Synthesis and Structural Characterization of a Monofunctionalized Phloroglucin-Derivative: A Precursor for Heterotrinuclear *meta*-Phenylene Bridged Complexes

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*Dedicated to Professor Wolfgang Jeitschko on the occasion of his 70th birthday*

As part of our synthetic efforts for new triplesalen derivatives, we reacted 2,4,6-triacetyl-1,3,5-trihydroxybenzene (**1**) with excess $Cu(ClO_4)_2 \cdot 6H_2O$, imidazole, and ethylenediamine. However, not the triple ketimine derivative was formed but the mononuclear Cu^{II} complex $[LCu^{II}(ImH)]ClO_4 \cdot 0.5EtOH \cdot 0.5H_2O$ (HL = 6-(1-(2-aminoethylimino)ethyl)-2,4-diacetyl-1,3,5-trihydroxybenzene) with only one ketimine function. This complex forms a one-dimensional coordination polymer in the solid state through the apical binding of a keto-oxygen atom of one cation to the Cu^{II} ion of a neighboring cation. Magnetic measurements reveal the presence of weak antiferromagnetic intra-chain interactions.

Key words: Cu Complexes, N Ligands, Magnetic Properties

Introduction

The design and synthesis of molecule-based magnets has attracted considerable interest over the past decade. The synthetic efforts focus on the assembly of molecular building blocks to form supramolecular magnetic materials [1]. As Kahn emphasized, the design of molecular building blocks with *ferromagnetic* interactions between the paramagnetic centers is essential for the development of new types of molecule-based magnets [2]. We are investigating three different approaches to stabilize ferromagnetic ground states in polynuclear transition metal complexes: (i) the use of orthogonal magnetic orbitals [3], (ii) the double exchange mechanism [4], and (iii) the spin-polarization mechanism [5]. The latter has been known for a long time for organic compounds in which *m*-phenylene brigded radicals exhibit ferromagnetic ground states while the analogous *o*- and *p*-phenylene bridged radicals exhibit antiferromagnetic ground states [6]. We and others have shown that a bridging phloroglucinol (1,3,5-trihydroxybenzene) acts as a ferromagnetic coupler in trinuclear transition metal complexes by the spin-polarization mechanism. Using the parent phloroglucinol as a bridging ligand between three $(Tp^*)Mo^VOCl$ fragments $(Tp^* = $ hydro-tris(3,5-dimethylpyrazolyl)borate) resulted in ferromagnetic interactions between the three Mo^V centers with a $S_t = 3/2$ spin ground state [7]. We have attached pendant arms at the 2,4,6-positions of phloroglucinol in order to enhance the stability of first-row transition metal complexes by the chelate effect [8]. This concept has been successfully applied to obtain ferromagnetic interactions between three Cu^{II} ions through the spin-polarization mechanism with $S_t = 3/2$ spin ground states [8, 9]. In order to introduce magnetic anisotropy we have been choosing a salen-like coordination environment which is known to establish a pronounced magnetic anisotropy by its strong ligand field in the basal plane [10, 11]. A well studied example is the Jacobsen catalyst $[(salen')Mn^{III}Cl]$ $(H_2salen' = (R,R)$-N,N'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine) [12] which is a Mn^{III} $(S = 2)$ species with a zero-field splitting of $D = -2.5$ cm^{-1} [10, 13]. In this respect, it is interesting to note that already a dimeric Mn^{III} salen complex behaves as a SMM [14]. The resulting trinucleating ligand which we call triplesalen (H_6talen) provides three salen-like ligand compartments where the three metal ions are *meta*-phenylene
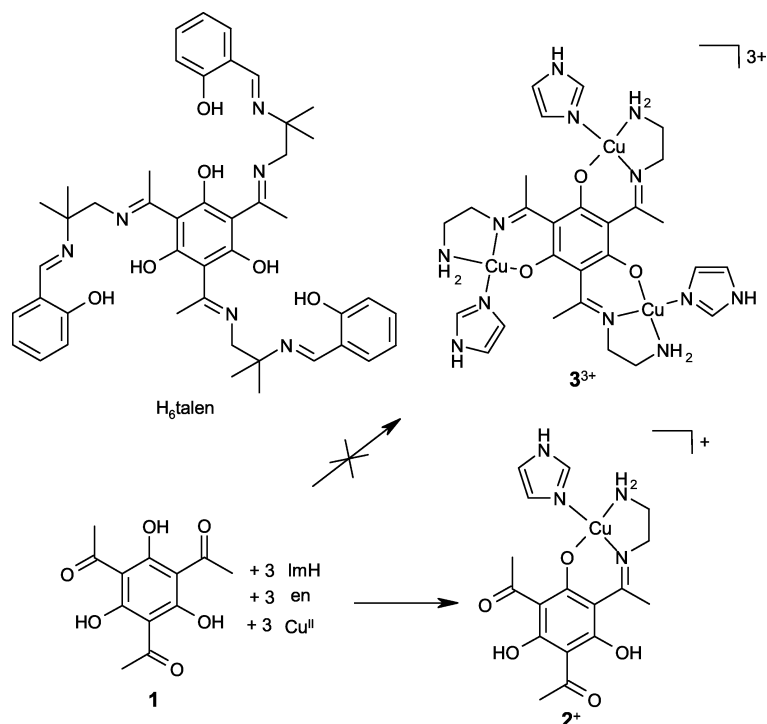
Scheme 1.

