A 1,8-naphthalenediol-based unsymmetrical dinucleating ligand

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A facile synthesis of 2-formyl-1,8-naphthalenediol is reported. Its potential as a general precursor for the preparation of unsymmetrical multidentate chelating ligand systems based on 1,8-naphthalenediol is demonstrated by the synthesis of the dinucleating ligand \mathbf{L}^{4-} ($\mathbf{H}_4 \mathbf{L} = N, N'$ -bis(2-(1,8-naphthalenediol)methylidene)propylenediamine). Reaction of $\mathbf{H}_4 \mathbf{L}$ with copper acetate results in the formation of the unsymmetrical dinuclear \mathbf{Cu}^{II} complex [\mathbf{LCu}_2] (3), which has been structurally characterized by single-crystal X-ray diffraction. One \mathbf{Cu}^{II} ion is coordinated by a N_2O_2 compartment of \mathbf{L}^{4-} and the other \mathbf{Cu}^{II} ion is coordinated by an O_4 compartment of \mathbf{L}^{4-} while they are bridged by two aryloxide functions of \mathbf{L}^{4-} . A dimerization of two molecules of 3 to a tetranuclear entity $\mathbf{3}_2$ occurs through formation of weak apical \mathbf{Cu} -O interactions. Analysis of the temperature dependent magnetic susceptibility measurements (2–290 K) established a strong intradimer exchange coupling $J_{12} = -371 \text{ cm}^{-1}$. This strong superexchange interaction fits nicely in a magneto-structural correlation which has been established for dinuclear bis(phenoxide)-bridged \mathbf{Cu}^{II} complexes demonstrating the electronic equivalence of the aryloxides of a phenol and 1,8-naphthalenediol.

Introduction

Phenolates are ubiquitous as coordinating groups in ligand systems. This is in contrast to the 'one ring- and one donor-increased' 1,8-naphthalenediol unit, which has only been sparingly used for coordination to metal ions. Wuest and coworkers used the dianion of 1,8-naphthalenediol to coordinate Ti^{IV.1} However, this is the only structurally characterized complex of the parent 1,8-naphthalenediol. Phenolates act only in a limited number of complexes as monodentate ligands. Usually, the phenolate is part of a chelating multidentate ligand system. To synthesize such multidentate ligand systems, suitable functionalized phenol precursor compounds must be available. In order to create a multidentate ligand system incorporating 1,8-naphthalenediol, Vidali et al. used 2-acetyl-3,6-dimethyl-1,8-naphthalenediol² and Robson et al. 2,7-diacetyl-3,6-dimethyl-1,8-naphthalenediol as precursor.3 While no structural characterization using the former precursor has been provided, only mono-Schiff base products have been obtained by Robson et al. upon condensation with mono-primary amines.³ These problems might be attributed to the general observation that ketones react more slowly than aldehydes with amines to form imines.⁴

In this respect, we described recently the synthesis of 2,7-diformyl-1,8-naphthalenediol which is the 'one ring- and one donor-increased' derivative of 2,6-diformylphenol.⁵ The latter was introduced in 1970 by Robson as building block for the synthesis of dinucleating ligands (compartmental ligands, Robson type ligands).⁶ Herein, we report a streamlined synthesis for the previously unknown building block 2-formyl-1,8-naphthal-enediol **II** as an extension of salicylaldehyde **I** (Scheme 1).



Salicylaldehyde I is a precursor for the preparation of a large number of ligand systems in coordination chemistry. One of

the most famous ligand systems are mono-nucleating salentype ligands, which have a long history in synthetic inorganic chemistry7,8 and a burgeoning significance in bioinorganic chemistry and homogenous catalysis.9 However, numerous metallo enzymes make use of the cooperative action of two (or even more) proximate metal ions within their active site, thus enabling very efficient catalytic transformations of biologically relevant substrate molecules.¹⁰ While salen-type ligands primarily form mononuclear complexes, we thought it might be interesting to study the cooperative action in dinuclear complexes of extended salen-type ligands. Accordingly, we tested the potential of the new precursor II for the synthesis of an extended salentype ligand based on the 1,8-naphthalenediol backbone, which provides a salen-like N2O2 ligand compartment and an O4 ligand compartment. The bridging aryloxides allow for strong cooperative interactions between the two metal ions. Thus, besides the synthesis of the building block 2-formyl-1,8-naphthalenediol II we report herein the preparation of the unsymmetrical dinucleating ligand L^{4-} which is the tetraanion of N, N'-bis(2-(1,8-naphthalenediol)methylidene)propylenediamine (H₄L). Its capability to form unsymmetrical dinuclear complexes is demonstrated by the synthesis of its dinuclear Cu^{II} complex [LCu₂] (3) whose structural and magnetic properties are described.

Experimental

All manipulations were performed in an atmosphere of dry argon by means of standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification unless otherwise noted. Et₂O and CH₂Cl₂ were distilled under argon from Na/benzophenone and CaH₂, respectively, prior to use. After addition of benzene and water, DMF was first fractionally distilled and then distilled from CaH₂ under argon. N,N,N',N'-Tetramethylethylenediamine (TMEDA) was purified by vacuum distillation from Na/benzophenone. 1,8-Bis(methoxymethoxy)naphthalene **1** was synthesized as previously described.⁵

Infrared spectra (400–4000 cm^{-1}) of solid samples were recorded on a Bruker Vector 22 spectrometer as KBr disks. Elemental analyses were obtained with a Vario EL III Elemental Analyzer at the Institut für Anorganische und Analytische Chemie der Westfälischen Wilhelms-Universität Münster. UV-Vis-NIR absorption spectra of solutions were measured on a Varian Cary 50 spectrophotometer in the range 190-1100 nm at ambient temperatures. EI and MALDI-TOF mass spectra were recorded on a Varian MAT 212 and a Bruker Reflex IV mass spectrometer, respectively. ¹H and ¹³C NMR spectra were measured on Bruker ARX300, Bruker AMX400, or Varian Unity plus 600 spectrometers using the solvent as internal standard. Temperature-dependent magnetic susceptibilities of finely grounded crystals were measured by using a SQUID magnetometer (Quantum Design) at 1.0 T (2.0-290 K). For calculation of the molar magnetic susceptibility, χ_M , the measured susceptibilities were corrected for the sample holder, the underlying diamagnetism of the sample by using tabulated Pascal's constants (3₂: $\chi_{dia} = 508 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$), and for the temperature independent paramagnetism (χ_{TIP}) which was obtained by a fitting procedure.

