Intramolecular Long-Range Exchange Coupling in Dinuclear Copper(II) Complexes with Cu···Cu Separations Greater than 10 Å

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Abstract: Magnetic long-range exchange coupling between two unpaired electrons of two copper(II) ions in a square-pyramidal ligand environment $(d_{x^2-y^2})^1$, which are rigidly separated by >10 Å by an organic spacer ligand (e.g., a μ-dicarboxylato ligand) has been systematically studied. The following complexes have been synthesized: $[\{LCu(OH_2)\}_2$(μ-terephthalato)]$(ClO_4)_2$ (**1**), $[LCu^{II}(OH_2)$(benzoato)](ClO_4) (**2**), $[\{LCu^{II}(NCS)\}_2$(μ-terephthalato)]$\cdot 2CH_3OH$ (**3**), $[\{LCu^{II}(NCS)\}_2$(μ-4,4′-oxybisbenzoato)]$\cdot 3CH_3OH$ (**4**), $[\{LCu^{II}(OH_2)\}_2$(μ-tetrafluoroterephthalato)]$(ClO_4)_2$ (**5**), $[\{LCu^{II}(OH_2)\}_2\{LCu^{II}\}_2$(μ-tetrafluorobenzoato)$_3](ClO_4)_2\cdot 6H_2O$ (**6**), $[\{LCu^{II}(OH_2)\}_2$(μ-biphenyl-4,4′-dicarboxylato)]$(ClO_4)_2$ (**7**), $[LCu^{II}$(μ-biphenyl-4,4′-dicarboxylato)$]_n(H_2O)_{2n}$ (**8**), $[\{LCu^{II}(NCS)\}_2$(μ-biphenyl-4,4′-dicarboxylato)] (**9**), $[\{LCu(OH_2)\}_2$(μ-*trans*,*trans*-2,4-hexadien-1,6-dicarboxylato)]$(ClO_4)_2$ (**10**) (L = 1,4,7-trimethyl-1,4,7-triazacyclononane). Complexes **1**, **2**, **3**, **4**, and **6** have been characterized by X-ray crystallography; the structure of **1** has been described previously.[15] Temperature-dependent magnetic susceptibility data for all complexes have been measured over the range 2.0–298 K. In complexes **2**, **3**, **4**, **6**, **8**, and **9** only very weak, if any, intermolecular antiferromagnetic or, in the case of **6**, ferromagnetic coupling has been observed ($|J| \le 2$ cm^{-1}; $H = -2JS_1\cdot S_2$, $S_1 = S_2 = {}^1/_2$). In contrast, in complexes **5** ($2J = -80$ cm^{-1}), **7** ($2J = -62$ cm^{-1}), and **10** ($2J = -100$ cm^{-1}) relatively strong intramolecular antiferromagnetic exchange coupling has been detected. The intramolecular Cu···Cu separation is 11.3 Å in **5**, 15.6 Å in **7**, and approximately 12.0 Å in **10**. These data demonstrate that intramolecular antiferromagnetic exchange coupling of considerable magnitude is possible over distances >15 Å, provided that the effective magnetic orbitals are favorably aligned.

Keywords
bridging ligands · coordination · copper compounds · exchange coupling · magnetic properties

Introduction

Dinuclear copper(II) complexes have played an important role in the elucidation of spin coupling or magnetic exchange phenomena between paramagnetic metal centers.[1–4] They exemplify the simplest case where two unpaired electrons at two paramagnetic ions are separated by organic spacer molecules which may mediate intramolecularly the stabilization of a singlet ($S = 0$; diamagnetic) or a triplet ($S = 1$) ground state. In general, the Goodenough–Kanamori[5,6] rules provide excellent guidelines for the analysis of orbital symmetry-governed exchange mechanisms, and our understanding of the factors that control an intramolecular anti- or ferromagnetic coupling of the unpaired electrons is well advanced and successful.[1–4]

One of the remaining fundamental questions in this area of magnetochemistry relates to the distance dependence of such exchange-mediated interactions: given a favorable orbital overlap for an intramolecular antiferromagnetic coupling between two paramagnetic metal ions, over how great a distance can exchange coupling be propagated? Is there a limit?[7] What is the singlet–triplet energy gap as a function of distance or, indeed, is there a correlation at all?

In the past inorganic chemists have addressed these questions by synthesizing suitable dinuclear copper(II) complexes where the metal ions are intramolecularly separated by about 11 Å by a coordinated μ-terephthalato bridge.[8–14] Table 1 lists these complexes. With the notable exception of $[Cu^{II}_2(bpy)_2(OH_2)_2$(μ-terephthalato)]$(ClO_4)_2$[9] the observed magnetic interaction was disappointingly small and was interpreted as being *inter*molecular rather than intramolecular in nature.

In 1988 we reported[15] the first case in which an antiferromagnetic coupling (in $[\{LCu(OH_2)\}_2$(μ-terephthalato)]$(ClO_4)_2$ (**1**); L represents the cyclic triamine 1,4,7-trimethyl-1,4,7-triazacyclononane) appeared to be *intra*molecular *and* surprisingly strong considering the intramolecular Cu···Cu separation of 11.25 Å (Fig. 1). The observed singlet–triplet energy gap is $-140(5)$ cm^{-1} ($2J$) from the isotropic spin Hamiltonian $H = -2JS_1\cdot S_2$ with $S_1 = S_2 = ½$ and $g_{iso} = 2.20(2)$. The crystal structure determination of **1** shows that the shortest *inter*molecular Cu···Cu distance is 7.587(1) Å, which is much smaller than the *intra*molecular Cu···Cu separation. It is therefore of the utmost importance to prove that the magnetic exchange interaction documented by measurements of the temperature-dependent susceptibility of crystalline **1** is *intra*- and not

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Table 1. Comparison of structural and magnetic data of dinuclear μ-terephthalato bridged copper(II) complexes.

	Complex [a]	Cu polyhedron [b]	$Cu-O_{carb}$ (Å)	$Cu\cdots Cu$ (Å) [c]	Magnetism [d]	Ref.
A	$[\{Cu(pmedien)(H_2O)\}_2(\mu\text{-tp})](ClO_4)_2$	approx. tbp	1.931(3)	11.129	– 2.7	[8]
B	$[\{Cu(petdien)\}_2(\mu\text{-tp})](ClO_4)_2$	approx. tpb	1.972(6) 2.347(6)	10.710	0	[8]
C	$[\{Cu(bpy)(H_2O)\}_2(\mu\text{-tp})](ClO_4)_2$	n.d.	n.d.	n.d.	– 25.9	[9]
D–G	$[\{Cu(polyamine)\}_2(\mu\text{-tp})]X_2(X = ClO_4,PF_6)$	n.d.	n.d.	n.d.	– 2.2– + 1.11	[10]
H	$[Cu(en)(H_2O)_2(\mu\text{-tp})]_m$	elongated octahedral	1.961(3)	11.167	weakly antiferromagnetic	[11]
I	$[\{Cu(dien)\}_2(\mu\text{-tp})](ClO_4)_2$	distorted octahedral	2.760(5) 2.484(5) 1.982(5)	11.006	weakly antiferromagnetic	[12]

[a] Ligand abbreviations: μ-tp = bridging terephthalate; pmedien = *N*-pentamethyldiethylenetriamine; petdien = *N*-pentaethyldiethylenetriamine; dien = diethylenetriamine; bpy = 2,2'-bipyridine; polyamine = diethylenetriamine in **D**, triethylenetetraamine in **E**, 2,2'-bipyridine in **F**, 1,10-phenanthroline in **G**; en = ethylenediamine. [b] tbp = trigonal bipyramidal; n.d. = not determined. [c] intramolecular $Cu\cdots Cu$ separation. [d] The coupling constant J (cm^{-1}) as defined by the Hamiltonian $H = -2JS_1\cdot S_2$; $S_1 = S_2 = {}^1/_2$.

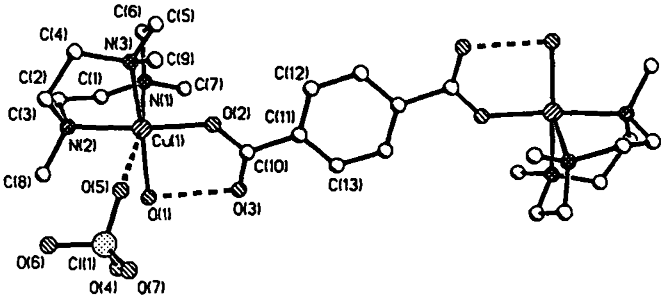

Fig. 1. Schematic representation of the neutral molecule $[\{LCu(OH_2)\}_2(\mu\text{-terephthalato})](ClO_4)_2$ in crystals of **1** (ref. [15]). The broken lines indicate the weak interaction between the Cu^{II} ions and one ClO_4^- anion ($Cu-O_{ClO4}$ = 2.992 Å) (the second ClO_4 is omitted for clarity) and the intramolecular hydrogen bonds between the coordinated water molecules and the carbonyl oxygen atoms of the coordinated carboxylate ($O(1)\cdots O(3)$ = 2.516 Å).

*inter*molecular. This is one aim of the present paper. If we can be reasonably sure that the exchange is intramolecular, is it possible to increase the intramolecular $Cu\cdots Cu$ separation by using more extended conjugated organic dicarboxylic acids to ensure intramolecular $Cu\cdots Cu$ separations >12 Å?

In order to address the above questions in a systematic fashion, we synthesized the complexes **1**–**10** depicted in Scheme 1, all of which contain the LCu^{II} fragment, where L represents the cyclic triamine 1,4,7-trimethyl-1,4,7-triazacyclononane. This fragment has in the past been successfully employed in the synthesis of dinuclear copper(II) complexes[16–19] where the coordination geometry around the copper(II) ion is five-coordinate square-pyramidal with a $(d_{x^2-y^2})^1$ electronic configuration.

