

Dinuclear Copper(II) Complexes with Bis-thiocarbohydrazone Ligands

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Copper(II) complexes with substituted bis(salicylaldehyde) thiocarbohydrazones (3-methoxy = H_4L^{Me} , 3-ethoxy = H_4L^{Et}), have been synthesized. These ditopic ligands form dinuclear copper(II) complexes containing the ligands in their triply deprotonated forms. The ligands entail two nonequivalent donor atom sites (ONN and ONS) for copper(II) coordination. Magnetic measurements of the complexes in the tempera-

ture range 2–290 K showed significant antiferromagnetic interactions between the two copper(II) ions, with $-2J$ around 180 cm^{-1} . The dinuclear molecules in turn also form face-to-face H-bonded dimers involving four coppers in total.

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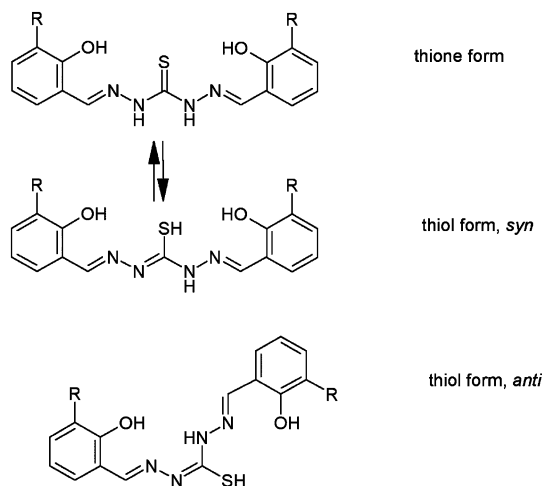
Introduction

During the last several years numerous papers dealing with compounds that are able to coordinate to two or more metal atoms have been published. Such centres are found in biological systems, e. g. ferritin,^[1,2] while those with high-spin ground states can act as single-molecule magnets,^[3,4] and some of them exhibit spin-transition behavior,^[5] or manifest catalytic activity.^[6]

Thiocarbohydrazide and its hydrazone Schiff bases constitute interesting ligand systems because of their versatile coordination ability toward metals. Thiocarbohydrazones have previously been used as building blocks in the self-assembly of tetranuclear molecular square structures. In particular, mixed-valence iron(II)/(III), nickel(II), zinc(II) and cadmium(II) clusters have been synthesized starting from 1,5-bis(2-acetylpyridine)thiocarbohydrazone or related derivatives.^[7–9] Reactions of the same ligands with copper(II) produced dimers of dimeric units held together by extraneous bridging ligands.^[9,10] Recently, two azine-bridged octanuclear copper(II) complexes, assembled from bis(2-hydroxybenzaldehyde) thiocarbohydrazone were re-

ported.^[11] In these 24-membered metallomacrocycles, the ligand used its maximal donor capacity in a manner unprecedented for thiocarbohydrazone coordination chemistry. Continuing our work^[11] on the coordination chemistry of bis(salicylaldehyde) thiocarbohydrazones, we have now prepared new copper(II) complexes, in order to establish the influence of the phenyl ring substituents on their nuclearity, geometry and magnetic properties. The substituents were placed at strategic positions with respect to the donor sets,

R	Ligand
OCH ₃	HL ^{Me}
OC ₂ H ₅	HL ^{Et}



Scheme 1.

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modifying the electronic environment around the metal centers (Scheme 1). In addition, we eschewed the use of added base, reasoning that the degree of self-association of the dicopper units may become limited by retention of protons on groups that act as bridging donors in the octanuclear systems.^[11] The crystal and molecular structures of these complexes $[\text{Cu}_2(\text{HL}^{\text{Me,Et}})(\text{HSO}_4)(\text{MeOH})_2] \cdot \text{MeOH}$ have been determined by single-crystal X-ray diffraction.

Results and Discussion

1. Synthesis and Characterization of the Ligands

The slightly photosensitive Schiff base ligands $\text{H}_4\text{L}^{\text{Me,Et}}$ (Scheme 1) were prepared by treatment of the salicylaldehyde derivatives with thiocarbohydrazide taken in a 2:1 molar ratio in refluxing ethanol and have been characterized by elemental analysis and ^1H NMR spectroscopy. In the NMR, the -NH and -OH are labile, while expression of the imine-H as two resonances presumably reflects the isomerism in Scheme 1. A recent report^[12] includes reference to unpublished structural data (CCDC-247503) for the methoxy ligand $\text{H}_4\text{L}^{\text{Me}}$.

