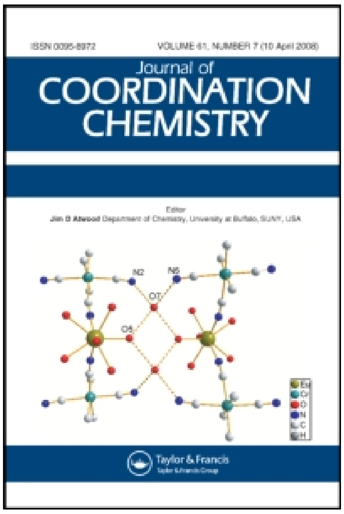

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SYNTHESIS AND CHARACTERIZATION OF A LINEAR μ-OXO DIIRON(III) COMPOUND AND A COPPER(II) NITRITE COMPLEX CONTAINING, A TRIPODAL POLYBENZIMIDAZOLE LIGAND

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SYNTHESIS AND CHARACTERIZATION OF A LINEAR μ-OXO DIIRON(III) COMPOUND AND A COPPER(II) NITRITE COMPLEX CONTAINING, A TRIPODAL POLYBENZIMIDAZOLE LIGAND

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Iron(III) and copper(II) complexes of the polybenzimidazole ligand, tris((benzimidazol-2-yl)methyl)amine (tmba) have been synthesized and structurally characterized. The mononuclear complex $[Cu(tmba)(NO_2)]^+[CH_3OH][NO_2^-]$, **1**, has been isolated and characterized by X-ray crystallography. The complex crystallizes in the triclinic space group P1 with two molecules in the unit cell of dimension $a = 8.891(5)$, $b = 11.775(6)$, and $c = 13.702(8)$ Å, and $\alpha = 67.76(1)$, $\beta = 71.79(2)$ and $\gamma = 88.96(1)°$, and volume = 1253.0(12) Å^3. The structure was refined to a final agreement factor $R = 0.0901$ using 4134 observed reflections. The complex consists of cationic copper(tmba) complex covalently bonded to a nitrite, and a pair of these cations is dibridged by a pair of nitrite anions. The gap between this dimer is occupied by a methanol molecule. The coordination environment around each copper can be described as trigonal bipyramidal, with the tertiary amine, a benzimidazole nitrogen and an oxygen from the nitrite providing the ligating atoms of the trigonal plane.

The μ-oxo bridged binuclear complex $[Fe_2O(tmba)_2Cl_2](H_2O)(EtOH)_2 \cdot Cl_2$, **2**, was also characterized by single crystal X-ray diffraction and magnetic susceptibility. The complex crystallizes in the triclinic space group P1 with one molecule in the unit cell of dimensions, $a = 11.5791(7)$, $b = 13.3369(8)$, and $c = 13.7002(9)$ Å, and $\alpha = 103.904(1)$, $\beta = 108.903(2)$ and $\gamma = 112.845(1)°$, and volume = 1674.1(2) Å^3. The structure was refined to a final agreement factor $R = 0.073$ using 5597 observed reflections. The complex is a centrosymmetric dimer, with the two iron(III) atoms bridged by an oxygen atom, with an Fe—O—Fe angle of 180°, and a Fe—Fe distance of 3.61(1)Å. The coordination around each iron(III) is best described as octahedral, with the bridging oxygen *trans* to one end of the benzimidazole group, and a chlorine atom *trans* to the tertiary amine nitrogen of the ligand.

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Keywords: Diiron(III); Tripodal ligand; Benzimidazole; Oxo bridged; Copper(II)

INTRODUCTION

Mono and binuclear metal centers are found to occur in several enzymes involved in catalysis of hydrolytic reactions such as the purple acid phosphatases, (using Fe) [1, 2]. The nitrite reductases responsible for reduction of nitrate and nitrite to gaseous NO, N_2O and/or N_2, a process responsible for depletion from soil of the nitrogen necessary in plant growth and also a key process in the global nitrogen cycle, have Fe and Cu as the metal [3–5]. Finally, ribonucleotide reductase uses Fe [6]. Very recently, attention has been focused on oxo-bridged iron(III) complexes. This interest is driven largely by the need to gain better understanding of the role of diiron sites in iron containing proteins such as the non-heme proteins hemerythrin, ribonucleotide reductase [6], and the purple acid phosphatases [2]. Recent structures of methemerythrin and the oxidized form of ribonucleotide reductase from Escherichia coli showed these enzymes to contain (μ-oxo), bis(μ-carboxylato), a μ-oxide and one μ-carboxylate bridged core units, respectively, and histidine imidazole as the ligand [6, 7]. More recent efforts in modeling the structure and reactivity of diiron protein active sites focused on the mechanism of O_2 binding in hemerythrin [8].