bridged by the phloroglucinol backbone (Scheme 1) [15, 16].

In order to prepare heterotrinuclear complexes bridged by a phloroglucinol derivative, a reproducible synthetic procedure for a mono- or difunctionalized derivative of the starting material 2,4,6-triacetyl-1,3,5-trihydroxybenzene **1** has to be established. Here, we report the template-directed synthesis and characterization of [LCu^{II}(ImH)](ClO$_4$), **2**-ClO$_4$, with HL = 6-(1-(2-aminoethylimino)ethyl)-2,4-diacetyl-1,3,5-trihydroxybenzene which represents a monofunctionalized ketimine derivative of **1**. The cationic **2**$^+$ forms a one-dimensional chain *via* coordination of the keto-group of one molecule to the copper ion of the next molecule. We envision **2**-ClO$_4$ as the starting point for heterotrinuclear complexes bridged by phloroglucinol.

Results and Discussion

Synthesis and characterization

We adapted a template-directed protocol developed by Costes *et al.* for the preparation of a salen 'half-unit', namely [(SE)Cu^{II}(ImH)](ClO$_4$) with HSE = *N*-(2-aminoethyl)salicylaldimine [17] for the synthesis of the analogous 'half-unit' **3**$^{3+}$ of our triplesalen ligands (Scheme 1) [16]. Under this protocol, we reacted **1** with three equivalents of Cu(ClO$_4$)$_2$ · 6H$_2$O, imidazole, and ethylenediamine in an EtOH/H$_2$O mixture and obtained green crystals in a low but reproducible yield. The FTIR spectrum indicates the presence of NH groups, imine groups, and ClO$_4$$^-$. The electrospray mass spectrum of exhibits a prominent ion at a mass-to-charge ratio (*m/z*) of 424.2, with mass and isotope distribution patterns corresponding to [LCu^{II}(ImH)]$^+$ (calculated *m/z* of 424.1). The elemental analyses combined with these data are in accordance with the formulation of the green product [LCu^{II}(ImH)]ClO$_4$ · 0.5EtOH · 0.5H$_2$O, **2**-ClO$_4$ · 0.5EtOH · 0.5H$_2$O, which was corroborated by an X-ray diffraction study. Instead of the formation of a triple 'half-unit' of a triplesalen ligand, a mono 'half-unit' of the triketone **1** has formed. The reaction of **1** with stoichiometric amounts of Cu(ClO$_4$)$_2$ · 6H$_2$O, imidazole, and ethylenediamine does not improve the yield of this reaction.