2. Synthesis and Characterization of Copper(II) Complexes

Copper(II) complexes of the general formula $[\text{Cu}_2(\text{HL}^{\text{Me,Et}})(\text{HSO}_4)(\text{MeOH})_2] \cdot \text{MeOH}$ were prepared by combination of copper(II) sulfate with the appropriate ligand in methanol as the reaction medium. Use of a 2:1 Cu/ligand molar ratio permitted the isolation of the dinuclear

complexes **1** (methoxy) and **2** (ethoxy). Despite the presence of the solvophilic alkoxy groups, they are insoluble in non-polar organic solvents, but soluble in polar coordinating solvents like DMF and DMSO and modestly soluble in MeOH. Figure 1 shows the FAB-mass spectra which offered the first confirmation of their dinuclear natures. Weak peaks corresponding to the tetranuclear species of atom composition $[\text{Cu}_4(\text{HL}^{\text{Et}})_2(\text{HSO}_4)]^+$ (1148) and $[\text{Cu}_4(\text{HL}^{\text{Et}})_2(\text{H})]^+$ (1052) were also seen.

3. Properties of the Compounds

Both complexes are deep brownish-green, forming essentially black crystals, and were obtained from the initial syntheses in crystalline forms $[\text{Cu}_2(\text{HL}^{\text{Me,Et}})(\text{HSO}_4)(\text{MeOH})_2] \cdot \text{MeOH}$ suitable for X-ray crystallography. However, it became evident that the methanol of crystallization is rather readily lost on exposure of the crystals to the atmosphere at ambient temperature, and is replaced by atmospheric water molecules, without visible effect on the crystal morphology. For the X-ray diffraction experiments, we were able to handle the crystals so as to avoid solvent loss or exchange.

Optical Spectra

The electronic spectra (vide infra) of the two compounds in DMF/MeOH solution are of course quite similar. A band near 630 nm (in DMF), although principally d-d in nature, is somewhat enhanced in intensity, as is often observed when sulfur donors are present;^[13] in MeOH, this band's maximum shifts 10 nm bathochromically and its apparent intensity is decreased about 10%. A more intense envelope is present around 415 nm, to which the main contribution is attributed to LMCT. Ligand-localised ($\pi-\pi^*$) bands appear near 295 and 230 nm.

Infrared Spectra

The IR spectra of all these compounds have considerable spectral density in the 600–1650 cm^{-1} region. Chromophores of interest which change frequency on coordination are exemplified by reference to the methoxy-substituted case. In $\text{H}_4\text{L}^{\text{Me}}$ there is a sharp but weak band at 1612 cm^{-1} , which we assign as $\nu_{\text{C}=\text{N}}$, and which shifts to 1598 cm^{-1} in the copper complex, gaining substantially in intensity, in the manner previously noted.^[14] A sharp band of medium intensity at 815 cm^{-1} in $\text{H}_4\text{L}^{\text{Me}}$ is attributed to mainly $\nu_{\text{C}=\text{S}}$ character, and is absent from the copper complexes, where a band of similar width and intensity now appears at 782 cm^{-1} . This is quite consistent with the shift normally observed^[15,16] on coordination of a conjugated thione, associated with the increased contribution of the thiolate resonance form (Scheme 1).

4. Structures of Complexes

Comparison of $\text{H}_4\text{L}^{\text{Me}}$ with its triply deprotonated, coordinated form, shows that the free ligand^[12] reconforms to accommodate the two coppers.