2-Formyl-1,8-bis(methoxymethoxy)naphthalene (2)

A solution of n-BuLi (2.5 M in hexane, 8.86 mL, 22.2 mmol) and TMEDA (2.57 g, 22.2 mmol) in Et₂O (130 mL) was added dropwise to a solution of 1,8-bis(methoxymethoxy)naphthalene (5.00 g, 20.1 mmol) in Et₂O (135 mL) at 0 °C. After stirring the mixture for 6 h at this temperature, DMF (3.11 mL, 40.2 mmol) was added and the resulting mixture stirred overnight (0 °C to r.t.). After addition of water (40 mL), the pH of the reaction solution was decreased to 5-6 by addition of dilute HCl. The aqueous solution was extracted with Et_2O (3 \times 50 mL). The organic extracts were combined, washed with brine and water, and dried over anhydrous MgSO₄. Volatiles were removed under reduced pressure to obtain 2 as an ochre solid. Yield: 4.89 g (88%). Crystals of 2 suitable for a single-crystal X-ray diffraction study were obtained by slow evaporation of a *n*-hexane solution. ¹H NMR (598.99 MHz, CDCl₃): δ 3.59 (s, 3 H; CH₃), 3.61 (s, 3 H; CH₃), 5.24 (s, 2 H; CH₂), 5.36 (s, 2 H; CH₂), 7.20 (dd, ${}^{3}J =$ 7.56 Hz, ${}^{4}J = 1.50$ Hz, 1H; H7), 7.50 (dd, ${}^{3}J = 7.56$ Hz, ${}^{3}J =$ 7.90 Hz, 1H; H6), 7.51 (dd, ${}^{3}J = 7.90$ Hz, ${}^{4}J = 1.50$ Hz, 1H; H5), 7.61 (dd, ${}^{3}J = 8.6$ Hz, J = 0.9 Hz, 1H; H4), 7.85 (d, ${}^{3}J =$ 8.6 Hz, 1H; H3), 10.61 (d, J = 0.9 Hz, 1H; CHO); ¹³C NMR $(150.63 \text{ MHz}, \text{CDCl}_3)$: δ 56.6 (CH_3) , 58.2 (CH_3) , 95.9 (CH_2) , 102.1 (CH₂), 111.8 (C7), 119.6 (C8a), 122.7 (C3 or C5), 122.8 (C3 or C5), 125.2 (C4), 127.3 (C2), 129.4 (C6), 140.5 (C4a), 154.3 (C8), 159.2 (C1), 191.1 (CHO); EI-MS: m/z (%) 276 (16) [M]⁺, $230(4)[M - CH_2OCH_3]^+, 200(100)[M - CHO - CH_2OCH_3]^+.$ 45 (56) [CH₂OCH₃]⁺; FT-IR (KBr): v/cm⁻¹ 1678 (C=O); UV-Vis (CH₃CN) λ_{max} /nm (ϵ /M⁻¹cm⁻¹) 361 (5400), 298 (5500), 255 (38300). Anal. Calc. for C₁₅H₁₆O₅: C 65.21, H 5.84. Found: C 64.95, H 6.11%.

2-Formyl-1,8-naphthalenediol (II)

An argon purged solution of HCl (5-6 M in isopropanol, 38 mL) was added dropwise at 0 °C to a solution of 2-formyl-1,8-bis(methoxymethoxy)naphthalene (1.55 g, 5.61 mmol) in CH_2Cl_2 (78 mL). After stirring the mixture for 6 h, the solvent was removed under reduced pressure. The residue was dissolved in CHCl₃ and dried over anhydrous MgSO₄. Volatiles were removed under reduced pressure to obtain II as an brownishyellow solid. Yield: 1.04 g (98%). ¹H NMR (300.14 MHz, $CDCl_3$): δ 6.95 (dd, ${}^{3}J = 8.0 \text{ Hz}, {}^{4}J = 0.9 \text{ Hz}, 1\text{H}; \text{H7}$), 7.27 (dd, ${}^{3}J = 8.0 \text{ Hz}, {}^{4}J = 0.9 \text{ Hz}, 1\text{H}; \text{H5}), 7.32 (d, {}^{3}J = 8.7 \text{ Hz}, 1\text{H}; \text{H4}),$ $7.39 (d, {}^{3}J = 8.7 Hz, 1H; H3), 7.55 (dd, {}^{3}J = 8.0 Hz, 1H; H6), 9.41$ (s, 1H; OH), 9.86 (s, 1H; CHO), 14.30 (br s, 1H; OH); ¹³C NMR (100.63 MHz, CDCl₃): δ 111.9 (C7), 113.2 (C3), 113.3 (C8a), 118.9 (C5), 120.5 (C4), 125.8 (C2), 132.7 (C6), 139.3 (C4a), 157.8 (C8), 163.7 (C1), 195.8 (CHO); EI-MS: m/z (%) 188 (100) [M]⁺; FT-IR (KBr): \tilde{v}/cm^{-1} 1641 (C=O); UV-Vis (CH₃CN) λ_{max}/nm $(\varepsilon/M^{-1} \text{ cm}^{-1})$ 423 (9900), 404 (9300), 333 (4000), 323 (4000),

261 (21900). Anal. Calc. for $C_{11}H_8O_3$: C 70.21, H 4.28. Found: C 69.81, H 4.19%.