Solid state structure

Fig. 1 shows the molecular structure of **2**$^+$ with the labeling scheme used. Selected bond distances and angles are given in Table 1. In accordance to the spec-
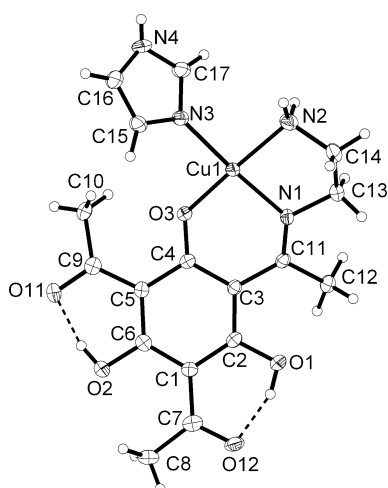
Fig. 1. Molecular structure of **2**$^+$ in crystals of **2**-ClO$_4$ · 0.5EtOH. Thermal ellipsoids are drawn at the 50% probability level.
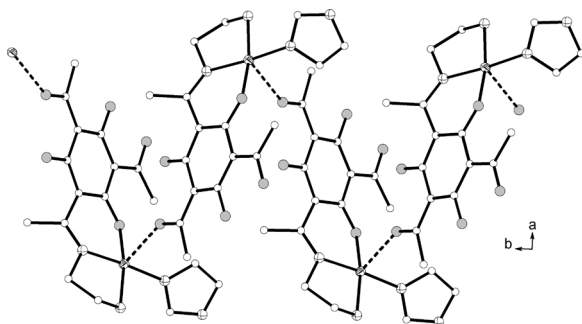

Fig. 2. Formation of a one-dimensional coordination polymer along the crystallographic *b*-direction by apical coordination of a keto-oxygen atom to copper(II).

Table 1. Selected bond lengths [Å] and bond angles [°] for **2**-ClO$_4$ · 0.5EtOH.

Cu(1)-O(3)	1.924(2)	C(2)-C(1)-C(7)	119.82(19)
Cu(1)-N(1)	1.949(2)	O(1)-C(2)-C(3)	117.49(18)
Cu(1)-N(3)	1.978(2)	O(1)-C(2)-C(1)	119.01(18)
Cu(1)-N(2)	2.022(2)	C(3)-C(2)-C(1)	123.48(19)
Cu(1)-O(12$^{\#1}$)	2.481(2)	C(2)-C(3)-C(4)	118.95(18)
C(1)-C(6)	1.419(3)	C(2)-C(3)-C(11)	119.34(18)
C(1)-C(2)	1.429(3)	C(4)-C(3)-C(11)	121.69(18)
C(1)-C(7)	1.441(3)	O(3)-C(4)-C(3)	122.46(19)
C(2)-O(1)	1.330(2)	O(3)-C(4)-C(5)	118.72(18)
C(2)-C(3)	1.396(3)	C(3)-C(4)-C(5)	118.82(18)
C(3)-C(4)	1.432(3)	C(6)-C(5)-C(4)	119.33(19)
C(3)-C(11)	1.467(3)	C(6)-C(5)-C(9)	118.24(19)
C(4)-O(3)	1.277(2)	C(4)-C(5)-C(9)	122.43(19)
C(4)-C(5)	1.446(3)	O(2)-C(6)-C(5)	119.72(19)
C(5)-C(6)	1.414(3)	O(2)-C(6)-C(1)	117.99(19)
C(5)-C(9)	1.447(3)	C(5)-C(6)-C(1)	122.27(19)
C(6)-O(2)	1.316(2)	O(11)-C(9)-C(5)	119.7(2)
C(9)-O(11)	1.259(3)	O(11)-C(9)-C(10)	115.5(2)
C(9)-C(10)	1.483(3)	C(5)-C(9)-C(10)	124.8(2)
C(12)-C(11)	1.503(3)	N(1)-C(11)-C(3)	121.18(18)
C(11)-N(1)	1.286(3)	N(1)-C(11)-C(12)	119.49(19)
C(13)-N(1)	1.471(3)	C(3)-C(11)-C(12)	119.26(19)
C(13)-C(14)	1.501(3)	N(1)-C(13)-C(14)	107.63(19)
C(14)-N(2)	1.473(3)	N(2)-C(14)-C(13)	107.6(2)
C(15)-C(16)	1.346(3)	C(16)-C(15)-N(3)	109.5(2)
C(15)-N(3)	1.374(3)	C(15)-C(16)-N(4)	105.9(2)
C(16)-N(4)	1.356(3)	N(3)-C(17)-N(4)	110.2(2)
C(17)-N(3)	1.323(3)	O(12)-C(7)-C(1)	120.0(2)
C(17)-N(4)	1.329(3)	O(12)-C(7)-C(8)	116.2(2)
C(7)-O(12)	1.255(3)	C(1)-C(7)-C(8)	123.8(2)
C(7)-C(8)	1.486(3)	C(11)-N(1)-C(13)	120.06(18)
O(3)-Cu(1)-N(1)	91.04(7)	C(11)-N(1)-Cu(1)	126.80(14)
O(3)-Cu(1)-N(3)	91.35(7)	C(13)-N(1)-Cu(1)	111.47(14)
N(1)-Cu(1)-N(3)	176.35(7)	C(4)-O(3)-Cu(1)	126.84(13)
O(3)-Cu(1)-N(2)	168.92(8)	C(14)-N(2)-Cu(1)	107.06(15)
N(1)-Cu(1)-N(2)	84.66(8)	C(17)-N(3)-C(15)	105.72(19)
N(3)-Cu(1)-N(2)	92.49(8)	C(17)-N(3)-Cu(1)	128.24(15)
C(6)-C(1)-C(2)	116.47(18)	C(15)-N(3)-Cu(1)	125.48(15)
C(6)-C(1)-C(7)	123.69(19)	C(17)-N(4)-C(16)	108.6(2)