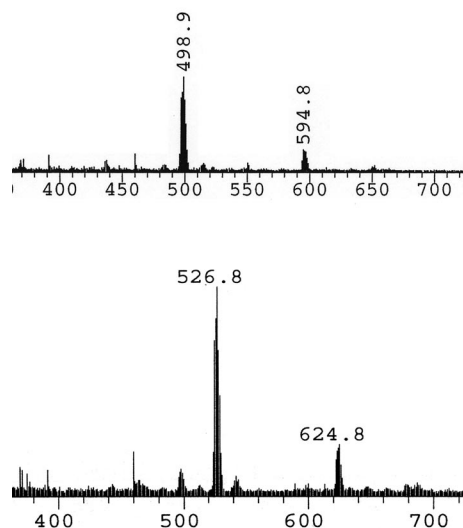


Figure 1. FAB-MS of the two compounds, showing (upper) superposition of $[\text{Cu}_2\text{HL}^{\text{Me}}]^+$ and $[\text{Cu}_2\text{H}_2\text{L}^{\text{Me}}]^+$ at $m/z = 498, 499$, with $[\text{Cu}_2\text{H}_2\text{L}^{\text{Me}}\text{HSO}_4]^+$ at $m/z = 595$, and (lower) superposition of $[\text{Cu}_2\text{HL}^{\text{Et}}]^+$ and $[\text{Cu}_2\text{H}_2\text{L}^{\text{Et}}]^+$ at $m/z = 526, 527$, and $[\text{Cu}_2\text{H}_2\text{L}^{\text{Et}}\text{HSO}_4]^+$ species centred around $m/z = 625$. Electron capture by Cu is implied.

The lower aryl group (Figure 2) rotates by ca. 180° around its C(aryl)–C(alimine) bond to make its phenolic oxygen atom O(2) available to form a six-membered metallocycle including the hydrazine nitrogen atom N(4). Consequently, the hydrazine–N(2) associated with the upper phenylhydrazone moiety becomes deprotonated and forms the five-membered chelate ring N2–C9–N3–N4–Cu. In H_4L^{Me} the two benzene rings are ca. 10° from being coplanar, whereas in the complex, this dihedral angle is reduced to less than 1° . Two tautomeric forms are possible for $H_4L^{Me,Et}$: the thione form and thiol form (Scheme 1), which are in equilibrium.^[17] The thiol tautomer can adopt a *syn* or *anti* configuration as a consequence of the double-bond character of the central N–C linkage (Scheme 1). These structures indicate that such ligands are potentially ditopic, and indeed, dinucleation has been proposed previously^[18] for a copper complex of somewhat different composition, but prepared from bis(2-hydroxy-3-methoxybenzaldehyde) thiocarbohydrazone. X-ray diffraction reveals that in **1** and **2** the thiocarbohydrazone ligands adopt the thiol *anti* configuration and thus provide two tridentate sites, one with NNO and the other with ONS donor atoms, each of which can accommodate one copper(II) ion (Figure 1). Thus, six donor atoms of triply deprotonated ligand HL^{3-} are bound to two metal ions and give a dicopper(II) unit $[Cu_2L]^+$.

Consonant with the shift from thione-hydrazine toward thiol-imine form,^[16] the C–S bond length increases from 1.68 Å in the free ligand to 1.71 Å in the copper complex, and the C–N bond complementarily shortens from 1.34 Å to 1.325 Å. In the dinuclear 3-methoxysalicylaldehyde-derived complex **1** (Figure 3), the left-hand Cu1 is square planar, with phenolate-O, aldimine-N, methanol-O and thiocarbonyl-S as the donors. The Cu^{II} are tightly bound, with Cu–N, Cu–O distances around 1.96 ± 0.07 Å, and Cu–S of 2.23 Å in their principal coordination plane.

The right-hand Cu2 is square pyramidal ($\tau = 0.07^{[13]}$), with methanol-O in the apical position. In the basal plane are imino-N, phenolate-O, sulfate-O and deprotonated (hydrazide) N from the left-hand hydrazine unit.

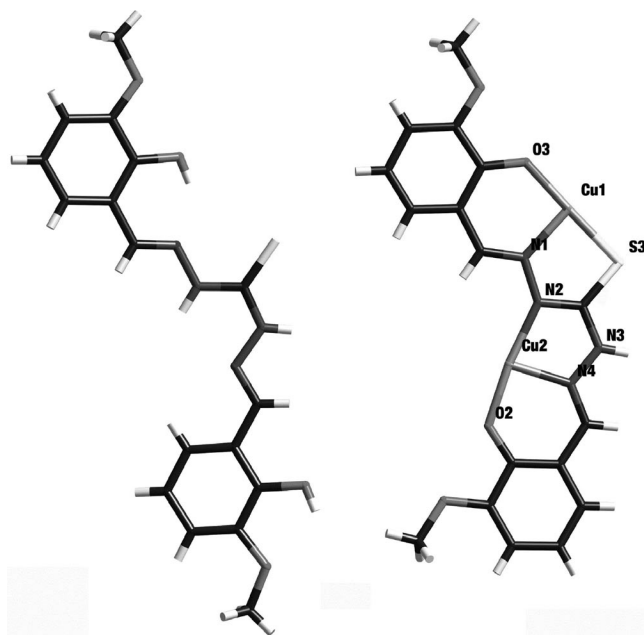


Figure 2. Comparison of the conformation of the free ligand H_4L^{Me} with its HL^{Me3-} copper complex. Only the coppers' chelating agent donors are shown.