N,N'-Bis(2-(1,8-naphthalenediol)methylidene)propylenediamine (H₄L)

A solution of 1,3-diaminopropane (0.08 M, 15 mL, 1.2 mmol) in EtOH (15 mL) was added to a solution of 2-formyl-1,8naphthalenediol (464 mg, 2.47 mmol) in CHCl₃ (27 mL). The reaction mixture was allowed to stir overnight, during which a precipitate formed. This was filtered off. Another crop of precipitate was obtained from the filtrate after slow evaporation of the solvent. The combined precipitates were washed three times with Et₂O resulting in a brownish-yellow solid. Crystals of H₄L suitable for a single-crystal X-ray diffraction study were obtained by slow evaporation of a CHCl₃-EtOH solution. Yield: 490 mg (98%). ¹H NMR (599.84 MHz, d_8 -THF): δ 2.19 (q, ³J = 6.9 Hz, 2 H; CH₂CH₂CH₂), 3.71 (m, 4 H; NCH₂CH₂), 6.58 (d, ${}^{3}J =$ 8.9 Hz, 2H; H4), 6.59 (dd, ${}^{3}J = 7.9$ Hz, ${}^{4}J = 1.0$ Hz, 2H; H7), 6.84 (d, ${}^{3}J = 8.9$ Hz, 2H; H3), 6.87 (dd, ${}^{3}J = 7.9$ Hz, ${}^{4}J =$ 1.0 Hz, 2H; H5), 7.31 (dd, ${}^{3}J = 7.9$ Hz, 2H; H6), 7.99 (d, J =12.6 Hz, 2H; N=C-H), 12.02 (br s, 2H; OH), 14.05 (s, 2H; OH); ¹³C NMR (150.85 MHz, d₈-THF): δ 32.7 (CH₂CH₂CH₂), 48.7 (NCH₂CH₂), 109.0 (C8a), 112.1 (C7), 115.8 (C4), 117.7 (C5), 118.6 (C2), 129.7 (C3), 134.0 (C6), 141.2 (C4a), 162.9 (C8), 164.5 (C1), 185.0 (N=C); MS-MALDI-TOF: *m*/*z* 415.4 [M + H]⁺; FT-IR (KBr): \tilde{v}/cm^{-1} 1623 (C=N); UV-Vis (CH₃CN) λ_{max}/nm $(\varepsilon/M^{-1} \text{ cm}^{-1})$ 450 (29000), 431 (28000), 274 (78000). Anal. Calc. for C₂₅H₂₄N₂O₅: C 69.43, H 5.59, N 6.48. Found: C 69.33, H 5.37, N 6.38%.

$[LCu^{II}_{2}]$ (3)

Solid H₄L (50 mg, 0.12 mmol) and solid $[Cu_2(OAc)_4(OH_2)_2]$ (72 mg, 0.18 mmol) were each placed in one arm of a Hshaped tube. The tube was filled carefully with DMF allowing for diffusion of the two solutions between the two arms. In the course of 12 days, black crystals deposited. Yield: 45 mg (69%). FT–IR (KBr): $\tilde{\nu}/cm^{-1}$ 1604 (C=N). Anal. Calc. for C₂₅H₁₈N₂O₄Cu₂: C 55.86, H 3.38, N 5.21. Found: C 55.63, H 3.33, N 5.42%.

X-Ray crystallographic data collection and refinement of the structures

X-Ray diffraction data were collected on a Bruker AXS APEX diffractometer equipped with a rotating anode using Mo-K α radiation (2) or on Nonius Kappa-CCD diffractometers using Cu-K α radiation (H₄L) or using Mo-K α radiation (3), in case of Mo-radiation equipped with a rotating anode generator. Programs used: data collection SMART¹¹ (2) and COLLECT¹² (H₄L, 3), data reduction SAINT¹¹ (2) and Denzo-SMN¹³ (H₄L, 3), absorption correction SADABS¹¹ (2) and Denzo¹⁴ (3), structure solution SHELXS-97,¹⁵ structure refinement SHELXL-97.¹⁶ Details of data collection and structure refinements are summarized in Table 1.

CCDC reference numbers 273592-273594.

See http://dx.doi.org/10.1039/b507579c for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis and characterization

Salicylaldehydes may be obtained by cleavage of the corresponding salicylaldehyde ethers prepared through directed *ortho*lithiation¹⁷ of the appropriate phenyl ethers and subsequent reaction with formaldehyde.¹⁸ This reaction sequence has been applied broadly for the formation of aromatic compounds with an *ortho*-hydroxyformyl unit.^{5,19} In this respect, we have chosen the di-MOM derivative 1⁵ of 1,8-naphthalenediol as starting material for the preparation of **II**. An ethereal solution

Table 1 Crystal data and structure refinement for 2, H_4L and 3

	2	$\mathrm{H}_4\mathbf{L}$	3	
Empirical formula	$C_{15}H_{16}O_5$	$C_{25}H_{22}N_2O_4$	$C_{25}H_{18}N_2O_4Cu_2\\$	
$M_{ m r}$	276.28	414.45	537.49	
T/K	173(2)	223(2)	198(2)	
λ/Å	0.71073	1.54178	0.71073	
Crystal system	Monoclinic	Monoclinic	Monoclinic	
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	
a/Å	4.5003(7)	14.731(1)	8.612(1)	
b/Å	13.713(2)	8.650(1)	18.755(1)	
c/Å	21.761(4)	16.954(1)	12.243(1)	
β/°	93.422(3)	109.91(1)	96.89(1)	
$V/Å^3$	1340.6(4)	2031.2(3)	1963.2(3)	
Z	4	4	4	
$D_{\rm c}/{\rm g~cm^{-3}}$	1.369	1.355	1.819	
μ/mm^{-1}	0.103	0.753	2.206	
Data/restraints/param.	3059/0/245	3209/0/288	4773/0/326	
Goodness of fit on F^2	1.024	1.008	1.025	
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0447	R1 = 0.0484	R1 = 0.0361	
	wR2 = 0.0947	wR2 = 0.1274	wR2 = 0.0813	
R indices (all data)	R1 = 0.0772	R1 = 0.0849	R1 = 0.0548	
	wR2 = 0.1045	wR2 = 0.1449	wR2 = 0.0894	

of 1 was treated with 1.1 equivalents of a 1 : 1 mixture of *n*-BuLi/TMEDA and subsequently with 2 equivalents of DMF. Acidic work-up resulted in the formation of 2 as an ochre solid in 88% yield (Scheme 2).

