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A tetranuclear copper(II) complex with bis(o-aminobenzaldehyde)thiocarbohydrazone

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1. Introduction

There has been a resurgence of interest in thiocarbohydrazone and thiosemicarbazone metal chelates, because of their interesting catalytic and magnetic properties, their mimicry of oligonuclearity in metalloproteins [1-3] and also recently because of their potential antimicrobial and antiproliferative activity [4–8].

For the copper chelates, mononuclear [9], dinuclear [10,11], paired dinuclear [5,12] and an octanuclear system [13] have been described. The paired dinuclear compounds entail a face-to-face dimerisation of dinuclear molecules [12]. Following on from our prior work [10,12], we now report a tetranuclear system of linear topology, prepared from a novel Schiff base derived from thiocarbohydrazide and o-aminobenzaldehyde. Tetranuclear copper(II) molecules are known with cubane [14–18], rectangular [5,19,20] 'butterfly' or 'chair' (out-of-phase butterfly) [21-23] and linear or pseudo-linear shapes [24,25].

Continuing our work [12] on the coordination chemistry of thiocarbohydrazones, we report here the structure and properties of a

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ABSTRACT

Bis(o-aminobenzaldehyde)thiocarbohydrazone (HL) forms with copper(II) nitrate a tetranuclear complex $[Cu_2(L)(NO_3)_3]_2$ ·2H₂O, in which two dinuclear units are joined by nitrate bridges. The dihydrazone ligand behaves ditopically, providing NNS and NNN binding sites, with the four coppers essentially in a squarepyramidal geometry. The tetranuclear molecule displays intramolecular magnetic interactions, with the antiferromagnetic exchange $(-2J = 210(1) \text{ cm}^{-1})$ between the copper(II) ions within each dinuclear moiety dominant over weak interdimer ferromagnetic coupling.

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tetranuclear copper(II) complex of a new ditopic chelating agent derived from o-aminobenzaldehyde, a molecule itself of enduring interest to inorganic chemists [26-29].

2. Experimental

Thiocarbohydrazide, o-nitrobenzaldehyde, N-allylimidazole and other reagents were used as received (TCI, Sigma-Aldrich, Fisher Scientific). Elemental analyses were from Robertson Microlit, Madison NJ. FAB/LSIMS mass spectra were run on Micromass-VG 70SE and Waters Micromass AutoSpec Ultima instruments (2-nitrobenzyl alcohol matrix), and infrared spectra on a Perkin-Elmer Spectrum One FT spectrometer furnished with a Universal ATR sampling accessory. Optical spectra were obtained mainly from MeOH solutions using a Perkin-Elmer Lambda-35 spectrophotometer. Variable-temperature magnetic susceptibility data were collected in the range 2-300 K on a Quantum Design MPMS5S squid magnetometer at 0.1T in DC mode. Background corrections were applied for the sample container assembly, and susceptibility data were corrected for diamagnetism using Pascal's constants [30]. Co[Hg(SCN)₄] was used as a calibration standard, and samples were placed in Al- or gel-capsules in 5 mm polymer straws. Data

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were fitted on a Macintosh G5 platform, using the Microsoft Excel Solver and the statistical macro SolvStat [31].

2.1. Synthesis and characterization of the thiocarbohydrazone and its copper(II) complex

2.1.1. HL

The carbonylic compound *o*-aminobenzaldehyde (anthranilaldehyde) was obtained by reduction of *o*-nitrobenzaldehyde with iron(II) sulfate [32]. The thiocarbohydrazone ligand HL was prepared by refluxing for 1 h the freshly-prepared aldehyde (0.60 g, 5 mmol) and thiocarbohydrazide (0.26 g, 2.5 mmol) in 50 mL of EtOH containing a drop of acetic acid. The product precipitated in 90% yield as yellow microcrystals, which were filtered off and air-dried. *Anal.* Calc. for C₁₅H₁₆N₆S·1/4H₂O: C, 56.9; H, 5.25; N, 26.5. Found: C, 56.9; H, 5.58; N, 26.9%. The mass spectrum shows m/z = 313.1 (MH⁺) as 100%. Optical spectrum λ_{max} (nm), (10⁻³ ε M⁻¹ cm⁻¹: in MeCN, 374 (16.9), 299 (17.4), 253 (15.7), 228 (20.6); in MeOH: 369 (15.1), 302 (17.5), 258 (sh, 20.9), 232 (26.9).