Editorial Board Member:[*] *Professor Karl Wieghardt was born in Germany in 1942. He studied chemistry at the Universities of Hamburg and Heidelberg and graduated in Inorganic Chemistry in 1969 under Professor Hans Siebert. In 1974 he was appointed junior lecturer at Heidelberg University; he became associate professor at the Technical University of Hannover in 1975. In 1981 he was appointed full professor at the Ruhr University, Bochum. He moved to the Max-Planck-Institut für Strahlenchemie, Mülheim an der Ruhr, as director in 1994. His research interests span bioinorganic chemistry, coordination chemistry with macrocycles, and inorganic reaction mechanisms. At present he is developing concepts for understanding metalloproteins containing dinuclear or polynuclear active sites, such as nonheme iron proteins and photosystem II.*

Results

Preparation of Complexes: The reaction of the triamine 1,4,7-trimethyl-1,4,7-triazacyclononane (L) with $Cu(ClO_4)_2\cdot 6H_2O$ and the piperidinium salt of an organic carboxylic or dicarboxylic acid in methanol in the ratio 1:1:1 or 1:1:0.5, respectively, yields deep blue or bluish-green solutions from which blue or bluish-green crystals of the perchlorate salts of the following composition were isolated: $[\{LCu(OH_2)\}_2(\mu\text{-terephthalato})](ClO_4)_2$ (**1**);[15] $[LCu(OH_2)(benzoato)](ClO_4)$ (**2**), $[\{LCu(OH_2)\}_2(\mu\text{-tetrafluoroterephthalato})](ClO_4)_2$ (**5**), $[\{LCu(OH_2)\}_2(\mu\text{-biphenyl-4,4'-dicarboxylato})](ClO_4)_2\cdot 3H_2O$ (**7**), and $[\{LCu(OH_2)\}_2(\mu\text{-}trans,trans\text{-2,4-hexadiene1,6-dicarboxylato})](ClO_4)_2$ (**10**). With the exception of **2**, these compounds have two $[LCu(OH_2)(carboxylato)]^+$ moieties separated by a covalently linked organic spacer, namely, phenyl in **1**, tetrafluorophenyl in **5**, 4,4-biphenyl in **7**, and *trans,trans*-butadienyl in **10**. The carboxylates are monodentate ligands, as is seen from the difference between the $\nu(C=O)$ and $\nu(C-O)$ stretching frequencies (> 190 cm^{-1}). Crystal structure determinations of **1** and **2** show that the carbonyl oxygen atoms of the coordinated carboxylate groups form a strong intramolecular $O-H\cdots O$ bond with the bound water molecule (Scheme 2). The CuN_3O_2 polyhedron is in all cases square-pyramidal with two Cu–O bonds to the oxygen atoms of the carboxylate and the water molecule and two relatively short $Cu-N_{amine}$ bonds in the basal plane, and a longer $Cu-N_{amine}$ bond in the apical position. In the solid state a perchlorate anion occupies the vacant sixth position at the copper(II). The $Cu\cdots OClO_3$ interaction is very weak ($Cu\cdots O$ = 2.8–3.4 Å) and probably electrostatic in nature rather than covalent. We assume that the same fragment is present in crystals of **5**, **7**, and **10**.

This conclusion is corroborated by the striking similarity of the visible spectra of the above complexes (Table 2 and Fig. 2) both in the solid state (reflectance spectra) and in solution, all of

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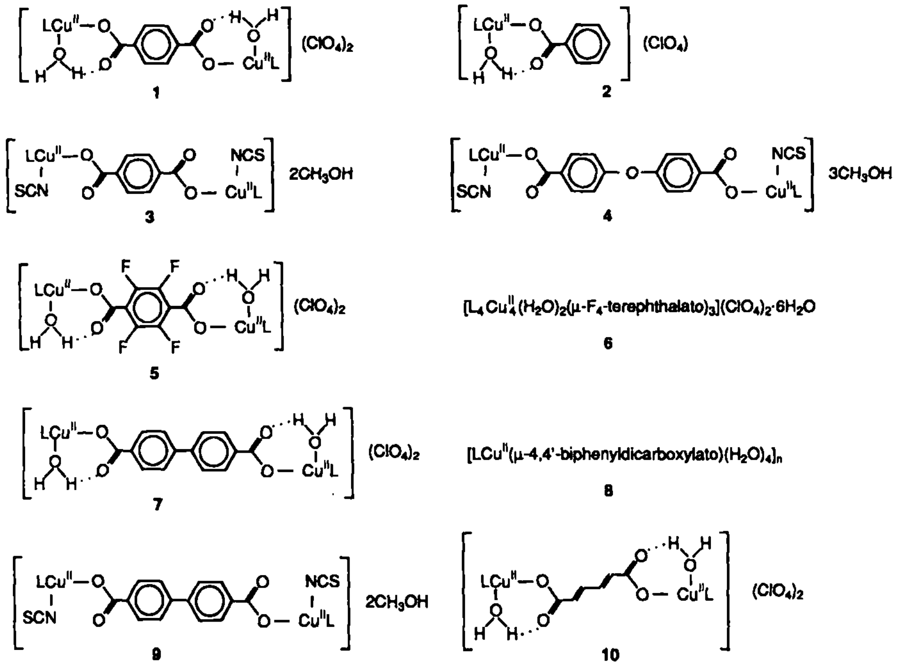
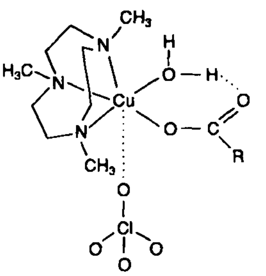


Scheme 1: Synthesized complexes (L = 1,4,7-trimethyl-1,4,7-triazacyclononane).



Scheme 2: [LCu(OH$_2$)(carboxylato)](ClO$_4$) polyhedron present in crystals of **1** and **2**, showing the intramolecular hydrogen bond.

which exhibit two d–d transitions at 648 ± 3 and 1064 ± 20 nm. This is quite characteristic for five-coordinate square-pyramidal copper(II) complexes where the unpaired electron resides in a $(d_{x^2-y^2})^1$ orbital.

The coordinated water molecule of the [LCu(OH$_2$)(carboxylato)]$^+$ fragment is readily substituted by an N-bound thiocyanate ligand by addition of NaSCN dissolved in methanol. The following dinuclear species have been isolated as crystalline materials: [{LCu(NCS)}$_2$(μ-terephthalato)]·2CH$_3$OH (**3**), [{LCu(NCS)}$_2$(μ-4,4'-oxybisbenzoato)]·3CH$_3$OH (**4**), and [{LCu(NCS)}$_2$(μ-biphenyl-4,4'-dicarboxylato)]·2CH$_3$OH (**9**).

Table 2. Electronic spectra of new complexes.

Complex	Solvent	λ_{max} (nm) (ε (L mol^{-1} cm^{-1}))
1	CH$_3$OH	642(167), 1060(70)
2	CH$_3$OH	229(13.1 × 10^3), 281(8.6 × 10^3), 649(75), 1114(40)
3	CH$_3$CN	242(17.3 × 10^3), 279(15.1 × 10^3), 350(1.1 × 10^3), 648(170), 1041(50)
4	CH$_3$CN	265(32.3 × 10^3), 370(2.0 × 10^3), 645(202), 1083(60)
5	CH$_3$CN	279(9.7 × 10^3), 370 sh, 642(207), 1052(72)
6	CH$_3$OH	234(25.3 × 10^3), 279(30.4 × 10^3), 666(282), 1144(108)
7	CH$_3$OH	290(40.9 × 10^3), 649(169), 1106(74)
8	CH$_3$OH	286(35.8 × 10^3), 647(89), 1124(40)
9	CH$_3$CN	288(43.1 × 10^3), 649(257), 1064(77)
10	CH$_3$OH	284(23.0 × 10^3), 647(162), 1067(61)

The electronic spectra are again consistent with a square-pyramidal geometry (CuN$_4$O) around the copper (Table 2). The crystal structure determinations of **3** and **4** confirm this. The N-bound NCS$^-$ ligand occupies a coordination site in the basal plane.

In an attempt to recrystallize complexes **5** and **7** from a methanol/water mixture (1:1) at ambient temperature in an open vessel, two new solid materials of different composition were obtained, namely the tetranuclear species [L$_4$Cu$_4$(H$_2$O)$_2$(μ-tetrafluoroterephthalato)$_3$](ClO$_4$)$_2$·6H$_2$O (**6**) and the polymeric species [LCu(μ-biphenyl-4,4'-dicarboxylato)(H$_2$O)$_2$]$_n$ (**8**). While the structure of **6** has been determined by X-ray crystallography it has not been possible to grow single crystals of **8**. From the infrared spectrum of **8** it clearly follows that the carboxylate groups are coordinated in a monodentate fashion. We propose a polymeric structure in analogy to the structure of **6** where each copper ion is coordinated to a cyclic triamine and two monodentate carboxylato groups *cis* to each other. This renders the copper ions five-coordinate (square-pyramidal) if the water molecules are not coordinated.

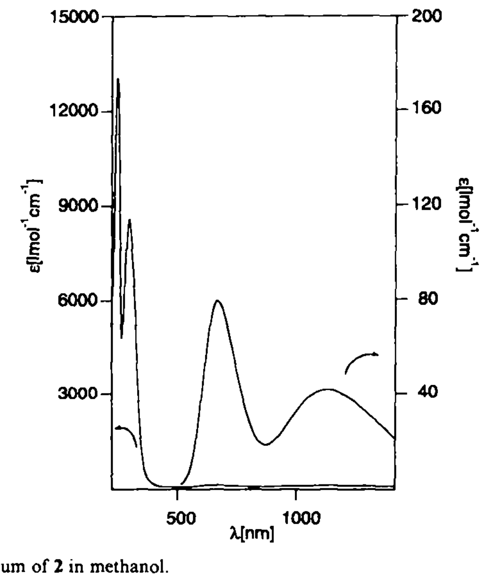


Fig. 2. UV/Vis spectrum of **2** in methanol.

This synthetic result demonstrates the difficulty in obtaining pure samples of the dinuclear species. The most probable contaminants of these complexes are oligomeric or even polymeric species.

Crystal Structures: Table 3 summarizes selected bond lengths and angles of crystal structures of **1**, **2**, **3**, **4**, and **6**.

It is very important to obtain a clear picture of the packing of the dications and the perchlorate anions in crystals of **1** if one wishes to assess the magnetic exchange pathways in **1**. Figure 3 shows the packing of these ions in the solid state. Clearly, the ion clusters {[{LCu(OH$_2$)}$_2$(μ-terephthalato)](ClO$_4$)$_2$} are packed

Table 3. Selected bond lengths (Å) and angles (°) of complexes.