Another uncommon feature is that the sulfate ion is actually bound as a hydrogen sulfate ligand. Its proton is stabilised by hydrogen-bonding interactions with the phenolate and methoxy oxygen atoms. In the methoxy compound these O–O distances are respectively 2.630 Å and 2.875 Å. These complexes were prepared without addition of any base; it is notable that sulfate acts as a base, with respect to deprotonation of the hydrazine-N. There are about a dozen instances of unidentately coordinated HSO_4^- in the literature, mostly with silver(I), while the compounds we report here add to the only two other copper examples so far structurally characterised.^[19] Meanwhile, there is a lattice methanol which is also H-bonded to an HSO_4^- oxygen (O–O of 2.665 Å) (Table 1, Table 2 and Table 3).

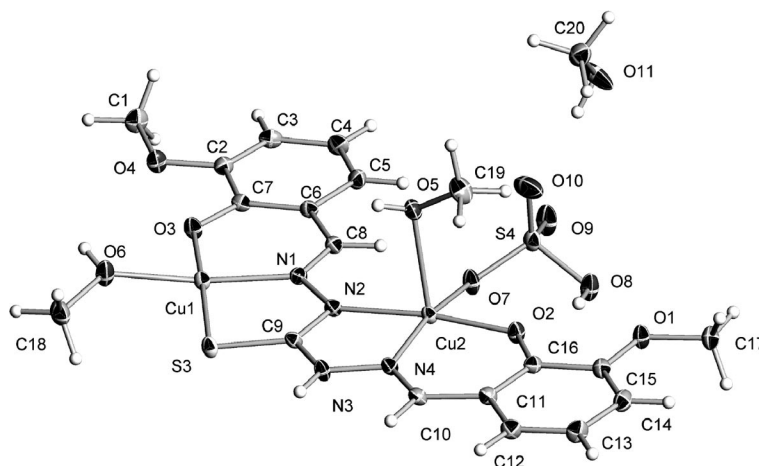


Table 1. Crystallographic data for complexes **1** and **2**.

	Complex 1	Complex 2
Crystal	black hexagon	black block
Dimensions [mm]	0.20 × 0.20 × 0.20	0.55 × 0.36 × 0.29
Chemical formula	C ₂₀ H ₂₈ Cu ₂ N ₄ O ₁₁ S ₂	C ₂₂ H ₃₂ Cu ₂ N ₄ O ₁₁ S ₂
Formula weight [M]	691.66	719.72
Crystal system	monoclinic, <i>P</i> 2 ₁ / <i>c</i>	monoclinic, <i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	7.4249(5)	7.6352(4)
<i>b</i> [Å]	17.3274(12)	17.5330(9)
<i>c</i> [Å]	20.2649(14)	20.8504(10)
β [°]	96.5240(10)	96.4590(10)
<i>V</i> [Å ³]	2590.3(3)	2773.5(2)
Temperature [°C]	100(2)	100(2)
<i>Z</i>	4	4

Table 2. Selected bond lengths [Å] for complexes **1** and **2**.

Bond lengths	Complex 1	Bond lengths	Complex 2
Cu(1)–O(3)	1.8941(18)	Cu(1)–O(2)	1.8930(12)
Cu(1)–N(1)	1.955(2)	Cu(1)–N(1)	1.9496(14)
Cu(1)–O(6)	1.982(2)	Cu(1)–O(9)	1.9712(13)
Cu(1)–S(3)	2.2295(7)	Cu(1)–S(3)	2.2381(5)
Cu(2)–O(2)	1.9227(19)	Cu(2)–O(3)	1.9094(13)
Cu(2)–N(4)	1.941(2)	Cu(2)–N(4)	1.9407(14)
Cu(2)–O(7)	1.9648(19)	Cu(2)–O(5)	1.9648(13)
Cu(2)–N(2)	2.034(2)	Cu(2)–N(2)	2.0296(14)
Cu(2)–O(5)	2.416(2)	Cu(2)–O(10)	2.5464(13)
C(9)–S(3)	1.712(3)	C(10)–S(3)	1.7170(17)
C(9)–N(2)	1.325(3)	C(10)–N(2)	1.331(2)
C(9)–N(3)	1.350(3)	C(10)–N(3)	1.349(2)

Its 3-ethoxy homologue is very similarly structured (Figure 4).