In these studies, both deoxyHr and metHr are known to contain an open coordination site on one of the iron centers that readily binds small anion ligands. In addition, the azide ligand in N_3MetHr is labile and known to exchange with other anionic ligands [8]. Dioxygen, on the other hand, is known to react with the diferrous center of deoxyHr, resulting in a bound hydroperoxide ion stabilized by intramolecular hydrogen bonding involving the bridging oxo group. It is our understanding that complexes capable of acting as functional models for the diiron non-heme proteins or nitrite reductase must have either a free coordination site or a ligand which can be replaced easily by an incoming substrate molecule.

The present work reports on the results of our search for model compounds having these features. The nonbridging ligators in the complexes reported here are provided by the tetradentate tripodal ligand tris(2-benzimidazolylmethyl)amine (tmba), which has served as a good substitute for the arrangement of histidine groups anchoring the metal centers in many metalloproteins [9, 10]. Monomeric tmba complexes have been reported with Cu(II), Fe(II), Mn(II) and Co(II), and geometries based on trigonal bipyramidal, octahedral, and capped octahedral, have all been represented among these complexes [10]. We report the synthesis and characterization of a diiron(III) oxo complex and copper(II) nitrite as models for the non-heme protein and the type 2 copper center in nitrite reductase, respectively.

EXPERIMENTAL

Materials

The chemicals for the synthesis of the compounds were used as purchased, TMBA-tris (2-benzimidazolylmethyl)amine was synthesized as previously reported [9], the iron(II) chloride tetrahydrate and copper(II) chloride dihydrate were purchased from Aldrich Co. All chemicals and solvents were reagent grade.

Physical Measurements

Infrared spectra (400–4000 cm^{-1}) were recorded on a Nicolet Impact-400 with KBr pellets. UV-vis spectra were recorded on a Perkin Elmer Lamda II Spectrophotometer.

Preparation of the Compounds

[Cu(TMBA)(NO$_2$)(1/2CH$_3$OH)](NO$_2$)

To a solution of 1.625 g (3.0 mmol) of copper(II) chloride TMBA (synthesized as reported in Ref. [9]), in 30 ml of methanol, was added 0.68 g (8 mmol) of potassium nitrite solution in 10 mL of methanol. The solution was stirred for about thirty minutes, the light green solution changed to a dark green color. Subsequent reduction in volume and slow crystallization over a period of one week yielded a green crystalline solid of [Cu(TMBA)(NO$_2$)](NO$_2$), **1**, 1.3 g (2.3 mmol) 77% yield. Anal Calc. for $CuC_{24}H_{21}N_9O_4$(%) C, 51.2 H, 3.76 N, 22.4 Observed: [11] C, 50.92 H, 3.83 N, 22.55 IR, 1630 (m), 1610 (m), v (C=N), 1550 (s), 1488 (s), 1468 (s), 1450 (vs) symmetric stretch (—C=N—C=C—), 1300 (s), 1250 (s), 1050 (s), 1020 (s), 826 (s) ionic non-coordinating nitrite, 800 (s), 780 (s) v (NO$_2$).

[Fe$_2$(TMBA)$_2$(O)(Cl)$_2$](Cl)$_2$ · 6ETOH · 2H$_2$O

To a solution of 0.59 g (3.0 mmol) of iron(II) chloride tetrahydrate in 30 mL of ethanol was added 1.22 g (3 mmol) of TMBA in 10 mL of ethanol. The solution was stirred for about two hours in air, followed by addition of 3 mmol of sodium acetate. The final solution was filtered and the filtrate allowed to slowly evaporate to give reddish brown crystals $[Fe_2(TMBA)_2(Cl_4)] \cdot 6EtOH \cdot 2H_2O$, **2**, 1.25 g (0.91 mmol) 61% yield. Anal Calc. for $Fe_2Cl_4C_{60}H_{82}N_{14}O_9$(%) C, 51.54 H, 5.92 N, 14.03 Observed: [11] C, 51.72 H, 5.69 N, 13.92, 1636 (m), 1615 (m), v (C=N), 1550 (s), 1490 (s), 1465 (s), 1454 (vs) symmetric stretch (—C=N—C=C—), 1306 (s), 1248 (m), 1050 (s), 826 (m).