Complex **2**:					
Cu1–N1	2.046(7)	O1–C1	1.268(12)		
Cu1–N2	2.198(7)	O2–C1	1.230(13)		
Cu1–N3	2.062(7)				
Cu1–O1	1.967(6)				
Cu1–O3	2.000(6)				
N1–Cu1–N2	84.9(3)	N1–Cu1–N3	84.7(3)	N2–Cu1–N3	83.8(3)
N1–Cu1–O1	90.3(3)	N2–Cu1–O1	97.3(3)	N3–Cu1–O1	174.8(3)
N1–Cu1–O3	168.0(3)	N2–Cu1–O3	106.8(3)	N3–Cu1–O3	93.8(3)
O1–Cu1–O3	90.7(3)				
Complex **3**:					
Cu1–O1	1.962(3)	S1–C14	1.613(4)		
Cu1–N4	1.960(3)	O2–C10	1.233(3)		
Cu1–N1	2.242(4)	N4–C14	1.157(5)		
Cu1–N2	2.075(3)	O1–C10	1.271(5)		
Cu1–N3	2.082(3)				
N4–Cu1–O1	92.4(1)	N2–Cu1–O1	91.4(1)	N3–Cu1–O1	172.5(1)
N1–Cu1–O1	91.2(1)	N2–Cu1–N4	168.9(1)	N3–Cu1–N4	93.3(1)
N1–Cu1–N4	107.0(1)	N2–Cu1–N1	83.3(1)	N3–Cu1–N1	82.4(1)
Cu1–N4–C14	167.6(3)	N4–C14–S1	178.2(4)	N3–Cu1–N2	83.9(1)
Complex **4**:					
Cu1–N1	1.957(8)	Cu2–N5	1.958(7)		
Cu1–N2	2.232(7)	Cu2–N6	2.082(6)		
Cu1–N3	2.070(7)	Cu2–N7	2.082(7)		
Cu1–N4	2.072(8)	Cu2–N8	2.258(6)		
Cu1–O1	1.934(5)	Cu2–O4	1.952(6)		
N1–Cu1–N2	104.1(3)	N1–Cu1–N3	93.6(3)		
N2–Cu1–N3	82.7(3)	N1–Cu1–N4	172.1(3)		
N2–Cu1–N4	83.3(3)	N3–Cu1–N4	84.4(3)		
N1–Cu1–O1	92.5(3)	N2–Cu1–O1	93.2(2)		
N3–Cu1–O1	173.4(3)	N4–Cu1–O1	89.9(3)		
N5–Cu2–N6	176.5(3)	N5–Cu2–N7	93.3(3)		
N6–Cu2–N7	84.0(3)	N5–Cu2–N8	99.2(3)		
N6–Cu2–N8	82.7(2)	N7–Cu2–N8	82.4(3)		
N5–Cu2–O4	91.4(3)	N6–Cu2–O4	91.4(2)		
N7–Cu2–O4	174.3(2)	N8–Cu2–O4	93.7(2)		
Complex **6**:					
Cu1–N1	2.056(4)	Cu2–N4	2.087(5)		
Cu1–N2	2.271(5)	Cu2–N5	2.244(4)		
Cu1–N3	2.059(4)	Cu2–N6	2.059(4)		
Cu1–O_w1	2.019(4)	Cu2–O3	1.954(3)		
Cu1–O1	1.970(3)	Cu2–O5	1.994(4)		
N1–Cu1–N2	83.1(2)	N1–Cu1–N3	85.7(2)		
N2–Cu1–N3	83.8(2)	N1–Cu1–O1	176.4(2)		
N2–Cu1–O1	93.5(1)	N3–Cu1–O1	92.7(1)		
N1–Cu1–O_w1	94.5(2)	N2–Cu1–O_w1	101.7(2)		
N3–Cu1–O_w1	174.4(2)	O1–Cu1–O_w1	87.4(1)		
N4–Cu2–N5	83.0(2)	N4–Cu2–N6	85.2(2)		
N5–Cu2–N6	83.9(2)	N4–Cu2–O3	91.8(2)		
N5–Cu2–O3	93.2(1)	N6–Cu2–O3	176.0(2)		
N4–Cu2–O5	175.0(1)	N5–Cu2–O5	101.7(2)		
N6–Cu2–O5	93.6(2)	O3–Cu2–O5	89.6(1)		

in such a fashion that each five-coordinate (square-pyramidal) copper(II) ion interacts very weakly with one oxygen atom of a perchlorate anion (Cu ··· $OClO_3$ = 2.992(6) Å), giving rise to a very distorted octahedral ligand environment at the Cu^{II} ions. It is noteworthy that, in contrast to the statement made in ref. [20], the ClO_4 ions in **1** are *not* bridging didentate but—at most—monodentate ligands. The clusters are then packed without formation of any significant hydrogen bonding contacts between clusters. Therefore, despite the existence of a relatively short *inter*molecular Cu ··· Cu distance of 7.587(1) Å, there is no favorable superexchange pathway between these dinuclear units.

Figure 4 shows two {$[LCu(OH_2)(benzoato)](ClO_4)$} ion pairs in crystals of **2**. The geometrical and metrical details of the

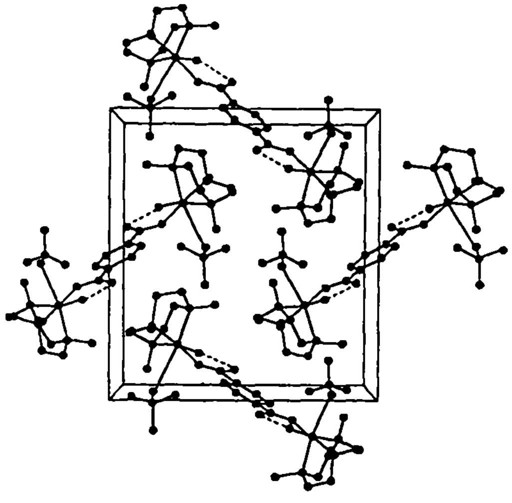


Fig. 3. Packing of dications and anions in crystals of **1** (ref. [15]).

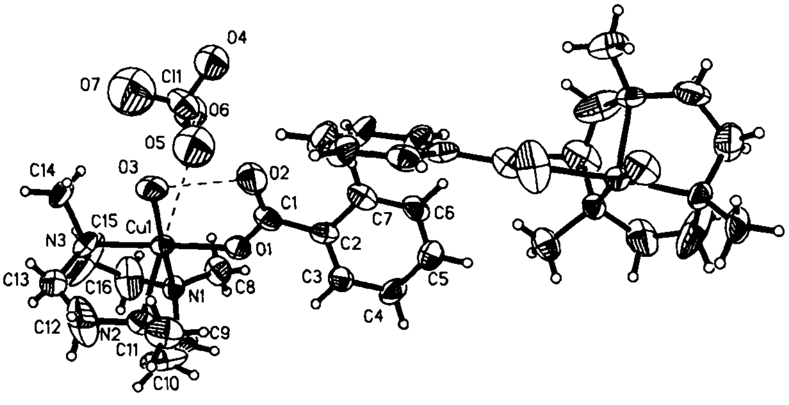


Fig. 4. Structure of an ion pair $[LCu(OH_2)(benzoato)](ClO_4)$ and its packing relative to a second pair in crystals of **2**. The broken lines indicate the weak interaction between the Cu^{II} ion and the ClO_4^- anion, and the intramolecular hydrogen bond between the coordinated water molecule and the carbonyl oxygen atom of the coordinated carboxylate.

$[LCu(OH_2)(carboxylato)]^+$ entity are, within experimental error, the same as for **1**. Thus, the Cu^{II} ion is five coordinate with two N_{amine} atoms, an oxygen atom of the carboxylato group, and a coordinated water molecule in the basal plane, and one apical N_{amine} donor atom. There is a strong intramolecular O–H ··· O bond between the water molecule and the carbonyl oxygen atom (O(2) ··· O(3) = 2.518(3) Å); the plane of the carboxylate group is nearly coplanar with the phenyl ring ($\theta = 11.3°$) and also nearly coplanar with the basal plane of the copper coordination square pyramid ($\theta = 15.4°$). The perchlorate anions may again be envisaged as monodentate O-bound ligands although the Cu ··· $OClO_3$ bond is extremely weak, at 3.348(3) Å, and the ClO_4 anion is disordered. Two $[LCu(OH_2)(benzoato)]^+$ cations are packed by a stacking interaction of two phenyl groups. The respective planes are not coplanar but tilted relative to each other. The shortest *inter*molecular Cu ··· Cu distance is at 7.231(2) Å. As in **1** there is no significant intermolecular hydrogen bonding between the cations (or anions) in **2**.

Figure 5 depicts a neutral molecule $[\{LCu(NCS)\}_2(\mu\text{-terephthalato})]$ in crystals of **3**; the molecule possesses crystallographic C_i symmetry. The copper(II) ions again have a square-pyramidal ligand environment comprising two N_{amine} atoms, one N-bound thiocyanate, and an oxygen atom of the coordinated carboxylate group in the basal plane, and one apical N_{amine} donor atom.

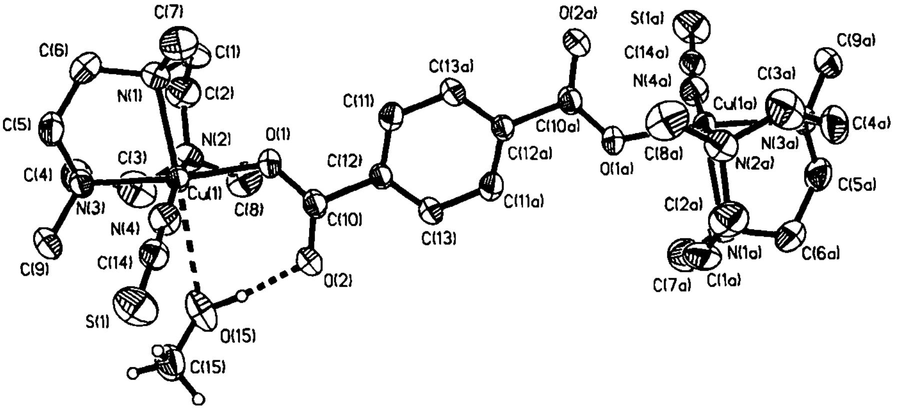


Fig. 5. Structure of the neutral molecule $[\{LCu(NCS)\}_2(\mu\text{-terephthalato})]\cdot 2CH_3OH$ in crystals of **3**. The broken lines indicate the weak interaction between the Cu^{II} ions and the oxygen atom of one methanol molecule which forms a hydrogen bonding contact $O-H\cdots O$ to the carbonyl oxygen of the coordinated carboxylate (the second MeOH molecule at Cu(1 a) is omitted for clarity).