IR (cm⁻¹): 3457, 3273, 3146 (ν_{N-H}), 3002 (ν_{C-H}), 1488, 1445, (ν_{C-C} , ν_{C-N}), 1228 (ν_{N-N}), 957 (ν_{C-S}), 791, 742 (δ_{C-H}).

2.1.2. [Cu₂(L)(NO₃)₃]₂·2H₂O (1)

For the preparation of the copper complex, 0.078 g of bis(oaminobenzaldehyde)thiocarbohydrazone was added to a solution of 0.116 g of copper(II) nitrate hemi(pentahydrate) in 20 mL MeOH. The suspension was stirred until the ligand dissolved, after which the resulting green solution was filtered and allowed to stand overnight. The small, dark green rectangular crystals which appeared were filtered off and air-dried. *Anal.* Calc. for $C_{30}H_{34}Cu_4N_{18}O_{20}S_2$: C, 28.0; H, 2.67; N, 19.6. Found: C, 28.1; H, 3.04; N, 19.6%. The complex is soluble in polar and/or coordinating solvents such as pyridine, 2-methoxyethanol, DMF and DMSO, and sparingly so in MeOH. Optical spectrum (MeOH): λ_{max} (nm), $(10^{-3} \varepsilon, M^{-1} \text{ cm}^{-1}$: 630 (1.8), 415(sh, 17.8), 325 (67). Changes in the spectrum with time suggest that the solutions are photosensitive.

IR (cm⁻¹): 3504, 3287, 3162 (v_{N-H}), 1466, 1378, (v_{C-C} , v_{C-N}), 1263 (v_{N-N}), 752 (v_{C-S}).

2.2. Crystallographic measurements

X-ray data for the complex were collected at 100 K on a Bruker AXS SMART APEX CCD diffractometer, using Mo K α radiation ($\lambda = 0.71073$ Å, $\mu = 7.08$ cm⁻¹) in the ω -scan mode. Structure solution and refinement were performed using SHELXTL [33]. The structure was solved using direct methods and all non-hydrogen atoms were located in the difference density Fourier map, their O–H distances were constrained to be 0.85 Å within a standard deviation of 0.02 and were isotropically refined. All other hydrogen atoms were placed in calculated positions and were isotropically refined with a displacement parameter of 1.5 (methyl) or 1.2 times (all others) that of the adjacent carbon or oxygen atom. Crystallographic data for complex **1** are in Table 1.

2.3. Computations

DFT calculations were performed with the GAMESS suite of codes [34] using the unrestricted Kohn–Sham formulation with the B3LYP exchange-correlation functional [35]. The Ahlrichs valence triple zeta (VTZ) basis set [36] was applied to all atoms. This

Table 1

Crystallographic data for complex 1.

	Complex 1
Crystal	Green rod
Crystal size (mm)	$0.29 \times 0.13 \times 0.13$
Formula	C30H34Cu4N18O20S2
Formula weight	1285.03
Crystal system	triclinic, P1
a (Å)	7.3594(11)
b (Å)	10.3702(15)
c (Å)	15.343(2)
α (°)	104.485(2)
β(°)	92.440(2)
γ (°)	102.396(2)
V (Å ³)	1101.6(3)
T (K)	100(2)
Ζ	1



Fig. 1. FAB-MS of the copper complex, showing the peak corresponding to Cu_2L^* at m/z = 437 (78%). The combination of copper contents and charges imply thermal electron capture, with generation of copper(1) for some ions.

functional and basis set was chosen for its previous success in determining J values of other Cu(II) complexes among other transition metal complexes [37-40].¹

As hardware/software limitations prevented us from obtaining a complete solution for the tetracopper system, we carried out two dicopper(II,II) calculations, firstly replacing Cu(3) and Cu(4) by Zn(II) to obtain an estimate of J_a , then similarly replacing Cu(1) and Cu(4) for estimating J_b .

3. Results and discussion

The FAB-mass spectrum (Fig. 1) shows the intended dinuclear moiety Cu_2L^+ preserved, as a strong peak, with another (de)protonated state superimposed. However, other higher-mass cupriferous ions are also seen, though appearing at much lower intensity; these include $Cu_2L(NO_3)H^+$ (500) and $[Cu_4L_2(NO_3)-2H]^+$ (935).