Aldehyde 2 exhibits a higher-order NMR spectrum due to the nearly identical chemical shifts of the aromatic hydrogen atoms H5 and H6. Therefore, the molecular structure of 2 was established by single-crystal X-ray diffraction (Fig. 1(a)). However, simulation of the 600 MHz ¹H NMR spectrum in conjunction with 2D NMR spectra resulted in a conclusive evaluation of the coupling constants, an rigorous assignment of all resonances, and thus an NMR confirmation of the structure of 2. The molecular structure in crystals of 2 reveals the formyl group almost coplanar to the plane of the naphthalene ring with the C=O function tilted away from the OMOM group (Fig. 1a).

Deprotection of the hydroxy groups was performed by dissolving **2** in CH_2Cl_2 and adding a solution of HCl in *i*-PrOH. This procedure resulted in pure **II** with 98% yield

(Scheme 2). The IR spectrum of II exhibits a C=O vibration at 1641 cm⁻¹ in comparison to 1678 cm⁻¹ in **2**. This low energy shift is indicative of a rotation of the formyl substituent by \sim 180° and the formation of a hydrogen bond between the hydroxyl proton and the oxygen atom of the formyl group in the unprotected monoaldehyde II.

The preparation of salen-type ligands is routinely achieved by the Schiff-base condensation of ethylenediamine or a related diamine with two equivalents of an aldehyde or ketone.⁸ In this respect, we reacted the new monoaldehyde II with 1,3diaminopropane and obtained the unsymmetrical dinucleating ligand H₄L as the first member of a new family of ligands based on the 1,8-naphthalenediol backbone (Scheme 2). The molecular structure of H₄L was confirmed by single-crystal X-ray diffraction (Fig. 1(b)). The two naphthalenediol units are located at opposite ends of the molecule. The two planes of the naphthalene rings form an angle of 107.6°. These orientation seems to originate from intermolecular π - π stacking



Scheme 2



Fig. 1 Molecular structures of (a) 2 and (b) H_4L with the atoms represented by thermal ellipsoids at the 50% probability level. Selected interatomic distances (Å): 2 O1–C1 1.376(2), O2–C7 1.369(2), O5–C15 1.207(2); H_4L O1–C5 1.278(2), O2–C7 1.351(3), O21–C25 1.277(2), O22–C27 1.333(3), N1–C3 1.302(3), N21–C23 1.296(3).

interactions with distances between neighboring naphthalene planes of ~ 3.4 A. Interestingly, difference Fourier synthesis establishes a double zwitterionic form for ligand H₄L. The electron density establishes two hydrogen atoms close to the imine nitrogen atoms N1 and N21 and two hydrogen atoms close to the phenolic oxygen atoms O2 and O22. That leads to a formulation with phenolate oxygen atoms O1 and O21 being deprotonated hydroxy groups. This assignment is corroborated by the shorter mean O-C bond distances for O1 and O21 of 1.278(2) and 1.277(2) Å, respectively, as compared to the analogous mean bond distances for O2 and O22 of 1.351(3) and 1.333(3) Å, respectively. Strong N–H \cdots O hydrogen bonds exists between N1 and O1 (distance 2.614 Å) and N21 and O21 (distance 2.620 Å). Beside these there are further strong hydrogen bonds between O1 and O2 (distance 2.530 Å) and O21 and O22 (distance 2.525 Å). O1 and N1 form a nearly planar five-membered ring with the three interstices carbon atoms (maximum deviation from best plane 0.004 Å) as do O21 and N21 (0.006 Å). In this respect it is interesting to note that the 600 MHz¹H NMR spectrum of ligand H₄L measured in d₈-THF exhibits a doublet for the imine hydrogen atom with a coupling constant of 12.6 Hz. 2D NMR spectra exhibit this coupling to the proton with δ 12.02 ppm assigned to the hydrogen atom of the protonated imine. The correlation of the structural and NMR spectroscopic data indicate that in the case of such a strong coupling a zwitterionic form might be present in solution. The 600 MHz ¹H NMR spectrum of ligand H₄L measured in d₆-DMSO does not show a coupling of the imine proton indicating that in DMSO solution not the zwitterionic forms but the convenient ortho-hydroxyimine tautomer dominates.

The reaction of H_4L with 1 or more equivalents of $[Cu_2(OAc)_4(OH_2)_2]$ results in the formation of an olive green solid (3) which analyses as one L^{4-} and two Cu^{II} . Coordination of the imine nitrogen atoms to copper in 3 is readily indicated by the red shift of the C=N stretch to 1604 from 1623 cm⁻¹ in H_4L .²⁰ However, this solid proofed to be insoluble in aprotic nonpolar solvents (hexane, heptane, toluene, ethyl acetate), in

aprotic polar solvents (acetonitrile, acetone, dichloromethane, chloroform), as well as in polar protic solvents (methanol, ethanol, DMF, water). Thus, single-crystals of this complex have been obtained by slow diffusion techniques of DMF solutions of H_4L and copper acetate. Structural characterization by single-crystal X-ray diffraction enabled the formulation of **3** as [LCu₂].