The sixth coordination site of the copper(II) is occupied by the oxygen atom of the methanol molecule of crystallization. The $Cu\cdots O_{methanol}$ distance is 2.968(3) Å, which indicates a very weak bond; the hydroxyl group of this CH_3OH molecule forms an intramolecular $O-H\cdots O$ contact with the carbonyl oxygen of the carboxylate group ($O(15)\cdots O(2) = 2.665(3)$ Å). The $Cu-N_{amine}$ bonds are very similar to those in **1** and **2** where the apical bond is longer than the two corresponding basal ones ($(Cu-N^{amine}_{apical})-(Cu-N^{amine}_{basal}) = 0.164$ Å). The $Cu-N_{NCS}$ bond is rather short at 1.960(3) Å, whereas the $Cu\text{-}O_{carboxylate}$ bond is in the same range as in all other structures reported here. Note that the two carboxylate groups of the bridging terephthalato ligand and the phenyl ring are tilted by 18.4°; the basal planes of the square-pyramidal polyhedra around the copper ions are both nearly *perpendicular* to the carboxylato plane ($\theta = 80.5°$). No intermolecular hydrogen bonding contacts are observed in the packing of the neutral molecules in **3**. The intramolecular $Cu\cdots Cu$ distance is very similar to that in **1**, at 11.195 Å, and the shortest intermolecular $Cu\cdots Cu$ distance is 7.956(2) Å.

The ligand environment of the copper ions in the dinuclear neutral molecule in crystals of **4** is identical to the one described above for **3**, as are the geometrical and metrical details of the square-pyramidal polyhedron (Fig. 6). As in **3**, the two copper(II) ions form a very weak bond to the oxygen atoms of two of the methanol molecules of crystallization ($Cu(1)\cdots O_{M1} = 3.029(6)$ and $Cu(2)-O_{M2} = 2.689(6)$ Å) giving rise to a very distorted octahedral (5+1) ligand environment. The planes of the two phenyl rings of the 4,4'-oxybisbenzoato bridging ligands are tilted and the basal planes of the square pyramids are nearly perpendicular with respect to the benzoato part of this bridge. Both carbonyl oxygen atoms of the carboxylates form an intramolecular hydrogen bond to the "coordinated" methanol molecule of crystallization ($O(2)\cdots O_{M1} = 2.645(7)$ and $O(5)\cdots O_{M2} = 2.639(7)$ Å). The intramolecular $Cu\cdots Cu$ separation is 13.72 Å.

Figure 7 shows the structure of the tetranuclear dication in crystals of **6**. Four copper ions are bridged by the monodentate carboxylate groups of three tetrafluoroterephthalate ligands. In the solid state the cation possesses a crystallographic center of symmetry and adopts the conformation of a zigzag chain. The two identical terminal copper ions have a square-pyramidal ligand environment composed of a cyclic triamine, one coordinated water molecule, and one oxygen atom of a carboxylate group as in

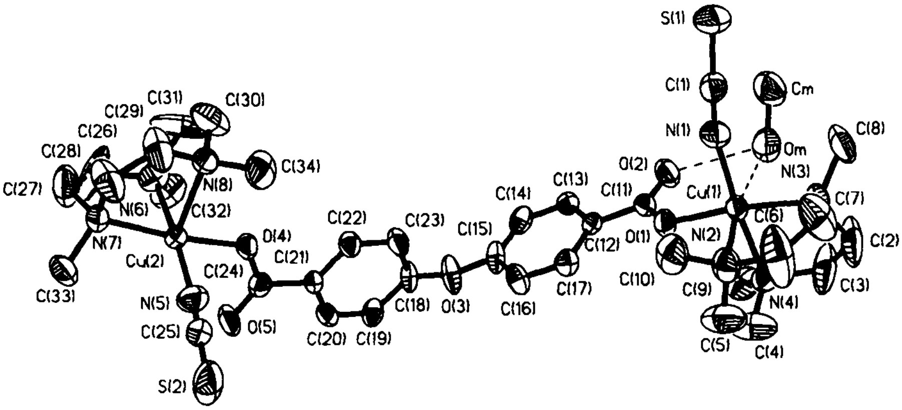


Fig. 6. Structure of the neutral molecule $[\{LCu(NCS)\}_2(\mu\text{-}4,4'\text{-oxybisbenzoato})]\cdot 2CH_3OH$ in crystals of **4**. The bonding interaction of only one methanol molecule at Cu(1) is shown. At Cu(2) the same coordination environment as at Cu(1) prevails; the MeOH molecule is omitted for clarity.

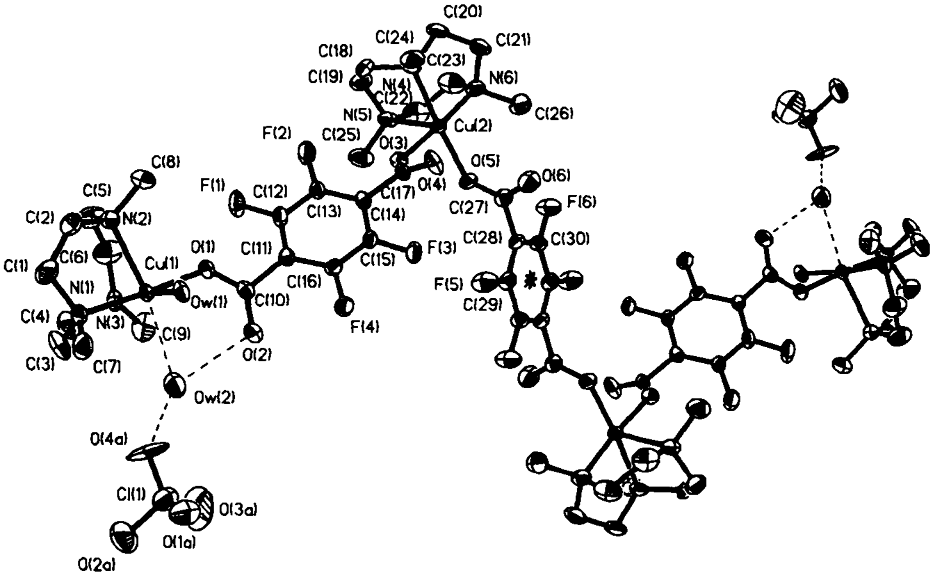


Fig. 7. Structure of the tetranuclear dication in crystals of **6**. The asterisk denotes a crystallographic center of symmetry. The broken lines indicate $O-H\cdots O$ hydrogen bonds between a water molecule ($O_w(2)$) and a ClO_4^- anion and a weak $Cu\cdots OH_2$ interaction.

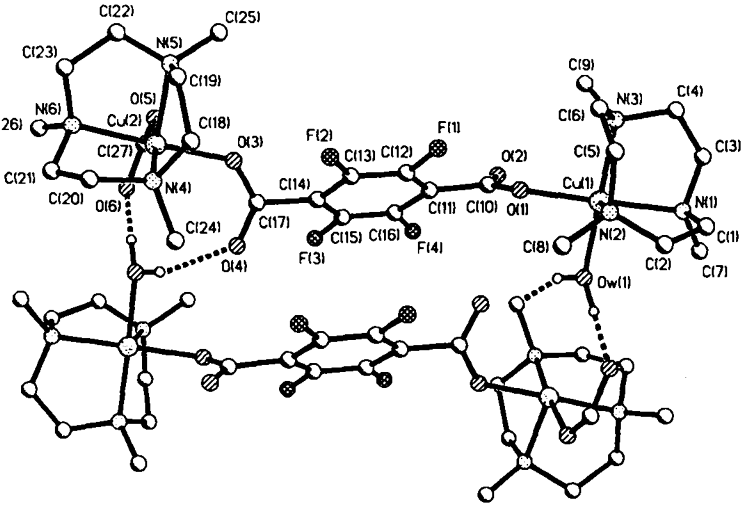


Fig. 8. Schematic representation of the intermolecular hydrogen bonding between two halves of two different dications in crystals of **6**. (Hatched circles represent oxygen atoms, cross-hatched circles are fluorine atoms, small dotted circles represent nitrogen atoms, and open circles are carbon atoms.)

1 and **2**. An interesting structural difference exists. The coordinated water molecules are not involved in *intramolecular* hydrogen bonding to the carbonyl oxygens of the coordinated carboxylate but each form two *intermolecular* O–H···O contacts to the carbonyl oxygens of the central copper ions of a second tetranuclear dication (Fig. 8) ($O_w(1)\cdots O(6) = 2.649(4)$; $O_w(1)\cdots O(4) = 2.679(5)$ Å). These two inner copper ions are also bound to a cyclic triamine. They do not bind to water but, instead, to two monodentate carboxylate groups that give rise to a square-pyramidal polyhedron around these copper ions. This leads to a situation where the carboxylate groups are not coplanar with the respective tetrafluorophenyl rings and, furthermore, the basal planes of the two terminal and of the two inner square pyramids are also not coplanar with the planes defined by the three atoms of the coordinated carboxylates. Thus, the crystal structure of **6** represents the only example of the present series where in the solid state *intermolecular* hydrogen bonding is unequivocally present. This packing leads to a quite short intermolecular Cu···Cu distance of 5.515(2) Å whereas the corresponding intramolecular distances are $Cu(1)\cdots Cu(2) = 11.018(2)$ and $Cu(2)\cdots Cu(2a) = 11.321(2)$ Å.

