

Linkage isomerism of two benzoato–copper(I) complexes containing bis(diphenylphosphino)methane bridging ligands. Crystal structures, TSDC measurements and reactivities of $[\text{Cu}_2(\mu\text{-dppm})_2(\text{O}_2\text{CPh})_2]$ and $[\text{Cu}_2(\mu\text{-dppm})_2(\text{O}_2\text{CPh})(\mu\text{-O}_2\text{CPh})] \cdot \text{H}_2\text{O}$

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Abstract

Here we report the molecular structures and reactivities of the two complexes $[\{\text{Cu}(\text{O}_2\text{CPh})\text{dppm}\}_2]$ (**A**) and $[\{\text{Cu}(\text{O}_2\text{CPh})\text{dppm}\}_2] \cdot \text{H}_2\text{O}$ (**B**), containing isomeric dibenzoato copper(I) moieties doubly bridged by dppm ligands (dppm = bis(diphenylphosphino)methane). In the isomeric unit $[\{\text{Cu}(\text{O}_2\text{CPh})\text{dppm}\}_2]$ of **B**, the two metal atoms are also bridged by one of the two benzoato ligands and a significant shortening of the transannular Cu...Cu distance (2.994(2) Å in **B** versus 3.359(2) Å in **A**) is observed. The eight-membered $\text{Cu}_2\text{P}_4\text{C}_2$ ring adopts an approximate chair conformation in **A** and a saddle conformation in **B**. The structures of **A** and **B** have been determined by single crystal X-ray diffraction method. The crystals of **A** are triclinic, space group $P\bar{1}$, with $Z=1$ in a unit cell of dimensions $a=11.841(2)$, $b=11.366(2)$, $c=10.769(2)$ Å, $\alpha=100.68(2)$, $\beta=101.45(2)$ and $\gamma=93.37(2)^\circ$. The crystals of **B** are monoclinic, space group $P2_1/a$, with $Z=4$ in a unit cell of dimensions $a=21.295(3)$, $b=13.295(2)$, $c=22.068(3)$ Å and $\beta=114.72(2)^\circ$. Final R was 0.032 (2553 reflections) for **A** and 0.058 (3909 reflections) for **B**. Bulky anions react with **A** and **B** metathetically removing one of the benzoato groups or, when coordinating, both of them. The characteristics of the new anions modulate the conformation of the $\text{Cu}_2(\text{dppm})_2$ unit. Thermally stimulated depolarization current (TSDC) measurements have also been performed on **B** to study the electric polarization phenomena induced by reorientation of dipole moments of the crystallization water molecules in the temperature range $100 \leq T \leq 350$ K. The reorientation ability of the dipole water molecules is probably favoured by the dynamic disorder of the atoms, which surround the water molecules in the crystal lattice.

Introduction

Dicopper unities are of particular interest in copper(I) chemistry, having been recognized as active sites of several copper biosystems [1], in which the proximity of the two metal atoms offers an appropriate two site binding to small molecules. In synthetic chemistry, the carboxylato group was found to have a good ability to form dinuclear complexes [2, 3] with copper(I) centers in close proximity [4], highly reactive with CO [3], acetylenes [5], quinoline [4], isocyanides and azocompounds [6].

Years ago, some of us prepared a series of $[\text{Cu}(\text{O}_2\text{CAr})\text{dppm}]_2$ complexes (dppm = bis(diphenylphosphino)methane) [7]. Among these the phenyl derivative was recognized to exist in two different forms, if crystallized from toluene (**A**) or MeOH/H₂O (**B**) respectively, **B** also differing from **A** by the presence of one crystallization water molecule. Their molecular structures, herein reported, evidence a different coordination mode for one of the carboxylato groups and, consequently, a significant difference in the Cu...Cu distances. Due to the presence of bridging dppm, the sites for reactions with the molecules above cited are already blocked; bulky anions, however, metathetically remove one of the carboxylato groups and, when co-

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ordinating, both of them, maintaining the dicopper(I) unit doubly bridged by the dppm ligands.

The compounds were also characterized by means of the dielectric technique thermally stimulated depolarization current (TSDC). This technique has been employed up to now to study a variety of electric polarization phenomena in insulating materials, such as ionic crystals [8], polymers and biopolymers [9, 10], whose electronic conductivity is negligible. The dielectric processes which have been analyzed are the reorientation of ionic dipoles, the space charge and the interfacial polarization phenomena originated in heterogeneous dielectrics. In the present case, the technique is exploited to evidence polarization phenomena induced by reorientation of groups endowed with an electric dipole moment. The TSDC approach allows us to monitor the changes in the dipole concentration and/or in the environment as a consequence of specific treatments.

Experimental

The two forms of $[\text{Cu}(\text{dppm})(\text{O}_2\text{CPh})]_2$ were prepared as previously reported [7] and crystals for the X-ray diffraction analysis were grown from toluene–*n*-hexane (**A**) and methanol–water (**B**), respectively. Further reactions were carried out in deaerated solvents utilizing commercial reagents.

$[\text{Cu}_2\text{dppm}_2(\text{O}_2\text{CPh})]\text{PF}_6$

A concentrated methanol solution of NH_4PF_6 (0.090 g; 0.55 mmol) was added to a solution of 0.30 g (0.26 mmol) of **B** in 10 ml of methanol. From the clear solution light needles began to precipitate after some hours. They were filtered and washed with a little methanol. The product has no definite melting point but shows softening and gradual decomposition starting above 265 °C.

$[\text{Cu}_2\text{dppm}_2(\text{O}_2\text{CPh})]\text{BPh}_4$

A concentrated methanol solution of 0.094 g (0.275 mmol) of NaBPh_4 was slowly added to a solution of 0.30 g (0.26 mmol) of **B** in 10 ml of the same solvent. A white flocky precipitate immediately formed, was stirred for 30 min, filtered, washed thoroughly with water and methanol and dried. The yield was almost quantitative. The product was not easily recrystallizable and we were unable to obtain crystals suitable for X-ray diffraction analysis. It revealed no definite melting point, but gradual softening from about 115 to 140 °C to a viscous mass.

The same product was obtained with a double amount of NaBPh_4 or, less easily, by reacting **A** and NaBPh_4 acetone solutions.

$[\text{Cu}(\text{dppm})\text{N}_3]_n$

Two isomeric forms (I and II) of complexes with this formula were obtained. Experimental conditions for the isolation of isomer I were not well defined: it seems to be the first formed, but less stable, so that by recrystallizations it changes to isomer II.

I and II were prepared by the followings methods:

(a) A solution of 0.23 g (0.20 mmol) of **B** in 10 ml of MeOH was treated with a concentrated methanol solution of NaN_3 (0.028 g; 0.43 mmol). From the clear solution large colorless crystals precipitated after some hours. The crystals faded immediately when removed from the mother liquor. Recrystallization from CH_2Cl_2 and MeOH gave white microcrystals which when heated turned to yellow at about 235 °C and decomposed at 250–253 °C with gas evolution.

(b) A solution of **A** (0.23 g, 0.20 mmol) in CH_2Cl_2 was allowed to react under stirring with an excess of finely powdered NaN_3 for one day. After evaporation to dryness, the residue was thoroughly washed with water.

(c) An acetone solution of $[\text{Cu}_2\text{dppm}_2(\text{O}_2\text{CPh})]\text{BPh}_4$ was treated with an excess of NaN_3 .

$[\text{Cu}_2\text{dppm}_2(\text{N}_3)\{\text{SCN}\}^*]$

(a) 0.06 g (0.6 mequiv.) of KSCN in 5 ml of MeOH were added to a saturated methanol solution of 0.20 g of $[\text{Cu}(\text{dppm})(\text{N}_3)]_n$ (0.41 (mequiv.)). After a few minutes, a white solid began to precipitate. It was filtered off, washed repeatedly with MeOH and dried. The powder darkened progressively when heated above 220 °C and decomposed with gas evolution at about 240 °C.