3.1. Structure of the complex

In addition to the hydrazone/imine and anilino-nitrogens, the dihydrazone ligand provides a thione sulfur and an additional

¹ The coupling constant (*J*) can be related to the energy difference between the broken symmetry (low-spin) and high-spin states, with the α and β densities being allowed to localize on different atomic centers (E. Ruiz, J. Cano, S. Alvarez, P. Alemany, J. Comput. Chem. 20 (1999) 1391–1400.) Using this approach, the coupling constant can be determined from: $J = \frac{E_{BS} - E_{BS}}{(25_1S_2 + S_2)}$ where E_{HS} is the energy of the high-spin state, E_{BS} is energy of the broken symmetry state, and S_1 and S_2 are the total spins for site 1 and 2, so that $J_{Cu-Cu} = E_{BS} - E_T$.



Fig. 2. Molecular structure, with numbering scheme, of the dinuclear unit of complex **1**. Nonessential H-atoms are omitted for clarity of presentation; atoms are shown at the 70% probability level. Atoms N1 and N6 are the sp³-hybridised aniline nitrogens. The two coppers are 4.88 Å apart.

nitrogen donor. The latter pertains as the result of deprotonation of one of the hydrazine α -nitrogens to yield a hydrazide. Note that no base was added during the chelation process; this ready displacement of the proton from the hydrazine-NH echoes the same phenomenon in the salicylaldehyde-derived copper complexes [12]. The ligand thus acts ditopically, with NNN and NNS binding sites for the coppers, as shown in Fig. 2. Selected bond distances and angles for 1 are listed in Table 2. The coppers are all pentacoordinate, with the additional two donors in each case being nitrate oxygens. Whereas the dinuclear salicylhydrazone molecules [12] are antiparallel-stacked to form noncovalent (H-bonded) dimers, the present dinuclear molecules are joined end-to-end by coordinate bonds with a pair of nitrate anions, which bridge the coppers Cu(2) in the NNS binding sites, to form a dimer of dinuclear molecules similar to one reported by Moubaraki et al. [41] (Fig. 3). These coppers are thus the 'inner' metal ions in a centrosymmetric pseudolinear tetranuclear structure, in which the dinucleating ligands' mean planes are antiparallel, to within 1°. The NNS donors occupy the basal plane of the essentially square-pyramidal inner coppers(II) $(\tau = 0.17 [42])$. A single nitrate–O acts as the bridging atom

Table 2						
Selected bond	lengths	(Å) and	l angles	(°) for	complex 1	

Bond lengths	Complex 1	Angles	Complex 1
Cu(1)-O(1)	2.316(3)	N(1)-Cu(1)-N(2)	91.6(1)
Cu(1) - O(4)	2.003(2)	O(4)-Cu(1)-N(2)	161.7(1)
Cu(1)-N(1)	1.988(2)	N(1)-Cu(1)-O(4)	88.4(1)
Cu(1)-N(2)	1.961(3)	N(2)-Cu(1)-N(4)	80.3(1)
Cu(1)-N(4)	2.005(3)	N(1)-Cu(1)-N(4)	171.8(1)
Cu(2)-S(1)	2.2407(10)	O(4)-Cu(1)-N(4)	99.7(1)
Cu(2)-N(5)	1.980(3)	N(2)-Cu(1)-O(1)	117.7(1)
Cu(2)-N(6)	1.985(3)	N(1)-Cu(1)-O(1)	92.7(1)
Cu(2) - O(7)	1.987(2)	O(4)-Cu(1)-O(1)	80.6(1)
Cu(2) - O(7)	2.398(2)	N(4)-Cu(1)-O(1)	90.3(1)
C(8)-S(1)	1.708(3)	N(5)-Cu(2)-N(6)	90.2(1)
C(8)-N(3)	1.355(4)	N(5)-Cu(2)-O(7)	170.0(1)
C(8)-N(4)	1.329(3)	N(6)-Cu(2)-O(7)	93.1(1)
		N(5)-Cu(2)-S(1)	87.4(1)
		N(6)-Cu(2)-S(1)	160.3 (1)
		O(7)-Cu(2)-S(1)	92.7(1)
		N(5)-Cu(2)-O(7)	95.8(1)
		N(6)-Cu(2)-O(7)	92.7(1)
		O(7)-Cu(2)-O(7)	74.6(1)
		S(1)-Cu(2)-O(7)	107.0(1)



Fig. 3. Inverse stereoview of the tetranuclear complex, viewed along the a-direction; nonessential H-atoms omitted for clarity of presentation, 75% thermal ellipsoids.