It should be noted that the two terminal copper ions (Cu(1)) adopt a 5 + 1 coordination sphere where the sixth coordination site is occupied by a loosely bound water molecule ($Cu(1)\cdots O_w(2) = 2.671(5)$ Å) whereas the inner copper ions remain essentially five-coordinate. This water molecule bound loosely to Cu(1) forms two O–H···O hydrogen-bonding contacts to a carbonyl oxygen ($O_w(2)\cdots O(2) = 2.763(4)$ Å) and a ClO_4^- anion ($O_w(2)\cdots O(4a) = 2.990(5)$ Å). Only the oxygen atom of a carbonyl group of a carboxylate is in the vicinity of the Cu(2) with a Cu(2)–O(6) distance of 3.273(5) Å, but it is not *trans* to the apical nitrogen atom of the square pyramid. The ClO_4^- anions are also not coordinated to copper(II).

The water molecules of crystallization $O_w(3)$ and $O_w(4)$ form an interesting O–H···O hydrogen-bonding network with the perchlorate anions and carbonyl oxygens of the carboxylate groups (Fig. 9). Four water molecules form a nearly perfect square, where two opposing water molecules each bind to one ClO_4^- anion and the other two bind to carbonyl oxygen atoms O(2).

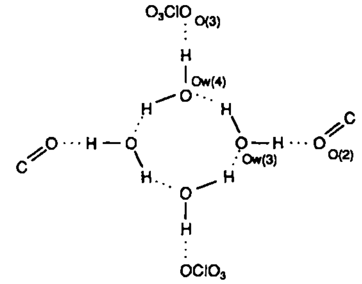


Fig. 9. Hydrogen bonding scheme of the ClO_4^- anions and water molecules of crystallization ($O_w(3)$ and $O_w(4)$) in crystals of **6**. O(2) is a carbonyl oxygen atom. Distances: $O_w(3)\cdots 0(2) = 2.855$; $O_w(3a)\cdots O_w(4) = 2.865$; $O_w(3)\cdots O_w(4) = 2.843$; $O_w(4)\cdots O(3a) = 2.786$ Å.

Magnetic Susceptibility: Variable-temperature magnetic susceptibility data for complexes **1**–**10** were measured between 2.0 and 298 K by using a Faraday balance or a SQUID magnetometer. The magnetic parameters were estimated

Table 4. X-ray structure determination data of complexes.

	2	**3**	**4**	**6**
empirical formula	$C_{16}H_{28}ClCuN_3O_7$	$C_{30}H_{54}N_8O_6S_2Cu_2$	$C_{37}H_{62}Cu_2N_8O_8S_2$	$C_{60}H_{100}Cl_2Cu_4F_{12}N_{12}O_{28}$
crystal system	orthorhombic	monoclinic	monoclinic	triclinic
space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	11.933(2)	7.956(2)	19.470(4)	10.764(2)
b (Å)	12.401(2)	14.342(5)	15.320(3)	11.980(2)
c (Å)	14.208(3)	16.654(5)	15.911(3)	16.671(3)
α (°)				79.01(3)
β (°)		93.33(2)	104.80(3)	78.57(3)
γ (°)				84.01(3)
V (Å^3)	2102.5(7)	1897.1(5)	4588.5(16)	2063.5(6)
Z	4	2	4	1
formula weight	473.4	814.0	938.1	1990.6
density (calcd.), $Mg m^{-3}$	1.496	1.42	1.36	1.60
$\mu_{MoK\alpha}$, mm^{-1}	1.208	1.28	1.07	1.19
T (K)	293	293	293	293
2θ range (°)	3.0–55.0	3.0–57.5	3.0–50.0	3.0–50.0
scan type	ω	ω	ω	ω
Observed reflections	1720 ($F > 4.0\sigma(F)$)	2893 ($I > 2.5\sigma(I)$)	4056 ($F > 4.0\sigma(F)$)	4910 ($F > 4.0\sigma(F)$)
no. of parameters	262	218	529	611
R [a]	0.060	0.049	0.060	0.048
R_w [b]	0.058	0.039	0.061	0.043
largest difference peak (eÅ^{-3})	0.50	0.35	0.46	0.61
largest difference hole (eÅ^{-3})	−0.51	−0.52	−0.46	−0.59

[a] $R = \sum||F_0| - |F_c||/\sum|F_0|$; [b] $R_w = [\sum w(|F_0| - |F_c|)^2/\sum w|F_0|^2]^{1/2}$; $w^{-1} = \sigma^2(F) + 0.0003 F^2$.

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as g_{mag} and J from a least-squares fitting of the susceptibility data to the Bleaney–Bowers equation (1) for dinuclear

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

copper(II) complexes, where $2J$ is the energy difference between the singlet and triplet states ($H = -2JS_1 \cdot S_2$; $S_1 = S_2 = {}^1/_2$) and the other constants have their usual meaning. The solid lines in Figures 10–15 represent these fits. A further parameter p, representing the percentage of a mononuclear copper(II) impurity with $S = {}^1/_2$, was introduced although the exact nature of the actual impurity (oligomer or polymer) was unknown. The variations in g_{mag} values are not significant and result from the fitting method.

Figure 10 shows the temperature dependence of the susceptibility and of the magnetic moment for dinuclear **1**. From the fit values, $g_{mag} = 2.2$, $J = -70.0\ \text{cm}^{-1}$, and $p = 2.8\%$ were calculated.[15] A substantial antiferromagnetic interaction is detected. At temperatures < 50 K the fit is not very good. This is most probably owing to the fact that the exact nature of the paramagnetic impurity and its temperature-dependent magnetism are not known. As pointed out above the impurity is most likely to be an oligomeric or polymeric species.

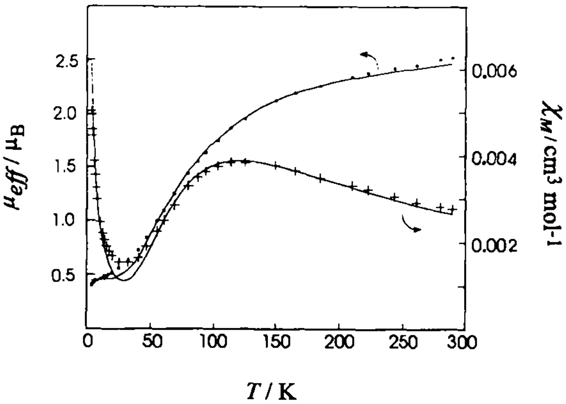


Fig. 10. Temperature dependence of the magnetic susceptibility, χ_M (+), and of the effective moment, μ_{eff}(·), of a solid sample of **1**.

In contrast to the results presented for **1**, the magnetic moment μ/μ_B for mononuclear [LCu(OH$_2$)(benzoato)](ClO$_4$) (**2**) is temperature-independent between 2 K (1.86 μ_B) and 295 K (1.89 μ_B). A fit of the susceptibility data to the Bleaney–Bowers equation (1) is possible if coupling within two [LCu(OH$_2$)(benzoato)](ClO$_4$) units is assumed, and yields values for g_{mag} of 2.16 and for J of $-0.55\ \text{cm}^{-1}$ (Fig. 11). Considering the packing in crystals of **2** this very weak antiferromagnetic interaction must be intermolecular. It should be noted that this formal fitting may not be physically meaningful. Within our experimental accuracy there appears to be no significant exchange coupling in **2**. We consider this to be an important observation because the structural similarities between **1** and **2** in the solid state are striking. It strongly suggests that the observed antiferromagnetic exchange in **1** is *intramolecular*.

This conclusion is further substantiated by the magnetism of **3**, which contains dinuclear molecules of [{LCu(NCS)}$_2$(μ-terephthalato)]·2CH$_3$OH. The magnetic moment per Cu^{II} ion varies between 2.0 μ_B at 284 K and 1.63 μ_B at 4.3 K. A fit to the Bleaney–Bowers equation (1) gives values for g_{mag} of 2.18, J of $-1.4\ \text{cm}^{-1}$, and p of 0. This small antiferromagnetic coupling may be intra- or intermolecular.

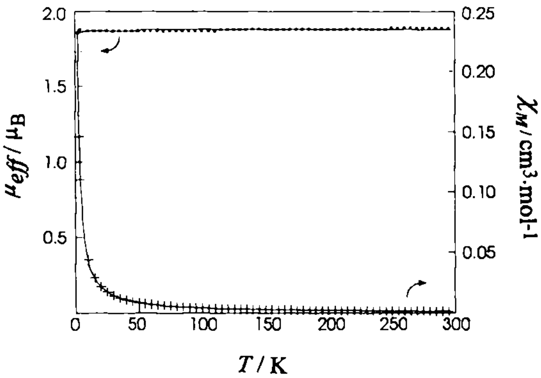


Fig. 11. Temperature dependence of χ_M (+) and μ_{eff}(·) of a solid sample of **2**.

Compound **4** also possesses a temperature-independent magnetic moment of 2.77 μ_B/dinuclear species at 295 K and 2.75 μ_B at 15 K. A fit to equation (1) produces $g_{mag} = 2.25$ and $J = -0.13\ \text{cm}^{-1}$. We conclude that no significant intramolecular exchange coupling occurs in **4**.

In complex **5** the μ-terephthalato bridge of **1** has been replaced by the μ-tetrafluoroterephthalato group. Figure 12 shows χ_M and μ_{eff} as functions of T for **5**. With decreasing temperature χ_M reaches a maximum at approximately 62 K and a minimum at approximately 15 K, beneath which temperature χ_M increases again because of the presence of a paramagnetic impurity. The maximum at 62 K is typical for an antiferromagnetic coupling of **5**. A fit to equation (1) in the temperature range 50–300 K yields numerical values of $g_{mag} = 2.22$, $J = -42\ \text{cm}^{-1}$, and $p = 0$. From this we conclude that the dications in **1** and **5** are isostructural in the solid state and that the antiferromagnetic coupling is intramolecular in both cases.

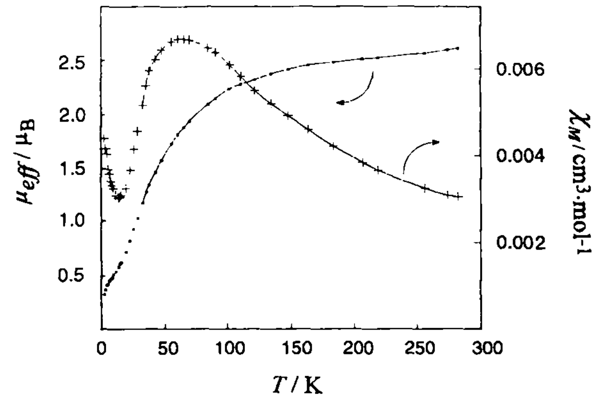


Fig. 12. Temperature dependence of χ_M (+) and μ_{eff}(·) of a solid sample of **5**. The solid line represents a fit between 50 and 300 K (see text).