Structural characterization of [LCu₂] (3)

Fig. 2 shows the molecular structure of the dinuclear complex [LCu₂] (3) and the labeling scheme used. The dinucleating ligand L^{4-} provides two tetradentate coordination compartments, one with an N₂O₂ donor set occupied by Cu1 and one with an O₄ donor set occupied by Cu2. Selected interatomic distances and angles are listed in Table 2.



Fig. 2 Molecular structure of 3 with the atoms represented by thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity.

The distances of Cu1 can be compared to the analogue distances in the mononuclear complexes [(salen)Cu] (H₂salen = N,N'-bis(salicylidene)ethylenediamine) and [(salen^{pr})Cu] (H₂salen^{pr} = N,N'-bis(salicylidene)propylenediamine). The range of Cu–N distances found in [(salen)Cu] is 1.92–1.96 Å²¹ and found in [(salen^{pr})Cu] is 1.94–1.99 Å.²² The Cu1–N distances of 1.93 and 1.95 Å in **3** fit well into these ranges. On the other hand, the Cu1–O bond distances of 1.97 and 1.98 Å found in **3** exceed the ranges of Cu–O distances found in [(salen)Cu] (1.89–1.91 Å)²¹ and found in [(salen^{pr})Cu] (1.84–1.90 Å).²² The aryloxides in **3** are bridging ligands (O1 and O3) while they are terminal ligands in [(salen)Cu] and [(salen^{pr})Cu]. A bridging ligand donates charge to two metal centers leading to a higher overall charge donation but a diminished charge donation per

 Table 2
 Selected interatomic distances (Å) and angles (°) for 3

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	Cu1–O1 Cu1–O3 Cu1–N1 Cu1–N2 Cu1–O2" Cu2–O1 Cu2–O3 Cu2–O2	1.978(2) 1.967(2) 1.950(3) 1.930(3) 2.415(2) 1.944(2) 1.913(2) 1.878(2) 1.878(2)	$\begin{array}{c} 01-C2\\ 02-C4\\ 03-C17\\ 04-C19\\ N1-C11\\ N2-C15\\ Cu1\cdots Cu2\\ Cu1\cdots Cu2^{a}\\ Cu1\cdots Cu2^{a}\\ Cu1 \cdots Cu2^{a}\\ Cu1 \cdots$	$\begin{array}{c} 1.337(3) \\ 1.323(3) \\ 1.331(3) \\ 1.308(3) \\ 1.277(5) \\ 1.280(5) \\ 3.012(1) \\ 3.221(1) \\ 5.129(1) \end{array}$
	Cu2-O4 Cu2-O4	1.853(2) 2.712(2)	$Cu1 \cdots Cu1^a$	5.139(1)
	Cu2-OI	2.712(2)	Cu2····Cu2	3.334(1)
	O1–Cu1–O3	77.77(7)	O2–Cu2–O4	93.41(7)
	O3–Cu1–N2	92.26(11)	O4–Cu2–O3	95.11(8)
	N2–Cu1–N1	99.04(13)	O3–Cu2–O1	79.89(8)
	N1–Cu1–O1	90.35(10)	Cu2–O1–Cu1	100.38(8)
	O1–Cu2–O2	91.46(7)	Cu2–O3–Cu1	101.87(8)

Symmetry transformations used to generate equivalent atoms: $a^{a} - x, -y, -z$.



Fig. 3 Two views on the molecular structure of the dimer of dimer 3_2 . Dashed lines indicate the weak apical Cu–O interactions leading to the dimerization.

metal–ligand bond.²³ The longer Cu1–O bond distances found in **3** provide clear evidence for the reduced Cu1–O covalency as compared to mononuclear salen copper complexes.

Two dinuclear complexes 3 dimerize by weak apical copperaryloxide interactions to a tetranuclear entity $\mathbf{3}_2$. This results in an overall square pyramidal coordination environment for each copper center (see Fig. 3). For Cu1 the basal plane is build by N1, N2, O3 and O1. Cu1 is positioned 0.10 Å above the best plane of these four basal ligand atoms toward the apical ligand which is formed by a coordinated aryloxide donor (O2#1) of the other dinuclear complex. The Cu1–O2#1 distance of 2.415(2) Å indicates only a weak apical interaction. On the other hand, Cu2 forms an apical bond with O1#1 of the other dinuclear complex which is even longer at 2.712(2) Å indicating an even weaker apical interaction. This is corroborated by the fact that in the case of the coordination environment of Cu2 not the metal ion is positioned above a best plane of its basal ligands (O1, O2, O4, O3) but one of the basal ligands (O2) is positioned above a best plan described by O1, O3, O4, and Cu2. This is due to the function of O2 as an apical donor for Cu1#1 of the other dinuclear complex.

Magnetic properties

The magnetic susceptibility was measured in the temperature range 2–290 K and analyzed for the tetranuclear entity 3_2 in order to take into account possible interdimer interactions. The effective magnetic moment, μ_{eff} , of the tetranuclear assembly 3_2 has a value of 1.14 μ_{B} at 290 K which is significantly lower than the theoretical value of 3.65 μ_{B} for four uncoupled Cu^{II} ions ($S_i = 1/2$, $g_i = 2.11$). Decreasing the temperature leads to a steadily decrease of μ_{eff} until it reaches at ~120 K a plateau of 0.27 μ_{B} (Fig. 4). This behavior is characteristic for strong antiferromagnetic exchange interactions between the Cu^{II} centers resulting in a $S_t = 0$ spin ground state. The plateau at low temperature originates from a trace amount of a paramagnetic impurity (probably a mononuclear Cu^{II} species).

The spin topology of $\mathbf{3}_2$ is indicated in the inset of Fig. 4. The relations $J_{12} = J_{1'2'}$ and $J_{12'} = J_{1'2}$ arise by consideration of the molecular symmetry of $\mathbf{3}_2$. The dominant intradimer coupling is presented by J_{12} , whereas $J_{12'}$ and $J_{22'}$ represent interdimer couplings.