The product obtained from the same reaction in acetone was mainly the $[\text{Cu}(\text{dppm})\{\text{SCN}\}]_n$ complex.

(b) The mixed complex was also obtained by starting with $[\text{Cu}(\text{dppm})\{\text{SCN}\}]_n$ and NaN_3 excess in MeOH.

$[\text{Cu}(\text{dppm})\{\text{SCN}\}]_n$

(III) A solution of 0.045 (0.46 mmol) of KSCN in acetone was added to a suspension of 0.2 g (0.17 mmol) of **A** in the same solvent and stirred for a day. The white solid, filtered off, was washed with water and acetone. The dried powder melted between 208 and 218 °C to a pale yellow glassy mass.

The same product was obtained from $[\text{Cu}_2\text{dppm}_2(\text{O}_2\text{CPh})]\text{BPh}_4$ and KSCN in acetone.

(IV) Solutions of 0.25 g (0.22 mmol) of **B** and 0.10 g (1.0 mmol) of KSCN in MeOH were mixed under stirring. The white precipitate, that immediately formed, was filtered after an additional 15 min, washed repeatedly with methanol and dried. When heated, the product melted, in part, at about 180 °C, then gave

*{SCN} denotes a group for which the point of attachment of the ligand to the metal(s) is not established.

an orange–brown viscous mass between 214 and 217 °C.

Techniques

(a) IR spectra were recorded as nujol mulls on a Perkin-Elmer 983 spectrophotometer. Molecular weights were measured in DCE at 45 °C with a Knauer vapour pressure osmometer. Conductivity measurements were performed at 25 °C with a B.E.103 digital conductivity meter.

(b) The TSDC measurements were performed by using a home-made apparatus. A typical measurement was done as follows. The sample was assembled in a gas exchange cryostat, put between two metal electrodes and polarized by an electric field E_p ($\sim 1.5 \times 10^3$ V cm^{-1}), at a temperature T_p (as a rule ~ 300 K) at which the electric dipoles were mobile, then it was cooled down to a temperature T_f (as a rule 143 K), at which the dipoles were no longer mobile: the electric field was turned off. The polarization induced by the field remained frozen in and the dipoles oriented. The sample was connected to an electrometer, then warmed up at a constant rate (~ 0.1 K/s). During this step the dipoles gained mobility and lost their preferred orientations, giving rise to a displacement depolarization current which was detected by an electrometer (Cary 401), capable of monitoring currents as low as 10^{-15} A. In this way, a plot of the thermally stimulated depolarization current (TSDC) versus temperature, displayed by a recorder (Bryans-272), was obtained. The electrometer signal and the e.m.f. of the Chromel-Constantan thermocouple, which monitored the sample temperature, were acquired by means of a Labmaster model interface and sent to an IBM personal computer for data elaboration. The TSDC spectra were monitored in the temperature range 110–350 K. For further details of the apparatus used for TSDC measurements, see ref. 8.

In order to avoid changes in the hydration level, the TSDC measurements were never performed in dynamic vacuum, but in dry nitrogen atmosphere at a pressure of 100 Torr. Between two subsequent TSDC runs, the nitrogen pressure was increased up to 600 Torr.

A clean dynamic vacuum (2×10^{-5} torr) for dehydrating the samples was obtained by means of a diffusion pump followed by a trap cooled to liquid nitrogen temperature.

The samples were prepared as pure compound pellets ($\phi = 13$ mm, $\times \approx 0.6$ mm).

X-ray data collection and refinement of the structures

Crystal data and the most significant parameters used in the X-ray diffraction experiments and in the crystal structures determination are reported in Table 1 for both **A** and **B** compounds. The intensities were de-

termined by profile analysis according to the method of Lehman and Larsen [11]. The intensity values were corrected for Lorentz and polarization effects. For both compounds, at the end of the isotropic refinements, the intensities were corrected for absorption effects [12] by the program ABSORB [13]. The structures were solved by Patterson methods with SHELX86 [14] and completed and refined with the SHELX76 [15] package. In both cases, full-matrix least-squares refinements were carried out for a total of 433 parameters for **A** and 485 parameters for **B**. 24 of the 27 hydrogen atoms of **A** were found in the Fourier ΔF map and then refined with isotropic temperature factors. The remaining three were calculated and refined 'riding' on their C atoms. All the hydrogen atoms of **B** were calculated and refined 'riding' on their corresponding C atoms. The atomic scattering factors were calculated by analytical approximation according to the literature [16]. Geometrical calculations were performed by PARST [17]. Molecular drawings were obtained by PLUTO [18]. Final atomic coordinates for the non-hydrogen atoms of **A** and **B** are given in Tables 2 and 3, respectively.

All of the calculations were carried out on the Gould 6040 Pownode at the Centro di Studio per la strutturistica diffrattometrica del CNR (Parma) and on the CRAY Y-MP8/432 computer at the 'Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale' (CINECA, Casalecchio, Bologna). See also 'Supplementary material'.

Results and discussion

Figures 1 and 2 give perspective views of the $\{[\text{Cu}(\text{O}_2\text{CPh})\text{dppm}]_2\}$ unities in **A** and **B**, respectively. Related bond distances and angles are given in Tables 4 (**A**) and 5 (**B**). In both complexes, two copper atoms are doubly bridged by two dppm ligands to form an eight-membered $\text{Cu}_2\text{P}_4\text{C}_2$ ring. In **A**, which possesses an imposed crystallographic C_i symmetry, the nearly trigonal planar arrangement around each copper atom is completed by one oxygen atom from a monodentate benzoate ligand; the Cu atom is slightly displaced (0.148(1) Å) from the plane defined by the O(1), P(1) and P(2') atoms towards its centrosymmetric copper, with a transannular Cu...Cu separation of 3.359(2) Å. In **B**, the metal atoms are held in a closer proximity (2.944(2) Å) by one benzoate ligand acting as a bridge through both the oxygen atoms, the other phenylcarboxylate behaving as a monodentate ligand. In **B**, Cu(1) is pseudotetrahedrally coordinated by two phosphorous of two dppm bridging ligands and by two oxygens of two different benzoate ligands; Cu(2) is in a nearly trigonal environment with the metal atom displaced,

TABLE 1. Crystal data and the most significant parameters of the crystal structure determination

Compound	A	B
Formula	C ₆₄ H ₅₄ Cu ₂ O ₄ P ₄	C ₆₄ H ₅₄ Cu ₂ O ₄ P ₄ ·H ₂ O
Molecular weight	1138.12	1156.13
Crystal system	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>a</i>
Cell dimensions		
<i>a</i> (Å)	11.841(2)	21.295(3)
<i>b</i> (Å)	11.366(2)	13.295(2)
<i>c</i> (Å)	10.769(2)	22.068(3)
α (°)	100.68(2)	90
β (°)	101.45(2)	114.72(2)
γ (°)	92.37(2)	90
<i>V</i> (Å ³)	1391.3(5)	5675(2)
<i>Z</i>	1	4
<i>D</i> _{calc} (Mg m ⁻³)	1.358	1.353
Crystal dimensions (mm)	0.3 × 0.2 × 0.3	0.4 × 0.2 × 0.3
Linear absorption coefficient (cm ⁻¹)	23.98	23.72
Diffractometer	Siemens AED	Siemens AED
Scan type	θ -2 θ	θ -2 θ
Scan width (°)	<i>a</i>	<i>a</i>
Radiation	Cu K α	Cu K α
θ range (°)	3–60	3–70
Reflections measured	$\pm h, \pm k, l$	$\pm h, k, l$
Total collected reflections	4396	11599
Observed reflections	2716 ($I \geq 2\sigma(I)$)	4025 ($I \geq 2\sigma(I)$)
Unique observed reflections	2553	3909
<i>F</i> (000)	588	2392
Final <i>R</i>	0.032	0.058
Final <i>R</i> _w	0.032	0.047
Weight, <i>w</i>	1.0	0.6306[$\sigma(F_o)$] ⁻²
Maximum residual in the ΔF map (e Å ⁻³)	0.38	0.37

$$^a(\theta - 0.65) \div [\theta + (0.65 + \Delta\theta)]; \Delta\theta = [\lambda_{\alpha_1} - \lambda_{\alpha_2}] / \lambda \tan \theta.$$

towards the Cu(1) atom, by 0.138(2) Å from the mean plane through the P(1), P(4), O(4) atoms.

