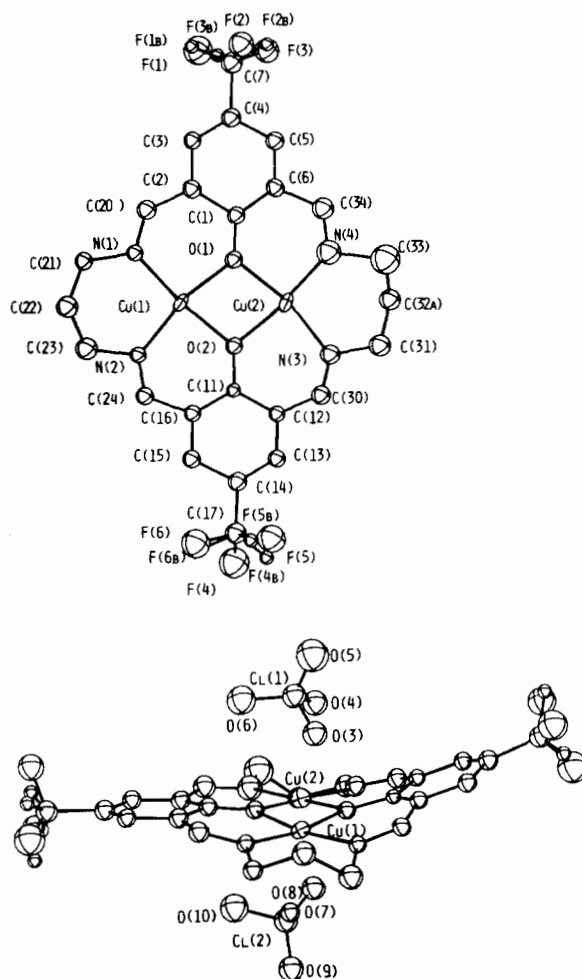


Fig. 1. Two perspective views of $[Cu_2(L_1CF_3)](ClO_4)_2$ (2) with the labeling scheme for the atoms.

0.38, respectively, for C(7)F₃ and 0.57 and 0.43, respectively, for C(17)F₃. The Cl(2)O₄ perchlorate group also occupies two positions. In contrast, the Cl(1)O₄ group located on the 'hollow side' of the molecule does not appear disordered and is less agitated. Concerning the propylene lateral chains, it is difficult to say whether they are only highly agitated or are actually disordered.

Electrochemical Properties

The cyclic voltammograms for compounds 1 to 4 were recorded under the same experimental conditions. Each of them exhibits the characteristic two-step reduction already observed for 1. The first step involves one electron and yields the mixed valence Cu^{II}Cu^I species and the second step involves two electrons and gives the fully reduced Cu^ICu^I species. The reduction potentials in DMF are compared in Table III. As an example, the cyclic voltammogram of 2 is shown in Fig. 2. The two reduction waves involve reversible processes as found in 1. The differ-

TABLE III. Electrochemical Data for Compounds 1–4^a

		$\text{Cu}^{\text{II}}\text{Cu}^{\text{II}} + e^- \rightarrow \text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ (V)	$\text{Cu}^{\text{II}}\text{Cu}^{\text{I}} + e^- \rightarrow \text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$ (V)
$[\text{Cu}_2(\text{L}_1\text{CH}_3)](\text{ClO}_4)_2$	(1)	-0.53	-0.91
$[\text{Cu}_2(\text{L}_1\text{CF}_3)](\text{ClO}_4)_2$	(2)	-0.39	-0.74
$[\text{Cu}_2(\text{L}_2\text{CH}_3)](\text{ClO}_4)_2$	(3)	-0.32	-0.81
$[\text{Cu}_2(\text{L}_2\text{CF}_3)](\text{ClO}_4)_2$	(4)	-0.16	-0.62

^aThe reduction potentials are given vs. normal hydrogen electrode.