Fig. 4 Temperature dependence of the effective magnetic moment, μ_{eff} , calculated for the tetranuclear assembly 3_2 at 1 T. The solid line is a fit to the experimental data using the appropriate spin-Hamiltonian with the values given in the text. Inset: Spin system of 3_2 imposed on its molecular structure. Note that the magnetic orbitals $(d_{x^2-y^2})$ of each Cu^{II} are oriented in the plane of its dimeric unit **3** perpendicular to the apical oxygen donor of the other dimeric unit.

Several studies have been dealing with the necessity to incorporate non-zero values for the interdimer J terms in dimer of dimer Cu^{II} complexes in which dimerization is achieved by weak apical Cu-ligand interactions. Differing magnitudes and signs have been reported for those interdimer coupling constants.²⁴⁻²⁶ Fallon et al. already pointed out that the interdimer interaction should be very small due to the large interdimer Cu-O distances (apical Cu-O bond of a square-pyramidal coordination geometry) as compared to the shorter intradimer Cu-O distances (equatorial Cu-O bonds of a square-pyramidal coordination geometry).26 They were able to fit their magnetic data without the use of an interdimer coupling constant. Moreover, by explicitly using the appropriate tetramer model, they obtained an interdimer coupling constant of zero.26 This argument also holds for 3_2 because the interdimer Cu–O distances are larger (2.42 and 2.71 Å) as compared to the intradimer Cu-O distances (1.91-1.98 Å).

Besides this distance point of view, the orientation of the magnetic orbitals should also contribute to the fact that the interdimer couplings are weak. The magnetic orbital of each Cu^{II} ion $(d_{x^2-y^2})$ is oriented towards the four equatorial ligand atoms of the dinuclear unit **3**. This leads to an effective superexchange pathway across the bridging oxygen atoms of the dinuclear complex. On the other hand, the magnetic orbital of each Cu^{II} $(d_{x^2-y^2})$ is of δ -type symmetry with regard to the Cu–O interaction with its apical ligand. As these oxygen atoms don't have δ -type symmetry orbitals, there is no interaction with the magnetic orbitals of the Cu^{II} ions. Hence, the superexchange pathway through the apical ligand has to be rather weak.²⁷

In order to reduce the parameter space we neglect the effect of $J_{22'}$ because this interaction involves two-times the longest apical Cu–O separation of 2.72 Å, while $J_{12'}$ (and $J_{21'}$) involves one apical Cu–O separations of 2.42 Å and only one of 2.72 Å.

The magnetic properties were analyzed by using the spin Hamiltonian in eqn (1) including the isotropic Heisenberg– Dirac–van Vleck (HDvV) exchange Hamiltonian and the singleion Zeeman interaction by means of a full-matrix diagonalization approach. The macroscopic magnetization is calculated by summing the microscopic magnetizations weighted according to the Boltzmann distribution.

$$H = H_{\rm HDvV} + \sum_{i} [\mu_{\rm B} g_i S_i B]$$

$$_{\rm HDvV} = -2J_{12}(S_1 S_2 + S_{1'} S_{2'}) - 2J_{12'}(S_1 S_{2'} + S_{1'} S_2)$$
(1)

Fitting the data resulted in an intradimer coupling constant of $J_{12} = -371 \text{ cm}^{-1}$ with g = 2.11, a paramagnetic impurity with

 $H_{\rm F}$

S = 1/2 (g = 2.00) of 2.4%, and $\chi_{\text{TIP}} = 82 \times 10^{-6}$ cm³ mol⁻¹ (Fig. 4).²⁸ The value of $J_{12'}$ showed no effect on the fit. Simulations using the values given above in combination with interdimer couplings $J_{12'} = -10$ cm⁻¹ or $J_{12'} = +10$ cm⁻¹ lead to μ_{eff} vs. T curves which are indistinguishable to that with $J_{12'} = 0$. The reason for this insensitivity to the interdimer exchange is easy to derive by analyzing the spin ladder of the tetranuclear unit **3**₂. Considering the intradimer exchange $J_{12} = -371$ cm⁻¹ only, results in a $S_t = 0$ spin ground state, two degenerate $S_t = 1$ spin states at 742 cm⁻¹, and three degenerate spin states of 6.55% each at the highest temperature used for the measurement of the susceptibility data (290 K). The three highest excited states exhibit only minor populations of 0.06% ($S_t = 0$), 0.17% ($S_t = 1$) and 0.28% ($S_t = 2$).

Introducing an interdimer coupling of $J_{12'} = -10 \text{ cm}^{-1}$ results into a splitting of the first excited $S_t = 1$ states of 20 cm⁻¹ and an overall splitting of the three highest states of 29.8 cm⁻¹. The spin states exhibit the following energies and thermal populations at 290 K: $S_t = 1$ at 733 cm⁻¹ (6.87%), $S_t = 1$ at 753 cm⁻¹ (6.23%), $S_t = 0$ at 1466 cm⁻¹ (0.06%), $S_t = 1$ at 1475.8 cm⁻¹ (0.17%), $S_t =$ 2 at 1495.8 cm⁻¹ (0.26%).

The splitting of the first two excited $S_t = 1$ states has no net effect on the μ_{eff} vs. *T* curve because both spin states have the same magnetic moment. The splitting of the spin states around 1500 cm⁻¹ is also negligible because they are thermally not accessible to a significant level due to their high energy. An analogous treatment by taking into account a ferromagnetic interdimer exchange coupling $J_{12'} = +10$ cm⁻¹ leads to similar effects and argumentation. In order to observe an effect on the μ_{eff} vs *T* curve, absolute values of the interdimer coupling constant in the order of 50 cm⁻¹ are necessary which are too large considering the associated exchange pathway.