between the axial coordination site of one Cu(II) and a basal site of the other Cu(II), trans- to the hydrazide-N. The Cu(II) are all closely bound, with inner Cu-donor atom distances of 1.980 Å (imine N), 1.985 Å (aniline N), 1.987 Å (O-basal), 2.241 Å (thione S) and 'outer' (Cu(1)) Cu-donor distances of 1.988 Å (aniline N), 1.961 Å (imine N) and 2.005 Å (hydrazide N). The outer two coppers, Cu(1), each have a basal and an axial unidentate nitrate to complete their square-pyramidal coordination ($\tau = 0.16$), with Cu–O (basal) of 2.002 Å. The axial nitrate oxygens are at 2.315 Å for the outer coppers, and 2.398 Å for the bridged inner coppers, all these bonds reflecting classical Jahn-Teller elongation. The hydrazide-N to Cu distance is relatively the longest in the basal plane, presumably reflecting the delocalisation of the anionic charge and its redistribution toward the sulfur atom. Although little evidence of any significant difference between Cu-S distances in protonated vs. deprotonated versions of similar thiocarbohydrazones has been observed. [43] it is generally the case that on deprotonation, the imino-thiolate (Scheme 1 (a)) resonance form's contribution increases relative to the amidato-thione's (b). This is evidenced by a modest increase of typically ca. 2% in the C-S bond length between the free and the coordinated deprotonated forms [12]. Sometimes the deprotonation and coordination contribute equally [12,34,43,44]. The decrease in C–S bond order on deprotonation is necessarily associated with shortening of the C-N4 bond to the hydrazide nitrogen (2% here), though this shortening is not general even within the limited pyridyl-thiosemicarbazone subset of chelates [41].

There are several hydrogen bonds associated with the structure. The lattice water molecule's O10 is an H-bond acceptor for H3A of the hydrazine nitrogen's N3. Simultaneously, the water's protons H10B and H10A link to an adjacent molecule's monodentate nitrates' O3 and O5, while the anilino-N's H1B is linked to nitrate O1 of an adjacent molecule. Consequently, the molecules include sheet-like segments which are linked laterally (Fig. 4) along the



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Scheme 1.
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b-direction. As each molecule is step-shaped, with the Cu(2) constituting the 'risers' and the ligands the 'treads', the lateral sheets form the treads of 'staircases' which run in the *c*-direction, and are stacked on top of one another.

3.2. Optical spectra

The optical spectrum shows a band maximizing at 630 nm (ε of ca. 450 M⁻¹ cm⁻¹ per Cu), which though principally *d*–*d* in nature, is somewhat enhanced in intensity, as is often seen when sulfur donors are present [42]. Ligand-localized transitions in the 250–350 nm region appear reproduced in the copper complex, while in the latter, absorption near 410 nm is likely associated with LMCT.

3.3. Infrared spectra

Broad bands assignable to $v(NH_2)$ appear at ca. 3400–311 cm⁻¹. On coordination of the imine nitrogen, v(C=N) shifts to lower frequency by ca. 10–35 cm⁻¹, so the band shifting from 1611 cm⁻¹ in the uncomplexed thiocarbohydrazone's spectrum to 1601 cm⁻¹ in the spectrum of the complex **1** is assigned as v(C=N). A sharp band of medium intensity at 791 cm⁻¹ in HL is attributed to a dominant contribution from v(C=S), and is absent from the copper complexes, where a new band appears at 752 cm⁻¹. This shift is consistent with the transformation from thione character (Scheme 1 (a)) to deprotonated pseudothiolate character (b).

3.4. Magnetic studies

The magnetic behavior of a polycrystalline sample of **1** is shown in Fig. 5. The value of $\chi_M T$ decreases from 1.357 cm³ K mol⁻¹ at ambient temperature to less than 0.0137 cm³ K mol⁻¹ by 30 K, evidencing a dominance of antiferromagnetic coupling within the tetranuclear molecule.

Several related tetracopper systems have appeared in the literature, and a treatment of this spin topology (Fig. 6) has been given by Fukuhara et al. [45], based on the original work by Hatfield and Inman [46].