To our knowledge, the **A** and **B** species molecular complexes can be considered the first pair of linkage isomers involving mono- and bidentate arylcarboxylate ligands in dicopper(I)-bridged units.

A comparison of the structural features of the Cu(O₂CPh) fragments involving monodentate benzoates in the two isomers shows only a significant lengthening of the Cu–O distance in **B** (2.087(6) versus 2.002(4) Å), due to the greater coordination number of the involved metal center. The monodentate CO₂ groups of the **A** and **B** species form different torsion angles (C(1)–O(1)–Cu–P(1) –61.2(4)° (**A**) and C(1)–O(1)–Cu(1)–P(2) –179.8(9)° (**B**)) with respect to the related eight-membered Cu₂(dppm)₂ ring. With respect to the associated phenyl moiety, they are quite coplanar in **A** and tilted by 4.3(7)° in the **B** species.

The different conformations of the [Cu₂(dppm)₂] moieties in the **A** and **B** species also influence the copper atoms trigonal arrangement, which is less distorted in **B** (P(1)–Cu(2)–P(4) 119.2(1), P(1)–Cu(2)–O(4) 116.9(2) and O(4)–Cu(2)–P(4) 122.6(2)°) than in **A**

(O(1)–Cu–P(1) 110.4(1), P(1)–Cu–P(2') 143.6(1) and O(1)–Cu–P(2') 104.4(1)°).

In the **B** species, the structural parameters of the O–C–O bridge, which furnishes one oxygen atom to the tetrahedral coordination of Cu(1) and another to the trigonal arrangement of Cu(2), are in the usual range and reflect the asymmetric bonding mode of the benzoate. This was previously observed in the structure of a dinuclear copper(I) benzoate quinoline complex [4]. The dihedral angle between the carboxylato group and the phenyl ring of the benzoato bridging ligand is 4.8(8)°.

The Cu–P bond distances, averaging 2.247(2) Å in both isomers, are almost similar to those reported for copper(I) derivatives containing [Cu₂(dppm)₂] rings [19, 20].

In the CuP(1)C(14)P(2)Cu' bridge of the **A** species, the P(1)CuCu'P(2) torsion angle (33.2(1)°) suggests an approximate chair conformation for the related eight-membered Cu₂P₄C₂ ring with the P(1) and C(14) atoms out by 1.229(2) and 1.429(5) Å, respectively, from the plane on which lie the Cu, P(2), Cu', P(2') atoms. Similar conformation was found for the centrosymmetric

TABLE 2. Fractional atomic coordinates ($\times 10^4$) with e.s.d.s in parentheses for the non-hydrogen atoms of $[\{\text{Cu}(\text{O}_2\text{CPh})\text{dppm}\}_2]$

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Cu	466(1)	1436(1)	671(1)
P(1)	292(1)	1050(1)	2599(1)
P(2)	531(1)	-1506(1)	1319(1)
O(1)	1976(3)	2368(3)	826(3)
O(2)	2559(3)	1289(3)	-836(3)
C(1)	2707(4)	2111(4)	114(5)
C(2)	3830(4)	2875(4)	489(5)
C(3)	4056(6)	3807(6)	1558(7)
C(4)	5102(8)	4507(7)	1875(10)
C(5)	5911(8)	4274(11)	1159(15)
C(6)	5700(7)	3334(10)	96(12)
C(7)	4664(5)	2636(6)	-229(7)
C(8)	1561(4)	1502(4)	3910(4)
C(9)	2333(6)	2397(5)	3832(5)
C(10)	3252(6)	2833(7)	4837(6)
C(11)	3410(5)	2381(6)	5928(6)
C(12)	2660(5)	1479(5)	6034(5)
C(13)	1750(4)	1044(5)	5037(4)
C(14)	-54(4)	-540(4)	2553(4)
C(15)	-869(4)	1789(4)	3271(4)
C(16)	-631(5)	2733(5)	4329(5)
C(17)	-1517(6)	3344(6)	4754(5)
C(18)	-2645(6)	3013(6)	4106(7)
C(19)	-2878(5)	2088(6)	3075(7)
C(20)	-2002(5)	1474(5)	2650(5)
C(21)	318(4)	-3002(4)	1659(4)
C(22)	-634(5)	-3336(4)	2121(5)
C(23)	-801(6)	-4490(6)	2308(6)
C(24)	-69(7)	-5341(5)	2011(6)
C(25)	874(6)	-5029(5)	1535(6)
C(26)	1066(5)	-3864(5)	1363(5)
C(27)	2082(4)	-1127(4)	1882(4)
C(28)	2668(5)	-1378(5)	3056(5)
C(29)	3823(5)	-983(6)	3508(6)
C(30)	4399(5)	-343(6)	2829(7)
C(31)	3828(5)	-118(6)	1663(7)
C(32)	2663(4)	-506(5)	1194(5)

TABLE 3. Fractional atomic coordinates ($\times 10^4$) with e.s.d.s in parentheses for the non-hydrogen atoms of $[\{\text{Cu}(\text{O}_2\text{CPh})\text{dppm}\}_2] \cdot \text{H}_2\text{O}$

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Cu(1)	342(1)	1936(1)	2474(1)
Cu(2)	1343(1)	401(1)	3271(1)
P(1)	2269(1)	1408(2)	3573(1)
P(2)	1280(1)	2899(2)	2605(1)
P(3)	28(1)	745(2)	1676(1)
P(4)	1145(1)	-714(2)	2470(1)
O(1)	-441(3)	3012(5)	2100(3)
O(2)	-1362(4)	2278(6)	2136(4)
O(3)	249(3)	1742(5)	3362(3)
O(4)	862(3)	369(4)	3862(3)
C(1)	-1065(6)	2917(8)	1938(6)
C(2)	499(5)	1157(8)	3836(5)
C(3)	2130(4)	2300(7)	2900(5)
C(4)	714(4)	-92(7)	1666(4)
C(5)	395(5)	1364(8)	4460(5)
C(6)	702(6)	795(9)	5027(5)
C(7)	630(7)	1005(11)	5595(7)
C(8)	228(8)	1788(11)	5612(8)
C(9)	-83(7)	2368(11)	5056(8)
C(10)	-5(5)	2160(8)	4480(6)
C(11)	3087(4)	792(7)	3709(4)
C(12)	3472(5)	1034(7)	3342(5)
C(13)	4096(5)	525(7)	3486(5)
C(14)	4310(6)	-188(7)	3975(5)
C(15)	3957(5)	-460(9)	4336(6)
C(16)	3334(5)	72(7)	4202(5)
C(17)	2502(4)	2187(6)	4315(4)
C(18)	3084(5)	2788(7)	4532(5)
C(19)	3282(6)	3371(8)	5131(5)
C(20)	2860(5)	3361(8)	5454(6)
C(21)	2279(5)	2753(7)	5230(5)
C(22)	2108(5)	2164(7)	4668(4)
C(23)	1435(5)	3941(7)	3178(4)
C(24)	1955(5)	4618(7)	3313(5)
C(25)	2062(6)	5440(9)	3761(5)
C(26)	1647(5)	5541(9)	4087(6)
C(27)	1133(6)	4852(8)	3967(6)
C(28)	1003(5)	4050(8)	3503(5)
C(29)	1241(5)	3537(7)	1848(5)
C(30)	1815(6)	3743(8)	1728(6)
C(31)	1750(8)	4280(9)	1144(6)
C(32)	1108(6)	4591(10)	709(7)
C(33)	529(7)	4365(8)	816(6)
C(34)	590(6)	3807(7)	1390(5)
C(35)	-655(5)	-128(8)	1583(5)
C(36)	-898(6)	-818(8)	1066(6)
C(37)	-1477(7)	-1461(11)	991(8)
C(38)	-1740(8)	-1363(11)	1439(7)
C(39)	-1520(7)	-684(10)	1950(7)
C(40)	-943(5)	-55(9)	2039(6)
C(41)	-324(5)	1326(7)	847(5)
C(42)	-974(6)	1709(8)	617(6)
C(43)	-1263(8)	2273(9)	9(6)
C(44)	-856(7)	2403(10)	-309(8)
C(45)	-192(8)	2094(10)	-97(7)
C(46)	77(7)	1515(9)	513(6)
C(47)	641(4)	-1848(7)	2436(5)
C(48)	591(6)	-2548(8)	1978(7)
C(49)	229(6)	-3495(11)	1967(7)