It is interesting to compare the coupling constant $(J_{12} =$ -371 cm⁻¹) obtained for the bis(µ-naphthoxide)-bridged dicopper(II) unit in 3 to analogous bis(µ-hydroxy)-, bis(µ-alkoxy)and bis(µ-phenoxide)-bridged dicopper(II) complexes. Using the well-established magneto-structural relationship for $bis(\mu$ hydroxy)-bridged dicopper(II) complexes (J = 1/2 (-74.53a + 7270) cm⁻¹ with *a* being the Cu–O–Cu angle²⁹ results in a range for J_{12} in 3 of -105 to -160 cm⁻¹. This predicted range implies a weaker exchange coupling as compared the observed value of $J_{12} = -371$ cm⁻¹. Inherently stronger exchange interactions have been established for bis(µ-alkoxide)-bridged dicopper(II) complexes.^{25,30} Recently, a magneto-structural relation for bis(µphenoxide)-bridged dicopper(II) complexes has been reported which exhibits no zero-crossing due to 'accidental orthogonality' for reasonable angles $(J = 1/2 (-31.95a + 2462) \text{ cm}^{-1})^{.31}$ This relation predicts the strongest inherent antiferromagnetic interactions in the series $Cu^{II}(OR)_2Cu^{II}$ (R = H < Alk < Ph) and results in values for 3 of $J_{12} = -373$ to -396 cm⁻¹. This range compares nicely to the experimental value for **3** of J_{12} = -371 cm⁻¹. Hence, the electronic properties of the aryloxide functions of 1,8-naphthalenediol closely resembles those of phenols.

Conclusions and outlook

We have for the first time synthesized 2-formyl-1,8naphthalenediol **II** as the 'one ring- and one donor-increased' derivative of salicylaldehyde **I** where numerous applications as precursor for the preparation of various ligand systems have been reported. The preparation of H_4L proves the ability of aldehyde **II** as a versatile precursor for multidentate chelating ligand systems. The tetra-anion L^{4-} provides a N₂O₂ ligand compartment closely related to that of salen-type ligands and an additional O₄ compartment. Other hetero-dinucleating ligands with a N₂O₂ and an O₄ compartment are based on 3formylsalicylic acid³² or 1-(*o*-hydroxyphenyl)-1,3-butanedione³³ and their derivatives.³⁴ The straightforward synthesis of the dinuclear complex [LCu₂] (**3**) with one Cu^{II} ion in the N₂O₂ ligand compartment and one Cu^{II} in the O₄ ligand compartment demonstrate the capability of ligand L⁴⁻ to form unsymmetrical dinuclear complexes. The structural analysis evidenced the formation of weak axial Cu–O interactions to result in **3**₂. The ligand L⁴⁻ allows for a strong exchange coupling between the two Cu^{II} ions of the dinuclear complex **3** with a coupling constants of $J_{12} = -371$ cm⁻¹. The comparison of this value to established magneto-structural correlations for Cu^{II}(OR)₂Cu^{II} demonstrates the electronic equivalence of the aryloxide functions of 1,8-naphthalenediol to that of phenols.

The synthesis of other homo- as well as heterodinuclear complexes with ligand L^{4-} and related ligands is currently performed in our laboratory. One interest in such dinuclear complexes lies in the area of magnetochemistry. Secondly, these complexes will be evaluated for their catalytic performance in transformations which are known to be catalyzed by mononuclear salen complexes. Especially the possible pre-binding of the substrate by the metal ion in the O₄ compartment seems to be a good candidate for catalyst improvements.

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References and notes

- 1 M. Poirier, M. Simard and J. D. Wuest, *Organometallics*, 1996, 15, 1296.
- 2 P. A. Vigato, U. Casellato, M. Vidali, R. Graziani, D. E. Fenton and C. M. Regan, *Inorg. Chim. Acta*, 1979, **32**, L27; R. Graziani, M. Vidali, P. A. Vigato, U. Casellato, D. E. Fenton and C. M. Regan, *Inorg. Chim. Acta*, 1980, **38**, 85.
- 3 B. F. Hoskins, C. J. McKenzie and R. Robson, J. Chem. Soc., Dalton Trans., 1992, 3083.
- 4 S. Dayagi and Y. Degani, in *The Chemistry of the Carbon–Nitrogen Double Bond*, ed. S. Patai, Interscience Publishers, London, 1970, p. 64.
- 5 T. Glaser and I. Liratzis, Synlett, 2004, 735.
- 6 R. Robson, *Inorg. Nucl. Chem. Lett.*, 1970, 6, 125; R. Robson, *Aust. J. Chem.*, 1970, 23, 2217; N. H. Pilkington and R. Robson, *Aust. J. Chem.*, 1970, 23, 2225.
- P. Pfeiffer, E. Breith, E. Lübbe and T. Tsumaki, *Liebigs Ann.*, 1933,
 503, 84; P. Pfeiffer, T. Hesse, H. Pfitzner, W. Scholl and H. Thielert, *J. Prakt. Chem.*, 1937, 149, 217; P. Pfeiffer, W. Christeleit, T. Hesse, H. Pfitzner and H. Thielert, *J. Prakt. Chem.*, 1938, 150, 261.
- 8 R. H. Holm, G. W. Everett and A. Chakravorty, *Prog. Inorg. Chem.*, 1966, 7, 83; M. Calligaris and L. Randaccio, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2, p. 715.
- 9 W. Zhang, J. L. Loebach, S. R. Wilson and E. N. Jacobsen, J. Am. Chem. Soc., 1990, **112**, 2801; R. Irie, K. Noda, Y. Ito, N. Matsumoto and T. Katsuki, *Tetrahedron Lett.*, 1990, **31**, 7345; E. N. Jacobsen, Acc. Chem. Res., 2000, **33**, 421.
- 10 N. Sträter, W. N. Lipscomb, T. Klabunde and B. Krebs, Angew. Chem., Int. Ed. Engl., 1996, 35, 2024; B. A. Averill, in Comprehensive Coordination Chemistry II, ed. J. A. McCleverty and T. J. Meyer, Elsevier Ltd., Oxford, 2004, vol. 8, pp. 641; R. H. Holm, P. Kennepohl and E. I. Solomon, Chem. Rev., 1996, 96, 2239.
- 11 Bruker AXS, 2000.
- 12 COLLECT, Nonius B. V., 1998.
- 13 Z. Otwinowski and W. Minor, Methods Enzymol., 1997, 276, 307.
- 14 Z. Otwinowski, D. Borek, W. Majewski and W. Minor, Acta Crystallogr., Sect. A, 2003, 59, 228.
- 15 G. M. Sheldrick, SHELXS-97, Program for solution of crystal structures, University of Göttingen, Germany, 1997.
- 16 G. M. Sheldrick, SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Germany, 1997.

