DALTON
FULL PAPER

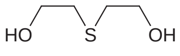
Thioalcohols as bridging ligands in polynuclear Pr^{III}/Cu^{II} and Ba^{II}/Cu^{II} complexes. Syntheses, structures and magnetic properties of $Pr_2Cu_4(tde)_3(Htde)_2(hfacac)_4(\mu_6\text{-}O)$, $Ba_2Cu_2(Htde)_2(hfacac)_4$ and $Cu_4(tde)_2(hfacac)_4$, ($H_2tde = HOCH_2CH_2SCH_2CH_2OH$) ‡

Steven R. Breeze,[a] **Suning Wang,***†[a] **John E. Greedan**[b] **and N. P. Raju**[b]

[a] *Department of Chemistry, Queen's University, Kingston, Ontario, K7L 3N6, Canada*
[b] *Department of Chemistry, McMaster University, Hamilton, Ontario, L8S 4M1, Canada*

The syntheses of heterometallic compounds involving praseodymium, barium and copper ions by using 2,2′-thiodiethanol (H_2tde) as the bridging ligand have been investigated. Three new polynuclear compounds, $Pr_2Cu_4(tde)_3(Htde)_2(hfacac)_4(\mu_6\text{-}O)$ **1**, $Ba_2Cu_2(Htde)_2(hfacac)_4$ **2** and $Cu_4(tde)_2(hfacac)_4$ **3** have been obtained and characterized structurally. The metal atoms in **1** have an octahedral arrangement with the two Pr^{III} occupying two opposite vertices. In the center of the octahedron is a μ_6-oxygen atom. The metal atoms in **2** have a rhombic arrangement with a long Cu · · · Cu separation distance (6.082 Å). The metal ions in **3** also have a rhombic arrangement with the copper atoms in close proximity to each other. The sulfur atoms of the $Htde^-$ or tde^{2-} ligand are bound exclusively to copper centers in all three compounds. The $Htde^-$ and tde^{2-} ligands display versatile bonding modes in the three compounds. Antiferromagnetic exchanges dominate in these compounds.

Heterometallic polynuclear lanthanide–copper and alkaline earth metal–copper compounds have attracted much research attention recently because of their potential applications in copper oxide based superconductors and molecular magnetism.[1–3] Our earlier research efforts focused on the syntheses of heterometallic Ln–Cu and M^{II}–Cu (M^{II} = alkaline earth metal) compounds by using bifunctional ligands such as aminoalcohols. A variety of polynuclear Ln–Cu and M^{II}–Cu compounds were obtained successfully by employing the aminoalcohol ligands.[3] Further to explore the chemistry of polynuclear Ln–Cu and M^{II}–Cu compounds, we investigated the utility of thio-containing alcohol ligands in the synthesis of mixed metal Ln–Cu and M^{II}–Cu compounds. The Ln–Cu compounds with thioalcohol ligands are not useful as precursors for superconductors due to the problem of sulfide contamination. They may, however, find use in the field of molecular magnetism. One advantage provided by thioalcohol ligands over aminoalcohol is that, as a soft donor, the sulfur atom has a high affinity for the copper center, making them better bifunctional ligands than aminoalcohols for selective binding to lanthanide or alkaline earth metal and copper centers. The thioalcohol ligand chosen for our study is 2,2′-thiodiethanol (H_2tde) for its simplicity. This ligand has two acidic protons which can be removed readily to form either the monoanion, $Htde^-$ or the dianion, tde^{2-}. The alkoxo oxygen atom of $Htde^-$ or tde^{2-} was anticipated to bridge a hard metal ion such as lanthanide(III) or barium(II) and the copper(II) ion in the same manner as those in aminoalcohol ligands. Indeed, we have succeeded in synthesizing several interesting polynuclear complexes by using the H_2tde ligand. We report herein the syntheses, structures and magnetic properties of two new heterometallic compounds, a μ_6-oxygen bridged Pr_2Cu_4 compound and a rhombic Ba_2Cu_2 compound and a tetranuclear Cu_4 compound as well, obtained by using the H_2tde ligand.



H_2tde

Experimental

All reactions and manipulations were performed under an atmosphere of nitrogen using either a Vacuum Atmospheres glove-box or standard Schlenk-line techniques. Solvents were reagent grade and distilled from appropriate drying agents under nitrogen prior to use. Copper(II) methoxide and 2,2′-thiodiethanol were purchased from the Aldrich Chemical Company and used as received. Praseodymium, barium and yttrium hexafluoroacetylacetonates were purchased from Strem Chemicals. The IR spectra were recorded on a Bomen FTIR spectrometer. The KBr used in the pellets for the IR studies was dried in an oven for several hours prior to use. Elemental analyses were performed by Canadian Microanalytical Service, Delta, British Columbia. Variable temperature magnetic susceptibility data were collected on a SQUID magnetometer at 1 kG. All molar susceptibility data were corrected for diamagnetism by using Pascal constants.[4]

Syntheses

$Pr_2Cu_4(tde)_3(Htde)_2(hfacac)_4(\mu_6\text{-}O)$ 1. The compound $Cu(OCH_3)_2$ (100 mg, 0.80 mmol) was treated with H_2tde (122 mg, 1.00 mmol) in CH_2Cl_2 (3 mL) at 25 °C, which yielded an insoluble purple solid. After allowing the mixture to stir for approximately 20 h, $Pr(hfacac)_3$ (Hhfacac = 1,1,1,5,5,5-hexafluoroacetylacetonate) (303 mg, 0.40 mmol), water (3.6 mg, 0.20 mmol) and CH_2Cl_2 (20 mL) were added. The solution became dark green and was stirred for 4 h before being filtered to remove a trace amount of precipitate. The filtrate was concentrated *in vacuo* to approximately 5 mL and hexane (2 mL) was added to crystallize the product. The crystals were dark green (153 mg, 0.079 mmol, 40%), m.p. 215–216 °C (Found: C, 24.17; H, 2.36. Calc. for $C_{40}H_{46}Cu_4F_{24}O_{19}Pr_2S_5$: C, 24.23; H, 2.34%). IR (KBr, cm^{-1}): 1660s, 1528m, 1259s, 1201s, 1142vs and 1073m. Magnetic moment at 300 K: 2.65 μ_B, Pascal constant = 8.10×10^{-4} $cm^3\ mol^{-1}$.

$Ba_2Cu_2(Htde)_4(hfacac)_4$ 2. The compound $Cu(OCH_3)_2$ (50 mg, 0.40 mmol) was treated with 2 equivalents of H_2tde (97 mg, 0.80 mmol) in CH_2Cl_2 (3 mL) at 25 °C. After allowing the mixture to stir for approximately 20 h, $Ba(hfacac)_2$ (220 mg,

---

† E-Mail: wangs@chem.queensu.ca

‡ *Non-SI units employed*: G = 10^{-4} T, $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

Table 1 Crystallographic data for compounds **1**–**3**

	1	**2**	**3**
Formula	$C_{40}H_{46}Cu_4F_{24}O_{19}Pr_2S_5$	$C_{36}H_{40}Ba_2Cu_2F_{24}O_{16}S_4$	$C_{28}H_{20}Cu_4F_{24}O_{12}S_2$
M	1983.04	1714.68	1322.72
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a/Å	12.081(2)	12.7094(2)	10.693(2)
b/Å	14.493(3)	9.2893(2)	10.8750(13)
c/Å	20.640(4)	25.6763(4)	11.130(2)
α/°	72.69(3)		66.214(13)
β/°	75.30(3)	100.391(1)	70.73(2)
γ/°	76.72(3)		72.356(9)
U/Å^3	3290.6(11)	2981.66(9)	1096.0(3)
Z	2	2	1
μ/cm^{-1}	30.1	22.8	21.6
Reflections measured	12 546	22 885	2943
Reflections used (R_{int})	12 439 (0.001)	5879 (0.045)	2762 (0.026)
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0537, 0.1553	0.0460, 0.1223	0.0567, 0.1265
(all data)	0.0732, 0.1726	0.0626, 0.1391	0.0899, 0.1479

$R1 = (\Sigma|F_o| - |F_c|)/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

0.40 mmol) and CH_2Cl_2 (20 mL) were added. The solution was stirred for 4 h before being filtered to remove a blue precipitate. The filtrate was concentrated *in vacuo* to approximately 5 mL and hexane (2 mL) was added to crystallize the product. The crystals of compound **2** were light blue (87 mg, 0.051 mmol, 25.3%), m.p. 162–165 °C (Found: C, 25.22; H, 2.35. Calc. for $C_{18}H_{20}BaCuF_{12}O_8S_2$: C, 25.22; H, 2.46%). IR (KBr, cm^{-1}): 1667s, 1537s, 1262s, 1203s, 1131vs and 1071m. Magnetic moment at 300 K: 1.50 μ_B, Pascal constant = 7.13×10^{-4} cm^3 mol^{-1}.