X-ray Structure Determination

Single crystals of the compounds **1** and **2** were glued to glass fibers and mounted on the Siemens SMART system for data collection at 173 K. An initial set of cell constants were calculated from reflections harvested from three sets of 30 frames. These initial sets of frames are oriented such that orthogonal wedges of reciprocal space were surveyed. This produces orientation matrices determined from 150 reflections for compound **1** and 44 reflections for compound **2**. Final cell constants for **1** are calculated from a set of 2565 strong reflections from the actual data collection. Final cell constants for **2** are calculated from a set of 3714 strong reflections from the actual data collection. Crystal and experimental data are summarized in Table I.

Structure Solution and Refinement for 1 and 2

The space group P1 was determined based on systematic absences and intensity statistics [12]. A successful direct methods solution was calculated which provided most non-hydrogen atoms from the E-map. Several full matrix least squares/difference fourier cycles were performed to locate the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with individual isotropic displacement parameters.

A major difficulty was obtaining a suitable specimen of **1** for data collection. These crystals are plates and crystallized in bunches. One small sample was liberated from a mass which was used for data collection. Frame duration was thirty seconds. The quality of the result is an effect of the quality and the size of the sample. All calculations were performed using SGI INDY R4400-SC or Pentium computers using the SHELXTL V5.0 suite of programs.

The final cycles of refinement for **1** converged at $R = [I > 2\sigma(I)] = 0.0901$ $wR_2 = 0.1925$ based on 4134 independent reflections $[I > 2.0s(I)]$.

TABLE I Summary of X-ray crystallographic data

Crystal data	1	2
Empirical formula	$C_{24.58}H_{23.31}CuN_9O_{4.58}$	$C_{30}H_{41}Cl_2FeN_7O_{4.50}$
Crystal habit, color	Plate, Green	Needle, Red – orange
Crystal size	0.25 × 0.15 × 0.05 mm	0.50 × 0.10 × 0.08 mm
Crystal system	Triclinic	Triclinic
Space group	P1	P1
a(Å)	8.891(5)	11.5791(7)
b(Å)	11.775(6)	13.3369(8)
c(Å)	13.702(8)	13.7004(9)
α(deg.)	67.759(12)	103.904(1)
β(deg.)	71.79(2)	108.903(1)
γ(deg.)	88.962(12)	112.845(1)
Volume	1253.0(12) $Å^3$	1674.1(2) $Å^3$
Z	2	2
Formula weight	581.61	698.45
density(calcd)	1.542 Mg/m^3	1.386 Mg/m^3
temp. (k)	173(2)	173(2)
Absorption Coefficient	0.926 mm^{-1}	0.657 mm^{-1}
F(000)	732	732
Diffractometer	Siemens SMART Platform CCD	Siemens SMART Platform CCD
Wavelength	0.71073 Å	0.71073 Å
Theta range data Coll.	1.70 to 25.10°	1.73 to 25.07°
Reflections collected	6349	9536
Independent reflections	4134 ($R_{\cdot int} = 0.0583$)	5597 ($R_{\cdot int} = 0.0296$)
System used	SHELXTL-V5.0	SHELXTL-V5.0
Solution	Direct methods	Direct methods
Refinement Method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Weighting scheme	$w = [\sigma^2(Fo^2) + (AP)^2 + (BP)]^{-1}$ where $P = ((Fo^2) + (2Fc^2))/3$, $A = 0.0610$, and $B = 6.5825$	$w = [\sigma^2(Fo^2) + (AP)^2 + (BP)]^{-1}$ where $P = ((Fo^2) + (2Fc^2))/3$, $A = 0.0964$, and $B = 1.1512$
Absorption Correction	Semi-empirical	SADABS (Sheidricks, 1996)
Max and Min. transm.	0.82274 and 0.52250	1.000 and 0.643
Data/restraints/Para.	4134/0/384	5597/9/403
R indices($l > 2\sigma(l) = 3497$	$R_1 = 0.0901$, $wR_2 = 0.1925$	$R_1 = 0.073$, $wR_2 = 0.1698$
R indices (all data)	$R_1 = 0.1214$, $wR_2 = 0.2144$	$R_1 = 0.1257$, $wR_2 = 0.1958$
Goodness of fit on F^2	1.166	1.032
Largest diff. peak and hole	0.793 and $-$ 0.978 eA^{-3}	0.718 and $-$ 0.465 eA^{-3}

The final cycles of refinement for **2** converged at $R = [I > 2\sigma(I)] = 0.0730$ $wR_2 = 0.1698$ based on 5597 independent reflections $[I > 2.0\sigma(I)]$.