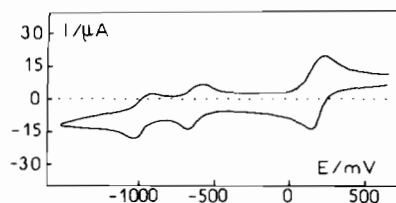


Fig. 2. Cyclic voltammogram for $[\text{Cu}_2(\text{L}_1\text{CF}_3)](\text{ClO}_4)_2$ (2). The concentration is 10^{-3} mol l^{-1} in DMF. The scan rate is 400 mV s^{-1} . The wave at ~ 500 mV is the ferrocene/ferricinium⁺ internal reference.

ences between anodic and cathodic peaks are 80 mV for $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}/\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ and 90 mV for $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}/\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$.

The replacement of the CH_3 substituent by CF_3 , everything else being unchanged, shifts the first reduction wave by *ca.* 0.15 V and the second one by *ca.* 0.18 V. By modifying the substituent on the aromatic ring ($\text{CH}_3 \rightarrow \text{CF}_3$), we displaced the first reduction wave by 0.37 V and the second one by 0.29 V, so that 4 is significantly more reducible than 1.

Magnetic Properties

One of the unsolved problems concerning the copper dinuclear systems is the following: what is the relation, if any, between the magnitude of the interaction in a $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ species and the redox properties of this species [10, 11]. More precisely, is the singlet–triplet energy gap J in the $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ complex related to the one-electron and the two-electron reduction potentials? The compounds 1 and 2 in principle offer a unique opportunity to approach this problem. Indeed, these compounds only differ by the nature of the substituent CH_3 or CF_3 on the aromatic ring and the electro-attractive character of CF_3 with regard to CH_3 makes 2 significantly more reducible than 1. We carefully studied the temperature dependence of the molar magnetic susceptibility χ_M for both compounds in the 70–300 K temperature range. The results for 2 are shown in Fig. 3. χ_M has a very low value at 290 K (340×10^{-6} $\text{cm}^3 \text{mol}^{-1}$) and decreases upon cooling down. χ_M reaches a minimum (80×10^{-6} $\text{cm}^3 \text{mol}^{-1}$)

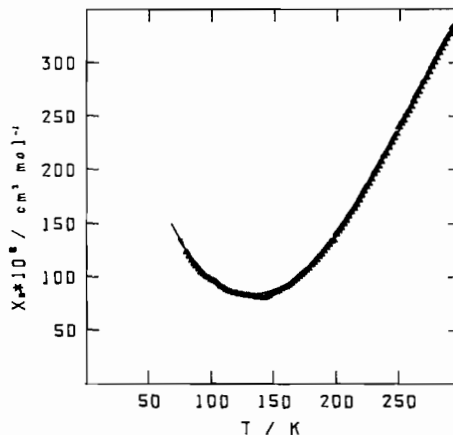


Fig. 3. Experimental (Δ) and calculated (—) temperature dependences of the molar magnetic susceptibility of 2.

around 140 K, then increases. This behavior is typical of a copper(II) dinuclear complex with a very large singlet–triplet energy gap. The increase of χ_M below 140 K is due to the presence of a small proportion ρ of uncoupled copper(II). The theoretical expression for χ_M is:

$$\chi_M = \frac{2N\beta^2 g^2}{kT} [3 + \exp(-J/kT)]^{-1} (1 - \rho) + \frac{N\beta^2 g^2}{2kT} \rho$$

where the symbols have their usual meaning. By least-squares fitting of the experimental data, J is found as $-710(10)$ cm^{-1} , with $g = 2.07(1)$ and $\rho = 0.023(2)$. The same investigation for 1 leads to $J = -712(10)$ cm^{-1} , $g = 2.05(2)$ and $\rho = 0.033(3)$. One sees, therefore, that the singlet–triplet energy gaps in 1 and 2 are equal within the experimental uncertainties. In other words, the replacement of CH_3 by CF_3 has no influence on the magnitude of the interaction in the $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ system, in spite of the modifications of the redox properties.

