Tuning the Magnetic Properties of a Dinuclear Copper Complex: From Ferromagnetic to Antiferromagnetic Coupling

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Keywords: Magnetism / Copper / Azides / Dinuclear complexes

A novel structural motif in oxalate bridged copper(II) complexes has been prepared namely a metallamacrocyclic compound of the dinucleating ligand 1,3-bis[bis(2-pyridylmethyl)-amino]benzene (= 1,3-tpbd). It could be demonstrated that the magnetic properties of copper(II) complexes of the 1,3-tpbd ligand can be adjusted from weakly ferromagnetic (J = +9.3 cm^{-1}) to strongly antiferromagnetic [J = –366(9) cm^{-1}] by variation of the additional ligands (e.g. perchlorate, azide, oxalate etc.).

Introduction

We have previously demonstrated that the ligand 1,3-tpbd {tpbd = 1,3-bis[bis(2-pyridylmethyl)amino]benzene}, a derivative of 1,3-phenylenediamine, provides a rigid structural framework in which two copper(I) or copper(II) ions can bind in close proximity to one another.[1] A magnetic study on the structurally characterised perchlorate bridged dinuclear copper(II) complex $[Cu_2(1,3\text{-tpbd})(H_2O)_2(ClO_4)_3](ClO_4)$ (**1**, Figure 1) showed that a significant ferromagnetic coupling ($J = +9.3$ cm^{-1}, the Hamiltonian being defined as $\mathbf{H} = -J\mathbf{S}_1\cdot\mathbf{S}_2$) mediated by the phenylenediamine unit could be observed[2] and the intramolecular Cu···Cu distance is 5.873(1) Å.[1] Ferromagnetic coupling has also been reported recently for a related dinuclear complex.[3] The ferromagnetic coupling following the spin polarisation mechanism was successfully interpreted for both complexes using density functional theory (DFT) calculations.[2,3]

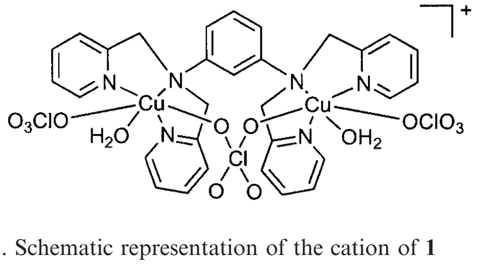

Figure 1. Schematic representation of the cation of **1**

In contrast, no magnetic exchange coupling was observed when the perchlorate group in **1** was substituted with acetate {which did not bridge the two copper(II) ions} or sulfate {the sulfate ion acting as both a terminal ligand and a one-atom bridging ligand in the tetranuclear complex $[Cu_4(1,3\text{-tpbd})_2(H_2O)_2(SO_4)_4]$}.[2]

Besides acetate, azide, and oxalate are typical multidentate ligands employed in copper(II) chemistry in order to achieve strong magnetic coupling between two metal centres.[4] Polynuclear copper(II) complexes with bridging azide ligands have received much attention due to the diverse range of their structural and magnetic properties.[4] Interest originates from the variety of coordination modes the azide anion can exhibit. It can act either as a terminal ligand or as a bridging ligand. For the latter case, three different types of structure may be observed: N_3^- can bridge through just one of the terminal nitrogen atoms (μ-1,1)[5–16] or through both terminal nitrogen atoms (μ-1,3) either symmetrically or asymmetrically.[5,17–23] The magnetic behaviour of the respective modes of coordination has been well established. The μ-1,1 mode mediates strong ferromagnetic exchange interactions and the symmetric μ-1,3 mode mediates strong antiferromagnetic exchange interactions.

During the last 20 years extensive theoretical and experimental studies by Kahn[9,24,25] and others[26,27] have been carried out in order to understand the exceptional ability of the oxalate bridge in mediating very weak to quite strong antiferromagnetic coupling between copper(II) centres separated by more than 5.5 Å. Kahn et al. elegantly demonstrated that in a series of dinuclear copper(II) μ-oxalate

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DOI: 10.1002/ejic.200300456

complexes it was possible to "tune" the singlet-triplet energy gap (2J) over a wide range ($0 < 2J < 400$ cm^{-1}) by keeping the [Cu(μ-oxalate)Cu]$^{2+}$ core constant and varying only the nature of the amine ligands.[28]

We decided to exploit the fact that the ligand 1,3-tpbd is capable of binding two metal ions at a fixed distance in order to prepare a novel dinuclear copper(II) bridging oxalate complex. It was envisaged that the 1,3-tpbd backbone would "fix" the [Cu(μ-oxalate)Cu]$^{2+}$ core in a rigid planar conformation leading to a strong antiferromagnetic interaction between the two copper(II) centres mediated by the oxalate bridge. Herein, we report the synthesis, structural characterisation, and magnetic behaviour of 1,3-tpbd copper(II) complexes with azide and oxalate as co-ligands.