RESULTS AND DISCUSSION

Description of the Structures

The molecular structure of $[Cu(TMBA)(NO_2)](1/2CH_3OH)(NO_2)$ is ionic and layered. The structure of $[Cu(II)(TMBA)(NO_2)]^+$ is depicted in

Figure 1. Like other Cu(II) complexes with tetradentate tripodal ligands [13], compound **1** has a severely distorted geometry and could not be described as distorted square pyramidal nor distorted trigonal bipyramidal, but a combination of both. This type of distortion has been observed with similar tripodal tetradentate ligands and was attributed to steric rather than electronic factors. In the cationic complex the nitrite is coordinated to the Cu(II) center through its oxygen with a Cu—O(11) distance of 1.988(6) Å. Three nitrite binding conformations have been reported for mononuclear Cu(II) structures [14–16]; the nitrite could bind to copper with one of its oxygens, as seen in $[Cu(terpy)(NO_2)OH_2]^+$ [14], it could bind to copper with its two oxygen atoms as observed in $Cu(bpy)(NO_2)_2$ and $[Cu(bpy)_2(NO_2)]^+$ [1a, 15b] and the third which is rarely observed is the binding through its nitrogen as observed in $[Cu(NO_2)_6]^{4-}$ [16]. In compound **1**, the nitrite binds through one of its oxygens, however, there are several hydrogen bonded interactions between the nitrite and the methylene hydrogen in the ligand. A pair of the cations are dibridged by a pair of nitrite anions as shown in (Fig. 2) and the gap between this dimer is also the gap between the layers as shown in the unit cell drawing (Fig. 3). There is an additional attraction

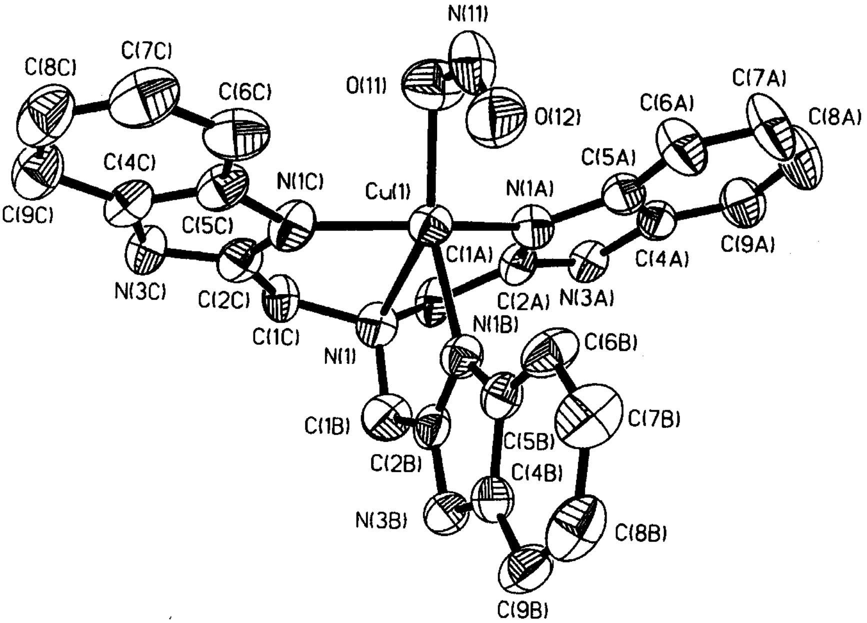

FIGURE 1 Molecular structure of the cation, $[Cu(II)(TMBA)(NO_2)]^+$, **1**.