$Cu_4(tde)_2(hfacac)_4$ 3. The compound $Cu(OCH_3)_2$ (100 mg, 0.80 mmol) was treated with H_2tde (122 mg, 1.00 mmol) in CH_2Cl_2 (3 mL) at 25 °C. After allowing the mixture to stir for approximately 20 h $Y(hfacac)_3$ (283 mg, 0.40 mmol), water (3.6 mg, 0.20 mmol) and CH_2Cl_2 (20 mL) were added. The solution was stirred for 4 h before being filtered to remove a trace amount of precipitate. The filtrate was concentrated *in vacuo* to approximately 5 mL and hexane (2 mL) was added to crystallize the product. The crystal were dark green (187 mg, 0.141 mmol, 71%), m.p. 185–187 °C (Found: C, 25.47; H, 1.55. Calc. for $C_{14}H_{10}Cu_2F_{12}O_6S$: C, 25.46; H, 1.53%). IR (KBr, cm^{-1}): 1648s, 1561w, 1468m, 1262s, 1211s and 1148vs. After the green crystals were collected, blue crystals were isolated from the remaining solution (50 mg) (Found: C, 22.93; H, 1.28%). This composition matches well with the formula of $Cu_2Y_2(tde)_2(hfacac)_3(O_2CCF_3)_2(OH)$ (C, 22.99; H, 1.41%). IR (KBr, cm^{-1}): 1663s, 1529w, 1503m, 1254s, 1142vs and 1077m. Magnetic moment at 300 K: 3.47 μ_B, Pascal constant = 5.30×10^{-4} cm^3 mol^{-1}.

Single-crystal X-ray diffraction analysis

X-Ray quality crystals were obtained from concentrated hexane–CH_2Cl_2 solutions at 0 °C. For compounds **1** and **2** the data were collected on a Siemens CCD X-ray diffractometer. For compound **3** a suitable crystal was mounted on a glass fiber with epoxy resin and the data were collected on a conventional Siemens P4 diffractometer with a Mo-Kα radiation source operating at 60 kV and 40 mA. Data were collected at 23 °C over the range $2 < 2\theta < 53°$ for **1**, $3.2 < 2\theta < 54°$ for **2** and $4 < 2\theta < 45°$ for **3**. Three standard reflections were measured every 197. The data for all the compounds were processed on a Pentium personal computer using the Siemens SHELXTL crystallographic package (version 5).[5] Data were corrected for Lorentz-polarization effects and empirical absorption corrections were applied in all cases. No significant decay was observed. Neutral atomic scattering factors were taken from the literature.[6] Some of the fluorine atoms in compounds **1**–**3** displayed a two-fold rotational disorder, which was successfully modeled and refined with 50% occupancy factors for each site. All of the non-hydrogen atoms were refined anisotropically except the disordered fluorine atoms in **1**. The positions of the hydrogen atoms bound to carbon atoms were calculated and included in the structure factor calculations. The crystal data are given in Table 1.

CCDC reference number 186/1009.

Results and Discussion

Synthesis and structure of $Pr_2Cu_4(tde)_3(Htde)_2(hfacac)_4(\mu_6\text{-}O)$ 1

The reaction between copper methoxide and H_2tde resulted in a sparingly soluble purple compound. Following the addition of $Pr(hfacac)_3$ the mixture immediately changed to dark green. When this solution was concentrated and a small amount of hexane was added dark green crystals were obtained. Attempts to determine the structure of the compound by single-crystal X-ray diffraction experiments on a conventional diffractometer were unsuccessful due to the insufficient number of data. The dark green color of the compound indicated the presence of copper(II). The IR spectrum of **1** showed that the hexafluoroacetylacetonato ligand is present. The structure and composition of **1** was ultimately established by a single-crystal X-ray diffraction experiment performed on a CCD diffractometer. The oxo ligand was believed to come from the trace amount of water present in the reaction medium. Indeed, the yield of compound **1** was improved when a stoichiometric amount of water was added to the reaction mixture.

An ORTEP[7] drawing of compound **1** with the fluorine atoms omitted for clarity is shown in Fig. 1. Selected bond lengths and angles are provided in Table 2. Compound **1** consists of four copper atoms and two praseodymium atoms in an octahedral arrangement, with the two praseodymium atoms occupying opposite vertices of the octahedron. The Pr^{III} and the Cu^{II} are linked together by an oxo ligand and eight oxygen atoms from the deprotonated 2,2′-thiodiethanol ligands. The Pr–Cu distances range from 3.285(1) [Pr(2)–Cu(1)] to 3.408(1) Å [Pr(2)–Cu(2)], comparable to those found in previously reported Ln–Cu complexes where the Ln^{III} and Cu^{II} are linked together by oxygen atoms from either hydroxypyridine or aminoalcohol ligands.[2,3] Several Ln–Cu compounds containing an octahedral Ln_2Cu_4 unit have been reported previously where hydroxypyridine ligands are used as the bridging ligands.[2c,3d] Compound **1** is, however, the first example of octahedral Ln–Cu complexes using thioalcohol ligands and the first example of Ln_2Cu_4 complexes containing a μ_6-oxo ligand [O(19)]. The μ_6 bridging mode of the oxo ligand, albeit

Table 2 Selected bond lengths (Å) and angles (°)

Compound 1

Pr(1)–O(11)	2.394(5)	Pr(2)–Cu(4)	3.396(2)	Pr(2)–O(12)	2.396(4)	Cu(3)–O(18)	1.904(5)
Pr(1)–O(14)	2.438(5)	Cu(1)–O(15)	2.412(5)	Pr(2)–O(18)	2.415(5)	Cu(3)–O(14)	1.905(5)
Pr(1)–O(16)	2.453(5)	Cu(1)–O(12)	1.892(5)	Pr(2)–O(13)	2.453(5)	Cu(3)–O(19)	2.006(4)
Pr(1)–O(9)	2.464(5)	Cu(1)–O(16)	1.898(5)	Pr(2)–O(7)	2.455(6)	Cu(3)–S(5)	2.335(2)
Pr(1)–O(4)	2.492(6)	Cu(1)–O(19)	2.034(4)	Pr(2)–O(5)	2.474(5)	Cu(4)–O(11)	1.893(5)
Pr(1)–O(1)	2.521(6)	Cu(1)–S(4)	2.336(2)	Pr(2)–O(15)	2.479(4)	Cu(4)–O(13)	1.895(5)
Pr(1)–O(2)	2.525(6)	Cu(2)–O(9)	1.902(5)	Pr(2)–O(8)	2.553(5)	Cu(4)–O(19)	2.137(4)
Pr(1)–O(3)	2.548(6)	Cu(2)–O(15)	1.914(4)	Pr(2)–O(6)	2.596(5)	Cu(4)–S(3)	2.490(2)
Pr(1)–O(19)	2.654(4)	Cu(2)–O(19)	2.039(4)	Pr(2)–O(19)	2.669(4)	Cu(4)–S(2)	2.573(2)
Pr(1)–Cu(2)	3.352(2)	Cu(2)–S(1)	2.358(2)	Pr(2)–Cu(1)	3.2848(11)	Cu(4)–Cu(3)	2.8968(12)
Pr(1)–Cu(4)	3.370(2)	Cu(2)–Cu(1)	2.7674(13)	Pr(2)–Cu(3)	3.3295(14)	Cu(4)–Cu(1)	2.980(2)
Pr(1)–Cu(1)	3.3740(14)	Cu(2)–Cu(3)	2.973(2)				

