A Unique Dinuclear Cu^{II} Compound with Two Phase Transitions Clearly Visible from Thermal and Magnetic Behaviour; Synthesis, Magnetism and X-ray Structures at Three Temperatures of Bis(di-2-pyridylamine)bis(μ-hydroxo)bis(μ-perchlorato-*O*,*O*)dicopper(II)

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A new compound, $[Cu(dpyam)(OH)]_2(ClO_4)_2$ (dpyam = di-2-pyridylamine) is studied in detail and characterised by magnetic susceptibility and heat capacity measurements. This unique compound exhibits two phase transitions at 192 and 116 K. To obtain more insight into the origin of this transition, X-ray crystal structures at 3 different temperatures, below (**1A**, 110 K), between (**1B**, 150 K) and above (**1C**, 200 K) the transitions are measured. The structure consists of a dinuclear Cu^{II} unit with two bridging hydroxo groups and with two ligands bound to each copper atom via N, while the axial sites are occupied by oxygen atoms of bridging perchlorate anions, providing a distorted tetragonal environment with a Cu–Cu distance which varies from 2.9328(6) to 2.9633(6) Å, and a Cu–O–Cu angle which varies from 99.00(9) to 100.53(9)°. In all three structures, the $Cu_2O_2L_2$ unit does not change significantly. The only changes involve the position of the perchlorate anions and their H bonds with the bridging OH groups. These anions have slightly different positions at different temperatures and appear to be the major origin of the crystallographic phase-transitions. Fitting the magnetic susceptibility measurements revealed a singlet-triplet separation (*J*) of $-37.2\ \mathrm{cm^{-1}}$ (antiferromagnetic), in the temperature ranges 275–190 K and 115–50 K. In the range 190–115 K a best fit, albeit inaccurate, of $29.3\ \mathrm{cm^{-1}}$ for *J* (ferromagnetic) is found. A small magnetic hysteresis of 0.5 K has been observed in the phase transition at 116 K. The heat capacity measurements have confirmed the transitions and the excess entropy (ΔS) and enthalpy (ΔH) have been calculated as 4.9 and 2.0 $\mathrm{J\ K^{-1}\ mol^{-1}}$ for ΔS (for 192.3 K and 116.4 K, respectively), and 0.96 and 0.25 $\mathrm{kJ\ mol^{-1}}$ for ΔH (for 192.3 K and 116.4 K, respectively).

Introduction

In the past decades a lot of work has been devoted to the magnetic and structural characterisation of square-planar dinuclear copper(II) complexes, formulated as $[LCu(OH)_2CuL]X(H_2O)_n$, where L = a didentate ligand and X = a variety of mono- and divalent anions.[1] Detailed analysis results in the linear correlation between the Cu−O−Cu angle and the singlet-triplet exchange parameter *J* established by Hodgson and Hatfield,[2] and is proposed as $J = -74.53 + 7270\ \mathrm{cm^{-1}}$ (where is the Cu−O−Cu angle).[1b,2]

From this correlation it has been concluded that when the Cu−O−Cu angle is larger than 97.55°, i.e. in cases where the Cu_2L_2 chromophore is almost coplanar, the overall magnetic behaviour is antiferromagnetic, and for smaller values, a ferromagnetic coupling is observed. At a Cu−O−Cu angle of 97.55°, the singlet-triplet splitting energy would be zero.[2]

These earlier studies have also revealed that the nature of exchange coupling and the geometry of the copper environment is strongly influenced by the nature of the terminal ligands and the coordination of counterions and solvent molecules.[3] Copper(II) compounds with the ligand 2,2′-bipyridine have been investigated extensively, and it is postulated that they exhibit ferromagnetic interactions,[1b] where as for dpyam complexes (dpyam = di-2-pyridylamine), only three systems have been prepared and structurally characterised, both spectroscopically and magnetically, and indicated an antiferromagnetic interaction.[4]

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In the literature many dinuclear dihydroxo-bridged copper(II) compounds containing other terminal ligands with ClO_4^- as a counteranion were characterised.[3a,5] Three copper environments are commonly observed: rhombic coplanar, CuN_2O_2;[5a,5f] square-based pyramidal, CuN_2O_2X;[5c−5e,5g] and elongated rhombic octahedral, $CuN_2O_2X_2$.[3a,5b,5h]

In order to investigate the magnetic and structural correlation in the H bond donor cases, such as the dpyam system, the compound $[Cu(dpyam)(OH)_2Cu(dpyam)](ClO_4)_2]$ has been synthesized and characterised.