(continued)

$\text{Au}(\text{dppm})_2\text{Au}$ ring in the $[\text{Au}_2(\text{dppm})_2\text{Cl}_2] \cdot 2\text{CH}_3\text{OCH}_3$ complex [21], although the $\text{Au}\dots\text{Au}$ separation of 2.962(1) Å is shorter than the $\text{Cu}\dots\text{Cu}$ distance in **A** and the $\text{P}(1)\text{AuAu}'\text{P}(2')$ torsion angle is lower (20.2(2)°) than the $\text{P}(1)\text{CuCu}'\text{P}(2)$ torsion angle. The pseudo-chair conformation of the $\text{Cu}_2(\text{dppm})_2$ ring promotes the increase of the $\text{P}(1)\text{-Cu-P}(2')$ bond angle (143.6(1)°), with respect to the corresponding one (119.3(1)°) in the trigonal coordination in **B**, and allows significant intramolecular $\text{C-H}\dots\text{O}$ interactions between the oxygens of the benzoate ligand and the phenyl C-H groups from the two centrosymmetric dppm bridges (see Table 4).

In the **B** species, the conformations of the two $\text{Cu}(\text{dppm})\text{Cu}$ fragments, as well as that of the $\text{Cu}(1)\text{O}(3)\text{C}(2)\text{O}(4)\text{Cu}(2)$ bridge, are all approximately 'eclipsed' and the eight-membered $\text{Cu}_2\text{P}_4\text{C}_2$ ring adopts a saddle conformation. The dihedral angle between the

TABLE 3. (continued)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
C(50)	17(6)	-3622(11)	2467(6)
C(51)	95(5)	-2919(9)	2923(6)
C(52)	425(4)	-1999(8)	2918(5)
C(53)	1951(5)	-1225(7)	2476(5)
C(54)	2224(7)	-2072(10)	2854(6)
C(55)	2911(8)	-2432(13)	2955(8)
C(56)	3219(8)	-1927(10)	2625(6)
C(57)	2947(7)	-1173(10)	2210(6)
C(58)	2294(6)	-774(10)	2127(6)
C(59)	-1542(6)	3669(10)	1437(6)
C(60)	-2244(7)	3631(12)	1182(7)
C(61)	-2666(10)	4314(16)	735(9)
C(62)	-2414(11)	5045(17)	486(11)
C(63)	-1716(9)	5140(13)	738(8)
C(64)	-1281(7)	4458(10)	1227(6)
O(1w)	3581(3)	3780(5)	3144(3)

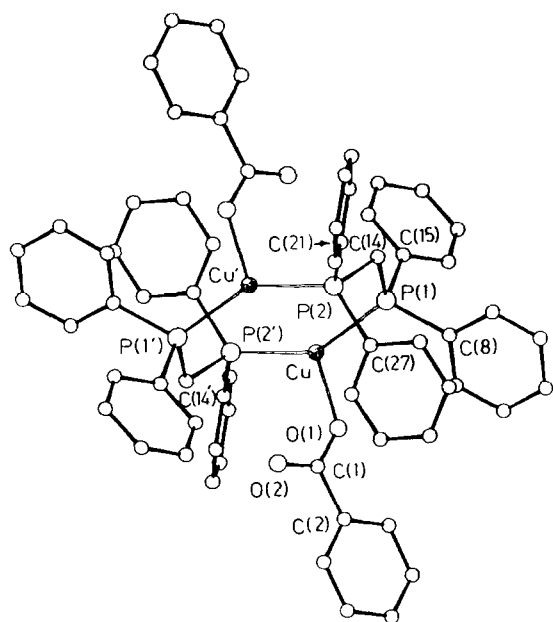


Fig. 1. Perspective view of the molecular complex **A**, $[\text{Cu}(\text{O}_2\text{CPh})\text{dppm}]_2$, with the atomic numbering scheme (the hydrogen atoms are omitted for clarity).

least-squares planes through Cu(1), P(2), P(1), Cu(2) and Cu(1), P(3), P(4), Cu(2) ($118.8(1)^\circ$) gives a rough estimation of the bending of the saddle, whereas the two dihedral angles ($116.6(1)$ and $124.2(1)^\circ$), formed by the latter planes with respect to the least-squares plane through Cu(1), O(3), O(4), Cu(2), roughly display the asymmetric orientation of the carboxylato bridge with respect to the saddle. This asymmetry may be due, at least in part, to intramolecular C-H...O interactions involving bridging carboxylato oxygens and phenyl rings C-H groups from only one dppm bridge (see Table 5). The conformation of the $\text{Cu}(\mu\text{-dppm})_2\text{Cu}$ ring in

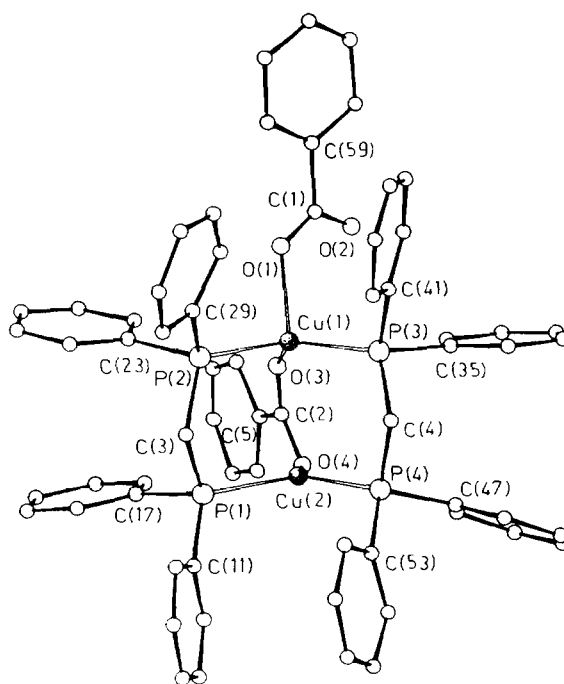


Fig. 2. Perspective view of the molecular complex of **B**, $[\text{Cu}(\text{O}_2\text{CPh})\text{dppm}]_2 \cdot \text{H}_2\text{O}$, with the labelling scheme (the hydrogen atoms are omitted for clarity).