Symmetry transformation used to generate equivalent atoms: $^{\#1}$ $-x+1/2, y-1/2, -z+1/2$.

troscopic and analytical data, triketone **1** reacted with one equivalent of ethylenediamine to form a ketimine which may be regarded as the 'single triplesalen half-unit'. A copper ion is coordinated by the phenolic oxygen atom O3 (Cu1-O3 1.92 Å), the ketimine nitrogen atom N1 (Cu1-N1 1.95 Å), and the amine nitrogen atom N2 (Cu1-N2 2.02 Å). The equatorial coordination is saturated by a imidazol ligand (Cu-N3 1.98 Å).

However, a fifth ligand is coordinated at the apical position of Cu1 to form an overall square-pyramidal coordination environment. This fifth ligand is the ketone oxygen atom O12 of a neighboring molecule giving rise to a one-dimensional coordination polymer (Fig. 2).

Magnetic properties

The magnetic susceptibility of [LCu^{II}(ImH)]ClO$_4$ · 0.5EtOH · 0.5H$_2$O was measured in the temperature range 2 – 290 K. The raw data were corrected for underlying diamagnetism by using tabulated Pascal constants and for temperature-independent paramagnetism, χ_{TIP} [18]. The value for χ_{TIP} was chosen such that no decrease of μ_{eff} at high temperatures results. The effective magnetic moment, μ_{eff}, has a value of 1.87 μ_B in the range 290 – 160 K and exhibits a slow decrease below 30 K to a value of 1.82 μ_B at 10 K followed by a rapid decrease to 1.77 μ_B at 2 K. Three effects may contribute the decrease of μ_{eff} at low temperatures: (*i*) saturation effects, (*ii*) zero-field splitting, and (*iii*) intermolecular antiferromagnetic exchange interactions. Zero-field splitting can be discarded due to the spin doublet state while saturation effects are in-
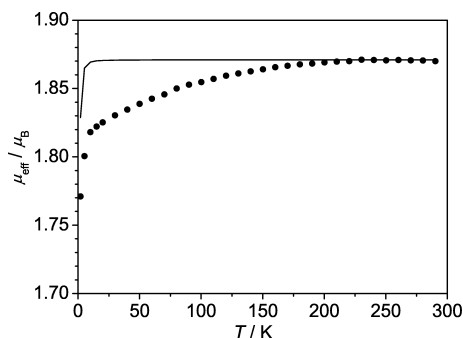
Fig. 3. Temperature dependence of the effective magnetic moment, μ_{eff}, of **2**-ClO$_4$ · 0.5EtOH · 0.5H$_2$O at 1 T. The solid line is a simulation using the spin-Hamiltonian for $S_{\text{t}} = 1/2$ with $g = 2.16$ and and $\chi_{\text{TIP}} = 114 \cdot 10^{-6}$ cm^3 mol^{-1} (subtracted from theoretical and experimental data) including saturation effects at low temperatures.

cluded in the simulation routine used. A simulation of the high temperature regime to the spin Hamiltonian for an $S_{\text{t}} = 1/2$ system results in $g = 2.16$ and $\chi_{\text{TIP}} = 114 \cdot 10^{-6}$ cm^3 mol^{-1}. The slow decrease of μ_{eff} must thus be assigned to weak antiferromagnetic exchange interactions propagated by the formation of the one-dimensional chain in the solid state.