By monitoring the temperature behaviour with respect to the magnetic properties, an abrupt change in the magnetism was noted at about 192 and about 116 K. Such an abrupt change is usually associated with a crystallographic phase transition. Reports on an abrupt variation in the magnetic interaction in coupled Cu^{II} systems are, however, very rare. In fact only a few reports on that phenomenon involving Cu^{II}, and which are fully magnetically and crystallographically investigated, are available.[6] $[[Cu(petdien)]_2(CO_3)](ClO_4)_2$ (petdien = *N*,*N*,*N*′,*N*′′,*N*''-pentaethyldiethylenetriamine)[6b] has a phase transition at 212−202 K, $[Cu(CH_3\text{-nso})NCS]$ {CH_3-nso = 2-[2-(dimethylamino)-ethylthio]ethanolato}[6a] has an abrupt phase transition at 240 and 180 K, while $[Cu(btaO)_2(MeOH)]_n$ [6c] (btaOH = 1-hydroxybenzotriazole) has a phase transition at 6.4 and 4.4 K. In this paper, $[Cu(dpyam)(OH)]_2(ClO_4)_2]$ is studied in detail and characterised by magnetic susceptibility and heat capacity measurements. The X-ray crystal structures at three different temperatures, above, between, and below the transitions are also studied in order to obtain an insight into the crystallographic changes of the compound.

Results and Discussion

Description of the Crystal Structures of $[Cu(dpyam)(OH)]_2(ClO_4)_2$ at 110 K (1A), 150 K (1B) and 200 K (1C)

According to the magnetic observations and heat capacity measurements (vide infra), two phase transitions are present, i.e. at about 192 and about 116 K. Therefore, it was decided to obtain the X-ray structures in all three temperature ranges. The X-ray data were collected at 110 K (structure **1A**), at 150 K (structure **1B**) and at 200 K (structure **1C**), all from the same single crystal. The structures of **1A** to **1C** all consist of a dinuclear $[Cu_2(OH)_2(dpyam)_2]^{2+}$ cation and two weakly coordinating, bridging ClO_4^- anions. The geometry of the cation is a distorted elongated octahedral with two bridging OH^- anions, two terminal bis(chelating) dpyam ligands as equatorial ligands, and two weak axial $O_{(ClO4)}$ interactions.

The unit cell of **1A** contains two chemically identical, but crystallographically independent dinuclear units. The unit cell of **1B** contains two dinuclear units related to each other by an inversion centre. The unit cell of **1C** contains one dinuclear unit located on a crystallographic inversion centre. Atomic displacement plots, together with the numbering scheme of the three compounds are shown in Figure 1, Figure 2 and Figure 3, for structures **1A**, **1B** and **1C**, respectively, with selected distances and angles in Table 1.

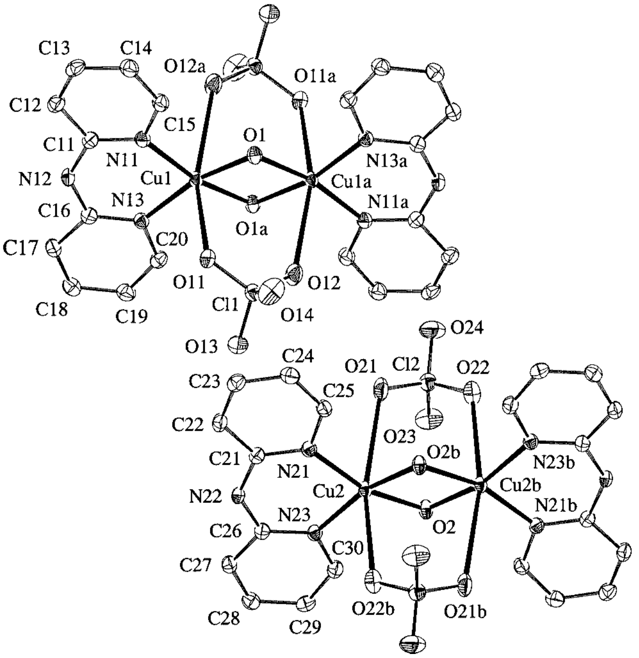

Figure 1. Atomic displacement plot (50% probability) of structure **1A** (110 K); both crystallographic dinuclear units are shown; atoms with suffix "a" are generated by symmetry operation $-x$, $-y$, $1-z$; atoms with suffix "b" are generated by symmetry operation $-x$, $1-y$, $-z$; hydrogen atoms are omitted for clarity

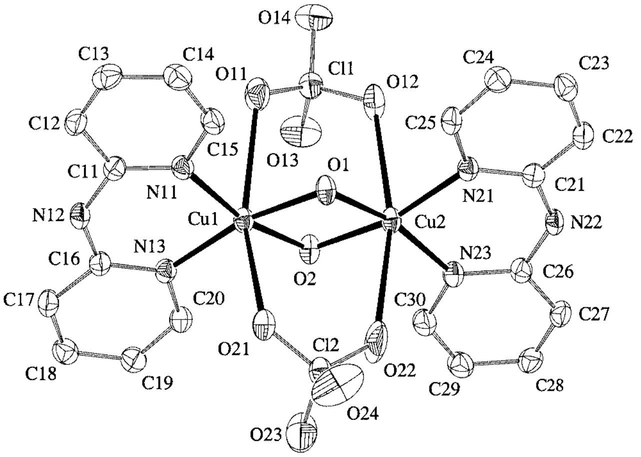

Figure 2. Atomic displacement plot (50% probability) of structure **1B** (150 K); hydrogen atoms are omitted for clarity