O(12)–Pr(2)–O(18)	127.4(2)	O(14)–Pr(2)–O(16)	126.3(2)	O(13)–Pr(2)–O(19)	63.05(14)	O(4)–Pr(1)–O(19)	135.1(2)
O(12)–Pr(2)–O(13)	80.2(2)	O(11)–Pr(1)–O(9)	127.5(2)	O(7)–Pr(2)–O(19)	134.6(2)	O(1)–Pr(1)–O(19)	133.0(2)
O(18)–Pr(2)–O(13)	77.4(2)	O(14)–Pr(1)–O(9)	79.4(2)	O(5)–Pr(2)–O(19)	134.3(2)	O(2)–Pr(1)–O(19)	123.4(2)
O(12)–Pr(2)–O(7)	145.8(2)	O(16)–Pr(1)–O(9)	77.0(2)	O(15)–Pr(2)–O(19)	61.75(13)	O(3)–Pr(1)–O(19)	122.2(2)
O(18)–Pr(2)–O(7)	79.1(2)	O(11)–Pr(1)–O(4)	81.8(2)	O(8)–Pr(2)–O(19)	125.1(2)	O(11)–Cu(4)–S(3)	102.7(2)
O(13)–Pr(2)–O(7)	86.5(2)	O(14)–Pr(1)–O(4)	81.6(2)	O(6)–Pr(2)–O(19)	119.00(14)	O(13)–Cu(4)–S(3)	85.4(2)
O(12)–Pr(2)–O(5)	79.7(2)	O(16)–Pr(1)–O(4)	141.7(2)	O(11)–Pr(1)–O(14)	77.1(2)	O(13)–Cu(4)–O(19)	83.2(2)
O(18)–Pr(2)–O(5)	141.6(2)	O(9)–Pr(1)–O(4)	139.3(2)	O(11)–Pr(1)–O(16)	80.4(2)	O(19)–Cu(4)–S(3)	140.05(12)
O(13)–Pr(2)–O(5)	139.4(2)	O(11)–Pr(1)–O(1)	140.3(2)	O(12)–Cu(1)–O(16)	172.8(2)	O(11)–Cu(4)–S(2)	83.8(2)
O(7)–Pr(2)–O(5)	90.8(2)	O(14)–Pr(1)–O(1)	140.9(2)	O(12)–Cu(1)–O(19)	87.6(2)	O(13)–Cu(4)–S(2)	106.2(2)
O(12)–Pr(2)–O(15)	74.0(2)	O(16)–Pr(1)–O(1)	81.0(2)	O(16)–Cu(1)–O(19)	86.2(2)	O(19)–Cu(4)–S(2)	133.61(12)
O(18)–Pr(2)–O(15)	80.9(2)	O(9)–Pr(1)–O(1)	81.2(2)	O(12)–Cu(1)–S(4)	98.7(2)	S(3)–Cu(4)–S(2)	86.34(8)
O(13)–Pr(2)–O(15)	124.7(2)	O(4)–Pr(1)–O(1)	91.8(2)	O(16)–Cu(1)–S(4)	88.5(2)	Pr(1)–O(19)–Pr(2)	177.5(2)
O(7)–Pr(2)–O(15)	137.6(2)	O(11)–Pr(1)–O(2)	73.7(2)	O(19)–Cu(1)–S(4)	154.71(13)	Cu(2)–O(9)–Pr(1)	99.5(2)
O(5)–Pr(2)–O(15)	82.3(2)	O(14)–Pr(1)–O(2)	141.0(2)	O(12)–Cu(1)–O(15)	85.1(2)	Cu(4)–O(11)–Pr(1)	103.1(2)
O(12)–Pr(2)–O(8)	78.2(2)	O(16)–Pr(1)–O(2)	73.4(2)	O(16)–Cu(1)–O(15)	96.4(2)	Cu(3)–O(19)–Pr(1)	91.71(14)
O(18)–Pr(2)–O(8)	135.7(2)	O(9)–Pr(1)–O(2)	139.5(2)	O(19)–Cu(1)–O(15)	72.5(2)	Cu(1)–O(19)–Pr(1)	91.10(14)
O(13)–Pr(2)–O(8)	72.3(2)	O(4)–Pr(1)–O(2)	69.2(2)	S(4)–Cu(1)–O(15)	83.58(12)	Cu(2)–O(19)–Pr(1)	90.20(14)
O(7)–Pr(2)–O(8)	67.7(2)	O(1)–Pr(1)–O(2)	67.5(2)	O(9)–Cu(2)–O(15)	168.9(2)	Cu(4)–O(19)–Pr(1)	88.75(13)
O(5)–Pr(2)–O(8)	69.3(2)	O(11)–Pr(1)–O(3)	140.0(2)	O(9)–Cu(2)–O(19)	84.9(2)	Cu(1)–O(16)–Pr(1)	100.9(2)
O(15)–Pr(2)–O(8)	143.3(2)	O(14)–Pr(1)–O(3)	74.2(2)	O(15)–Cu(2)–O(19)	84.0(2)	Cu(4)–O(13)–Pr(2)	102.0(2)
O(12)–Pr(2)–O(6)	133.8(2)	O(16)–Pr(1)–O(3)	139.4(2)	O(9)–Cu(2)–S(1)	88.4(2)	Cu(3)–O(18)–Pr(2)	100.2(2)
O(18)–Pr(2)–O(6)	74.7(2)	O(9)–Pr(1)–O(3)	73.3(2)	O(15)–Cu(2)–S(1)	102.3(2)	Cu(3)–O(19)–Pr(2)	89.66(14)
O(13)–Pr(2)–O(6)	145.2(2)	O(4)–Pr(1)–O(3)	67.0(2)	O(19)–Cu(2)–S(1)	165.07(13)	Cu(1)–O(19)–Pr(2)	87.52(14)
O(7)–Pr(2)–O(6)	68.3(2)	O(1)–Pr(1)–O(3)	67.8(2)	O(18)–Cu(3)–O(14)	171.2(2)	Cu(2)–O(19)–Pr(2)	91.75(14)
O(5)–Pr(2)–O(6)	67.2(2)	O(2)–Pr(1)–O(3)	114.4(2)	O(18)–Cu(3)–O(19)	85.5(2)	Cu(4)–O(19)–Pr(2)	89.22(14)
O(15)–Pr(2)–O(6)	70.5(2)	O(11)–Pr(1)–O(19)	64.94(14)	O(14)–Cu(3)–O(19)	85.8(2)	Cu(3)–O(19)–Cu(1)	177.2(2)
O(8)–Pr(2)–O(6)	115.9(2)	O(14)–Pr(1)–O(19)	62.91(14)	O(18)–Cu(3)–S(5)	87.8(2)	Cu(3)–O(19)–Cu(2)	94.6(2)
O(12)–Pr(2)–O(19)	64.66(14)	O(16)–Pr(1)–O(19)	63.36(14)	O(14)–Cu(3)–S(5)	100.9(2)	Cu(1)–O(19)–Cu(2)	85.6(2)
O(18)–Pr(2)–O(19)	62.7(2)	O(9)–Pr(1)–O(19)	62.56(14)	O(19)–Cu(3)–S(5)	173.30(13)	Cu(3)–O(19)–Cu(4)	88.7(2)
				O(11)–Cu(4)–O(13)	167.7(2)	Cu(1)–O(19)–Cu(4)	91.2(2)
				O(11)–Cu(4)–O(19)	84.6(2)	Cu(2)–O(19)–Cu(4)	176.6(2)