- 17 V. Snieckus, Chem. Rev., 1990, 90, 879.
- 18 H. Christensen, Synth. Commun., 1975, 5, 65.
- N. S. Narasimhan, R. S. Mali and M. V. Barve, Synthesis, 1979, 906; R. G. Harvey, C. Cortez, T. P. Ananthanarayan and S. Schmolka, J. Org. Chem., 1988, 53, 3936; A. S. Parsons, J. M. Garcia and V. A. Snieckus, Tetrahedron Lett., 1994, 35, 7537; H. Brunner and H. Schießling, Bull. Soc. Chim. Belg., 1994, 103, 119; M. M. G. Antonisse, B. H. M. Snellink-Ruel, A. C. Ion, J. F. J. Engbersen and D. N. Reinhoudt, J. Chem. Soc., Perkin Trans. 1, 1999, 1211; H.-C. Zhang, W.-S. Huang and L. Pu, J. Org. Chem., 2001, 66, 481; A. Arroult, J.-Y. Mérour, J-M. Léger, C. Jarry and G. Guillaumet, Helv. Chim. Acta, 2001, 84, 2198.
- 20 R. Hernández-Molina and A. Mederos, in *Comprehensive Coordination Chemistry II*, ed. J. A. McCleverty and T. J. Meyer, Elsevier Ltd., Oxford, 2004, vol. 1, p. 411.
- 21 E. N. Baker, D. Hall and T. N. Waters, J. Am. Chem. Soc., 1970, 406, 406; H. Milburn, M. R. Truter and B. L. Vickery, J. Chem. Soc., Dalton Trans., 1974, 841.
- 22 G. B. Drew Michael, R. N. Prasad and R. P. Shama, Acta Crystallogr., Sect. C., 1985, 41, 1755; R.-G. Xiong, B.-L. Song, J.-L. Zuo and X.-Z. You, Polyhedron, 1996, 15, 903; B. H. Chen, H. H. Yao, W. T. Huang, P. Chattopadhyay, J. M. Lo and T. H. Lu, Solid State Sci., 1999, 1, 119; M. Hasegawa, K. Kumagai, M. Terauchi, A. Nakao, J. Okubo and T. Hoshi, Monatsh. Chem., 2002, 133, 285; L. C. Nathan, J. E. Koehne, J. M. Gilmore, K. A. Hannibal, W. E. Dewhirst and T. D. Mai, Polyhedron, 2003, 22, 887.
- 23 T. Glaser, B. Hedman, K. O. Hodgson and E. I. Solomon, Acc. Chem. Res., 2000, 33, 859.

- L. Merz and W. Haase, J. Chem. Soc., Dalton Trans., 1978, 1594; L. Schwabe and W. Haase, J. Chem. Soc., Dalton Trans., 1985, 1909;
 R. Wegner, M. Gottschaldt, H. Görls, E.-G. Jäger and D. Klemm, Chem. Eur. J., 2001, 7, 2143; J. Sletten, A. Sorensen, M. Julve and Y. Journaux, Inorg. Chem., 1990, 29, 5054.
- 25 L. Merz and W. Haase, J. Chem. Soc., Dalton Trans., 1980, 875.
- 26 G. D. Fallon, B. Moubaraki, K. S. Murray, A. M. Vandenbergen and B. O. West, *Polyhedron*, 1993, **12**, 1989.
- 27 T. Glaser, T. Lügger and R. Fröhlich, *Eur. J. Inorg. Chem.*, 2004, 394.
 28 The routine JULIUS was used for spin Hamiltonian simulations of the data (C. Krebs, E. Bill, F. Birkelbach and V. Staemmler, unpublished results). For the calculation of the magnetic susceptibility of the paramagnetic impurity JULIUS uses the molar mass of the main component. Thus the obtained value for the paramagnetic impurity of 3₂ (2.4%) is far overestimated if a mononuclear Cu^{II} species is anticipated.
- 29 V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, 1976, **15**, 2107; D. J. Hodgson, *Inorg. Chem.*, 1976, **15**, 3174.
- 30 M. Handa, N. Koga and S. Kida, Bull. Chem. Soc. Jpn., 1988, 61, 3853.
- 31 L. K. Thompson, S. K. Mandal, S. S. Tandon, J. N. Bridson and M. K. Park, *Inorg. Chem.*, 1996, **35**, 3117.
- 32 H. Okawa, M. Tanaka and S. Kida, Chem. Lett., 1974, 987.
- 33 D. E. Fenton, S. E. Gayda, U. Casellato, P. A. Vigato and M. Vidali, Inorg. Chim. Acta, 1978, 27, 9.
- 34 U. Casellato, P. A. Vigato, D. E. Fenton and M. Vidali, *Chem. Soc. Rev.*, 1979, **8**, 199; D. E. Fenton and H. Okawa, *Chem. Ber.*, 1997, **130**, 433.