B is similar to that found for the corresponding moiety in our previously investigated complex $[\text{Cu}_2(\mu\text{-dppm})_2(\text{S}_2\text{CC}_6\text{H}_4\text{Me-}o)_2]$ [19] and in the $[\text{Cu}_2(\mu\text{-dppm})_2(\mu\text{-mpyO})]^+$ cationic complex [20]. In the latter compounds, the Cu...Cu separations were $3.426(3)$ and $2.679(6)$ Å and the folding of the eight-membered rings along the Cu...Cu direction was $135.0(1)$ and $124.8(2)^\circ$, respectively.

In **A** the packing of the molecular complexes is determined by intermolecular C-H...O hydrogen bonds (see Table 4 and Fig. 3) involving the coordinated oxygens, whereas in **B** the molecular units are packed by intermolecular hydrogen bonds between the uncoordinated carboxylate oxygens (see Table 5 and Fig. 4) and the co-crystallized water molecules (1:1 ratio).

An additional insight on the behaviour of such water molecules has been obtained by means of TSDC measurements. The TSDC spectra of the $[\text{Cu}(\text{O}_2\text{CPh})\text{dppm}]_2 \cdot \text{H}_2\text{O}$ pellet were measured in the temperature range 100–350 K: the samples were previously polarized in the range $T_p = 316$ K and $T_f = 143$ K (T_p = polarization temperature, at which dipoles can be easily oriented by the field; T_f = temperature at which the field is switched off, since the polarization is already frozen in).

The displacement current is negligible at low temperatures and only a broad TSDC peak appears at 322 K in a freshly prepared sample (see curve a in Fig. 5). When the sample is subjected to dynamic vacuum

TABLE 4. Molecular geometry of $[\text{Cu}(\text{O}_2\text{CPh})\text{dppm}]_2$ (A): bond distances (Å) and bond angles ($^\circ$)

In the coordination polyhedron of the Cu atom					
Cu–P(1)	2.246(2)		Cu–O(1)	2.002(4)	
Cu–P(2')	2.249(2)				
O(1)–Cu–P(1)	110.4(1)		O(1)–Cu–P(2')	104.4(1)	
P(1)–Cu–P(2')	143.6(1)				
In the organic ligands					
C(1)–O(1)	1.274(7)		P(1)–C(15)	1.840(5)	
C(1)–O(2)	1.229(5)		P(2)–C(14)	1.827(5)	
C(1)–C(2)	1.499(6)		P(2)–C(21)	1.822(5)	
P(1)–C(8)	1.828(4)		P(2)–C(27)	1.823(5)	
P(1)–C(14)	1.826(5)				
O(1)–C(1)–O(2)	125.0(5)		Cu–P(1)–C(14)	113.1(2)	
O(1)–C(1)–C(2)	116.5(4)		Cu–P(2)–C(14)	100.7(2)	
O(2)–C(1)–C(2)	118.6(5)		Cu–O(1)–C(1)	125.9(3)	
P(1)–C(14)–P(2)	111.9(3)				
Relevant intra- and intermolecular hydrogen bonds					
X...Y (Å)		H...Y (Å)		X–H...Y ($^\circ$)	
C(9)...O(1)	3.17(1)	H(9)...O(1)	2.45(5)	C(9)–H(9)–O(1)	142(5)
C(20)...O(2')	3.34(1)	H(20)...O(2')	2.48(4)	C(20)–H(20)–O(2')	164(4)
C(25)...O(1'')	3.30(1)	H(25)...O(1'')	2.39(6)	C(25)–H(25)–O(1'')	162(5)

Symmetry codes: ' = $-x, -y, -z$; '' = $x, -1+y, z$.

treatment at room temperature, the TSDC spectrum is considerably reduced (see curve b); moreover, the peak shifts to slightly higher temperatures. If the sample is then exposed to moist atmosphere at room temperature, the TSDC peak recovers (see curve c).

The results obtained can be explained by considering the structure and the packing of **B** (see Fig. 4): water molecules, which are endowed with a dipole moment of 1.85D, are present in the structure and can reorient as a consequence of the application of the electric field at the temperature, such as T_p , at which they are mobile. The depolarization current peak monitored at 322 K in the freshly prepared pellet (see Fig. 5, curve a) is due to the thermally stimulated disorientation of the water molecules. Due to water molecule reorientation, TSDC peaks in the same temperature range were reported in biopolymers such as melanine [9] and lysozyme [10] and, more recently, in some homo-bi-nuclear and trinuclear iron complexes [22]. Such a hypothesis is further supported by the results displayed by curves b and c. In fact, the pellet storage in dynamic vacuum causes the partial desorption of the water molecules, therefore the TSDC peak decreases (see curve b). A subsequent exposure of the partially dehydrated sample to moist atmosphere induces the signal recovery (see curve c). These results point out that the crystallization water molecules are able to reorient their dipole vectors already at r.t. (room temperature), the displacement current not being negligible at 300 K (see curves a and c in Fig. 5). This observation agrees with the X-ray diffraction analysis, which shows that each

crystallization water molecule is involved, as a hydrogen donor, in only one intermolecular hydrogen bond with the uncoordinated oxygens of the complexes, so that the rotation of the water molecule around the axis of such O–H...O intermolecular contacts is possible. The reorientation ability of water molecule dipoles seems favoured, moreover, by the high thermal motion of the atoms (C(7),C(8),C(9); C(43),C(44),C(45); C(54),C(55)) on the border of the niches surrounding the water molecules in the lattice, as confirmed by the significantly high thermal parameters found for all these carbon atoms. The TSDC spectra show how the molecule mobility increases by increasing the temperature: in fact, at $T > 350$ K the displacement current vanishes because all the molecules, which are quite mobile, no longer remain oriented along their preferred orientations. The decrease of the TSDC peak, as a consequence of the sample treatment in dynamic vacuum at r.t., suggests that the water molecules are not strongly bound to the structure. Moreover, the TSDC peak is rather broad: it has been found that it shifts towards lower temperatures (while its amplitude is decreasing) if the sample is polarized at polarization temperatures lower than those chosen for obtaining the spectra of Fig. 5. Such a result points out that disorientation of the water molecules is not ruled by a unique relaxation time, but rather by a relaxation time distribution [8]. It is very likely that this means the water molecules are surrounded by slightly different environments, therefore they exhibit a relaxation time distribution. This can be expected, for instance, when they are involved

TABLE 5. Molecular geometry of $[\{\text{Cu}(\text{O}_2\text{CPh})\text{dppm}\}_2] \cdot \text{H}_2\text{O}$ (**B**): bond distances (Å) and bond angles (°)