As seen from Table 1, the geometry of the $[Cu_2(OH)_2(dpyam)_2]^{2+}$ cation is basically the same in all three structures. Each copper atom has a distorted elongated octahedral geometry with two oxygen atoms of the bridging hydroxo groups and two nitrogen atoms of the dpyam ligand forming the basal plane; both axial sites of each copper atom are occupied by oxygen atoms of perchlorate anions at long (semi-coordinating) distances ($Cu-O_{(ClO4)}$ distances vary from 2.70 to 2.95 Å). The Cu−N distances vary from 1.975 to 2.004 Å, while the

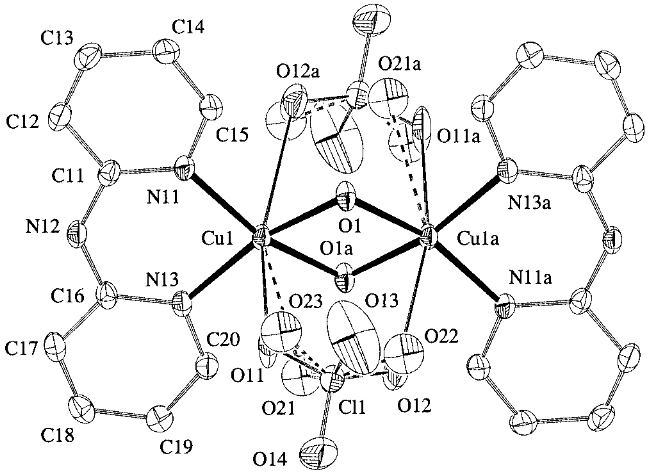

Figure 3. Atomic displacement plot (30% probability) of structure **1C** (200 K); atoms with suffix "a" are generated by symmetry operation $1 - x$, $1 - y$, $1 - z$; hydrogen atoms are omitted for clarity

$Cu-O_{(OH)}$ distances vary from 1.916 to 1.937 Å. These values are in accordance with earlier observations made for Cu^{II} dinuclear hydroxo-bridged compounds.[4,11b] The Cu−Cu distances in the three structures and the Cu−O−Cu angles are almost the same in all 3 structures with values of 2.933 and 2.963 Å for **1A**; 2.948 Å for **1B** and 2.941 Å for **1C**; and with Cu−O−Cu angles of 99.00 and 100.53° for **1A**; 99.76 and 99.54° for **1B**; and 99.53° for **1C**.

However, the main differences in the three structures are the orientation and distances of the perchlorate anions with respect to the CuN_2O_2 plane, as detailed below.

Due to the abrupt change in symmetry, the three structures are different with respect to the orientation of the perchlorate anion. This is shown in Figure 4, where the "canting" (tilting) of the perchlorate anions is projected in each case.

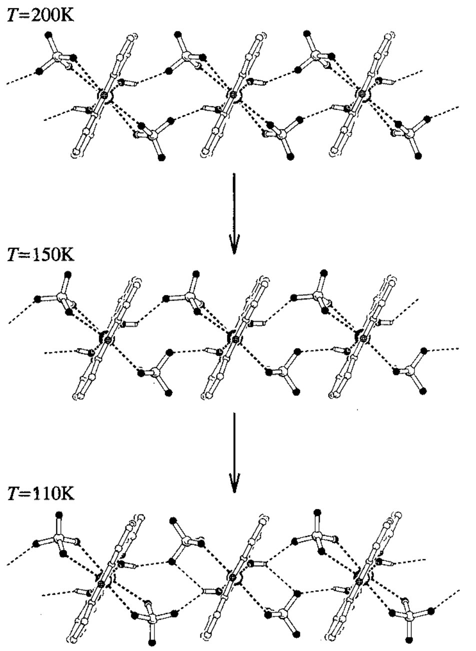

Figure 4. Plot showing the perchlorate orientations and the hydrogen bonds; projections are along the Cu···Cu axis

At 200 K (structure **1C**), the perchlorate is disordered along the Cl1−O14 axis and has to be refined in two positions. The ClO_4^- ions are centrosymmetrically located with respect to the $Cu(OH)_2Cu$ core. At 150 K (structure **1B**), this centrosymmetric arrangement is broken, and both ClO_4^- anions take their own position. In structure **1A** (110 K), after the second abrupt transition, the ClO_4^- anions are once again centrosymmetrically arranged around the dinuclear copper core, albeit that the unit cell now contains two different centrosymmetric units.