These alkoxy-Schiff base dinuclear chelates display an interesting framework of hydrogen-bond interactions in the solid state. Figure 5 indicates how the two dinuclear units are stacked so as to entail a centre of inversion.

Table 3. Selected bond angles [°] for complexes **1** and **2**.

Angles	Complex 1	Angles	Complex 2
O(3)–Cu(1)–N(1)	94.68(9)	O(2)–Cu(1)–N(1)	95.15(6)
O(3)–Cu(1)–O(6)	86.64(8)	O(2)–Cu(1)–O(9)	85.13(5)
N(1)–Cu(1)–O(6)	170.54(10)	N(1)–Cu(1)–O(9)	169.61(6)
O(3)–Cu(1)–S(3)	176.60(6)	O(2)–Cu(1)–S(3)	174.14(4)
N(1)–Cu(1)–S(3)	87.03(7)	N(1)–Cu(1)–S(3)	86.97(4)
O(6)–Cu(1)–S(3)	92.16(6)	O(9)–Cu(1)–S(3)	93.78(4)
O(2)–Cu(2)–N(4)	90.98(8)	O(3)–Cu(2)–N(4)	90.57(6)
O(2)–Cu(2)–O(7)	87.93(8)	O(3)–Cu(2)–O(5)	88.27(6)
N(4)–Cu(2)–O(7)	167.07(9)	N(4)–Cu(2)–O(5)	167.35(7)
O(2)–Cu(2)–N(2)	171.52(8)	O(3)–Cu(2)–N(2)	171.33(6)
N(4)–Cu(2)–N(2)	81.18(9)	N(4)–Cu(2)–N(2)	80.95(6)
O(7)–Cu(2)–N(2)	98.98(8)	O(5)–Cu(2)–N(2)	99.60(6)
O(2)–Cu(2)–O(5)	97.09(8)		
N(4)–Cu(2)–O(5)	93.88(8)		
O(7)–Cu(2)–O(5)	99.04(8)		
N(2)–Cu(2)–O(5)	86.72(8)		

Each dinuclear moiety, though substantially planar, has the coordinated methanol protruding from the plane, so that its H-atom is H-bonded to the phenolate-O and alkoxy-O of the complementary dimer, the two O–O distances being respectively 2.802 Å and 2.866 Å in the methoxy compound **1**. This pair of noncovalent interactions is further reinforced by a third H-bond from the coordinated methanol of the complementary square-planar copper (2.686 Å). Another lattice methanol is H-bonded to the square-planar copper's imine-N (2.720 Å). This structural motif resembles a precursor or transition state for a penetrative dimerisation of the type recently reported by Ueng et al.^[20]

There are no significant structural differences between complexes **1** and **2**, except for the MeOH molecule coordinated axially to Cu(2), which in complex **2** is a little more distant (2.416 vs. 2.546 Å, respectively).

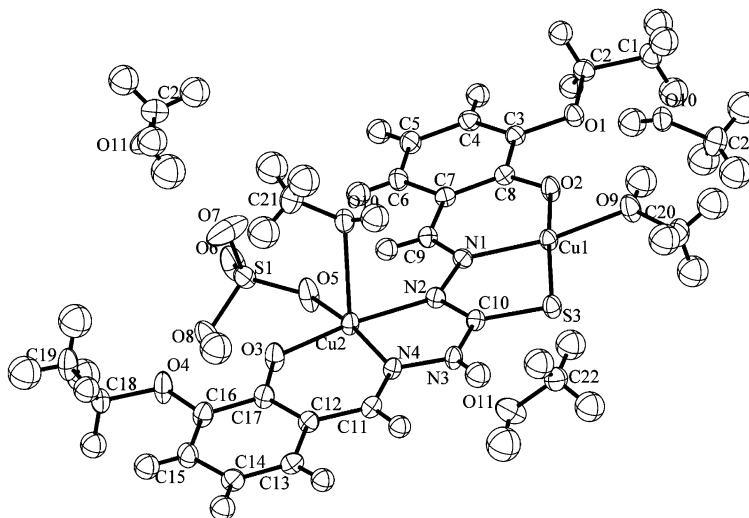


Figure 4. ORTEP representation of the molecular structure of the ethoxy-substituted complex **2** (thermal ellipsoids are shown at the 50% level).