In the coordination polyhedra of the Cu atoms			
Cu(1)–O(1)	2.087(6)	Cu(2)–O(4)	1.967(8)
Cu(1)–O(3)	2.067(8)	Cu(2)–P(1)	2.242(3)
Cu(1)–P(2)	2.287(3)	Cu(2)–P(4)	2.208(3)
Cu(1)–P(3)	2.252(3)		
O(1)–Cu(1)–O(3)	94.8(3)	P(2)–Cu(1)–P(3)	116.8(1)
O(1)–Cu(1)–P(2)	100.2(2)	P(1)–Cu(2)–O(4)	116.9(2)
O(1)–Cu(1)–P(3)	104.2(2)	P(4)–Cu(2)–O(4)	122.6(2)
O(3)–Cu(1)–P(2)	112.0(2)	P(1)–Cu(2)–P(4)	119.3(1)
O(3)–Cu(1)–P(3)	122.6(2)		
In the organic ligands			
C(1)–O(1)	1.230(14)	C(2)–O(3)	1.232(12)
C(1)–O(2)	1.243(16)	C(2)–O(4)	1.289(12)
C(1)–C(59)	1.521(15)	C(2)–C(5)	1.509(17)
P(1)–C(3)	1.825(11)	P(3)–C(4)	1.844(10)
P(1)–C(11)	1.832(9)	P(3)–C(35)	1.804(11)
P(1)–C(17)	1.822(9)	P(3)–C(41)	1.833(10)
P(2)–C(3)	1.830(9)	P(4)–C(4)	1.820(8)
P(2)–C(23)	1.811(9)	P(4)–C(47)	1.834(10)
P(2)–C(29)	1.844(12)	P(4)–C(53)	1.841(12)
O(1)–C(1)–O(2)	128.0(11)	O(4)–C(2)–O(3)	126.1(9)
O(1)–C(1)–C(59)	117.1(11)	O(3)–C(2)–C(5)	118.9(9)
O(2)–C(1)–C(59)	114.9(11)	O(4)–C(2)–C(5)	115.0(9)
Cu(1)–P(2)–C(3)	118.9(3)	Cu(1)–P(3)–C(4)	117.1(3)
P(2)–C(3)–P(1)	111.8(5)	P(3)–C(4)–P(4)	110.0(5)
Cu(2)–P(1)–C(3)	108.8(3)	Cu(2)–P(4)–C(4)	109.0(3)
Cu(1)–O(1)–C(1)	129.2(7)	Cu(1)–O(3)–C(2)	134.9(7)
Cu(2)–O(4)–C(2)	115.0(6)		
Relevant intra- and intermolecular hydrogen bonds			
X...Y (Å)		H...Y (Å)	
C(22)...O(4)	3.46(1)	H(22)...O(4)	2.50(1)
C(28)...O(3)	3.42(1)	H(28)...O(3)	2.55(1)
C(34)...O(1)	3.36(2)	H(34)...O(1)	2.42(2)
O(1w)...O(2')	2.68(1)		
		X–H...Y (°)	
		C(22)–H(22)–O(4)	159(1)
		C(28)–H(28)–O(3)	145(1)
		C(34)–H(34)–O(1)	156(1)

Symmetry code: ' = $\frac{1}{2} + x, \frac{1}{2} - y, z$.

in the dynamic disorder due to the high thermal motion of the surrounding atoms in the lattice.

In a freshly prepared sample, the peak of curve c is a little higher than that of curve a. It is possible that the sample treatment in dynamic vacuum causes a minor alteration of the crystal structure, which afterwards is capable of hosting a slightly higher number of water molecules in the rehydration step.

Reactivity of the $[\text{Cu}(\text{dppm})(\text{O}_2\text{CPh})_2]$ complexes

The reactivity of the two $[\text{Cu}(\text{dppm})(\text{O}_2\text{CPh})_2]$ species is not strictly comparable, because the presence of **A** or **B** is conditioned by the polarity of the solvent, which also plays a crucial role in the solubility of co-reagents and by-products. The reactions with **A**, which require solvents of low polarity, primarily have to be carried out in suspension and the isolated products are often

mixtures of copper complexes and of insoluble inorganic side-compounds, which can be removed only by washing with methanol or water.

Both **A** and **B** give exchange reactions of the carboxylato groups with the anions of several salts. While with PF_6^- and BPh_4^- the substitution, also with reagent excess, involves only one of the carboxylato groups and unique products are formed, both the carboxylato anions are substituted by N_3^- and SCN^- and the corresponding derivatives each exist in different solid forms. The starting structure does not seem to influence that of the products.

An overview of the **A** and **B** reactivity is given in Scheme 1 and some characteristics of the complexes in Table 6. All the products are soluble in chlorinated solvents and the PF_6^- and BPh_4^- derivatives are also soluble in acetone and CH_3CN . The azido derivatives react with CS_2 and CH_3CN , as expected [23a].

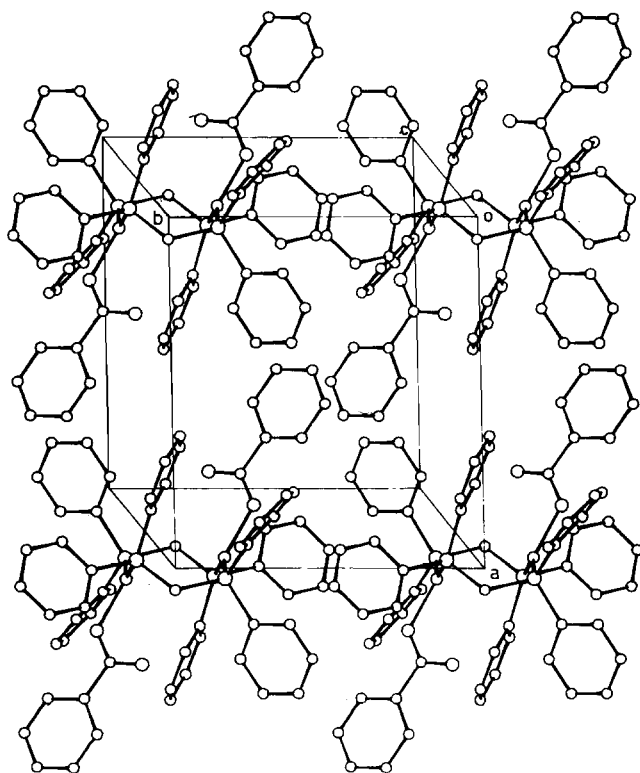


Fig. 3. View of the molecular packing of A.

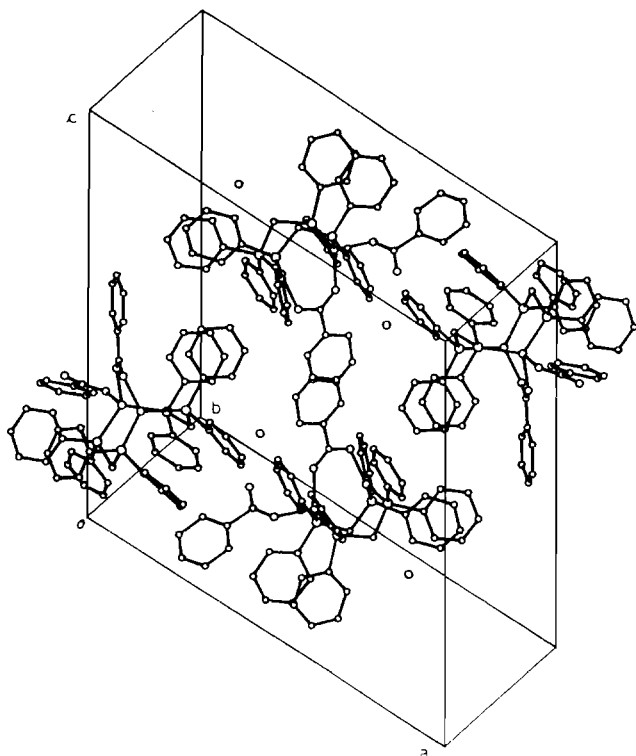


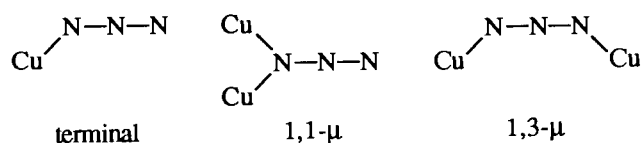
Fig. 4. View of the molecular packing of B.