Since the planar CuO_2N_2 unit does not display significant differences (dihedral angles in the $Cu_2N_4O_2$ planes vary from 16 to 20°), the phase transitions must originate from

Table 1. Selected bond lengths [Å] and bond angles [°] for the crystal structure determinations of **1A** (110 K), **1B** (150 K) and **1C** (200 K); molecule 1 of structure **1A** refers to the complex containing Cu1; molecule 2 refers to the complex containing Cu2; part 1 of structure **1B** refers to the part containing Cu1; part 2 refers to the part containing Cu2

	1A Molecule 1	**1A** Molecule 2	**1B** Part 1	**1B** Part 2	**1C**
Cu−OH	1.934(2)	1.937(2)	1.934(2)	1.935(2)	1.930(3)
	1.9231(18)	1.9160(18)	1.926(2)	1.920(2)	1.923(3)
Cu−N	1.993(2)	1.975(2)	1.997(2)	1.989(2)	1.988(3)
	2.004(2)	2.001(2)	2.000(3)	2.003(3)	1.996(3)
$Cu-OClO_3$	2.822(2)	2.945(2)	2.908(2)	2.834(3)	2.942(5)
	2.760(2)	2.781(2)	2.705(2)	2.732(2)	2.709(6)
Cu···.Cu	2.9328(6)	2.9633(6)	2.9477(8)	2.9477(8)	2.9412(8)
HO-Cu−OH	81.00(8)	79.47(8)	80.28(9)	80.41(9)	80.47(11)
N−Cu−N	92.43(9)	92.55(9)	92.32(10)	92.35(10)	92.68(12)
N−Cu−OH *cis*	94.04(9)	95.24(9)	94.04(9)	94.31(9)	95.02(12)
	94.79(8)	96.33(9)	94.18(10)	95.62(10)	95.33(12)
N−Cu−OH *trans*	166.99(9)	163.27(9)	167.54(9)	165.48(10)	163.09(12)
	167.54(9)	165.15(9)	168.03(9)	166.76(9)	165.87(12)
Cu−OH−Cu	99.00(9)	100.53(9)	99.76(9)	99.54(10)	99.53(12)

Table 2. Hydrogen bond details (distances [Å] and angles [°])

1A (110 K) Donor−H···Acceptor [ARU]	D−H	H···A	D···A	D−H···A
O(1)−H(1)···O(23) [x, y, 1 + z]	0.74(3)	2.22(3)	2.931(3)	162(3)
O(2)−H(2)···O(14) [x, y, −1 + z]	0.78(3)	2.24(3)	2.890(3)	141(3)[a]
O(2)−H(2)···O(23) [x, y, z]	0.78(3)	2.59(3)	3.224(3)	139[a]
N(12)−H(12A)···O(22) [1 + x, y, 1 + z]	0.88	2.09	2.922(3)	157
N(22)−H(22A)···O(11) [1 − x, 1 − y, 1 − z]	0.88	2.07	2.940(3)	172

1B (150 K) Donor−H···Acceptor [ARU]	D−H	H···A	D···A	D−H···A
O(1)−H(1)···O(13) [−1 + x, y, z]	0.73(4)	2.21(4)	2.915(3)	164(4)
O(2)−H(2)···O(24) [1 + x, y, z]	0.77(4)	2.35(4)	2.959(3)	138(3)
N(12)−H(12A)···O(12) [x, 1 + y, z]	0.88	2.11	2.951(3)	160
N(22)−H(12B)···O(21) [x, −1 + y, z]	0.88	2.03	2.902(3)	168

1C (200 K) (major disordered component) Donor−H···Acceptor [ARU]	D−H	H···A	D···A	D−H···A
O(1)−H(1)···O(13) [−x, 1 − y, 1 − z]	0.77(4)	2.16(4)	2.844(8)	148(5)
N(12)−H(12A)···O(11) [1 − x, −y, 1 − z]	0.88	2.07	2.923(6)	162

[a] Bifurcated hydrogen bond; the sum of the angles involving H(2) is 359(4)°.

the tilting of the perchlorate anions, and their effect on the H bonds.

The lattice structures are stabilised by stacking between the pyridine groups, and by moderate to weak hydrogen bonding between the hydroxo atom and an oxygen atom of the perchlorate anion [D···A distances vary from 2.844(8) to 2.959(3) Å] and between the amine nitrogen atom and an oxygen atom of the perchlorate anion [distances vary from 2.902(3) to 2.951(3) Å]. Details of the hydrogen bonds are given in Table 2.

Spectroscopy

The most relevant features of the IR spectra are those involving the presence of hydroxo bridges and the perchlorate counteranion. The presence of the $Cu(OH)_2Cu$ unit is supported by the occurrence of a weak, but sharp peak of medium intensity at 3550 cm^{-1} (bridging OH stretching). The ν_3 mode of the ClO_4^- anion appears as a strong absorption, split into three broad components at about 1100, 1046 and 1015 cm^{-1}, consistent with its didentate and relatively long Cu−O bonding distance of 2.72 Å.[5h,7]

The electronic reflectance spectra of **1** measured as a powder at room temp. shows a broad band at 15430 cm^{-1} consistent with the distorted elongated octahedral geometry.[8] No spectroscopic data were recorded at low temperature.