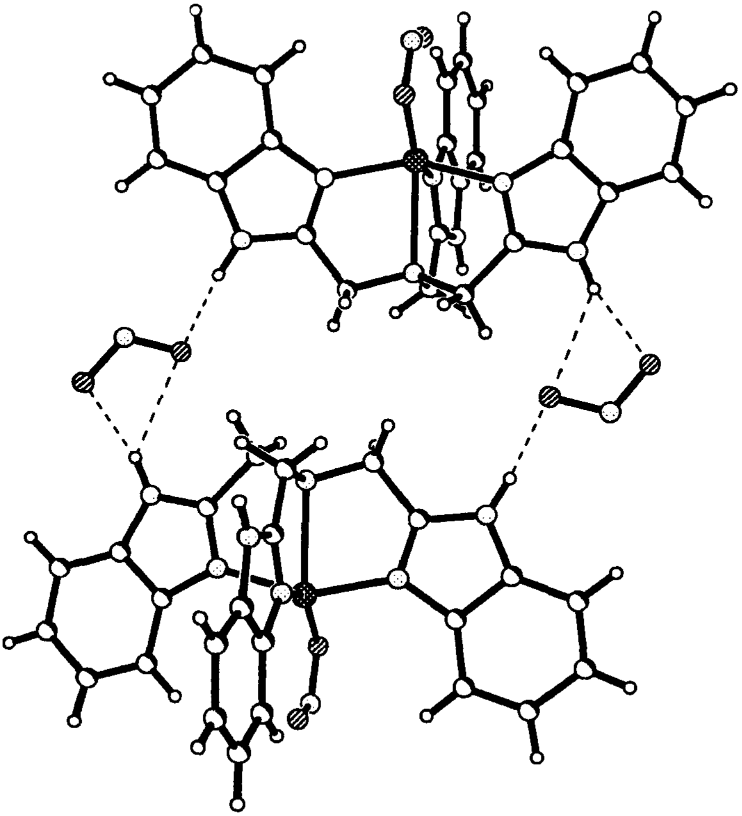

FIGURE 2 Molecular structure of the pair of cations [Cu(II)(TMBA)(NO_2)]$^+$ with bridging nitrite anions in **1**.

between pairs in the same layers that is considerably weaker. Between the layers a partially occupied methanol solvent molecule is found. The copper to nitrogen distances range from 1.951(6) Å for Cu(1)—N(1c) to 2.405(6) Å for Cu(1)—N(1), *i.e.*, the tertiary nitrogen of the *tmba* ligand. The lengthening in this latter Cu—N(1) distance may be a consequence of the steric nature of the ligand. Similar lengthening were observed in other metal complexes of *tmba* ligands [10].

The O—N—O angle of 122.8° in the coordinating nitrite is about 9° wider than the angle in the non-coordinating nitrite anion, where the O—N—O angle is 113.9°, and are within the range of nitrite O—N—O angles in Cu(II)–NO_2 complexes [14, 15]. The principal bond lengths and bond angles are given in Table II.

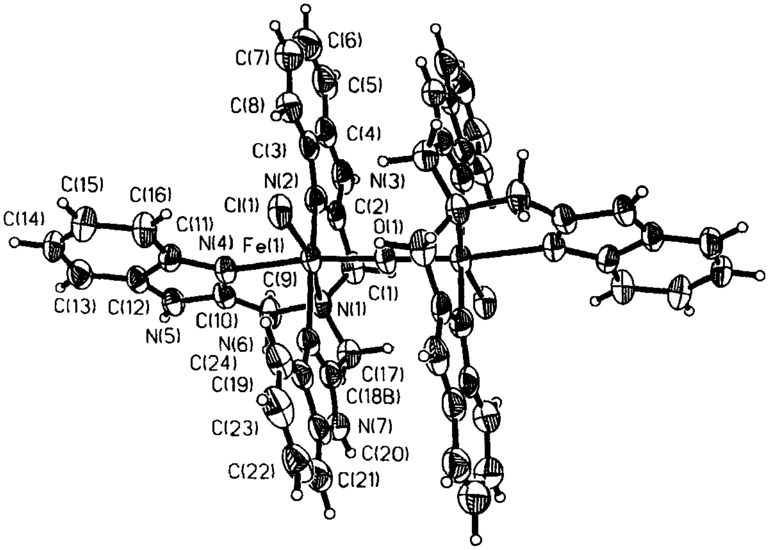

FIGURE 3 Molecular structure of the cation, $[Fe_2O(tmba)_2Cl_2]$, **2**.

The molecular structure of the (μ-oxo) diiron(III) complex, **2**, of the tripodal benzimidazolyl ligand consists of the cation $[tmba(Cl)Fe—O—Fe(Cl)tmba]^{2+}$, a water molecule and three ethanols located in a complex hydrogen-bonding scheme, and two chloride anions. The cation, depicted in Figure 3 lies in a crystallographic two-fold axis with perfect two-fold symmetry where the bridging oxygen lies in the center of symmetry, with Fe—(μ-O) distances of 1.8054(7) Å, and the Fe—O—Fe angle of 180.0° which is not significantly different from values in (μ-oxo)diiron(III) core structures [17]. Each iron (III) center is in a distorted octahedral geometry, where the iron atoms are each coordinated to one chlorine atom, with, an Fe(1)—Cl(1) distance of 2.304(2) Å, the bridging oxygen atom, and four nitrogen atoms from the tmba ligand. The bond distances and bond angles are listed in Table III. The tertiary amine of the two tmba ligands occupies a position *cis* to the μ-oxo bridge and *trans* to the ligating Cl. A similar configuration was observed in $[tpa(Cl)FeOFe(Cl)tpa]^{2+}$, where tpa is tris(2-pyridylmethyl)amine [18], the geometry is a consequence of steric constraints imposed by the tripodal ligands. In the absence of such constraints, one would have predicted the tertiary ligating nitrogen to occupy a position *trans* to the bridging oxygen based on electronic preference for a weaker ligand *trans* to the oxo bridge [19].