The product obtained by reacting A or B with NH_4PF_6 is a complex of the formula $[\text{Cu}_2\text{dppm}_2(\text{O}_2\text{CPh})]\text{PF}_6$, whose molecular weight in DCE is compatible with that of a dinuclear form, partially ionized in solution. The IR spectrum, apart from the new PF_6^- absorptions and a reduction in the intensity of the carboxylato bands, is very close to that of B, suggesting a saddle conformation of the Cu_2dppm_2 ring similar to that of the parent compound. To achieve the tricoordination of both copper atoms, the residual benzoate must be the bridging one. The $[\text{Cu}_2\text{dppm}_2(\text{O}_2\text{CPh})]\text{BPh}_4$ complex, on the basis of the IR dppm pattern, seems to prefer a chair conformation of the Cu_2dppm_2 moiety.

The compounds $[\text{Cu}_2\text{dppm}_2(\text{O}_2\text{CPh})]\text{X}$ ($\text{X} = \text{PF}_6, \text{BPh}_4$) give exchange reactions with N_3^- and SCN^- by substitution at first of the coordinated carboxylato group and then also of the counterion. The final complexes are not electrolytes.

The reaction of A and B with NaN_3 gave compounds of rough formula $\text{Cu}(\text{dppm})\text{N}_3$, which exist in two isomeric forms (I and II). The original product (I) shows a fair solubility in some common solvents, but then reprecipitates spontaneously from the solutions in a more stable form (II) in a short time. This conversion also causes some variations in the IR spectra, suggesting that the saddle conformation of the Cu_2dppm_2 ring moves towards the pseudo-chair one.

It is well known that the coordination mode of the azido group cannot be unequivocally established from IR data, different modes having shown $\nu_{\text{asym}}\text{N}_3^-$ absorptions at the same frequencies [23]*.



For copper(I) complexes with phosphines, the azido products known from the literature are: μ -diazido-tetrakis(triphenylphosphine)dicopper(I), $[\text{Cu}(\text{N}_3)(\text{PPh}_3)_2]_2$ [24, 25] with 1,3- μ diazido groups ($\text{Cu}\dots\text{Cu}$ distance 4.956(2) Å); diazido- μ -1,2-bis(diphenylphosphino)ethane-bis(1,2-bis(diphenylphosphino)ethane)dicopper(I), $\text{Cu}_2(\text{N}_3)_2(\text{diphos})_3$ [26] with terminal azido groups ($\text{Cu}\dots\text{Cu}$ distance 7.31 Å) and the monomeric $\text{CuN}_3\text{PPh}_3(\text{L}-\text{L})$ ($\text{L}-\text{L} = 1,10\text{-phen}; 3,4,7,8\text{-tetramethyl-phen}$) [27]. Our complexes maintain the

*Also NMR spectra are not decisive for structural assignments; the interpretation of their data in solution is furthermore complicated by dissociation equilibria.

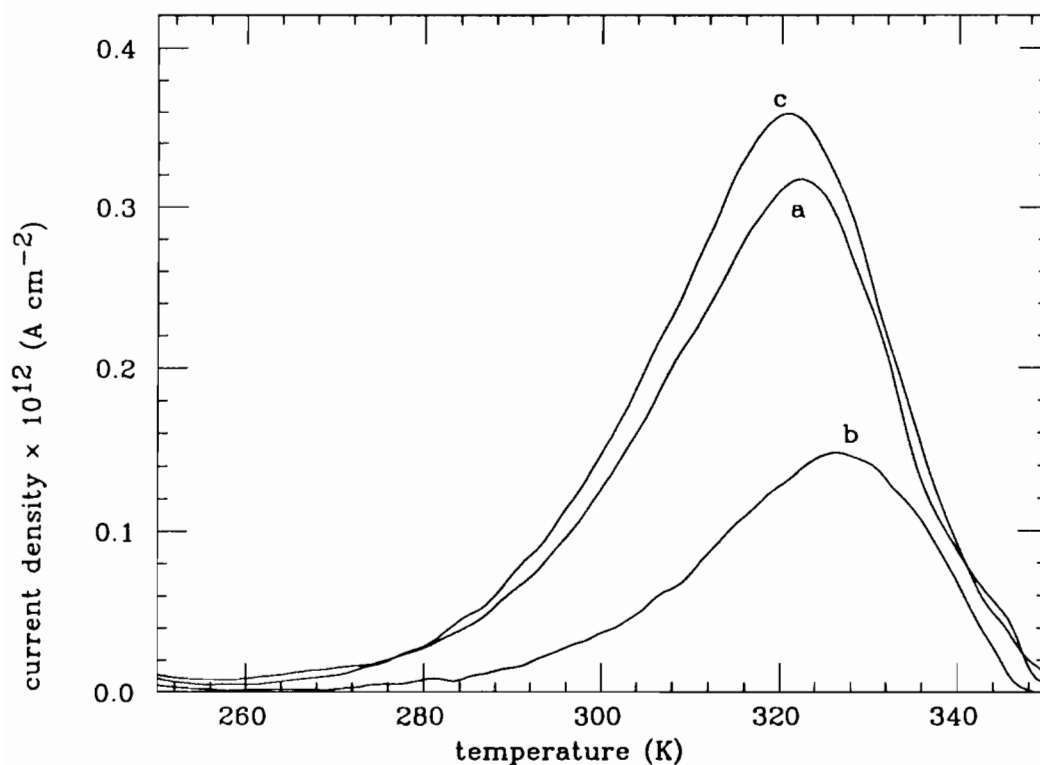


Fig. 5. TSDC spectra of $[\{\text{Cu}(\text{O}_2\text{CPh})\text{dppm}\}_2] \cdot \text{H}_2\text{O}$: $T_p = 316 \text{ K}$, $T_f = 143 \text{ K}$, $E_p = 1.5 \times 10^3 \text{ V/cm}$. Curve a, pellet freshly prepared; curve b, the same pellet submitted to dynamic vacuum treatment at r.t. for 17 h 30 min; curve c, the same pellet of curve b exposed to moist atmosphere at r.t. for 22 h 20 min.

Cu_2dppm_2 moiety and, hence, also the Cu...Cu distances must be approximately those of the parent carboxylates (**A**, 3.36 Å; **B**, 2.94 Å). For bridging azido ligands, these short distances suggest a 1,1- μ (Cu...Cu 3.185 Å* [23b]), rather than a 1,3- μ bridging mode (Cu...Cu 3.61 to 5.15 Å*, [28]).

In accordance with the results of the elemental analysis, in the IR spectra of the isomeric forms I and II of the $\text{Cu}(\text{dppm})\text{N}_3$ complexes, the carboxylato bands have disappeared and new intense absorptions are present in the 2100–2000 cm^{-1} region, due to the antisymmetric stretches of coordinated azido groups. The spectrum of I exhibits a single $\nu_{\text{asym}}(\text{N}_3^-)$ band at about 2040 cm^{-1} and probably a very weak $\nu_{\text{sym}}(\text{N}_3^-)$ band at 1300 cm^{-1} , masked in part by a peak of the framework; the spectrum of II shows two $\nu_{\text{asym}}(\text{N}_3^-)$ absorptions, of different intensity, at 2054 and 2035 cm^{-1} and a weak $\nu_{\text{sym}}(\text{N}_3^-)$ band at 1290 cm^{-1} .