EPR and Magnetic Properties

The X-band polycrystalline powder EPR spectra of this compound, up to 800 mT at 77 K, exhibits a typical triplet spectrum with four features at 150, 325, 590, 690 and 755 mT. The spectrum is qualitatively similar to that reported for other coupled copper(II) pairs with $D > h\nu$.[5c,9] The feature at 325 mT is most certainly from a mononuclear Cu^{II} impurity, which is often present in dinuclear species, and the weak absorption at low field (150 mT) comes from the $\Delta M_s = \pm 2$ transition. The presence of the other peaks at high field values is as expected for cases in which the value of the axial zero-field splitting parameter D is larger than the incident quantum (about 0.3 cm^{-1}). Although it is not the intention of this paper to perform a detailed EPR study, including variable frequencies, to determine the parameters D and E, an approximate analysis[10] yields a D value of about 0.5 cm^{-1}.

In a frozen solution (DMF/MeOH, 1:1), only a mononuclear $S = 1/2$ signal is observed with a $g_{\perp}$ value of 2.04, a $g_{//}$ of 2.28 and an $A_{//}$ value of about 15.8 mT, indicating that the compound dissociates in this solution.

The temperature dependence of the molar magnetic susceptibility χ_m^{-1} of **1** down to 5 K, measured on a powder sample, is shown in Figure 5. At 275 K, χ_M is equal to 2.87 × 10^{-3} cm^3 mol^{-1}, which is very close to what is expected for two noninteracting copper(II) ions ($g = 2$). When cooled to 50 K, χ_M slowly increases to 11.14 × 10^{-3} cm^3 mol^{-1}. The absence of any maximum indicates, at best, weakly antiferromagnetically coupled copper(II) ions within the dinuclear units. However, two discontinuities are observed at 192 K and 116 K. The magnetic data therefore point at the presence of two phase changes that are likely to have a consequence for the magnetic behaviour of compound **1**. The susceptibility increases at 192 K and decreases again at 116 K, but in an asymmetric manner, the decrease at 116 K being larger than the increase at 192 K. This indicates that a difference in g value cannot be the origin of these changes. Most likely, the interaction between the two copper ions changes quite drastically. Below 50 K χ_M increases more sharply, to reach 0.113 cm^3 mol^{-1} at 5 K. In the same range, the effective magnetic moment of **1** remains almost

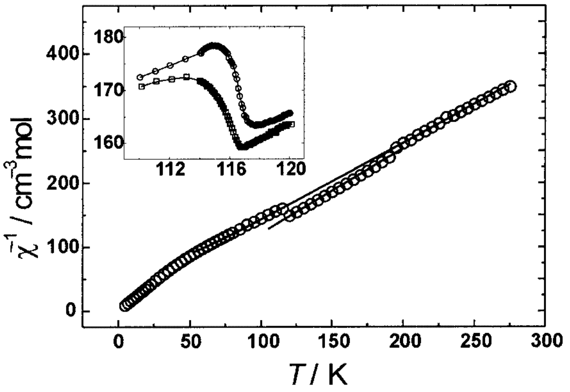

Figure 5. A plot of temperature dependence of χ_m^{-1} vs. T for compound **1**; the full lines correspond to fits of the different temperature ranges (see text); insert: variation of χ_M^{-1} in the 110−120 K temperature range on cooling (○) and warming (□)

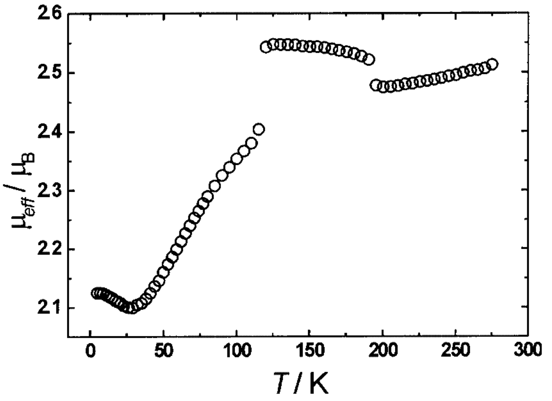

Figure 6. A plot of temperature dependence of μ_{eff} vs. T for compound **1**

constant at a value of 2.12 μ_B (Figure 6). This low-temperature behaviour cannot be attributed to a paramagnetic impurity, and is not understood yet, and therefore omitted from the present analysis. Full analysis would also require X-ray structures below 50 K. Subsequently, the fitting procedure was performed from 275 to 50 K (vide infra). The magnetic data above 50 K, and above and below the two discontinuities, can be reproduced (see Figure 5), with the theoretical expression of the magnetic susceptibility of a copper(II) pair given in the following equation, where J is the singlet-triplet energy gap (a positive or negative J value corresponds to a ferromagnetic or antiferromagnetic interaction, respectively) and the other parameters have their usual meaning.[1b]

$$\chi_M = \frac{2N_A\beta^2 g^2}{k_B T}\left[3+\exp\left(\frac{-J}{k_B T}\right)\right]^{-1}$$