Complex **5** is converted to the tetranuclear complex **6** upon recrystallization from a methanol/water mixture. Interestingly, the magnetism of **6** differs markedly from that of **5**. The magnetic moment per tetranuclear unit increases slightly with decreasing temperature from 3.49 μ_B at 295 K to 3.88 μ_B at 5 K; below 5 K the magnetic moment decreases again (Fig. 13). This behavior indicates some weak ferromagnetic coupling in **6**. If all four spins in the tetranuclear species were fully aligned, a magnetic moment of 4.90 μ_B would be expected. On the other hand, if these spins were completely uncoupled, a temperature-independent magnetic moment of 3.46 μ_B ($2\sqrt{1.73^2}$) would be observed. Although it has not been possible to find a satisfactory fit of the

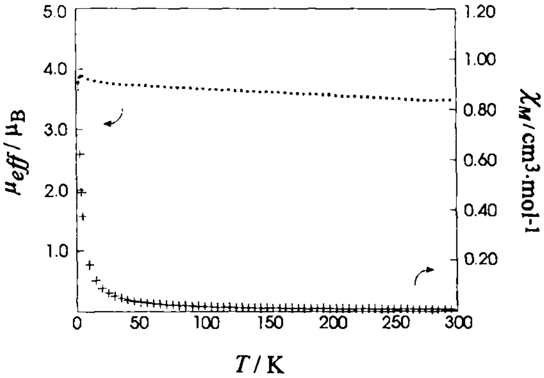


Fig. 13. Temperature dependence of χ_M (+) and $\mu_{eff}(\cdot)$ of a solid sample of **6**.

data to equation (1), it is clear that no significant intramolecular antiferromagnetic coupling exists. It is conceivable that an intermolecular ferromagnetic exchange through the intermolecular O–H ··· O hydrogen bonds (Fig. 8) exists. Similar magnetic behavior has been reported for $[Cu(en)(H_2O)_2(\mu\text{-terephthalato})]_n$, which is a polymer forming zigzag chains.[11]

In the dinuclear complex **7** the two $[LCu(H_2O)]^{2+}$ fragments are bridged by the biphenyl-4,4′-dicarboxylato ligand. Figure 14 shows a plot of χ_M vs. T and μ_{eff} vs. T. The magnetism of **7** is very similar to that of **1** and **5**; a moderately strong antiferromagnetic coupling is observed. Thus, the fit to equation (1) in the temperature range 50–295 K yields $g_{mag} = 2.12$, $J = -31$ cm^{-1}, and $p = 8.8\%$. The fit is poor due to an unknown oligomeric or polymeric impurity (see below). The magnitude of the antiferromagnetic coupling together with all the magnetic data for complexes **1**–**6** suggest that the exchange coupling in **7** is intramolecular and that the structure of **7** involves coplanar $(d_{x^2-y^2})^1$ magnetic orbitals and a planar organic spacer ligand as in **1** and, probably, **5**.

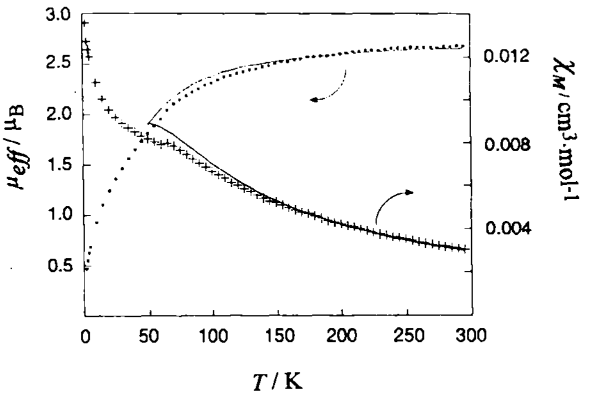


Fig. 14. Temperature dependence of χ_M (+) and $\mu_{eff}(\cdot)$ of a solid sample of **7**.

This is corroborated by the observation that the spins in polymeric **8** are essentially uncoupled. The magnetic moment/Cu^{II} ion decreases slightly with decreasing temperature from 1.95 μ_B at 295 K to 1.81 μ_B at 4 K. Substitution of the coordinated water molecules in **8** by a thiocyanato ligand in dinuclear **9** also yields an effectively uncoupled system. The magnetic moment decreases from 1.90 μ_B/Cu^{II} at 284.5 K to 1.70 μ_B at 6 K and 1.64 μ_B at 4.2 K. A very small intermolecular antiferromagnetic coupling cannot be ruled out by these data.

Finally, with a *trans,trans*-2,4-hexadiene-1,6-dicarboxylato spacer between two coordinated $[LCu(OH_2)]^{2+}$ fragments, as in **10**, an intramolecular antiferromagnetic exchange coupling is observed. The fit of the susceptibility data in Figure 15 at temperatures above 50 K yields values for g_{mag} of 2.16, for J of -50 cm^{-1}, and for p of 6.2%. Here as elsewhere the nature of the impurity is not known and, consequently, the fit below 50 K is rather poor.

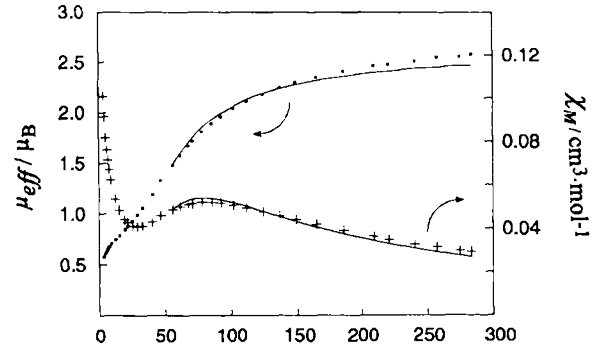


Fig. 15. Temperature dependence of χ_M (+) and $\mu_{eff}(\cdot)$ of a solid sample of **10**.

Discussion

As has been noted previously, when coordinated to a copper(II) ion, the macrocyclic ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (L) prefers to impose a slightly distorted square-pyramidal geometry around the metal ion where two additional donor atoms are bound in the basal plane.[16–19] In this and previous studies, one amine nitrogen of L occupies the apical position with a long $Cu-N_{amine}$ bond (in the range 2.20–2.27 Å) and two shorter $Cu-N_{amine}$ bonds *cis* to each other in the basal plane (2.03–2.09 Å). In addition, two coordination sites in the basal plane are occupied by i) an oxygen atom of a monodentate carboxylato group and a bound water molecule (**1**, **2**, **5**, **6**, **7**, **8**, **10**) or ii) by an N-bound thiocyanato ligand or an additional monodentate carboxylate (**3**, **4**, **9**). Two inner copper(II) ions in the tetranuclear cation in **6** also form a square-pyramidal CuN_3O_2 polyhedron in which two oxygen atoms of monodentate carboxylate groups are coordinated in the basal plane. This leads to a $(d_{x^2-y^2})^1$ electronic ground-state configuration at all the copper(II) ions in complexes **1**–**10**, which is in agreement with the electronic spectra. According to Hathaway,[22] a square-pyramidal CuX_5 chromophore gives rise to two clearly resolved d–d transitions in the visible, which is the case for complexes **1**–**10** (Table 2).

As noted above, the square-pyramidal LCu^{II}XY chromophores in complexes **1**–**10** interact very weakly with a sixth oxygen donor atom of either a ClO_4^- anion, a water molecule of crystallization, or a methanol molecule, formally giving rise to a 5 + 1 coordination (distorted octahedron), but the Cu ··· O distance is in all cases >2.7 Å. This interaction is therefore probably electrostatic rather than covalent. In the following discussion of the exchange phenomena we will consider the coordination geometry at copper(II) as square-pyramidal with a $(d_{x^2-y^2})^1$ ground state. This magnetic orbital points to the four donor atoms in the basal plane (x,y coordinates) and is ideally positioned to propagate electronic interactions between two CuX_5 chromophores of this kind through a suitable organic spacer molecule provided that favorable orbital interactions prevail.

In the following we analyze and compare complexes **1** and **2** in terms of possible inter- and intramolecular exchange coupling. It is important first to recognize the structural similarities:

1) Both **1** and **2** contain the same $[LCu(OH_2)(carboxylato)]^+$ chromophore; their metrical details are identical within experimental error (3σ). In both complexes the coordinated water molecule and the carbonyl oxygen of the carboxylato groups form a strong intramolecular O–H···O hydrogen bond that ensures the near coplanarity of the basal plane ($d_{x^2-y^2}$ orbital) and the plane defined by the three atoms of the coordinated $-CO_2^-$ group. This dihedral angle is 8.4° in **1** and 15.4° in **2**.

2) Furthermore, in both **1** and **2** the planes of these carboxylates are nearly coplanar with the phenyl rings of the terephthalato spacer in **1** and the benzoato ligand in **2**; this dihedral angle θ is 8.7° in **1** and 11.3° in **2**. Interestingly, in potassium hydrogenphthalate,[23] $C_8H_5O_4K$, the planar carboxylate groups are also tilted by 8.0° with respect to the plane of the benzene ring.

3) In both **1** and **2** the ClO_4^- anions occupy the sixth coordination site of the CuN_3O_2 chromophore (5 + 1 coordination). Thus the ClO_4^- anions are bound in a monodentate fashion (if at all); they are *not* bridging ligands.

4) The packing of the $[\{LCu(OH_2)\}_2(\mu\text{-terephthalato})](ClO_4)_2$ and $[LCu(OH_2)(benzoato)](ClO_4)$ neutral entities in the solid state is not achieved by any significant *inter*molecular hydrogen bonding contacts. It is noteworthy that the shortest nonbonding intermolecular Cu···Cu distance in **1** is 7.587 Å and in **2** is 7.231 Å. It is also worth pointing out explicitly that the two phenyl rings of a dimer $[LCu(OH_2)(benzoato)]_2(ClO_4)_2$ in **2** are directed towards each other but are not coplanar and, thus, no genuine π-stacking interaction is present in **2**.