The presence of two $\nu_{\text{asym}}\text{N}_3^-$ bands should, however, be indicative of two differently bonded azido groups. The absence of $\nu_{\text{sym}}(\text{N}_3^-)$ stretches should be diagnostic [29] of 1,3- μ symmetric bonded azido groups, so that in isomer II two different kinds of coordinated azido

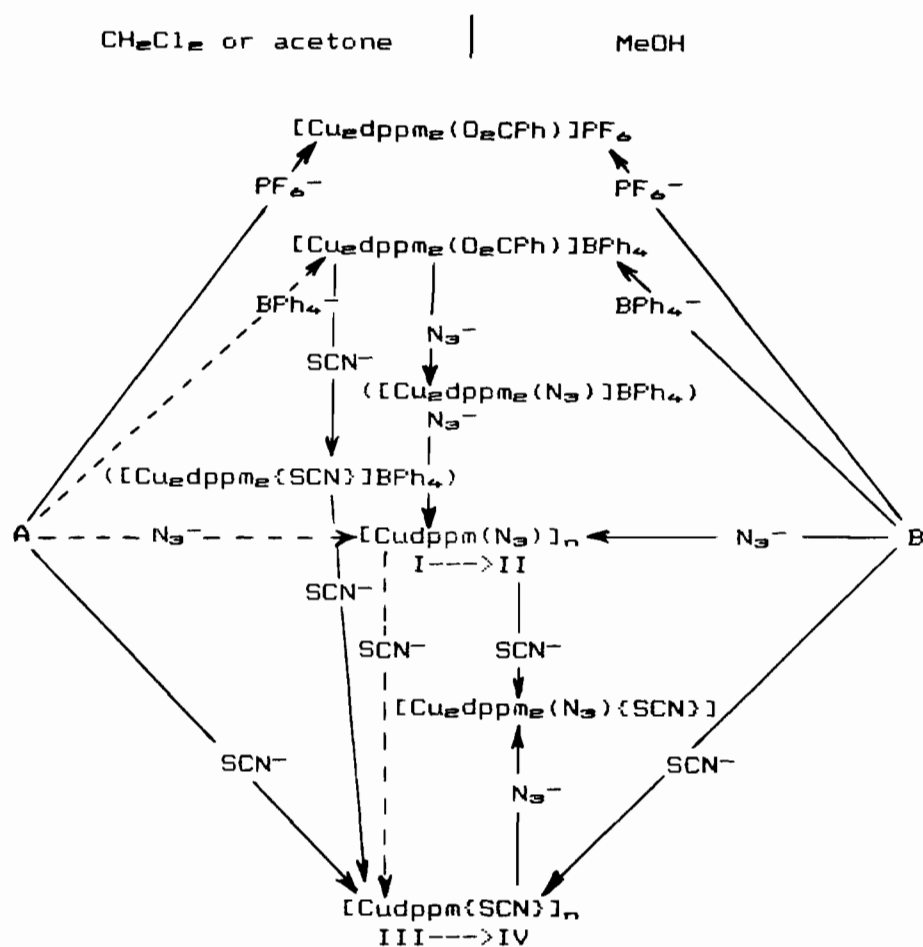
ligands should be present, one of which is 1,3- μ symmetrically bonded.

It is to be noted, however, that the bridging mode could also interest copper atoms of different dinuclear unities, originating oligomeric structures. This is in agreement with the decreasing solubility of the products and also with molecular weight measurements in DCE at 45 °C, which always resulted in higher values than the theoretical one expected for the dinuclear complex, in spite of some ionization in solution. On the basis of the molecular weights, formation of complexes more than tetranuclear is unlikely.

The situation is even more intriguing for the $\text{Cu}(\text{dppm})\{\text{SCN}\}$ complexes because the $\{\text{SCN}\}$ group, when acting as a terminal ligand, may coordinate to the metal either via the nitrogen or via the sulfur atom, its ambidentate nature being well known [30].

Bridging thiocyanates usually involve binding of the nitrogen to one metal atom and of the sulfur to the other. This kind of structure was also recognized for $\text{Cu}(\text{I})$, with a Cu...Cu distance of about 5.30 Å [31]. Unusual 1,1- μS bindings were furthermore observed [32, 33]: in these cases the Cu...Cu distance is shorter, close to 2.8 Å and, hence, similar to those expected for the $\text{Cu}(\text{dppm})\{\text{SCN}\}$ complexes.

*These values refer to $\text{Cu}(\text{II})$ complexes



Scheme 1.

TABLE 6. Analytical data of the new complexes

Compound	Analysis ^a (%)					Mol. weight DCE (%wt./wt.)	Conductivity ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) DCE ^b
	C	H	Cu	N	S		
[Cu ₂ dppm ₂ (O ₂ CPh)]PF ₆	58.6 (58.92)	4.21 (4.25)	10.87 (10.94)			970 (1.7) (1162)	38.6
[Cu ₂ dppm ₂ (O ₂ CPh)]BPh ₄	72.6 (72.80)	5.10 (5.20)	9.50 (9.51)			1075 (2.0) (1336)	19.8
[Cu ₂ dppm(N ₃)] _n	61.2 (61.28)	4.46 (4.53)	12.93 (12.97)	8.50 (8.58)		1263 (1.6) (490 <i>xn</i>)	6.8 ^c
[Cu ₂ dppm ₂ N ₃ {SCN}]	61.2 (61.5)	4.35 (4.45)	12.91 (12.76)	5.52 (5.62)	3.19 (3.22)	916 (1.0) (996)	4.8
[Cu ₂ dppm{SCN}] _n	61.5 (61.71)	4.43 (4.38)	12.83 (12.56)	2.79 (2.77)	6.38 (6.33)	1259 (1.2) (506 <i>xn</i>)	7.4 ^c

^aCalculated values in parentheses. ^bThe ionization degree does not change appreciably in MeOH and acetone. ^cValues calculated for $n=2$.

The IR spectra of the latter again suggest the presence of two different isomeric forms (III and IV), with some differences in the structure of the Cu₂dppm₂ moiety,

which is close to the saddle conformation of the [Cu₂S₂CPh(dppm)]₂ complex [19] for isomer III. The spectra of both forms show two $\nu_{\text{asym}} \text{CNS}^-$ bands (III:

2112, 2088 cm^{-1} ; IV: 2095, 2073 cm^{-1}), indicative of two different species of SCN^- groups in each form of the complex; the intensities of these peaks are very different for III and comparable for IV, which is the more stable. Small shifts in the frequencies of $\nu_{\text{asym}}\{\text{SCN}\}$ absorptions are produced by recrystallization from various solvents.

The modes of coordination of the $\{\text{SCN}\}$ ligands are not clear. Frequencies near or above 2100 cm^{-1} are usually attributed to S-bonding; below this value to N-bonding [34]. However, the presence of thiocyanate in III and isothiocyanate in IV complexes should also cause differences of intensities and frequencies for the ν_{cs} absorptions (860–780(ms) cm^{-1} in the N-bonded forms; 720–690(w) cm^{-1} in the S-bonded), which were not noticed in our spectra. Following the criterion proposed for assigning the bonding mode in solid $\{\text{SCN}\}$ complexes by comparison of the IR intensities ratio between $\nu_{\text{asym}}\{\text{SCN}\}^-$ and $\nu_{\text{asym}}\text{CO}$ of a standard (salicylic acid) [34], the ligand should be mainly present as S-bonded in both types.

The almost perfect correspondence of the spectra of the $\{\text{SCN}\}$ derivatives with those of azido complexes, with the exception of bands due to the anions, suggests that there are only minor differences in the coordination geometry about the copper atom and in the conformation of the eight-membered $\text{Cu}_2\text{P}_4\text{C}_2$ ring in the two series. Molecular weight measurements indicate the presence of molecules greater than dinuclear units in DCE solutions also for the $\{\text{SCN}\}$ complexes.

The mixed $[\text{Cu}_2\text{dppm}_2(\text{N}_3)\{\text{SCN}\}]$ shows an IR spectrum with absorption bands due to the inorganic ligands at 2065(m), 2040(s), 1290(w) cm^{-1} , while the dppm pattern suggests a pseudo-chair rather than a saddle conformation of the Cu_2dppm_2 ring.

Supplementary material

Tables of anisotropic thermal parameters, coordinates of hydrogen atoms, selected torsion angles and a complete list of bond distances and angles are available from the authors upon request.

Acknowledgements

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