The minimisation of $R = \Sigma\,(\chi_M^{calcd.} - \chi_M^{obs.})^2/\Sigma(\chi_M^{obs})^2$ led to $J = -37.2$ cm^{-1} and $g = 2.09$, with $R = 3.37 \times 10^{-3}$. Applying the same expression to the data between the two discontinuities, yields $J = 29$ cm^{-1} and $g = 2.0$ with $R = 5.1 \times 10^{-3}$. Although the exact value of J may not be precisely defined because of the small number of data points fitted, a change in the sign of J is clearly observed. Indeed, the effective magnetic moment of **1** in that temperature range increases, whereas it decreases in the other fitted regions, also indicating a change in the sign of the exchange interaction. Such a drastic change of the magnetic interaction in a polynuclear compound upon a crystallographic phase transition is unprecedented. Sletten et al.[6b] have observed a change of 7 cm^{-1} in the strength of the antiferromagnetic interaction in $\{[Cu(petdien)]_2(CO_3)\}(ClO_4)_2$, but the perchlorate anions are not coordinated and the two copper ions are bridged by a carbonato anion. In that case, the change in the S-T energy gap has been related to a subtle change of the character of the magnetic orbital.

Here, the present phase transitions must mainly result from changes in the perchlorate anion orientation with respect to the $Cu_2(dpym)_2$ plane. Considering the Hatfield−Hodgson relationship[2] between J and the Cu−O−Cu angle for bis(μ-dihydroxo)copper dimers, the expected value for the S-T energy gap in **1** would range from −148 to −157 cm^{-1}. Such a discrepancy from the measured value was already observed in two of the rarely studied bis(μ-dihydroxo)copper dinuclear compounds having perchlorate anions coordinated, or semi-coordinated via two oxygen atoms.[11] It is thought[11a] that the perchlorate coordination greatly, but indirectly, affects the exchange interaction, and hence in two possible ways. The electronic perturbation due the additional coordination can affect the superexchange mechanism through the hydroxo oxygen atom, by altering the electron density available to it.

Alternatively, the very small changes in the Cu geometries (deviations from planarity) may be the origin.[11c,11d] None of these origins can be excluded in **1**. The abrupt change in behaviour from the ordering and change in orientation of the perchlorate anions only proves the strong influence of their coordination on the magnetic interaction. What is clear in this case is that the magnetic properties cannot be explained on the basis of Cu−Cu distances and Cu−OH−Cu angles alone.

The two ranges of temperature showing discontinuities were reinvestigated by cooling and heating at a much lower rate. A small hysteresis of 0.5 K is detected at the low-temperature transition, with $T^{\downarrow} = 116.2$ K and $T^{\uparrow} = 116.6$ K (see insert in Figure 5), which is in good agreement with the calorimetric measurements (see separate section). However, the step at high temperature occurs at $T = 5$ K on cooling and heating, which differs from the calorimetric measurements in which a hysteresis of 2 K was detected.

Heat Capacity Measurements

To understand more of these two phase transitions, calorimetric analyses have been performed on **1**. The sample was first rapidly cooled down to 250 K, measurements were then carried out on cooling to 85 K and warming back to 240 K. The temperature dependence of the molar heat ca-

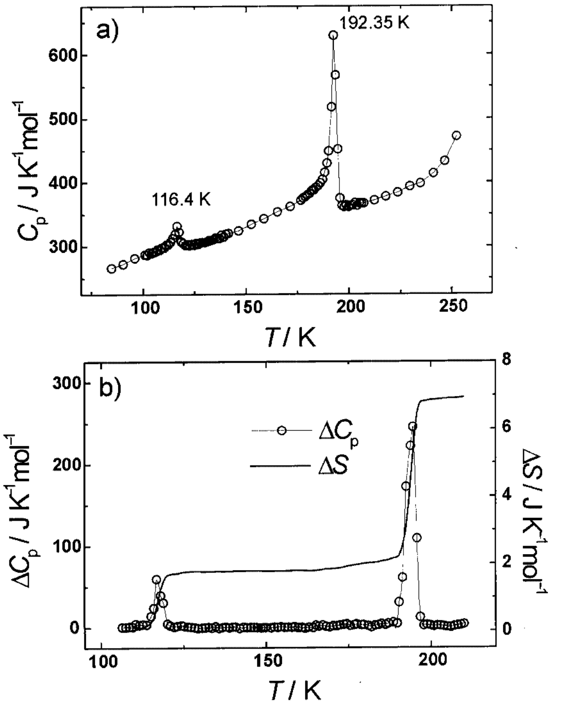

Figure 7. Temperature dependence of a) the heat capacity of compound **1** in the cooling mode and b) the excess heat capacity (empty circles) and the derived entropy gain (full line) in the warming mode