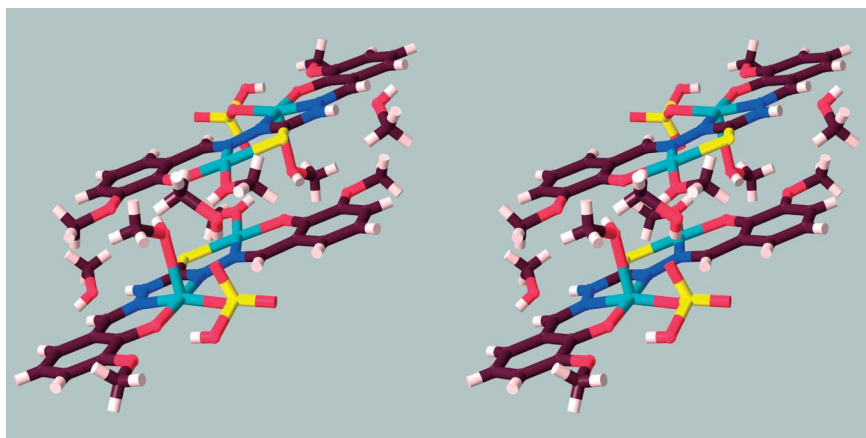


Figure 5. Stick rendering (inverse stereoview) of the stacked pair of dimers of **1**.

Magnetic Properties

The magnetic behavior of polycrystalline samples of **1** and **2** in the temperature range 2–300 K in a field of 1 T is shown in Figure 6. The values of $\chi_{\text{M}}T$ decrease from $0.72 \text{ cm}^3 \text{ K mol}^{-1}$ at ambient temperature to less than $0.01 \text{ cm}^3 \text{ K mol}^{-1}$ by 30 K, evidencing substantial antiferromagnetic coupling.

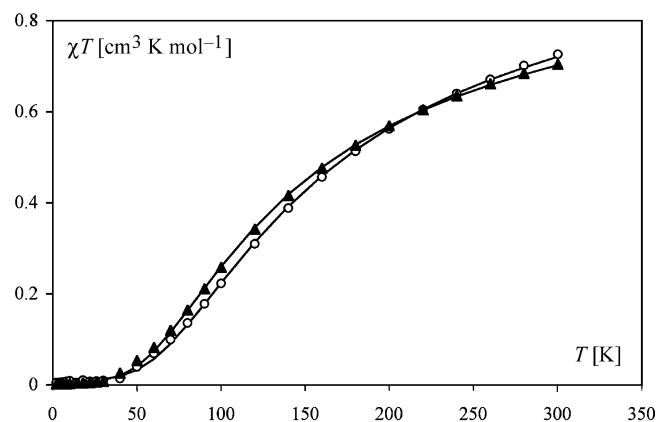


Figure 6. Plots of χT vs. T for the methoxy (o) and ethoxy compounds (▲).

A standard Bleaney–Bowers model^[21] for the coupling of the two neighbouring spins

$$H = -2J\mathbf{S}_1\mathbf{S}_2$$

was used to obtain fits of the data, approximating for the two copper environments by a single g value. For the methoxy compound with $g = 2.17(1)$, $-2J = 189(1) \text{ cm}^{-1}$, $\rho = 0.006(1)$, $R^2 = 1.4 \times 10^{-4}$; for its ethoxy analogue, $g = 2.10(1)$, $-2J = 167(1) \text{ cm}^{-1}$, $\rho = 0.003(1)$, $R^2 = 1.1 \times 10^{-4}$. It is quite unlikely that any water or alcohol H-bond-mediated interdimer interaction (orthogonal to the magnetic orbitals) would be of significance vs. these intradimer couplings. The sign and magnitude of the coupling seem appropriate to the structural features. The essentially coplanar relationship between the two coppers' primary coordination cores