Compound 2

Ba(1)–O(5)	2.760(3)	Ba(1)–O(5′)	2.834(3)	Ba(1)–O(1)	2.784(4)	Cu(1)–O(5)	1.944(3)
Ba(1)–O(4)	2.761(4)	Ba(1)–O(7)	2.841(3)	Ba(1)–O(3)	2.787(4)	Cu(1)–S(1)	2.348(2)
Ba(1)–O(2)	2.780(4)	Cu(1)–O(7)	1.937(3)	Ba(1)–O(7′)	2.830(3)	Cu(1)–S(2)	2.349(2)

O(5)–Ba(1)–O(4)	116.08(13)	O(1)–Ba(1)–O(5′)	124.76(12)	O(1)–Ba(1)–O(3)	70.77(13)	O(5′)–Ba(1)–O(7)	68.25(9)
O(5)–Ba(1)–O(2)	169.61(13)	O(3)–Ba(1)–O(5′)	163.30(12)	O(5)–Ba(1)–O(7′)	69.43(9)	Cu(1)–O(7)–Ba(1)	96.88(12)
O(4)–Ba(1)–O(2)	73.1(2)	O(7′)–Ba(1)–O(5′)	43.14(9)	O(4)–Ba(1)–O(7′)	81.90(12)	Ba(1′)–O(7)–Ba(1)	85.97(9)
O(5)–Ba(1)–O(1)	108.57(11)	O(5)–Ba(1)–O(7)	54.77(9)	O(2)–Ba(1)–O(7′)	118.34(12)	O(7)–Cu(1)–O(5)	83.23(14)
O(4)–Ba(1)–O(1)	100.69(14)	O(4)–Ba(1)–O(7)	170.85(13)	O(1)–Ba(1)–O(7′)	177.30(11)	O(7)–Cu(1)–S(1)	171.25(11)
O(2)–Ba(1)–O(1)	63.41(13)	O(2)–Ba(1)–O(7)	116.00(13)	O(3)–Ba(1)–O(7′)	110.04(11)	O(5)–Cu(1)–S(1)	88.30(11)
O(5)–Ba(1)–O(3)	75.14(10)	O(1)–Ba(1)–O(7)	83.30(12)	O(5)–Ba(1)–O(5′)	92.57(9)	O(7)–Cu(1)–S(2)	88.83(11)
O(4)–Ba(1)–O(3)	62.92(11)	O(3)–Ba(1)–O(7)	111.41(10)	O(4)–Ba(1)–O(5′)	114.89(10)	O(5)–Cu(1)–S(2)	171.67(11)
O(2)–Ba(1)–O(3)	106.69(13)	O(7′)–Ba(1)–O(7)	94.03(9)	O(2)–Ba(1)–O(5′)	87.45(12)	S(1)–Cu(1)–S(2)	99.52(6)

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

Compound 3

Cu(1)–O(5)	1.941(5)	Cu(1)–S	2.654(3)	Cu(1)–O(3)	1.985(5)	Cu(2)–O(1)	1.935(6)
Cu(1)–O(6)	1.970(5)	Cu(2)–O(5′)	1.897(6)	Cu(1)–O(6′)	2.434(6)	Cu(2)–O(2)	1.952(6)
Cu(1)–O(4)	1.984(6)	Cu(2)–O(6)	1.928(5)				

O(5)–Cu(1)–O(6)	96.1(2)	O(3)–Cu(1)–S	103.2(2)	O(6)–Cu(1)–O(6′)	86.2(2)	O(1)–Cu(2)–O(2)	90.1(2)
O(5)–Cu(1)–O(4)	89.3(2)	O(6′)–Cu(1)–S	150.09(13)	O(4)–Cu(1)–O(6′)	92.2(2)	Cu(2′)–O(5)–Cu(1)	108.8(3)
O(6)–Cu(1)–O(4)	173.6(2)	O(5′)–Cu(2)–O(6)	85.2(2)	O(3)–Cu(1)–O(6′)	104.1(2)	Cu(1)–O(6)–Cu(1′)	93.8(2)
O(5)–Cu(1)–O(3)	175.6(2)	O(5′)–Cu(2)–O(1)	91.8(2)	O(5)–Cu(1)–S	81.3(2)	Cu(2)–O(6)–Cu(1)	111.4(2)
O(6)–Cu(1)–O(3)	84.5(2)	O(6)–Cu(2)–O(1)	175.3(2)	O(6)–Cu(1)–S	84.4(2)	Cu(2)–O(6)–Cu(1′)	90.6(2)
O(4)–Cu(1)–O(3)	89.9(2)	O(5′)–Cu(2)–O(2)	171.5(3)	O(4)–Cu(1)–S	99.9(2)		
O(5)–Cu(1)–O(6′)	71.6(2)	O(6)–Cu(2)–O(2)	93.4(2)				

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

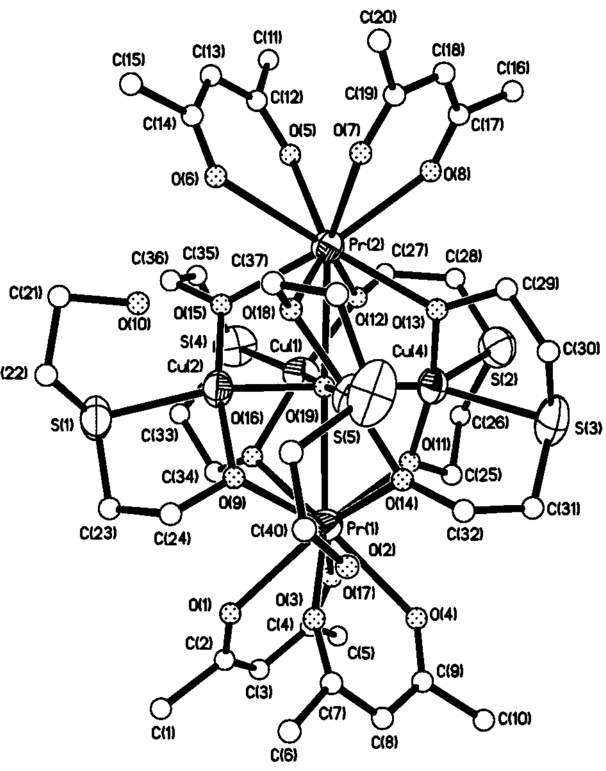


Fig. 1 Molecular structure of compound **1** with 50% thermal ellipsoids and labeling scheme. For clarity, fluorine and hydrogen atoms are omitted and only the metal atoms and sulfur atoms are shown as anisotropic thermal ellipsoids (50%)

uncommon, has been observed recently in $Na_2Fe_6(\mu_6\text{-}O)(OCH_3)_{18}(HOCH_3)_6$,[8] $H_4Ba_6(\mu_6\text{-}O)(OCH_2CH_2OCH_3)_{14}$,[9] and $Y_4Ba_2(\mu_6\text{-}O)(\mu_3\text{-}OC_2H_5)_8[Bu^tC(O)CHC(O)Bu^t]_6$.[10] The average praseodymium–oxo distance of 2.661 Å and the average copper–oxo distance of 2.054 Å are longer than the praseodymium–alkoxo and copper–alkoxo distances averaging 2.478 and 1.900 Å, respectively. There are three doubly deprotonated 2,2′-thiodiethanol and two singly deprotonated 2,2′-thiodiethanol ligands. As anticipated, the sulfur atoms are bound exclusively to the copper centers with the Cu–S bond lengths ranging from 2.335(2) to 2.573(2) Å which are within the normal range of Cu^{II}–S bond lengths.[11] The Cu–O–Cu angles between the oxo ligand and the copper atoms range from 85.6(2) to 94.6(2)°. The Cu–Cu separation distances in **1** range from 2.7674(13) Å between Cu(1) and Cu(2) to 2.980(2) Å between Cu(1) and Cu(4).