pacity of **1** in the cooling mode is shown in Figure 7a. Two thermal anomalies are found at 192.3 ($T_{c1}^{\downarrow}$) and 116.4 K ($T_{c2}^{\downarrow}$), and the same is observed in the warming mode at 116.8 ($T_{c2}^{\uparrow}$) and 194.4 K ($T_{c1}^{\uparrow}$). These values are in good agreement with the steps observed in the magnetic properties. The presence of hysteresis in the phase change at high temperature is also confirmed, with $T_{c1}^{\uparrow}$ and $T_{c1}^{\downarrow}$ differing by 2 K. The presence of hysteresis in the high-temperature transition, where no hysteresis could be detected by magnetic measurements, may indicate that the magnetic change does not occur while the structural phase transition takes place, but just after it has occurred. Since the hysteresis is so small, the magnetic change then appears at the same temperature on cooling and warming. The enthalpy gain ΔH and the entropy gain ΔS, associated with the excess heat capacities ΔC_p, were determined by integration of ΔC_p with respect to T and ln$T$, respectively, both in the cooling and warming mode. The temperature dependence of ΔC_p and the excess entropy in the warming mode are shown in Figure 7b. The ultimate value at high temperatures corresponds to $\Delta S = (6.9 \pm 0.7)$ J K^{-1} mol^{-1}, while the excess enthalpy was found to be $\Delta H = (1.2 \pm 0.1)$ kJ mol^{-1}. Similar calorimetric values were found in the cooling mode, the only marked difference being the temperatures. This confirms the reversibility of the phase changes in compound **1**. Large errors are due to the ambiguity in the determination of normal heat capacity curves, which were done by fitting the experimental data above, below and between the C_p anomalies, to a polynomial function. Since the two C_p anomalies are well separated, an approximation of the excess entropy and enthalpy associated with the two transitions is possible, e.g. $\Delta S(T_{c1}) = 4.9$ J K^{-1} mol^{-1}/$\Delta H(T_{c1}) = 0.96$ kJ mol^{-1} and $\Delta S(T_{c2}) = 2.0$ J K^{-1} mol^{-1}/ $\Delta H(T_{c2}) = 0.25$ kJ mol^{-1}. The entropy variation ΔS is usually[12] written as $\Delta S = \Delta S_{el} + \Delta S_{vib,intra} + \Delta S_{vib,inter}$.

In the present case, there is almost no variation in the metal−ligand bond lengths, and the intramolecular geometry is not modified, as shown by the very similar Cu−O−Cu angles. Therefore, $\Delta S_{vib,intra}$ is negligible. The observed change in magnetic interaction may result in a small contribution of the electronic entropy ΔS_{el}, while the dominant term is probably the lattice term $\Delta S_{vib,inter}$. The high-temperature transition entropy is approximated, within the error, in terms of Rln 2 (5.76), which agrees with an order-disorder phenomenon occurring between two positions. This is indeed in agreement with the structural data at 200 and 150 K. On the other hand, the phase change between the 150 and 110 K structures only involves changes in the crystal lattice. This is in agreement with the amount of entropy gain measured at T_{c2}, which can reasonably arise from lattice vibrations.

Conclusions

The results described above have shown a unique double phase transition for a dinuclear hydroxo-bridged Cu^{II} compound. X-ray structures were measured at three different temperatures (below, between and above the two phase transitions), and it can be concluded that the main reason for the crystallographic phase transition must originate from the abrupt change in the positions (canting or tilting) of the perchlorate anions, and therefore influencing the Cu−O$_{(ClO4)}$ bonds and Cu geometries. The abrupt change in behaviour from the ordering and change in orientation of the perchlorate anions confirms the influence of their coordination on the magnetic interaction.

More insight in the exact mechanism of the transition from more studies using other examples would be desirable. In fact, it is likely that such phase transitions, involving the movements of (semi)coordinated anions do occur, since many coordination compounds are studied only at one temperature and in many cases no magnetic susceptibility measurements are performed.

Experimental Section

General: All reagents were commercial-grade materials and were used without further purification. C,H,Cu,N determinations were performed by the Microanalytical Service of Science and Technological Research Equipment Centre, Chulalongkorn University. Infrared spectra were taken with a Biorad FTS-7/PC FTIR spectrophotometer as KBr pellets in the 4000−450 cm^{-1} region. Solid-state (diffuse reflectance) electronic spectra were recorded as polycrystalline samples with a Perkin−Elmer Lambda 2S spectrophotometer over the range 8000−18000 cm^{-1}. X-band EPR spectra were recorded on polycrystalline samples with a Jeol RE2X electron spin resonance spectrometer using DPPH (g = 2.0036) as a standard.