Results and Discussion

Crystal Structure of [Cu_2(1,3-tpbd)$(N_3)_4$] (2)

The mode of azide binding which would occur in the copper(II) complex of 1,3-tpbd [Cu_2(1,3-tpbd)$(N_3)_4$] (**2**) was not at all predictable. We assumed the azide ligands would most likely adopt an intra- or intermolecular bridging mode (the common case). A structural determination of **2** revealed, however, two terminal azide anions coordinated to each copper(II) ion (the less common case). An ORTEP[29] representation of the crystal structure of **2** is shown below in Figure 2. Crystallographic data for **2** are presented in Table 2 with selected bond lengths and angles in Table 1.

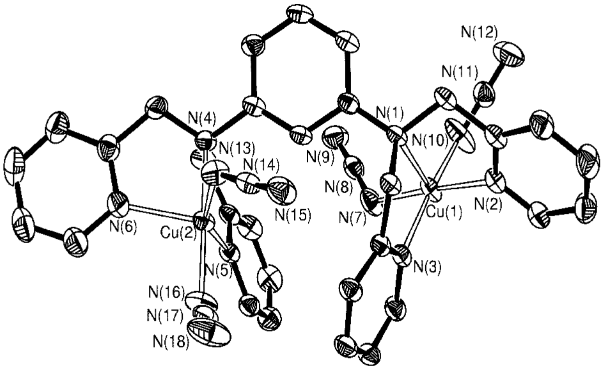

Figure 2. ORTEP[29] representation (50% probability displacement ellipsoids) of **2**. Hydrogen atoms omitted for clarity

Table 1. Selected bond lengths [Å] and angles [°] in **2** and **3**

2			
Cu(1)−N(1)	2.474(2)	Cu(2)−N(4)	2.138(2)
Cu(1)−N(2)	2.036(2)	Cu(2)−N(5)	2.029(2)
Cu(1)−N(3)	2.044(2)	Cu(2)−N(6)	2.176(2)
Cu(1)−N(7)	1.955(2)	Cu(2)−N(13)	1.979(2)
Cu(1)−N(10)	1.975(2)	Cu(2)−N(16)	1.959(2)
Cu(1)···Cu(2)	6.160(2)		
N(1)−Cu(1)−N(2)	75.08(6)	N(2)−Cu(1)−N(3)	90.88(6)
N(1)−Cu(1)−N(3)	77.42(5)	N(2)−Cu(1)−N(7)	176.16(6)
N(1)−Cu(1)−N(7)	105.04(7)	N(3)−Cu(1)−N(10)	172.58(8)
N(1)−Cu(1)−N(10)	110.00(8)		

3			
Cu(1)···N(1)	2.509(2)	Cu(1)−O(1)	2.013(2)
Cu(1)−N(2)	2.026(3)	Cu(1)−O(2)	1.996(2)
Cu(1)−N(3)	2.027(3)	Cu(1)−O(5)	2.242(2)
Cu(1)···Cu(2)	5.188(2)	C(31)−C(32)	1.540(4)
N(2)−Cu(1)−N(3)	99.6(1)	N(3)−Cu(1)−O(2)	87.73(9)
N(2)−Cu(1)−O(1)	88.07(9)	N(3)−Cu(1)−O(5)	91.54(9)
N(2)−Cu(1)−O(2)	163.38(9)	O(1)−Cu(1)−O(2)	83.21(9)
N(2)−Cu(1)−O(5)	92.32(9)	O(1)−Cu(1)−O(5)	94.79(8)
N(3)−Cu(1)−O(1)	169.88(9)	O(2)−Cu(1)−O(5)	102.46(8)