means that the exchange is $d_{x^2-y^2} - d_{x^2-y^2}$ in nature, leading to antiferromagnetic coupling, with the rather flat Cu–N–N–Cu bridges providing an efficient σ pathway for exchange. Other azine-bridged dicopper systems with roughly parallel copper coordination planes also exhibit moderate to large antiferromagnetic coupling.^[10–11,22,23] Indeed, Thompson et al.^[24] have elucidated the way in which the coupling crosses over (i.e., $-2J = 0$) at an interplane twist angle of about 85° . The coupling is antiferromagnetic at lower twist angles, $-2J$ approaching 225 cm^{-1} when the coordination planes are parallel (interplane angle 0°). In the present instances, the CuNNCu torsion angles for the methoxy- and ethoxy-substituted compounds are respectively 4.5° (**1**) and 8.5° (**2**).

The EPR spectra, lacking any fine structure and of low intensity in both the solid state and solution, are not highly informative; the methoxy compound exhibits a broad resonance (H_{pp} ca. 400 G) centred around $g = 2.11$ and a weak half-field ($\Delta M_S = \pm 2$) resonance. Both compounds display a trace of ligand-based free radical at $g = 2.002$.

Conclusions

2:1 alkoxy-salicylaldehyde thiocarbohydrazones form dinuclear copper(II) structures under circumstances in which a second hydrazine nitrogen is kept protonated. The flatness of the Cu–azine–Cu moiety leads to substantial antiferromagnetic coupling. Hydrogen-bond-mediated dimerisation of the dinuclear molecules is effected in an inversion-symmetric modality resembling a pair of plates linked by complementary pin-and-grommet structures.

Experimental Section

General: All reagents, including 3-methoxysalicylaldehyde (*o*-vanillin) were used as received from Aldrich Chemical Co. The 1,5-bis(2-alkoxybenzaldehyde) thiocarbohydrazones were prepared by a slight modification of the reported procedure.^[25] Elemental analyses were from Robertson Microlit, Madison NJ. Fast-atom bom-

bardment (FAB) mass spectra were run with a Micromass-VG 70SE instrument (2-nitrobenzyl alcohol matrix) and infrared spectra with a Perkin–Elmer Spectrum One FT spectrometer furnished with a Universal ATR sampling accessory. EPR spectra were obtained with a Varian E-12 X-band instrument, calibrated near $g = 2$ with DPPH, and NMR spectra with Varian INOVA 300 and 500 MHz spectrometers. Optical spectra were obtained with a Perkin–Elmer Lambda-35 spectrophotometer; samples in DMF for the 450–1,000 nm region were diluted into MeOH for the UV. Variable-temperature magnetic susceptibility data were collected in the range 2–290 K using a Quantum Design SQUID magnetometer, employing a main solenoid field of 1 T and a gradient field of 10 T m^{-1} . Samples were placed in aluminum or gelatin capsules inside 5-mm plastic straws. Susceptibility data were corrected for diamagnetism using Pascal's constants,^[26] $\text{Co}[\text{Hg}(\text{SCN})_4]$ being used as a calibration standard. Data were fitted on a Macintosh G5 platform, using the Microsoft Excel Solver and the statistical macro Solvstat.^[27] X-ray data sets for the complexes **1** and **2** were collected at 100 K with a Bruker AXS SMART APEX CCD diffractometer, using $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$, $\mu = 7.08 \text{ cm}^{-1}$) in the ω scan mode. Structure solution and refinement were performed using SHELXTL.^[28] Both structures were solved by direct methods and all non-hydrogen atoms were refined anisotropically. Hydroxy hydrogen atoms in **1** were located in difference density Fourier maps and all O–H distances were restrained to be the same (within a standard deviation of $0.02 \text{ \AA}$). The hydroxy H-atom H9b in **2** was located similarly and its O–H distance was restrained to be $0.84(2) \text{ \AA}$. The other two O–H hydrogen atoms were placed in calculated positions, but were allowed to rotate around the oxygen atom to best fit the experimental electron density; a like procedure was applied to the methyl groups. All other hydrogen atoms in both structures were placed in calculated positions and refined with an isotropic displacement parameter of 1.5 (methyl, hydroxy) or 1.2 times (all others) that of the adjacent C, O or N atom.