In conclusion, in our synthetic efforts to synthesize a triple half-unit of our triplesalen ligand we observed the formation a single 'half-unit' of the triplesalen ligand, **2**$^+$. This compound forms a one-dimensional coordination polymer in the solid state which results in weak antiferromagnetic interactions. We are investigating the capability of **2**$^+$ to function as a precursor for the synthesis of heterotrinuclear *meta*-phenylene bridged complexes which appear to have interesting magnetic properties.

Experimental Section

Physical techniques

Infrared spectra (400 – 4000 cm^{-1}) of solid samples were recorded on a Bruker Vector 22 spectrometer as KBr disks. ESI spectra were recorded using an Esquire 3000 ion trap mass spectrometer (Bruker Daltronic GmbH, Bremen, Germany) equipped with a standard ESI source. Temperature-dependent magnetic susceptibilities of powdered samples were measured by using a SQUID magnetometer (Quantum Design) at 1.0 T (2.0 – 300 K).

X-ray diffraction

Data of [LCu$^{\text{II}}$(ImH)]ClO$_4$ · 0.5EtOH were collected [19] at −120 °C on a Bruker AXS APEX diffractome-

Table 2. Crystallographic data for **2**-ClO$_4$ · 0.5EtOH.

Habit	green transparent plates
Crystal size [mm]	$0.13 \times 0.10 \times 0.02$
Formula	C$_{18}$ H$_{24}$ Cl N$_4$ O$_{9.50}$ Cu
fw, amu	547.40
a [Å]	31.994(2)
b [Å]	9.2152(7)
c [Å]	14.5501(11)
β (deg)	90.389(2)
V [Å^3]	4289.8(5)
Calculated density [g cm^{-3}]	1.695
Crystal system	monoclinic
Space group	$C2/c$
Z	8
λ [Å]	0.71073
Monochromator	graphite
Temperature [K]	153(2)
Scan type	omega and phi scans
2θ Range [deg]	5 – 54
hkl limits	$-40 \leq h \leq 40$
	$-11 \leq k \leq 11$
	$-18 \leq l \leq 18$
μ [mm^{-1}]	1.206
Reflections measured	19698
Independent reflections	4656
Observed [$I > 2\sigma(I)$]	3698
R (observed)	$R1 = 0.0339, R_{\text{w}} = 0.0782$
R (all)	$R1 = 0.0465, R_{\text{w}} = 0.0829$
GOF	0.911
No. of variables	400
Res. el. dens. [eÅ^{-3}]	0.415 / −0.318

ter equipped with a rotating anode using Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Structure solution and refinement were performed with the SHELXS-97 [20] and SHELXL-97 [21] programs using anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms of the ligand were located by difference Fourier techniques and were refined with isotropic displacement parameters. The hydrogen atoms of the disordered solvent molecule were refined in calculated positions. Additional data collection and refinement details are listed in Table 2. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre, CCDC-297384. Copies of the data can be obtained free of charge on application to The director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code+(1223)336-033; e-mail: for inquiry: fileserv@ccdc.cam.ac.uk).

*[LCu$^{\text{II}}$(ImH)](ClO$_4$) (**2**-ClO$_4$)*

A solution of 5.55 g (15 mmol) Cu(ClO$_4$)$_2$ · 6H$_2$O in water (10 ml) is added to a suspension of 1.26 g (5 mmol) **1** in ethanol (50 ml) and heated to reflux for 10 min to give a greenish suspension. After addition of 2.04 g (30 mmol) of solid imidazole (ImH) the reaction mixture is

heated to reflux for another 10 min. A solution of 900 mg (15 mmol) of ethylenediamine in ethanol (10 ml) is added while the reaction mixture is still hot and is then allowed to cool to r. t. The filtered solution is slowly evaporated to give green crystals which are washed with water and iso-propanol and dried in air. Yield: 100 mg, 4%. IR (KBr): $\tilde{v} = 3389, 3273, 3142, 3014, 2968, 2929, 2854, 1603, 1560, 1489, 1404, 1364, 1283, 1121, 1111, 1094, 1070, 916, 806, 772, 623$ cm^{-1}. – MS (ESI in CH_2Cl_2/MeOH 9 : 1, positive ion mode): *m/z* (%) = 424.2 [LCu^{II}(ImH)]$^+$. –

2-ClO$_4$ · 0.5EtOH · 0.5H$_2$O C$_{18}$H$_{25}$ClN$_4$O$_{10}$Cu (556.42): calcd. C 38.86, H 4.53, N 10.07; found C 38.55, H 4.25, N 10.06.

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