Table 2. Crystallographic data for **2** and **3**

	2	**3**
Formula	$C_{30}H_{28}Cu_2N_{18}$	$C_{41}H_{49}Cl_2Cu_2N_9O_{15}$
M	767.78	1105.87
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	9.0968(7)	12.6529(7)
b [Å]	12.769(1)	12.9553(8)
c [Å]	15.804(2)	15.5846(9)
α [°]	66.918(1)	78.084(1)
β [°]	81.261(1)	67.703(1)
γ [°]	74.051(1)	81.976(1)
U [Å^3]	1621.7(2)	2307.4(2)
Z	2	2
D_c [g·cm^{-3}]	1.572	1.592
μ [mm^{-1}]	1.366	1.117
Reflections measured	17240	25012
Unique reflections	7655	11012
R_{int}	0.0195	0.0476
Parameters	460	645
R (F, $F^2 > 2σ$)	0.0293	0.0453
R_w (F^2, all data)	0.0814	0.1055

Each copper(II) ion in **2** is five-coordinate [intramolecular separation Cu(1)···Cu(2) = 6.160(2) Å] being ligated by five nitrogen donor atoms, three nitrogen atoms from the 1,3-tpbd ligand and two azide ions. The coordination geometry around Cu(1) and Cu(2) is best described as distorted square-based pyramidal, with Cu(1) adopting a closer to ideal square-based pyramidal geometry than Cu(2). For Cu(1) the trigonality index parameter[30] $\tau = 0.06$ [where $\tau = (\beta - \alpha)/60$, with α and β being the two largest coordination angles around the metal centre. For ideal square-pyramidal geometry $\tau = 0$, while for perfect trigonal-bipyramidal geometry $\tau = 1$]. The equatorial plane around Cu(1) consists of the pyridyl donor atoms N(2) and N(3) of the ligand and the azide donor atoms N(7) and N(10) [Cu(1)−N(2) = 2.036(2) Å, Cu(1)−N(3) = 2.044(2) Å, Cu(1)−N(7) = 1.955(2) Å, Cu(1)−N(10) = 1.975(2) Å]. Occupying the apical coordination site is the tertiary amine atom N(1) of the ligand [Cu(1)−N(1) = 2.474(2) Å]. Around Cu(2) the coordination geometry is significantly distorted from square pyramidal towards trigonal bipyramidal (τ[30] = 0.36). The apical coordination site of Cu(2) however is occupied by the pyridyl donor atom N(6) of the ligand [Cu(2)−N(6) = 2.176(2) Å] and not by the tertiary amine atom N(4), which is in contrast to what is evident for Cu(1). The equatorial plane around Cu(2) consists of the tertiary amine atom N(4) and the pyridyl donor atom N(5) of the ligand and the donor atoms N(13) and N(16) of the two azide ligands [Cu(2)−N(4) = 2.138(2) Å, Cu(2)−N(5) = 2.029(2) Å, Cu(2)−N(13) = 1.979(2) Å, Cu(2)−N(16) = 1.959(2) Å]. Cu(2) deviates from the mean plane of the square pyramid towards the apical N(6) by ca. 0.22 Å.

Asymmetric azide stretching vibrations generally occur above 2000 cm^{-1}, and the appearance of more than one band is a good indication that more than one type of azide ligand is present. In the solid state the N_3^- stretching frequency in **2** appears as a sharp band at 2048 cm^{-1}, a value which is in agreement with other structurally and spectroscopically characterised dinuclear copper(II) complexes containing terminal azide ligands.[11,31]

[Cu_2(1,3-tpbd)(C_2O_4)$(DMF)_2$]$(ClO_4)_2$·DMF (3)

Reacting sodium oxalate with **1** led to the initial isolation of a turquoise coloured precipitate. Recrystallisation of the precipitate by slow diffusion of diethyl ether into a DMF containing solution led to the formation of the dinuclear complex [Cu_2(1,3-tpbd)(C_2O_4)$(DMF)_2$]$(ClO_4)_2$·DMF (**3**). An ORTEP[29] representation of the crystal structure of the cation of **3** is shown below in Figure 3. Crystallographic data for **3** are presented in Table 2 and selected bond lengths and angles are in Table 1.