One of the alkoxo oxygen atoms of the tde^{2-} ligand chelates to the copper center while the other functions as a bridging ligand between the Pr^{III} and the second Cu^{II}. The two non-deprotonated hydroxyl oxygen atoms, O(10) and O(17), are not bound to any metal ions, but form hydrogen bonds with the oxygen atoms of the hfacac ligands, O(6) and O(4), respectively, as indicated by the distances of O(6)···O(10) 2.925 and O(4)···O(17) 2.971 Å. Another important feature of compound **1** is that it is a chiral molecule with each of the copper(II) ions having a distinct chemical environment. As shown in Fig. 2, the Cu(1) and Cu(2) ions have a distorted square planar geometry while Cu(3) has a nearly ideal square planar geometry [S(5)–Cu(3)–O(19) 173.30(13), O(18)–Cu(3)–O(14) 171.2(2)°]. In contrast, the Cu(4) ion is co-ordinated by three oxygen atoms and two sulfur atoms in an approximate trigonal bipyramidal geometry. There are weak axial bonds associated with the Cu(1), Cu(2) and Cu(3) centers, as evidenced by the distances of Cu(1)–O(15) 2.412(5), Cu(2)–O(18) 2.749(6) and Cu(3)–O(13) 2.574(5) Å. The O(12)–Cu(4) distance, 2.734(6) Å, could also be considered as a weak Cu–O bond. Interestingly, the four copper(II) units in **1** have a propeller arrangement around the Pr(1)–O(19)–Pr(2) axis, as shown in Fig. 2. We believe that such a propeller arrangement is likely dictated by non-bonding interactions between the 2,2′-thiodiethanolato ligands. Polynuclear metal complexes with propeller structures are rare. One of the examples is $Cu_6(\mu_3\text{-}O)(\mu_3\text{-}OH)(bdmap)_3Cl_6$ [bdmap = 1,3-bis(dimethylamino)propan-2-olate], reported recently by our group, where the six copper(II) ions are in a propeller arrangement with a C_3 symmetry.[12]

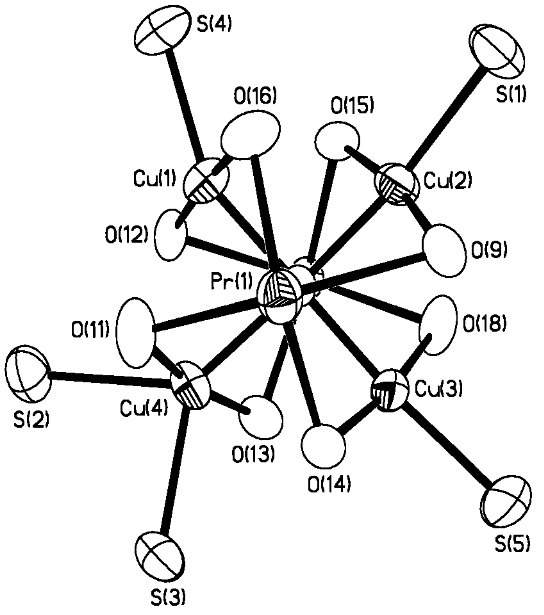


Fig. 2 View of the propeller core structure of compound **1** projected down the Pr–O–Pr vector

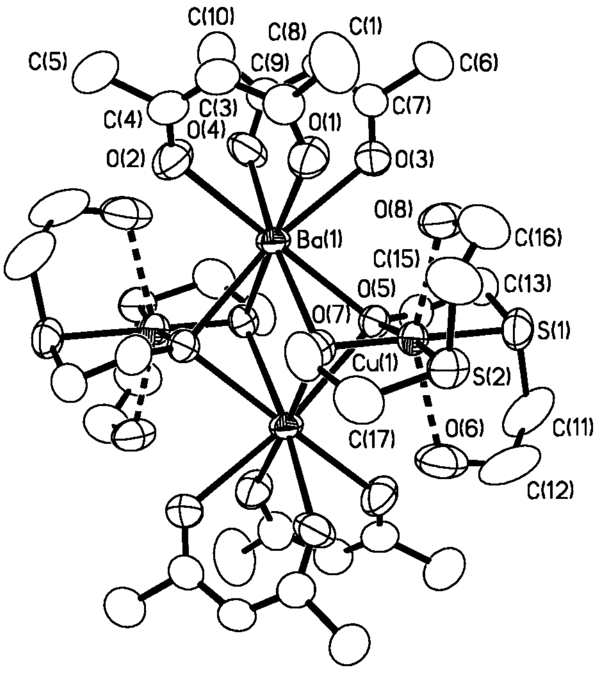


Fig. 3 Molecular structure of compound **2** with 50% thermal ellipsoids and labeling scheme. For clarity, hydrogen and fluorine atoms are omitted

Synthesis and structure of $Ba_2Cu_2(Htde)_4(hfacac)_4$ 2

The Ba_2Cu_2 compound was initially isolated from an analogous synthetic procedure as used for compound **1**. Compound **2** was subsequently synthesized using a logical procedure in which $Cu(OCH_3)_2$, H_2tde and $Ba(hfacac)_2$ reacted in a 1 : 2 : 1 ratio in CH_2Cl_2. The composition and structure of the compound was determined by single-crystal X-ray diffraction and elemental analysis. An ORTEP diagram displaying the structure of this compound is shown in Fig. 3. Selected bond lengths and angles are provided in Table 2.

Compound **2** consists of two copper(II) and two barium ions in a rhombic arrangement with the Ba(1)···Cu(1) and Ba(1)···Cu(1′) distances being 3.5817(6) and 3.6251(6) Å, respectively, and the Ba(1)–Cu(1)–Ba(1′) and Cu(1)–Ba(1)–Cu(1′) angles being 64.89(1) and 115.11(1)°, respectively. The molecule of **2** has an inversion center and contains four Htde$^-$ ligands. The four alkoxo oxygen atoms of the four Htde$^-$ ligands function as triply bridging atoms to the copper and barium centers. The barium ion is surrounded by eight oxygen atoms, four alkoxo oxygen atoms and four from the two hfacac ligands, with the Ba–O bond lengths ranging from 2.760(3) to 2.841(3) Å, comparable to those reported previously. The geometry of the barium ion is almost an ideal square prism, which resembles that found in $YBa_2Cu_3O_{7-x}$ superconductor.[1] The sulfur atoms co-ordinate exclusively to the copper(II) centers in a similar manner as was observed **1**.

Each copper center is chelated by two Htde$^-$ ligands *via* the alkoxo oxygen and sulfur atoms at the equatorial sites with the O(7)–Cu(1)–S(1) and O(5)–Cu(1)–S(2) angles being 171.3(1) and 171.7(1)°, respectively. As observed in **1**, the four non-deprotonated hydroxyl oxygen atoms form four intramolecular hydrogen bonds with the oxygen atoms of the hfacac ligands as evidenced by the distances of O(8)···O(1) 2.891(5) and O(6)···O(4′) 2.919(6) Å. However, unlike compound **1**, where the non-deprotonated hydroxyl oxygen atoms are not bound to any metal ions, those of the Htde$^-$ ligands in **2** occupy the axial positions of the copper(II) centers as evidenced by the long bond lengths of O(8)–Cu(1) 2.523(5) and O(6)–Cu(1) 2.542(5) Å. The O(8)–Cu(1)–O(6) bond angle of 150.3(5)° is significantly off linearity, perhaps due to steric interactions. The geometry of the copper(II) center can be therefore best described as a distorted elongated octahedron. The distance between the two copper centers is 6.082(5) Å. The arrangement of the four metal ions in **2** resembles that in the Ba_2Cu_2 compound $Ba_2Cu_2(acac)_4(tme)_4 \cdot 2(Htme)$ (tme = 2-methoxyethoxide), reported by Ryan and co-workers.[2g] Compound **2** is, however, the first BaCu bimetallic complex employing thioalcohol as the bridging ligand.