Preparation of Schiff Base Ligands: The ligands $\text{H}_4\text{L}^{\text{Me}}$ and $\text{H}_4\text{L}^{\text{Et}}$ were prepared by first dissolving thiocarbohydrazide (0.265 g, 2.5 mmol) in 20 mL of $\text{H}_2\text{O}/\text{EtOH}$ (1:3). The 3-alkoxy-2-hydroxy-benzaldehyde (5 mmol) in 25 mL of EtOH was then added to this solution, and the resulting reaction mixture was refluxed for 1 h. The pale yellow solids which formed were filtered off, washed with ethanol, diethyl ether and dried in air. Yields were 85–95%.

Bis(3-methoxysalicylaldehyde) Thiocarbohydrazone ($\text{H}_4\text{L}^{\text{Me}}$): Yellow powder. MS: $m/z = 375.1$ $[\text{MH}^+]$. $\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_4\text{S}$ (374.4): calcd. C 54.5, H 4.86, N 15.0; found C 54.5, H 5.19, N 15.4. ^1H NMR ($[\text{D}_6]\text{DMSO}$): $\delta = 3.79$ (s, 6 CH_3), 6.64 (s, OH/NH), 6.82 (d, 2 H, m), 6.84 (d, 4 H, op), 8.51 (s, 1 H, imine), 8.71 (s, 1 H, imine) ppm.

Bis(3'-ethoxysalicylaldehyde) Thiocarbohydrazone ($\text{H}_4\text{L}^{\text{Et}}$): Yellow powder, MS: $m/z = 403.1$ $[\text{MH}^+]$. $\text{C}_{19}\text{H}_{22}\text{N}_4\text{O}_4\text{S}$ (402.5): calcd. C 56.7, H 5.52, N 13.9; found C 56.4, H 5.70, N 14.2. ^1H NMR ($[\text{D}_6]\text{DMSO}$): $\delta = 1.33$ (t, $J = 4.2 \text{ Hz}$, 6 CH_3), 4.04 (q, $J = 4.2 \text{ Hz}$, 4 CH_2), 7.63 (s, OH/NH), 6.81 (d, 2 H, m), 6.99 (d, 4 H, op), 8.52 (s, 1, imine), 8.72 (s, 1 H, imine) ppm.

Synthesis of Copper(II) Complexes: A suspension of the appropriate Schiff base ligand (0.25 mmol) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.125 g, 0.5 mmol) in 25 mL of methanol was heated to reflux and stirred for 10 min. The brown crystalline solid which formed on cooling was filtered off, washed with methanol and placed in a capped vial. Samples for magnetochemistry were further air-dried. Yields were 60–65%.

The copper complex **1** was obtained as a brown crystalline solid after air-drying. $\text{Cu}_2(\text{HL}^{\text{Me}})(\text{HSO}_4) \cdot \text{MeOH} \cdot 3\text{H}_2\text{O}$. $\text{C}_{18}\text{H}_{26}\text{Cu}_2\text{N}_4\text{O}_{12}\text{S}_2$ (682): calcd. C 31.7, H 3.85, N 8.22; found C 31.9, H 3.50,

N 8.54. UV/Vis: λ_{max} [ϵ ($\text{M}^{-1} \text{ cm}^{-1}$ per 2Cu)] = 627 [500], 425 [1.8×10^4], 400 sh [1.6×10^4], 337 sh [2.2×10^4], 306 [3.4×10^4], 236 [3.2×10^4], 205 nm [3.7×10^4].

The copper complex **2** was obtained as a brown crystalline solid after air-drying. $\text{Cu}_2(\text{HL}^{\text{Et}})(\text{HSO}_4) \cdot 0.5\text{MeOH} \cdot 3.5\text{H}_2\text{O}$; $\text{C}_{19.5}\text{H}_{29}\text{Cu}_2\text{N}_4\text{O}_{12}\text{S}_2$ (703): calcd. C 33.3, H 4.17, N 8.00; found C 33.5, H 3.64, N 8.11. UV/Vis: λ_{max} [ϵ ($\text{M}^{-1} \text{ cm}^{-1}$)] = 628 [470], 425 [1.9×10^4], 400 sh [1.6×10^4], 340 sh [2.1×10^4], 304 [3.4×10^4], 236 [3.3×10^4], 208 nm [3.7×10^4].

CCDC-665237 (for **1**) and -665236 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/datarequest/cif.

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