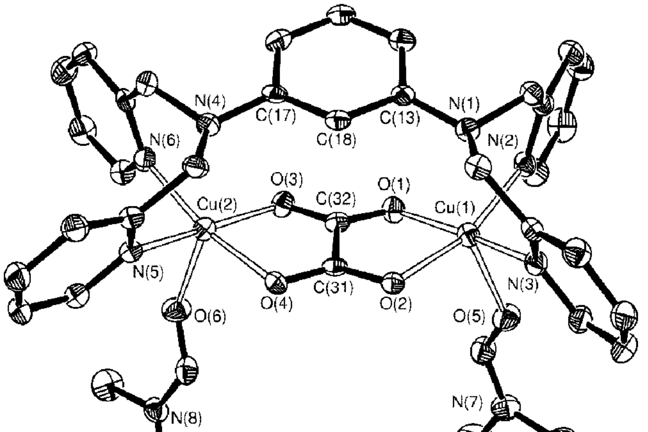

Figure 3. ORTEP[29] representation (50% probability displacement ellipsoids) of **3**. Hydrogen atoms and one DMF solvent molecule omitted for clarity

The cation of **3** consists of two copper(II) ions [intramolecular separation Cu(1)···Cu(2) = 5.188(2) Å] with the copper(II) ions being bridged by the bis-bidentate oxalate ion. Both the copper(II) centres are best described as having a "4+1" square pyramidal coordination geometry and the geometrical parameters around each copper(II) centre do not differ significantly from one another. The basal plane around Cu(1) consists of the two pyridine nitrogen atoms of the ligand [Cu(1)−N(2) = 2.026(3) Å and Cu(1)−N(3) = 2.027(3) Å] and two oxygen atoms of the oxalate anion [Cu(1)−O(1) = 2.013(2) Å and Cu(1)−O(2) = 1.996(2) Å]. A DMF solvent molecule occupying the apical site [Cu(1)−O(5) = 2.242(2) Å] completes the coordination environment around Cu(1). The tertiary amine nitrogen N(1) forms a very weak interaction with Cu(1) [Cu(1)···N(1) = 2.509(2) Å]. This is most likely the reason for the much smaller distance between the copper(II) ions in **3** compared with **1** or **2**. The dimensions of the oxalate anion show no abnormalities and are typical of those found in other structurally characterised copper(II) complexes. The basal planes around Cu(1) and Cu(2) do not lie perfectly coplanar with the plane containing the oxalate bridge: the oxalate bridge is slightly "puckered", giving rise to a "boat type" conformation.[27] The oxalate anion and the central aromatic ring of the 1,3-tpbd moiety are not coplanar with one another and, moreover, the oxalate anion does not lie directly beneath the aromatic ring. However, the central aromatic ring carbon atoms C(13), C(17), and C(18) make several close contacts with the oxalate anion: [C(13)···O(1) = 3.333 Å, C(18)···C(31) = 3.018 Å, C(18)···C(32) = 3.171 Å, and C(17)···O(3) = 3.262 Å].

Many structurally characterised oxalate bridged complexes are known: a search of the Cambridge Structural Database[32] for dinuclear copper(II) complexes of amine ligands containing a bridging bis-bidentate oxalate unit reveals there to be between 40 and 50 such structures.[28,33−37]

However, in contrast to these compounds, complex **3** presents a novel structural motif in which the two copper(II) ions are furthermore bridged by the dinucleating 1,3-tpbd ligand, thus leading to a metallamacrocyclic complex when oxalate is coordinated. There are only two other examples of structurally characterised dinuclear copper(II) complexes that use oxalate only as an additional bridging ligand.[38,39] However, these complexes contain macrocyclic ligands prior to their binding to oxalate and the magnetic properties of these complexes have not been described.

Magnetic Measurements

Measurements of the magnetic properties on powder samples of **2** and **3** were performed. A plot of $m{\cdot}T/B$ vs. temperature for **2** at a magnetic field of 5.5 T showed no maximum which is characteristic of antiferromagnetic coupling and is shown below in Figure 4.