Synthesis and structure of $Cu_4(tde)_2(hfacac)_4$ 3

Compound **3** was obtained from a reaction intended to produce a structural analogue of **1** with the non-paramagnetic yttrium ion in place of the praseodymium ion. However, instead of obtaining the Y_2Cu_4 compound, dark green crystals of **3** were isolated along with a blue microcrystalline compound. The structure and composition of **3** were determined by single crystal X-ray diffraction and elemental analyses. The blue compound did not form crystals suitable for X-ray diffraction analysis. The fact that it has a similar color as compound **2** and was obtained in good yield makes us suggest that the blue compound likely contains both copper and yttrium. The results of elemental analysis appeared to match well the formula of $Cu_2Y_2(tde)_2(hfacac)_3(O_2CCF_3)_2(OH)$, where the trifluoroacetate ligand would be originated from the decomposition of the hfacac ligand.[3f] However, the exact nature of this blue compound still remains a mystery. An ORTEP diagram showing the structure of **3** is given in Fig. 4. Selected bond lengths and angles are provided in Table 2.

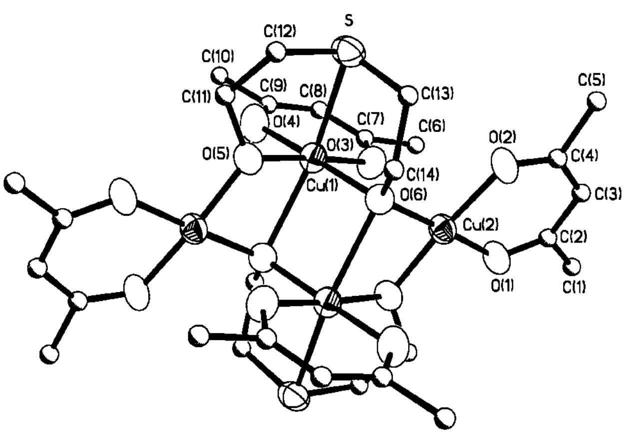


Fig. 4 Molecular structure of compound **3** with 50% thermal ellipsoids and labeling scheme. The hydrogen and fluorine atoms are omitted for clarity

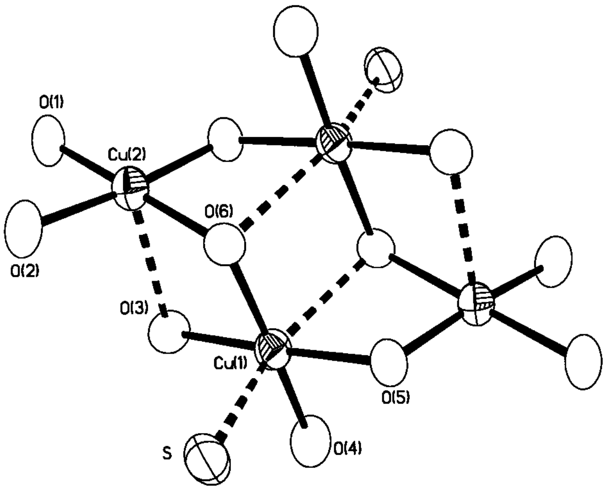


Fig. 5 Core structure and the geometry surrounding the copper centers in compound **3**

Compound **3** consists of four Cu(hfacac)$^+$ units which are linked together by the alkoxo oxygen atoms of two tde^{2-} ligands. Two of the oxygen atoms act as double bridges while the remaining two function as triple bridges. In contrast to compounds **1** and **2**, where the tde^{2-} and Htde$^-$ ligands function as a bidentate chelate to the copper(II) ion, in **3** the tde^{2-} chelates to the Cu(1) center as a tridentate ligand such that the alkoxo oxygen atoms bind to the equatorial positions while the sulfur donor occupies one of the axial positions [Cu(1)–S 2.654(3) Å]. The second axial positions of Cu(1) is occupied by an inversion center symmetry related O(6′) atom with a long bond length of 2.434(6) Å. The S–Cu(1)–O(6′) angle of 150.09(13)° is significantly deviated from linearity. The geometry of Cu(1) can be therefore best described as a distorted elongated octahedron. The Cu(2) center is co-ordinated by two alkoxo oxygen atoms from the bridging tde^{2-} ligands and a chelating hexafluoroacetylacetonato ligand in a square-planar geometry. As shown in Fig. 5, the fifth position of the Cu(2) atom is occupied by a weakly bound O(3) atom from a neighbouring hfacac ligand [O(5)–Cu(2) 2.521(6) Å]. The geometry of Cu(2) is therefore a square pyramid. The four copper ions are coplanar with the separation distances being Cu(1)···Cu(2) 3.220(5), Cu(1)···Cu(2′) 3.121(5), Cu(1)···Cu(1′) 3.230(5) and Cu(2)···Cu(2′) 5.458(6) Å, respectively. The arrangement of the copper atoms in **3** can be therefore described as a rhombus or two oxygen-capped copper triangles sharing an edge which is unusual for tetranuclear copper(II) compounds. A tetrahedral arrangement is most common for tetranuclear copper(II) compounds.[13] Rectangular or square arrangements of cyclic tetranuclear copper(II) complexes, albeit rare, have been reported in compounds such as $Cu_4Zr_4O_3(OPr^i)_{18}$,[14] $[Cu_2(bpim)(im)]_2(NO_3)_4 \cdot 3H_2O$ [bpim = 4,5-bis{[(2-pyridin-2-ylethyl)imino]methyl}-2*H*-imidazole],[15] $Cu_4(MPZ)_4(acMPZ)_2(ONO_2)_2$ [HMPZ = 3,5-dimethyl-1*H*-pyrazole, HacMPZ = 1-(5-methyl-1*H*-pyrazol-1-yl)ethan-1-ol],[16a] and $[Cu_4(bdmap)_2(O_2CCH_3)_4][PF_6]_2$.[17] Compound **3** is one of the rare examples of rhombic Cu^{II}_4 compounds. A rhombic Cu_4 arrangement has also been observed in a heteropolyoxotungstate anion,[16b] $[Cu_4(H_2O)_2(PW_9O_{34})_2]^-$.[10] Despite the

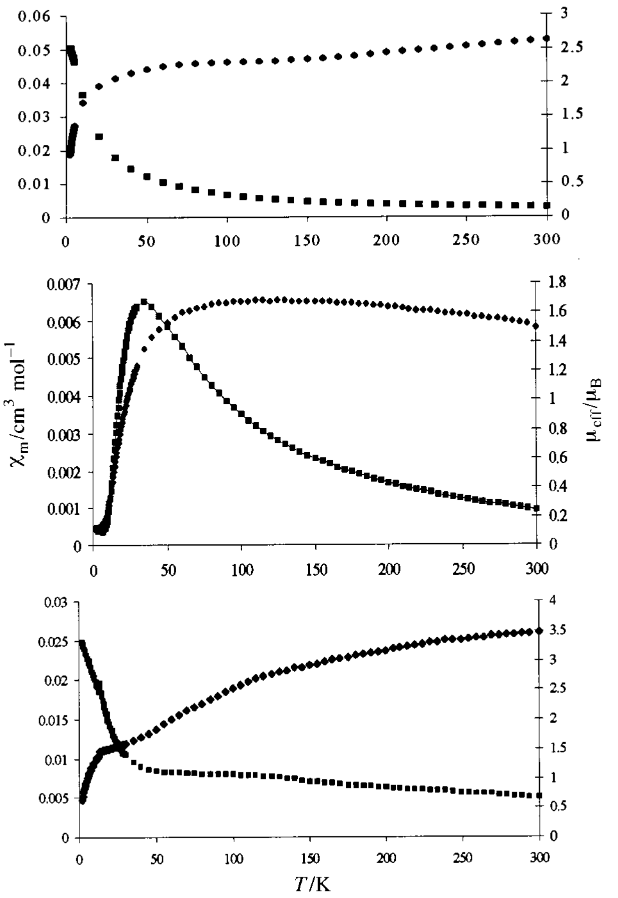


Fig. 6 Plots of magnetic moment (diamond) and molar susceptibility (square) *versus* temperature for compounds **1** (top), **2** (middle) and **3** (bottom)

coplanarity of the four copper centers in **3**, the four square-planar CuO_4 units are not coplanar. The two CuO_4 units involving Cu(1) are parallel to each other. The dihedral angle between the CuO_4 unit of Cu(1) and that of Cu(2) is 75.2°, almost orthogonal.