Conclusion

Two main results emerge from this work. The replacement of CH_3 by CF_3 in the 4-position of the Robson-type binucleating ligand makes the copper(II)

dinuclear species more reducible, as expected. The first reduction wave is displaced by *ca.* 0.15 V and the second one by *ca.* 0.19 V. This effect is significative but however limited in the sense where the redox potential of $[\text{Cu}_2(\text{L}_1\text{CF}_3)](\text{ClO}_4)_2$ is still too low to allow an electron transfer if the perchlorate anion is replaced by TCNQ^- . As a matter of fact, we synthesized the compound $[\text{Cu}_2(\text{L}_1\text{CF}_3)](\text{TCNQ})_2$ and actually we did not observe any electron transfer. The magnetic properties of $[\text{Cu}_2(\text{L}_1\text{CF}_3)](\text{TCNQ})_2$ are very similar to that of **2**, which indicates that the TCNQ^- units form essentially diamagnetic $(\text{TCNQ}^-)_2$ dimers, as had been found in $[\text{Cu}_2(\text{L}_1\text{CH}_3)](\text{TCNQ})_2$ [1]. Even by playing on both the nature of the substituent in the 4-position (CF_3) and that of the lateral chains (butylene), the first reduction wave remains too apart from that of the $\text{TCNQ}/\text{TCNQ}^-$ couple.

In another respect, the replacement of CH_3 in **1** by CF_3 in **2** does not modify the magnetic properties in spite of the shift of the reduction waves. In both compounds, the singlet state is stabilized by *ca.* 710 cm^{-1} with regard to the triplet state. At first, this result is rather surprising. The crystal structure of **1** is not known. Maybe, some slight geometrical changes, for instance the value of the bridging angles or the more or less planarity of the molecular skeleton, compensate the purely electronic effect due to $\text{X} = \text{CH}_3$ or CF_3 . In other

words, our result does not mean that the problem of the relation between J and the redox properties of a copper(II) dinuclear species is a false problem, but much more data will be necessary before getting an overview on this important question.

References

- 1 P. Lacroix, O. Kahn, A. Gleizes, L. Valade and P. Casoux, *Nouv. J. Chim.*, **8**, 643 (1984).
- 2 R. C. Wheland, *J. Am. Chem. Soc.*, **98**, 3926 (1976).
- 3 N. H. Pilkington and R. Robson, *Aust. J. Chem.*, **23**, 2225 (1970).
- 4 R. R. Gagné, C. A. Koval, T. J. Smith and M. C. Cimolino, *J. Am. Chem. Soc.*, **101**, 4571 (1979).
- 5 M. L. Kaplan, R. C. Haddon, F. B. Bramwell, F. Wudl, J. H. Marshall, D. O. Cowan and S. Gronowitz, *J. Phys. Chem.*, **84**, 427 (1980).
- 6 R. C. Long and D. N. Hendrickson, *J. Am. Chem. Soc.*, **105**, 1513 (1983).
- 7 D. N. Hendrickson, R. C. Long, Y. T. Hwang and H. R. Chang, in K. D. Karlin and J. Zubiela (eds.), 'Biological and Inorganic Copper Chemistry', Vol. 1, Adenine Press, New York, 1986, p. 223.
- 8 J. Leroy, C. Wakselman, P. Lacroix and O. Kahn, *J. Fluorine Chem.*, in press.
- 9 R. R. Gagné, C. A. Koval and G. C. Lisensky, *Inorg. Chem.*, **19**, 2854 (1980).
- 10 T. R. Felthouse and D. N. Hendrickson, *Inorg. Chem.*, **17**, 2636 (1978).
- 11 O. Kahn, in R. D. Willett, D. Gatteschi and O. Kahn (eds.), 'Magneto Structural Correlations in Exchange Coupled Systems', Reidel, Dordrecht, 1985, p. 57.