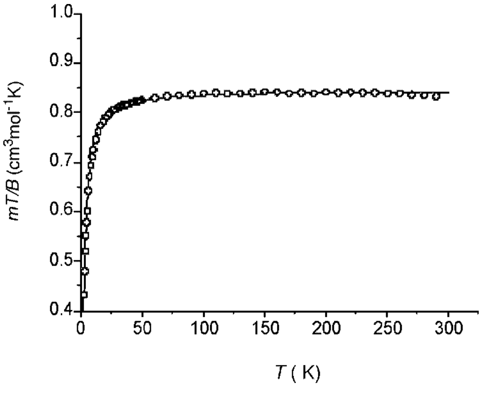

Figure 4. $m{\cdot}T/B$ vs. temperature of **2**. Circles represent experimental data, the solid line represents the fit

For $T > 50$ K the system behaves like an uncoupled dimer as the signal is constant at a value of 0.8 cm^3·mol^{-1}·K. At low temperatures, the signal decreases with temperature, an indication that the value of $|J|$ is small. Quantitative analysis of the data using the Hamiltonian $H = -J\,\boldsymbol{S}_1\cdot\boldsymbol{S}_2 + \mu_B g\boldsymbol{S}\cdot\boldsymbol{B}$, where J denotes the exchange coupling parameter, g the Zeeman factor, $\boldsymbol{S}_1$, $\boldsymbol{S}_2$, and **S** the Spin Operators for each copper(II) ion and for the coupled system] revealed as a best fit the following parameters: $J = -2.1(4)$ cm^{-1}, $g = 2.10(8)$ with $R = 1.25\cdot10^{-5}$ ($R = \{\Sigma[(\chi_m T)_{exp} - (\chi_m T)_{calc}]^2\}/[\Sigma(\chi_m T)^2_{exp}]\}$. As the azide anions do not act as bridging ligands, no suitable magnetic exchange pathway is available between the unpaired electrons of each copper(II) ion. Ferromagnetic coupling is no longer possible because one of the amine nitrogen donor atoms N(1) occupies the axial site of Cu(1) and is no longer in an equatorial position of the complex.

The magnetic behaviour of **3** is shown in Figure 5 as a plot of $\chi_m\cdot T$ vs. temperature, where χ_m denotes the molar susceptibility. The signal decreases with temperature down to 100 K. At lower temperatures the signal vanishes indicating an antiferromagnetic **S** = 0 ground state. For theoretical analysis the same spin Hamiltonian as above was employed. At 300 K the signal is well below the value expected for two isolated copper(II) ions (0.8 cm^3·mol^{-1}·K) indicating a huge value for $|J|$. The parameters obtained from a best fit obtained from a least-squares analysis are: $J = -366(9)$ cm^{-1}, $g = 2.18(2)$ and $R = 7.3\cdot10^{-6}$. The theoretical curve using the above parameters is shown in Figure 5.

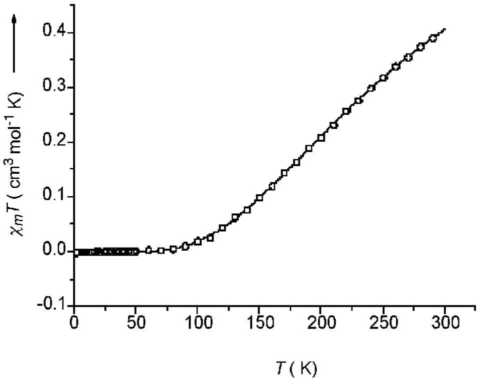

Figure 5. $\chi_m\cdot T$ vs. temperature of **3**. Circles represent experimental data, the solid line represents the fit

In contrast to **1**, ferromagnetic coupling in **3** via a spin polarisation pathway through the phenylenediamine backbone is completely excluded because the tertiary amine nitrogen atoms N(1) and N(4) of the ligand (see Figure 3 above) are not coordinated to the copper(II) ions. However, in contrast to **2**, the bridging oxalate ligand in **3** offers a pathway for strong antiferromagnetic coupling. The J value lies in the expected range for a square pyramidal copper(II) centre, albeit towards the strongest coupling observed for a Cu(ox)Cu complex containing only nitrogen donor ligands. The antiferromagnetic coupling is only slightly smaller than that found in the $[\mathrm{tmen(H_2O)Cu(\mu\text{-}C_2O_4)Cu(H_2O)tmen}]^{2+}$ cation ($J = -384.5$ cm^{-1}).[4]

Conclusion

From the results presented herein together with an earlier report we have clearly demonstrated that the magnetic properties of copper(II) complexes of the 1,3-tpbd ligand can be adjusted from weakly ferromagnetic to strongly antiferromagnetic. However normal magnetic behaviour of magnetically isolated copper(II) ions (data following the Curie Law) as well as very weak antiferromagnetic behaviour can also be achieved. Often changes in the magnetic properties of dinuclear copper(II) complexes can be achieved by varying the nature of the ligand, and not the magnetic coupling unit e.g. azide or oxalate.