As soft donors, thiol ligands are often associated with copper(I) compounds. Copper(II) compounds containing sulfur donors are much less common than those of oxygen or nitrogen as donor atoms due to the reducing property of the sulfur atom. Most of the previously known sulfur-containing copper(II) compounds are limited to thiocarbamate-type ligands and dimercaptomalionitrile.[18] One of the rare examples of copper(II) complexes, $\{Cu(R\text{-}sno)\}_2][ClO_4]_2$, containing a thioalcohol ligand was reported by Kida and co-workers[19] where R-sno = *N*-(2-alkylsulfanylethyl)-3-aminopropanolate. The stability of the copper(II) ions in compounds **1**–**3** can be attributed to the chelate effect of the tde^{2-} or $Htde^-$ ligand.

Magnetic properties

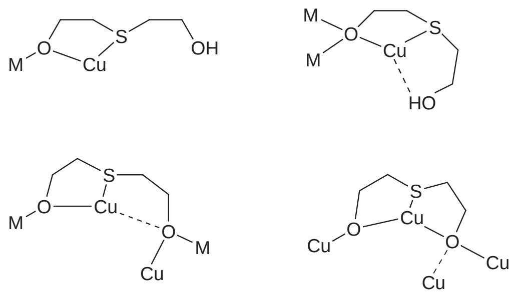
Compound 1. Compound **1** contains six paramagnetic metal ions linked by a central oxo ligand and alkoxo oxygen atoms as well. Substantial magnetic interactions between the metal ions are therefore anticipated. The susceptibility data at 2 to 300 K are shown in Fig. 6. Compound **1** appears to be dominated by antiferromagnetic exchanges, since the room temperature magnetic moment (2.64 μ_B) is much less than that expected for the non-interacting four copper(II) and two praseodymium centers (≈7 μ_B).[4] In addition, the magnetic moment decreases slowly with decreasing temperature from 300 to 40 K, and drops rapidly after 40 K, which is again consistent with the dominance of antiferromagnetic exchange in the system. If one assumes that magnetic interactions between Pr and Pr and Cu and Pr are negligible, the magnetic exchange behavior of **1** would be dictated by the four copper(II) centers. To confirm it, an analogous compound, Y_2Cu_4 or La_2Cu_4, where no paramagnetic lanthanides are present, is required. Unfortunately, we have not been able to synthesize these analogues. The Cu_4O portion in **1**, however, resembles that in $Cu_4Zr_4O_3(OPr^i)_{18}$, reported by Caulton and co-workers,[14] which has been shown to have a singlet ground state. The magnetic behavior of **1** appears to be similar to that of Caulton's compound. The fact that the magnetic moment of 2.64 μ_B at 300 K is also much smaller than that of two non-interacting praseodymium(III) ions (≈4.9 μ_B) further suggests that Pr–Pr and Cu–Pr magnetic interactions are also present and likely dominated by antiferromagnetic exchange as well, which has been observed frequently in Ln–Cu complexes reported previously.[2,3]

Compound 2. As shown in Fig. 3, the copper(II) ions in compound **2** are far apart [6.082(5) Å]. In addition, there is no bridging ligand linking these two copper(II) ions directly. One therefore would anticipate that there is either a very weak magnetic interaction or no interaction at all between the two copper(II) ions. To find out the truth, we measured magnetic susceptibility data for this compound over the temperature range of 2–300 K. The plots of magnetic susceptibility and the effective magnetic moment *versus* temperature for **2** are shown in Fig. 6 (middle). The susceptibility data have a maximum at 35 K, which is an indication of the presence of a fairly strongly coupled antiferromagnetic ground state.[1c,4] To determine the magnitude of the exchange constant *J*, the susceptibility data were fitted by a modified Bleaney–Bowers equation (1)[1c,4] that

$$\chi = (1 - \rho)\{(2Ng^2\beta/3kT)\,[1 + \tfrac{1}{3}\exp(-2J/kT)]^{-1}\} + \rho\chi_{\text{monomer}} + \chi_{\text{tip}} \quad (1)$$

takes into account the effects of paramagnetic impurities (ρ) and temperature independent paramagnetism (tip) using a non-linear regression program. The results of the fitting yielded $J = -19.2(1)$ cm^{-1}, $\rho = 0.012$, $g = 2.25$, tip = −0.000542 and $R = 0.0056$. The *J* value of **2**, although not large, is appreciable, considering that the two copper centers are far apart with no direct ligand links. It is likely that the dipolar interaction is operative in **2** and responsible for the sizable *J* value.[1c,4] Exchange pathways involving Cu–O–Ba–O–Cu are also possible.

Compound 3. Compound **3** contains four copper atoms in close proximity to each other. One might therefore expect the presence of significant magnetic interactions between the copper centers. However, the fact that there is no bridging ligand linking the two $d_{x^2-y^2}$ orbitals of the two Cu(1) centers and the two $d_{x^2-y^2}$ orbitals of the Cu(1) and Cu(2) [or Cu(1a) and Cu(2)] centers are 75.2° with respect to each other, albeit linked by the O(6) atom [O(5) in the case of Cu(1a) and Cu(2)], is not in favor of a strong magnetic exchange *via* superexchange pathways.[1c,4] To establish the nature of magnetic exchanges in **3**, magnetic susceptibility measurements were performed over the temperature range 2–300 K. The susceptibility data were corrected for diamagnetic contributions using Pascal constants. Plots of the molar susceptibility and the effective magnetic moment *versus* temperature are shown in Fig. 6 (bottom). The magnetic moment of 3.48 μ_B at 300 K is slightly less than that of four non-interacting copper(II) ions (≈3.80 μ_B, assuming $g = 2.2$, similar to that of compound **2**), suggesting that the magnetic exchange between the copper centers is fairly weak. The decreasing trend of magnetic moment with decreasing temperature implies that this compound is dominated by antiferromagnetic exchanges. The drastic decrease of magnetic moment from 1.5 μ_B at about 15 K to 0.5 μ_B at about 2 K appears to suggest that the ground state of this compound is a singlet. To obtain the magnitude of exchange constants, we attempted to fit the data by a tetramer model[13] where four



Scheme 1 Bonding modes of the $Htde^-$ and tde^{2-} ligands; M = Pr^{III} or Ba^{II}

independent J values are employed ($J_{Cu1-Cu2}$, $J_{Cu1a-Cu2}$, $J_{Cu1-Cu1a}$, $J_{Cu2-Cu2a}$). Unfortunately, we were unable to obtain satisfactory fitting of the susceptibility data.