TABLE II Bond lengths [Å] and angles [°] for **1** [Cu(TMBA)(NO_2)(1/2CH_3OH)](NO_2)

Cu(1)—N(1C)	1.951(6)	Cu(1)—N(1A)	1.964(6)
Cu(1)—O(11)	1.988(6)	Cu(1)—N(1B)	2.056(6)
Cu(1)—N(1)	2.405(6)	O(11)—N(11)	1.245(9)
N(11)—O(12)	1.052(9)	N(1)—C(1B)	1.467(10)
N(1)—C(1A)	1.473(9)	N(1)—C(1C)	1.494(9)
N(1A)—C(2A)	1.292(9)	N(1A)—C(5A)	1.403(9)
C(1A)—C(2A)	1.500(10)	C(2A)—N(3A)	1.352(9)
N(3A)—C(4A)	1.366(9)	C(4A)—C(9A)	1.382(11)
C(4A)—C(5A)	1.424(11)	C(5A)—C(6A)	1.379(11)
C(6A)—C(7A)	1.364(12)	C(7A)—C(8A)	1.398(14)
C(8A)—C(9A)	1.359(13)	N(1B)—C(2B)	1.300(9)
N(1B)—C(5B)	1.374(9)	C(1B)—C(2B)	1.492(10)
C(2B)—N(3B)	1.346(9)	N(3B)—C(4B)	1.380(10)
C(4B)—C(9B)	1.379(11)	C(4B)—C(5B)	1.391(10)
C(5B)—C(6B)	1.376(10)	C(6B)—C(7B)	1.364(11)
C(7B)—C(8B)	1.391(13)	C(8B)—C(9B)	1.368(12)
N(1C)—C(2C)	1.311(10)	N(1C)—C(5C)	1.411(9)
C(1C)—C(2C)	1.491(10)	C(2C)—N(3C)	1.350(10)
N(3C)—C(4C)	1.378(10)	C(4C)—C(5C)	1.397(11)
C(4C)—C(9C)	1.399(11)	C(5C)—C(6C)	1.384(11)
C(6C)—C(7C)	1.390(13)	C(7C)—C(8C)	1.372(13)
C(8C)—C(9C)	1.363(13)	N(21)—O(22)	1.226(9)
N(21)—O(21)	1.268(9)	O(31)—C(31)	1.23(2)
N(1C)—Cu(1)—N(1A)	150.2(3)	N(1C)—Cu(1)—O(11)	91.1(3)
N(1A)—Cu(1)—O(11)	92.7(3)	N(1C)—Cu(1)—N(1B)	97.2(3)
N(1A)—Cu(1)—N(1B)	94.9(2)	O(11)—Cu(1)—N(1B)	148.4(3)
N(1C)—Cu(1)—N(1)	78.0(2)	N(1A)—Cu(1)—N(1)	78.2(2)
O(11)—Cu(1)—N(1)	134.1(2)	N(1B)—Cu(1)—N(1)	77.6(2)
N(11)—O(11)—Cu(1)	105.4(6)	O(12)—N(11)—O(11)	122.8(9)
C(1B)—N(1)—C(1A)	114.6(6)	C(1B)—N(1)—C(1C)	112.6(6)
C(1A)—N(1)—C(1C)	114.0(6)	C(1B)—N(1)—Cu(1)	107.4(4)
C(1A)—N(1)—Cu(1)	103.9(4)	C(1C)—N(1)—Cu(1)	103.1(4)
C(2A)—N(1A)—C(5A)	107.6(6)	C(2A)—N(1A)—Cu(1)	118.2(5)
C(5A)—N(1A)—Cu(1)	134.2(5)	N(1)—C(1A)—C(2A)	109.5(6)
N(1A)—C(2A)—N(3A)	112.2(7)	N(1A)—C(2A)—C(1A)	124.4(7)
N(3A)—C(2A)—C(1A)	123.4(6)	C(2A)—N(3A)—C(4A)	107.8(6)
N(3A)—C(4A)—C(9A)	133.1(7)	N(3A)—C(4A)—C(5A)	106.0(6)
C(9A)—C(4A)—C(5A)	120.8(7)	C(6A)—C(5A)—N(1A)	132.6(8)
C(6A)—C(5A)—C(4A)	121.0(8)	N(1A)—C(5A)—C(4A)	106.3(6)
C(7A)—C(6A)—C(5A)	117.0(9)	C(6A)—C(7A)—C(8A)	121.9(9)
C(9A)—C(8A)—C(7A)	122.2(9)	C(8A)—C(9A)—C(4A)	117.0(8)
C(2B)—N(1B)—C(5B)	106.0(6)	C(2B)—N(1B)—Cu(1)	117.5(5)
C(5B)—N(1B)—Cu(1)	136.1(5)	N(1)—C(1B)—C(2B)	112.1(6)
N(1B)—C(2B)—N(3B)	113.1(7)	N(1B)—C(2B)—C(1B)	125.2(7)
N(3B)—C(2B)—C(1B)	121.7(7)	C(2B)—N(3B)—C(4B)	106.4(6)
C(9B)—C(4B)—N(3B)	131.5(7)	C(9B)—C(4B)—C(5B)	122.8(7)
N(3B)—C(4B)—C(5B)	105.7(6)	N(1B)—C(5B)—C(6B)	131.9(7)
N(1B)—C(5B)—C(4B)	108.9(6)	C(6B)—C(5B)—C(4B)	119.2(7)
C(7B)—C(6B)—C(5B)	119.0(8)	C(6B)—C(7B)—C(8B)	120.6(8)
C(9B)—C(8B)—C(7B)	122.0(8)	C(8B)—C(9B)—C(4B)	116.3(8)
C(2C)—N(iC)—C(5C)	105.8(7)	C(2C)—N(iC)—Cu(1)	118.3(5)
C(5C)—N(1C)—Cu(1)	135.7(5)	C(2C)—C(iC)—N(1)	108.9(6)
N(1C)—C(2C)—N(3C)	112.8(7)	N(1C)—C(2C)—C(1C)	124.0(7)
N(3C)—C(2C)—C(1C)	123.2(7)	C(2C)—N(3C)—C(4C)	107.3(6)
N(3C)—C(4C)—C(5C)	106.2(7)	N(3C)—C(4C)—C(9C)	132.8(8)
C(5C)—C(4C)—C(9C)	121.0(8)	C(6C)—C(5C)—C(4C)	121.5(8)
C(6C)—C(5C)—N(1C)	130.5(8)	C(4C)—C(5C)—N(1C)	107.9(7)
C(5C)—C(6C)—C(7C)	116.5(9)	C(8C)—C(7C)—C(6C)	121.4(9)