Experimental Section

General Remarks: The ligand 1,3-tpbd was synthesised as described previously.[1] Reagents and solvents were of commercially available reagent grade quality and were used without further purification. Magnetic susceptibility data for **2** and **3** were collected in the temperature range of 1.8−300 K on a Quantum Design MPMS-7 SQUID magnetometer. Two samples of each compound were investigated. The powder samples (typically 0.5 mg) were mixed with apiezon grease and fixed on a plastic straw. The signal of the grease could be subtracted from the experimental measurements, whereas the signal due to the straw was negligible.

Caution! *The syntheses and procedures described below involve compounds that contain perchlorate and azide ions, which can detonate explosively and without warning. Although we have not encountered any problems with the compounds used in this study, they should be handled with extreme caution.*

$[\mathrm{Cu_2(1,3\text{-}tpbd)(N_3)_2}]$ (2): 1,3-tpbd (0.100 g, 0.21 mmol) was suspended in acetonitrile (3 cm^3). To this suspension was added $\mathrm{Cu(OAc)_2\cdot H_2O}$ (0.085 g, 0.42 mmol) in water (2 cm^3). The green coloured solution was stirred for a few minutes and sodium azide (0.055 g, 0.84 mmol) in water (2 cm^3) was added dropwise. The solution became dark green. Within the period of a few hours a precipitate had formed which was removed and discarded. The remaining dark green coloured solution was allowed to evaporate slowly at room temperature. Within one week small dark green coloured needles of **2** appeared which were suitable for a single-crystal X-ray structural determination; found C 46.64, H 3.75, N 33.00. $\mathrm{C_{30}H_{28}Cu_2N_{18}}$ (767.770) requires C, 46.93, H 3.68, N 32.84%.

$[\mathrm{Cu_2(1,3\text{-}tpbd)(C_2O_4)(DMF)_2}](\mathrm{ClO_4})_2\cdot\mathrm{DMF}$ (3): 1,3-tpbd (0.100 g, 0.21 mmol) was suspended in methanol (3 cm^3). To this suspension was added $\mathrm{Cu(ClO_4)_2\cdot 6H_2O}$ (0.157 g, 0.42 mmol) in water (2 cm^3). The dark green coloured solution was stirred for a few minutes and sodium oxalate (0.0284 g, 0.21 mmol) in water (2 cm^3) was added dropwise. A turquoise coloured precipitate appeared immediately. The precipitate was filtered, washed with a little water and diethyl ether, and dried (0.178 g, 0.19 mmol, 91%). The blue coloured powder was dissolved in dimethylformamide (2 cm^3). Diethyl ether was allowed to slowly diffuse into the solution and within the period of a few days small light green coloured crystals appeared which were suitable for a single-crystal X-ray structural determination; found C 44.62, H 4.74, N 11.14. $\mathrm{C_{41}H_{49}Cl_2Cu_2N_9O_{15}}$ (1105.897) requires C 44.53, H 4.47, N 11.40%. IR (KBr disc): $\tilde{\nu}$/cm^{-1}: 1661 ($\tilde{\nu}_{asym}$OCO oxalate); 1348, 1306 ($\tilde{\nu}_{sym}$OCO oxalate); 774 (δ_{sym}OCO oxalate).

X-ray Crystallographic Studies: The details of structure solution and refinement are given in Table 2. Cell dimensions and intensity data for **2** and **3** were measured at 200(2) K on a Siemens SMART 1000 CCD diffractometer with graphite-monochromated Mo-K_{α} radiation ($\lambda = 0.71073$ Å). The collected reflections were corrected for Lorentz, polarisation, and absorption effects. The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2.[40–42] Anisotropic displacement parameters were refined for all non-hydrogen atoms, and isotropic hydrogen atoms were included with riding model constraints.

CCDC-207005 for **2** and -207004 for **3** 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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Received July 11, 2003