Table 3. Crystal and refinement data

Compound	**1A** (110 K)	**1B** (150 K)	**1C** (200 K)
Empirical formula	$C_{20}H_{20}Cu_2N_6O_2(ClO_4)_2$	$C_{20}H_{20}Cu_2N_6O_2(ClO_4)_2$	$C_{20}H_{20}Cu_2N_6O_2(ClO_4)_2$
T/K	110	150	200
Crystal system	triclinic	triclinic	triclinic
Space Group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	10.0337(12)	7.4898(12)	7.4730(12)
b/Å	11.1292(14)	9.4322(16)	9.4614(18)
c/Å	13.1017(15)	18.700(4)	9.697(2)
α/°	104.334(10)	100.933(10)	73.092(10)
β/°	98.705(10)	91.431(10)	80.652(10)
γ/°	115.985(10)	108.268(10)	71.048(10)
V/Å^3	1216.2(3)	1226.7(4)	618.7(2)
Z	2	2	1
$D_{calcd.}$/g·cm^{-3}	1.918	1.902	1.885
μ/mm^{-1}	2.039	2.022	2.004
F(000)	708	708	354
Crystal size [mm]	0.05 × 0.10 × 0.35	0.05 × 0.10 × 0.35	0.05 × 0.10 × 0.35
Total refl.	23865	21228	12098
Indep.refl. (R_{int})	5515 (0.0793)	5445 (0.0721)	2789 (0.0644)
No. parameters used	367	367	194
GOF	1.027	1.032	1.042
Final R[a] indices	$R1 = 0.0383$	$R1 = 0.0414$	$R1 = 0.0450$
indices	[4308, $I > 2\sigma(I)$]	[4258, $I > 2\sigma(I)$]	[2306, $I > 2\sigma(I)$]
	$wR2 = 0.1041$	$wR2 = 0.1084$	$wR2 = 0.1247$
Min./max. resd.dens. [e Å^{-3}]	−0.90/0.57	−0.86/0.53	−0.68/0.71

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Magnetic susceptibility measurements (5−275 K) were carried out using a Quantum Design MPMS-5 5T SQUID magnetometer (measurements carried out at 0.1 and 1 T). Data were corrected for magnetisation of the sample holder and for diamagnetic contributions, which were estimated from Pascal constants. Heat-capacity measurements were carried out using the heat-capacity option of a Quantum Design PPMS model 6000. A few crystals (total mass = 2.3 mg) were mounted onto the sample platform of the heat capacity puck with a little Apiezon N grease, which was previously measured as an addendum (puck + grease). The heat-capacity option uses a relaxation technique, fitting the whole thermal response to a heating period followed by a cooling period with a model that accounts for both thermal relaxation from the sample platform to the bath and the relaxation between the platform and the sample.

Synthesis of the Title Compound: Solid sodium carbonate (0.052 g, 0.5 mmol) was slowly added under continuous stirring to an aqueous solution (60 mL) containing copper(II) perchlorate hexahydrate (0.370 g, 1.0 mmol) and di-2-pyridylamine (0.171 g, 1.0 mmol). The greenish-blue solution was allowed to concentrate at room temperature. After several days, purple-blue rod-shaped crystals were formed. They were filtered off, washed with the mother liquor and air-dried. Yield: ca. 0.32 g (45%). $C_{20}H_{20}Cl_2Cu_2N_6O_{10}$ (702.4): calcd. C 34.0, H 2.6, Cu 17.8, N 11.8; found C 34.2, H 2.9, Cu 18.1, N 12.0. ***Caution:*** Perchlorate salts are potentially explosive, caution is advised and handling of only small quantities is recommended.

X-ray Data Collection and Structure Determination: A crystal was mounted on top of a glass fibre (using the inert-oil technique) and transferred to a cold nitrogen stream of a Nonius Kappa-CCD diffractometer for data collection at 200, 150 and 110 K (rotating anode, graphite-monochromated Mo-K_α radiation, $\lambda = 0.71073$ Å). The unit-cell parameters were checked for the presence of higher lattice symmetry.[13c] No absorption correction was applied. The structure was solved by automated direct methods (SHELXS-86).[13a] Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-97).[13b] For the structure determination of **1C**, a two-site disorder model was adopted for the ClO_4^- ion. The occupancy of the major component was refined to 0.811(5). Mild distance restraints and a common displacement parameter were applied to the minor component. Anisotropic displacement parameters were used for all non-hydrogen atoms, except for those belonging to the minor disorder component. Hydroxo hydrogen atoms were located on a difference Fourier map and their positions were refined. All other hydrogen atoms were introduced at calculated positions and included in the refinement riding on their carrier atoms. Geometrical calculations, including the ORTEP illustrations were performed with the PLATON package.[13c] Crystallographic details are tabulated in Table 3. CCDC-173825, -173824 and CCDC-173823 for structures **1A**, **1B** and **1C** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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