TABLE III Bond lengths [Å] and angles [°] for **2**. $[Fe_2(TMBA)_2(O)(Cl)_2](Cl)_26ETOH \cdot 2H_2O$

Fe(1)—O(1)	1.8054(7)	Fe(1)—N(6)	2.098(5)
Fe(1)—N(2)	2.112(5)	Fe(1)—N(4)	2.251(4)
Fe(1)—C1(1)	2.304(2)	Fe(1)—N(1)	2.351(4)
O(1)—Fe(1)#1	1.8055(7)	N(1)—C(9)	1.488(6)
N(1)—C(17)	1.490(7)	N(1)—C(1)	1.501(6)
C(1)—C(2)	1.470(8)	C(2)—N(2)	1.315(7)
C(2)—N(3)	1.357(7)	N(2)—C(3)	1.386(7)
N(3)—C(4)	1.388(8)	C(3)—C(8)	1.387(9)
C(3)—C(4)	1.402(8)	C(4)—C(5)	1.384(9)
C(5)—C(6)	1.352(11)	C(6)—C(7)	1.384(11)
C(7)—C(8)	1.375(9)	C(9)—C(10)	1.478(7)
C(10)—N(4)	1.313(7)	C(10)—N(5)	1.367(6)
N(4)—C(11)	1.403(6)	N(5)—C(12)	1.371(7)
C(11)—C(16)	1.383(8)	C(11)—C(12)	1.405(7)
C(12)—C(13)	1.394(7)	C(13)—C(14)	1.354(8)
C(14)—C(15)	1.390(8)	C(15)—C(16)	1.394(7)
C(17)—C(18B)	1.503(7)	C(18B)—N(6)	1.309(7)
C(18B)—N(7)	1.335(7)	N(6)—C(19)	1.400(7)
N(7)—C(20)	1.390(7)	C(19)—C(20)	1.383(8)
C(19)—C(24)	1.399(8)	C(20)—C(21)	1.407(8)
C(21)—C(22)	1.348(10)	C(22)—C(23)	1.383(10)
C(23)—C(24)	1.388(8)	O(101)—C(101)	1.455(11)
C(101)—C(102)	1.40(2)	O(201)—C(201)	1.392(9)
C(201)—C(202)	1.443(12)	O(301)—C(301)	1.419(9)
C(301)—C(302)	1.364(11)		
O(1)—Fe(1)—N(6)	90.37(11)	O(1)—Fe(1)—N(2)	91.36(11)
N(6)—Fe(1)—N(2)	150.9(2)	O(1)—Fe(1)—N(4)	165.58(12)
N(6)—Fe(1)—N(4)	85.9(2)	N(2)—Fe(1)—N(4)	85.2(2)
O(1)—Fe(1)—Cl(1)	102.67(4)	N(6)—Fe(1)—Cl(1)	104.50(13)
N(2)—Fe(1)—Cl(1)	103.5(2)	N(4)—Fe(1)—C1(1)	91.75(12)
O(1)—Fe(1)—N(1)	89.99(10)	N(6)—Fe(1)—N(1)	75.4(2)
N(2)—Fe(1)—N(1)	75.5(2)	N(4)—Fe(1)—N(1)	75.6(2)
Cl(1)—Fe(1)—N(1)	167.33(10)	Fe(1)—O(1)—Fe(1)#1	180.0
C(9)—N(1)—C(17)	111.5(4)	C(9)—N(1)—C(1)	110.9(4)
C(17)—N(1)—C(1)	113.1(4)	C(9)—N(1)—Fe(1)	112.3(3)
C(17)—N(1)—Fe(1)	105.0(3)	C(1)—N(1)—Fe(1)	103.5(3)
C(2)—C(1)—N(1)	108.3(4)	N(2)—C(2)—N(3)	111.6(6)
N(2)—C(2)—C(1)	122.5(5)	N(3)—C(2)—C(1)	125.8(5)