Considering the above structural similarities between **1** and **2**, the vastly differing magnetism can reasonably be accounted for only by the fact that in **1** two $\{LCu(OH_2)(carboxylato)\}$ chromophores are covalently linked by a phenyl spacer, whereas in **2** no such covalent linkage exists. In other words, the strong antiferromagnetic coupling in **1** must be *intramolecularly* propagated over a Cu···Cu distance of 11.25 Å, as proven by the nonexistence of such an exchange interaction in **2**, because all other structural features in **1** and **2** are very similar. The structure of **2** demonstrates nicely that the lack of significant bonding interactions (intra- or intermolecular) between the centers carrying the unpaired electron leads to only very small magnetic ordering in complexes of the present type ($|J| < 2\ cm^{-1}$), if any.

The apparent importance of the coplanar assembly of the terephthalato spacer in **1** with the basal plane of the two $\{LCu(OH_2)(carboxylato)\}$ chromophores or the presence of the intramolecular O–H···O bond is demonstrated in complex **3**. In this dinuclear compound the coordinated water molecule is substituted by an N-coordinated thiocyanate. The packing of the neutral molecules in **3** and of the methanol molecules of crystallization is again not accompanied by intermolecular hydrogen bonding. Therefore, the lack of strong antiferromagnetic exchange coupling is either attributed to the unfavorable orbital overlap between the magnetic $(d_{x^2-y^2})^1$ orbitals and the relevant orbitals of organic spacer terephthalate or the lack of the intramolecular O–H···O contact or both.

Complex **4** simply underscores the point that intermolecular interactions do not provide favorable exchange pathways in the solid state.

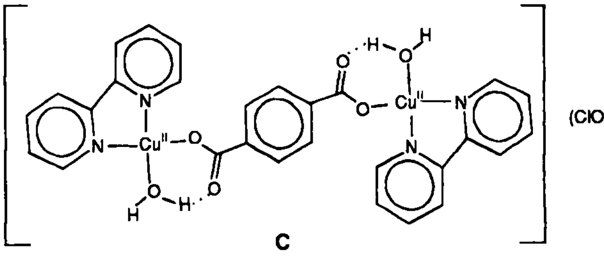
Complex **6**, which contains the tetranuclear dication $[L_4Cu_4(OH_2)_2(\mu\text{-tetrafluoroterephthalato})_3]^{2+}$, provides the first example of the present series where *inter*molecular O–H···O hydrogen bonding is present in the solid state. The coordinated water molecules of the two terminal $\{LCu(OH_2)(carboxylato)\}$ chromophores form intermolecular O–H···O bonds to the carbonyl oxygen atom of a second tetranuclear dication. We suggest that this packing scheme in solid **6** provides an intermolecular pathway for the observed weak ferromagnetic exchange interaction.[11]

At this point we may summarize the observed magnetostructural correlations as follows: The ligand L enforces a square-pyramidal coordination geometry around the copper(II) ions that yields a $(d_{x^2-y^2})^1$ magnetic orbital. A suitable organic spacer mediates intramolecular antiferromagnetic exchange coupling. In complexes of the type $[\{LCu(OH_2)\}_2(\mu\text{-dicarboxylate})](ClO_4)_2$ this is achieved by a strong intramolecular O–H···O hydrogen bond between the H_2O molecule and the carbonyl oxygen of the coordinated carboxylate. If this bond is destroyed by the introduction of another monodentate ligand X^-, the effective antiferromagnetic exchange pathway is cancelled. Intermolecular exchange pathways are weak or nonexistent if intermolecular hydrogen bonding or other covalent linkages are absent.

From this we can safely conclude that the structure of the dication in crystals of **6** is virtually identical with that of **1**, although the crystal structure has not been determined. *The observed strong antiferromagnetic coupling is only explicable if we assume the presence of the intramolecular O–H···O bond.*

Exactly the same arguments hold for complexes **7** and **10**, which contain a biphenyl-4,4'-dicarboxylato and a *trans,trans*-2,4-hexadiene-1,6-dicarboxylato bridge, respectively, between two $\{LCu(OH_2)(carboxylato)\}^+$ chromophores. Both compounds exhibit significant antiferromagnetic coupling. That this exchange interaction is intramolecular in nature is corroborated by the observation that replacement of the coordinated H_2O molecule in **7** by thiocyanate to form **9** immediately destroys this coupling. The formation of the polymer **8**, the structure of which is not known but which probably consists of zigzag chains of the type indicated in the tetranuclear species **6** (omitting the terminal $\{LCu(OH_2)(carboxylato)\}^+$ fragments), also leads to complete quenching of the antiferromagnetic pathway.

Having established that the exchange coupling in complexes **1**, **5**, **7**, and **10** is intra- rather than intermolecular, we now investigate the nature of this superexchange pathway in more detail. A number of extended Hückel molecular orbital (EHMO) calculations for dinuclear copper(II) complexes containing either bis(monodentate)- or bis(didentate)-bound terephthalato bridges have shown that the most suitable orbital pathways propagating the magnetic exchange interaction are predominantly of the σ-type.[9–12] It is dependent on the stereochemistry around the magnetic centers and binding mode of the spacer. As is clearly seen from the compilation of structural and magnetic data in Table 1, all previously investigated μ-terephthalato bridged complexes—with the notable exception of $[\{Cu(bpy)(H_2O)\}_2(\mu\text{-terephthalato})](ClO_4)_2$ (**C**)[9]—show very weak exchange coupling phenomena ($|J| \leq 2.7\ cm^{-1}$), although



C

Scheme 3. Proposed structure of $[\{Cu(bpy)(H_2O)\}_2(\mu\text{-terephthalato})](ClO_4)_2$ (**C**).

theoretical analysis of the orbital pathways clearly shows that σ-type superexchange pathways are available. From these data one must conclude that i) the $Cu-O_{carboxylato}$ bonds in complexes with monodentate or didentate coordination are rather weak, that is, the overlap integral is small, and ii) since the superexchange is of σ-type there should be no dependence of the coupling on the dihedral angle between the basal planes of the two Cu coordination polyhedra (square-pyramidal, square, or octahedral) as long as the magnetic orbitals are of the $(d_{x^2-y^2})^1$ type.

The question then arises: what makes complexes **1** and **C** so different from the other species? We conclude that the coordinated water molecule in the *cis* position relative to the bound oxygen atom of the carboxylate group is involved in the σ superexchange pathway. The strong intramolecular $O-H \cdots O$ contact facilitates the exchange coupling in a quite dramatic fashion. The proposed σ pathway is shown in Figure 16. It is important to recall that Muhonen[24] has shown for two complexes that $O-H \cdots O$ hydrogen bonding between basal oxygen atoms of two square-pyramidal copper(II) polyhedra with $(d_{x^2-y^2})^1$ magnetic orbitals leads to a significant antiferromagnetic coupling ($J = -13.5$ and -24.5 cm^{-1}). It is also noteworthy that the two basal planes in this instance are not coplanar ($\chi = 26.7$ and $80.1°$).

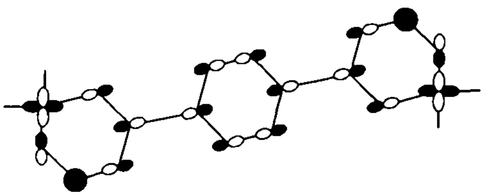


Fig. 16. Proposed σ superexchange pathway in 1.

Therefore, we conclude that the presence of a *cis*-H_2O ligand in the basal plane and the resulting intramolecular $O-H \cdots O$ contact are essential for the observed strong coupling in **1**, **5**, **7**, **10**, and in **C**, and that the coplanarity of the two basal planes is not an important feature for magnetic superexchange. On replacement of the coordinated H_2O in **1** by NCS^- to form **3**, we still have a dinuclear species which could show intramolecular antiferromagnetic coupling via σ superexchange pathway, but its strength is significantly diminished (or nonexistent) as a consequence of the absence of the *cis*-coordinated H_2O.

The same argument holds for terminal and inner copper(II) ions in **6** where the bridging terephthalato group, in theory, provides a σ superexchange pathway. Since the coordinated water molecule at the terminal Cu^{II} center forms an ineffective *inter*molecular $O-H \cdots O$ contact and the inner Cu^{II} ion lacks such a contact altogether, the absence of significant intramolecular coupling is caused by the absence of two intramolecular $O-H \cdots O$ bonds.

The isotropic interaction between two copper(II) ions is strongly intramolecularly propagated over the large distance of 11.2 Å, as is demonstrated by complexes **1** and **5**. This is in contrast to an earlier statistical analysis by Coffman and Buettner[7] who suggested the distance dependence in Equation (2), where J_{limit} is the maximum singlet–triplet

$$J_{limit}(\mathrm{cm}^{-1}) = -1.35 \times 10^7 \exp[-1.80\, r(\text{Å})] \quad (2)$$

energy gap at a given distance r between the two paramagnetic centers. At $r = 11.25$ Å the calculated J_{limit} is -0.02 cm^{-1}, which is smaller by nearly four orders of magnitude than the experimental value of -140 cm^{-1}. Recently, Erasmus and Haase[20] have performed self-consistent field Möller–Plesset (SCF–MP) calculations on a series of dinuclear copper(II) complexes, including complex **1**, and have found that the calculated J values fit the limiting function Equation (2) well. In particular, the calculated J values reported for **1** are in the range -0.085 to $+0.057$ cm^{-1} depending on geometrical details. These results are at variance with experiment.

In the light of the above discussion it is therefore significant and important that strong intramolecular antiferromagnetic exchange coupling in complex **7** has been observed. The intramolecular $Cu \cdots Cu$ distance in this compound has been calculated to be 15.6 Å by a molecular modeling program. For complex **10** this distance has been calculated to be 12.0 Å and again a strong antiferromagnetic interaction is observed. These results demonstrate that, provided that a suitable superexchange pathway is available, even at a separation between the two interacting magnetic centers of 15.6 Å, a limiting distance—if it exists at all—has not been reached.