Variations in the molecular structure details have often enabled certain of the J_a - J_d values to be approximated to zero in different systems [21–23,25,47,48]. In anticipation of the analysis of the magnetic data, it might be noted that the basal plane-basal plane interactions Cu(1)–Cu(2) and Cu(3)–Cu(4) are similar to previously described cases [5,12,42,49,50] with $-2J_a$ in the range of 100 to 300 cm⁻¹, while it would appear unlikely that coupling of non-adjacent coppers would be significant relative to such J_a values. Indeed a simple dinuclear model [12,51] on J_a (approximating as usual for the two copper environments by a single g-value) yields a good fit ($R^2 = 1.2 \times 10^{-4}$) of the data, with $-2J_a = 210(1)$ cm⁻¹, g = 2.143(5), with *TIP* = 60 × 10⁻⁶ cgsu per Cu, and 0.2% paramag-



Fig. 4. Lattice view along the c-direction, showing 'staircase' stacking of the molecules (inverse stereoview).



Fig. 5. Plot of χT vs. *T* for the copper compound. The solid line represents the fit model.



Fig. 6. Scheme for the magnetic interactions amongst the four coppers. Connector lengths reflect interaction weakness. The molecule's outer Cu(1) correspond to the spin locations 1 and 4, and the inner Cu(2) to locations 2 and 3.

netic impurity estimated from the low-*T* floor. Although Cu(2) and Cu(3) are physically close, at 3.50 Å, the structure shows that the nitrate bridge oxygens are disposed axially/equatorially. As a consequence, these copper(II) ground state orbitals are mutually orthogonal, so that significant antiferromagnetic coupling is not expected. In any case, any outcome of this coupling is overwhelmed by the strong Cu(1)–Cu(2) interaction. In at least one prior tetranuclear case [19], the value of J_b was similarly so small as to be negligible, and the data were likewise fitted by a Bleaney–Bowers model.

Some further points relevant to this situation are:

- (1) An allylimidazole complex structurally very similar to the Cu(2), Cu(3) core in our tetranuclear system has been described [52], and this has $-2J = -2.1 \text{ cm}^{-1}$ (Fig. S2), confirming the absence of marked Cu(2)–Cu(3) coupling.
- (2) The DFT calculations (Tables 3 and S1) support these conclusions, estimating $J_a = -125 \text{ cm}^{-1}$ and $J_b = +5 \text{ cm}^{-1}$.
- (3) Fitting of the data to the full tetranuclear Hatfield–Fukuhara model yielded very large standard deviations for J_b , J_c and J_d , and fits involving physically incompatible values of the *J*'s were also easily realised, suggesting overparametrization. Exploration of the dependence of R^2 on the *J*-values as previously described [21,53,54] showed that even for a two-*J* model (giving $J_b = +1 \text{ cm}^{-1}$), the value of R^2 remains low for

Table 3

UB3LYP/Ahlrichs-TZV-calculated energies (Hartrees) for the high-spin (E_{HS}) and broken symmetry spin (E_{BS}) states, and the calculated J values.

Coupling constant	E _{BS}	E _{HS}	$J(cm^{-1})$
Ja	-11133.76308	-11133.76251	-125
Jb	-11133.77343	-11133.77345	+5

a wide range of positive J_b values, but rises steeply if J_b becomes negative.

The sign and magnitude of the couplings correlate satisfactorily with 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, [12,13,41,49,50] as elucidated by Thompson et al. [55]; the coupling crosses over (i.e., -2J = 0) at an interplane twist angle of about 85°. In the present instance, the Cu-N-N-Cu torsion angle is 15° away from parallel, and the angle between the two 5 atom coordination basal mean planes is 36°. These angles are slightly larger than in our previously reported systems, where -2I was about 180 cm⁻¹ [12–13]. It is also of interest to compare these results with those for two tetranuclear Schiff base complexes described by Mukherjee et al. [24]; these molecules have a metal/ ligand/bridge layout very similar to 1, but the phenolate bridges at 94° between the central coppers lead to a $-2I_b$ of 70 cm⁻¹.

4. Conclusions

A tetranuclear Cu(II) compound with NNN and NNS binding sites for the copper has been described. Two dinuclear entities are joined end-to-end by bridging nitrate anions, which mediate a small ferromagnetic coupling. However, the magnetic properties of the tetranuclear molecule are dominated by antiferromagnetic interactions between the two coppers in each dinuclear chelate. The molecule provides a rare example of a tetracopper system with this numerical pattern of spin couplings.

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Appendix A. Supplementary material

CCDC 744024 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica. 2010.02.002.

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