C(2)—N(2)—C(3)	106.7(5)	C(2)—N(2)—Fe(1)	114.9(4)
C(3)—N(2)—Fe(1)	137.6(4)	C(2)—N(3)—C(4)	107.8(5)
N(2)—C(3)—C(8)	131.2(6)	N(2)—C(3)—C(4)	108.9(6)
C(8)—C(3)—C(4)	119.9(6)	C(5)—C(4)—N(3)	132.2(7)
C(5)—C(4)—C(3)	122.7(7)	N(3)—C(4)—C(3)	105.0(6)
C(6)—C(5)—C(4)	115.9(7)	C(5)—C(6)—C(7)	122.7(8)
C(8)—C(7)—C(6)	122.0(8)	C(7)—C(8)—C(3)	116.8(7)
C(10)—C(9)—N(1)	111.6(4)	N(4)—C(10)—N(5)	112.4(5)
N(4)—C(10)—C(9)	126.2(4)	N(5)—C(10)—C(9)	121.4(5)
C(10)—N(4)—C(11)	106.1(4)	C(10)—N(4)—Fe(1)	114.1(3)
C(11)—N(4)—Fe(1)	139.7(3)	C(10)—N(5)—C(12)	107.0(4)
C(16)—C(11)—N(4)	132.5(5)	C(16)—C(11)—C(12)	119.6(5)
N(4)—C(11)—C(12)	107.9(5)	N(5)—C(12)—C(13)	131.3(5)
N(5)—C(12)—C(11)	106.5(4)	C(13)—C(12)—C(11)	122.2(5)
C(14)—C(13)—C(12)	117.3(5)	C(13)—C(14)—C(15)	121.7(5)
C(14)—C(15)—C(16)	121.5(6)	C(11)—C(16)—C(15)	117.8(5)
N(1)—C(17)—C(18B)	108.6(4)	N(6)—C(18B)—N(7)	113.0(5)
N(6)—C(18B)—C(17)	122.0(5)	N(7)—C(18B)—C(17)	124.8(5)

TABLE III (Continued)

C(18B)—N(6)—C(19)	105.7(5)	C(18B)—N(6)—Fe(1)	116.0(4)
C(19)—N(6)—Fe(1)	136.1(4)	C(18B)—N(7)—C(20)	107.0(5)
C(20)—C(19)—C(24)	121.0(6)	C(20)—C(19)—N(6)	108.4(5)
C(24)—C(19)—N(6)	130.6(6)	C(19)—C(20)—N(7)	105.8(5)
C(19)—C(20)—C(21)	122.0(6)	N(7)—C(20)—C(21)	132.2(6)
C(22)—C(21)—C(20)	116.0(7)	C(21)—C(22)—C(23)	123.2(6)
C(22)—C(23)—C(24)	121.6(7)	C(23)—C(24)—C(19)	116.2(6)
C(102)—C(101)—O(101)	109.8(14)		
O(201)—C(201)—C(202)	116.2(8)		
C(302)—C(301)—O(301)	112.1(8)		

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y+1$, $-z+1$.

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Supplementary Material

Tables of atomic positional parameters, anisotropic thermal motion parameters, H atom coordinates, torsional angles and observed and calculated structure amplitudes are available from the authors.

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