Finally, we note that the antiferromagnetic coupling in $[\{Cu^{II}(bpy)(H_2O)\}_2(\mu\text{-terephthalato})](ClO_4)_2$ (**C**)[9] with a singlet–triplet gap of 51.8 cm^{-1} may be intramolecular in nature, if the structure of the dinuclear species is as depicted in Scheme 3. Two square-pyramidal Cu^{II} polyhedra with a $(d_{x^2-y^2})^1$ magnetic orbital are then bridged in exactly the same fashion as in **1**. It would be highly desirable to determine the crystal structure of this compound but, like the original authors, we have not succeeded in growing suitable single crystals. However, the reported physical data (IR, UV/Vis, and ESR spectra) do not rule out this structure.

Experimental Section

Preparation of Complexes: The synthesis of $[\{LCu(OH_2)\}_2(\mu\text{-terephthalato})]X_2$ ($X = ClO_4$ (**1a**), PF_6 (**1b**)), where L represents 1,4,7-trimethyl-1,4,7-triazacyclononane, has been described previously [15]. The dicarboxylato ligands were introduced by using the following solution (if not stated otherwise): the dicarboxylic acid (0.25 mmol) was dissolved in piperidine (0.50 mmol) and methanol (10 mL) while heated.

$[LCu(OH_2)(benzoato)](ClO_4)$ (2): A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.38 g; 1.0 mmol), the macrocycle L (0.19 g; 1.10 mmol), and sodium benzoate (0.15 g; 1.0 mmol) in methanol (30 mL) was heated under reflux for 30 min until a clear blue solution was obtained and left to stand in an open vessel; blue crystals precipitated within 2–3 days. These crystals were suitable for X-ray crystallography. Yield: 0.32 g (68%). Anal calcd. for $C_{16}H_{28}N_3O_7ClCu$: C, 40.6; H, 6.0; N, 8.9; found: C, 40.5; H, 5.9; N, 8.9. IR (KBr disc): $\tilde{\nu} = 3392$ (b) (H_2O), $\tilde{\nu} = 1550$ (C=O), $\tilde{\nu} = 1391$ cm^{-1} (C–O).

$[\{LCu(NCS)\}_2(\mu\text{-terephthalato})] \cdot 2CH_3OH$ (3): To a solution of $Cu(CH_3CO_2)_2 \cdot H_2O$ (0.10 g; 0.50 mmol) and L (0.10 g; 0.58 mmol) in methanol (20 mL) was added the above piperidinium terephthalate solution (1 mL). To the resulting blue solution was added a solution of NaSCN (0.04 g; 0.49 mmol) in methanol (10 mL) whereupon the color changed to bluish-green. From this solution blue crystals precipitated within 24 h in an open vessel at room temperature; they proved to be suitable for X-ray crystallography. These crystals slowly lose methanol of crystallization at ambient temperature and become turbid. Yield: 0.36 g (88%). Anal calcd. for $C_{30}H_{54}N_8O_6S_2Cu_2$: C, 44.3; H, 6.7; N, 13.8; Cu, 15.6; found: C, 44.3; H, 6.4; N, 14.0; Cu, 15.9. IR (KBr): $\tilde{\nu} = 1596$ (C=O), $\tilde{\nu} = 1363$ (C–O), $\tilde{\nu} = 2092$ cm^{-1} (SCN).

$[\{LCu(NCS)\}_2(\mu\text{-4,4'-oxybisbenzoato})] \cdot 3CH_3OH$ (4): This complex was prepared completely analogously to the preparation of **3** by using a methanolic solution of piperidinium 4,4'-oxybisbenzoate. Yield: 0.53 g (56%). Anal calcd. for $C_{37}H_{62}N_8O_8S_2Cu_2$: C, 47.4; H, 6.7; N, 11.9; found: C, 47.4; H, 6.2; N, 11.9. IR (KBr): $\tilde{\nu} = 1604$ (C=O), $\tilde{\nu} = 1376$ (C–O), $\tilde{\nu} = 2094$ cm^{-1} (NCS).

$[\{LCu(OH_2)\}_2(\mu\text{-tetrafluoroterephthalato})](ClO_4)_2$ (5): To a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.19 g; 0.51 mmol) and L (0.10 g; 0.58 mmol) in methanol (30 mL) was added a methanolic 0.25 M solution of piperidinium tetrafluoroterephthalate (10 mL). Upon standing in an open vessel at ambient temperature for 24 h bluish-green, needle-shaped crystals precipitated. Yield: 0.33 g (69%). Anal calcd. for

$C_{26}H_{46}N_6O_{14}F_4Cl_2Cu_2$: C, 33.2; H, 4.9; N, 8.9; found: C, 32.8; H, 5.2; N, 9.2. IR (KBr): $\tilde{\nu}$ = 1635 (C=O), $\tilde{\nu}$ = 1412 cm^{-1} (C–O).

[L$_4$Cu$_4$(H$_2$O)$_2$(μ-tetrafluoroterephthalato)$_3$](ClO$_4$)$_2$·6H$_2$O (6): A solution of **5** (0.5 mmol) in methanol/water (1:1) mixture (30 mL) was allowed to stand in an open vessel for 3–4 d after which time blue microcrystals had precipitated; these were collected by filtration. Yield: 0.6 g (60%). Anal calcd. for $C_{60}H_{100}N_{12}O_{28}F_{12}Cl_2Cu_4$: C, 36.2; H, 5.1; N, 8.4; found: C, 36.4; H, 5.2; N, 8.5. IR (KBr): $\tilde{\nu}$ = 1656 (C=O), 1631; $\tilde{\nu}$ = 1395, 1376 cm^{-1} (C–O).

[{LCu(OH$_2$)}$_2$(μ-biphenyl-4,4′-dicarboxylato)](ClO$_4$)$_2$·3H$_2$O (7): To a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.19 g; 0.5 mmol) and L (0.10 g; 0.58 mmol) in methanol (30 mL) was added a methanolic solution (1.0 mL) of piperidinium biphenyl-4,4′-dicarboxylate (0.25 M). When this was left to stand in an open vessel for 24 h, blue-green, needle-shaped crystals precipitated. Yield: 0.34 g (71%). Anal calcd. for $C_{32}H_{60}N_6O_{17}Cl_2Cu_2$: C, 38.5; H, 6.0; N, 8.4; found: C, 38.2; H, 6.0; N, 9.0. IR (KBr): $\tilde{\nu}$ = 1595 (C=O), $\tilde{\nu}$ = 1394 cm^{-1} (C–O).

[LCu(μ-biphenyl-4,4′-dicarboxylato)(OH$_2$)$_4$]$_n$ (8): From a clear blue solution of **7** (0.30 g) in a water/methanol mixture (1:1) blue, needle-shaped crystals precipitated slowly upon reducing the volume at ambient temperature. Anal calcd. for $C_{23}H_{37}O_8N_3Cu$: C, 50.5; H, 6.8; N, 7.7; found: C, 50.1; H, 6.4; N, 7.5. IR (KBr): $\tilde{\nu}$ = 1597 (C=O), $\tilde{\nu}$ = 1392 cm^{-1} (C–O).

[{LCu(NCS)}$_2$(μ-biphenyl-4,4′-dicarboxylato)]·2CH$_3$OH (9): The compound was prepared analogously to complex **3**. Blue, needle-shaped crystals. Yield: 0.36 g (82%). Anal calcd. for $C_{36}H_{58}N_8O_6S_2Cu_2$: C, 48.6; H, 6.6; N, 12.6; found: C, 48.3; H, 6.4; N, 13.0. IR (KBr): $\tilde{\nu}$ = 1610 (C=O), $\tilde{\nu}$ = 1366 (C–O), $\tilde{\nu}$ = 2093 cm^{-1} (NCS).

[{LCu(OH$_2$)}$_2$(μ-trans,trans-2,4-hexadiene-1,6-dicarboxylato)](ClO$_4$)$_2$ (10): This compound was prepared analogously to complexes **5** and **7** by using a methanolic solution of piperidinium 2,4-hexadiene-1,6-dicarboxylate. Bluish-green crystals. Yield: 0.26 g (60%). Anal calcd. for $C_{24}H_{50}N_6O_{14}Cl_2Cu_2$: C, 34.1; H, 6.0; N, 10.0; found: C, 33.8; H, 5.9; N, 10.2. IR (KBr): $\tilde{\nu}$ = 1570 (C=O); $\tilde{\nu}$ = 1380 cm^{-1} (C–O).

Physical Measurements: Temperature-dependent magnetic susceptibility measurements on powdered solid samples were carried out on a Faraday balance (**1**, **5**) or a SQUID magnetometer (Quantum Design) (**2**, **3**, **4**, **6**, **7**, **8**, **9**, **10**) over the temperature range 2.0–293 K. The observed susceptibility data were corrected for underlying diamagnetism by using Pascal's constants and for temperature-independent paramagnetism (60×10^{-6} cm^{3}mol^{-1} per Cu^{II}) which yielded χ_M. The electronic spectra were recorded in solution and the solid state (reflectance spectra) on a Perkin–Elmer Lambda 9 UV/Vis–NIR spectrophotometer over the range 210–1400 nm. Infrared spectra were measured with KBr disks on a Perkin–Elmer FT-IR 1720X spectrometer.

Crystal Structure Determinations: Intensity data and lattice parameters of single crystals of **2**, **3**, **4**, and **6** were measured at 293 K on a Siemens P4 diffractometer by using graphite-monochromated Mo$_{K\alpha}$ X-rays (λ = 0.71073 Å). Table 4 summarizes the crystallographic data. Intensity data were corrected for Lorentz, polarization, and absorption effects (ψ scans) in the usual manner. The structures were solved by direct methods by using the SHELXTL-PLUS programme package [25]. The function minimized during full-matrix least-squares refinement was $\sum w(|F_0|-|F_c|)^2$; neutral atom scattering factors and anomalous dispersion corrections for nonhydrogen atoms were taken from ref. 26. The positions of hydrogen atoms bound to carbon atoms were calculated and included with fixed isotropic thermal parameters. The hydrogen atoms bound to oxygen atoms of CH_3OH or H_2O were located in the final difference Fourier map. These were included in fixed positions in the last refinement cycle. Further details of the crystal structure investigation (including tables of atom coordinates, bond lengths and angles, anisotropic thermal parameters, calculated positions of hydrogen atoms, and structure factor tables ($F_{\rm obs}$, $F_{\rm calc}$)) may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-58967.

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