Conclusion

It has been shown that the 2,2′-thiodiethanol ligand is effective in forming heterometallic complexes containing copper(II) and lanthanide or alkaline earth metal ions. The sulfur atoms of the tde^{2-} and $Htde^-$ bind to the copper center exclusively. Despite their simplicity, the $Htde^-$ and tde^{2-} ligands display versatile bonding patterns to metal ions as summarized in Scheme 1. Compounds **1** and **2** are the first examples of thioalcohol bridged Ln–Cu and Ba–Cu compounds with unusual structural features. These compounds may not be useful as precursors for oxides due to the sulfur contamination, but they provide valuable information on the construction of polynuclear heterometallic compounds using thioalcohols as ligands. The environments surrounding the copper(II) centers in compounds **1**–**3** are distinctively different: in **1** all four copper(II) ions are linked together by a central oxo ligand and alkoxo ligands as well; in **2** there is no direct ligand bridge between the two copper centers; and in **3** the copper centers are linked by alkoxo oxygen atoms in either a nearly orthogonal fashion or a face-to-face parallel manner, leading to their distinct magnetic behavior. Although quantitative analyses on the magnetic exchange of compounds **1** and **3** could not be achieved, the experimental data show that antiferromagnetic exchanges dominate in all three compounds.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for financial support, Professor C. V. Stager for use of the magnetometer and Jim Britten for crystal data collection for compounds **1** and **2**.

References

1 (*a*) *Ceramic Superconductors*, ed. M. F. Yan, American Ceramic Society, Westerville, OH, 1988; (*b*) *Chemistry of High Temperature Superconductors*, *ACS Symp. Ser.*, 1987, **351**; (*c*) O. Kahn, *Molecular Magnetism*; VCH, Weinheim, 1993; (*d*) D. Gatteschi, O. Kahn, J. S. Miller and F. Palacio (Editors), *Magnetic Molecular Materials*, Kluwer, Dordrecht, 1991.

2 (*a*) O. Guillou, R. L. Oushoorn, O. Khan, K. Boukekeur and P. Betail, *Angew. Chem.*, *Int. Ed. Engl.*, 1992, **31**, 626; (*b*) A. J. Blake, P. E. Y. Milne, P. Thornton and R. E. P. Winpenny, *Angew. Chem.*, *Int. Ed. Engl.*, 1991, **30**, 1139; (*c*) D. M. L. Goodgame, D. J. Williams and R. E. P. Winpenny, *Polyhedron*, 1989, **8**, 1531; (*d*) C. P. Love, C. C. Torardi and C. J. Page, *Inorg. Chem.*, 1992, **31**, 1784; (*e*) W. Bidell, J. Doring, H. W. Bosch, H.-U. Hund, E. Plappert and H. Berke, *Inorg. Chem.*, 1993, **32**, 502; (*f*) W. Bidell, H. W. Bosch, D. Veghini, H.-U. Hund, J. Doring and H. Berke, *Helv. Chim. Acta*, 1993, **76**, 596; (*g*) N. N. Sauer, E. Garcia, K. V. Salazar, R. R. Ryan and J. A. Martin, *J. Am. Chem. Soc.*, 1990, **112**, 1524; (*h*) C. Benelli, A. Caneschi, D. Gatteschi, O. Guilou and L. Pardi, *Inorg. Chem.*, 1990, **29**, 1750; (*i*) M. Andruh, I. Ramade, E. Codjovi, O. Guillou, O. Kahn and J. C. Trombe, *J. Am. Chem. Soc.*, 1993, **115**, 1822; (*j*) J. L. Sanz, R. Ruiz, A. Gleizes, F. Lloret, J. Fans, M. Julve, J. J. Borrás-Almenar and Y. Journaux, *Inorg. Chem.*, 1996, **35**, 7384.

3 (*a*) S. Wang, S. J. Trepanier and M. J. Wagner, *Inorg. Chem.*, 1993, **32**, 833; (*b*) S. R. Breeze and S. Wang, *Inorg. Chem.*, 1994, **33**, 5114; (*c*) S. R. Breeze and S. Wang, *Inorg. Chim. Acta*, 1996, **250**, 163; (*d*) S. Wang, Z. Pang and M. J. Wagner, *Inorg. Chem.*, 1992, **61**, 1613; (*e*) L. Chen, S. R. Breeze, R. Rousseau, S. Wang and L. K. Thompson, *Inorg. Chem.*, 1995, **34**, 454; (*f*) S. Wang, Z. Pang, K. D. L. Smith, C. Deslippe and Y. Hua, *Inorg. Chem.*, 1995, **34**, 908; (*g*) S. Wang, Z. Pang, K. D. L. Smith and M. J. Wagner, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 955.

4 R. Carlin, *Magnetochemistry*, Springer, Berlin, 1986; R. S. Drago, *Physical Methods in Chemistry*, W. B. Saunders Co., Philadelphia, 1977, W. E. Hatfield, in *Magneto-Structural Correlations in Exchange Coupled Systems*, eds. R. D. Willett, D. Gatteshi and O. Kahn, NATO ASI, Reidel, Dordrecht, 1985, p. 555.

5 SHELXTL, version 5, crystal structure analysis package, Bruker Axs, Analytical X-ray System, Madison, WI, 1995.

6 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, Table 2.2A.

7 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

8 K. Hegetschweiler, H. W. Schmalle, H. M. Streit, V. Gramlich, H.-U. Hund and I. Erni, *Inorg. Chem.*, 1992, **31**, 1299.

9 K. G. Caulton, M. H. Chisholm, S. R. Drake and J. C. Huffman, *J. Chem. Soc.*, *Chem. Commun.*, 1990, 1498.

10 P. Miele, J. D. Foulon, N. Hovnanian and L. Cot, *J. Chem. Soc.*, *Chem. Commun.*, 1993, 29.

11 E. Bouwman, R. Day, W. L. Driessen, W. Tremel, B. Brebs, J. S. Wood and J. Reedijk, *Inorg. Chem.*, 1988, **27**, 4614; M. Zoeteman, E. Bouwman, R. A. G. de Graff, W. L. Driessen, J. Reedijk and P. Zanello, *Inorg. Chem.*, 1990, **29**, 3487.

12 S. Wang, Z. Pang, J. C. Zheng and M. J. Wagner, *Inorg. Chem.*, 1993, **32**, 5975.

13 S. R. Breeze, S. Wang and L. Chen, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 1341; S. Teiplel, K. Griesar, W. Haase and B. Krebs, *Inorg. Chem.*, 1994, **33**, 456; J. W. Hall, E. D. Estes, R. P. Scaringe and W. E. Hatfield, *Inorg. Chem.*, 1977, **16**, 1527; R. Mergehenn, L. Merz and W. Haase, *J. Chem. Soc.*, *Dalton Trans.*, 1980, 1703; E. D. Estes and D. J. Hodgson, *Inorg. Chem.*, 1975, **14**, 334; S. Wang, J. C. Zheng and J. R. Hall, *Polyhedron*, 1994, **13**, 1039.

14 J. A. Samuels, B. A. Vaartstra, J. C. Huffman, K. L. Trojan, W. E. Hatfield and K. G. Caulton, *J. Am. Chem. Soc.*, 1990, **112**, 9623.

15 G. Kolks and S. J. Lippard, *Acta Crystallogr.*, *Sect. C*, 1984, **40**, 261.

16 (*a*) R. W. M. Ten Hoedt, F. B. Hulsbergen, G. C. Verschoor and J. Reedijk, *Inorg. Chem.*, 1982, **21**, 2369; (*b*) J. Gómez-Garcia, E. Coronado and J. J. Borrás-Almenar, *Inorg. Chem.*, 1992, **31**, 1667.

17 S. Wang, S. J. Trepanier, J. C. Zheng, Z. Pang and M. J. Wagner, *Inorg. Chem.*, 1992, **31**, 2118.

18 M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago and L. Zambonelli, *Acta Crystallogr.*, 1965, **19**, 886; C. K. Schauer, K. Akabori, C. M. Elliot and O. P. Anderson, *J. Am. Chem. Soc.*, 1984, **106**, 1127.

19 M. Mikuriya, H. Okawa and S. Kida, *Inorg. Chim. Acta*, 1979, **34**, 13.

Received 25*th March* 1998; *Paper* 8/02333F