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PAPER

Synthesis, structure and magnetism of homodinuclear complexes of Co, Ni and Cu supported by a novel bitriazine scaffold[†]

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Btzn (1), an amine-functionalized bi(1,3,5-triazine) 4,4'-(NH₂)₂-6,6'-(NHC₆H₅)₂-2,2'-(1,3,5-C₃N₃)₂, is reported, and its coordination with Co, Ni and Cu is explored. Reactions of metal salts (2 equiv) with Btzn (1 equiv) result in dimeric species [(Btzn)Co₂(NCS)₄(EtOH)₂(DMF)₂], (2), [(Btzn)Ni₂(η^1 -ONO₂)₂(MeOH)₄(DMF)₂]·2[NO₃], (3), [(Btzn)Cu₂Cl₄(DMF)₂], (4), and [(Btzn)Cu₂(η^2 -O₂NO)₂(OH₂)₂(DMF)₂]·2[NO₃], (5). These complexes are the first examples of the coordination of transition metals with bi(1,3,5-triazine) ligands. Their structures display a bridging bis-bidentate coordination mode for Btzn. Variable-temperature magnetic susceptibility of the complexes reveals antiferromagnetic exchange between the spin carriers, with calculated exchange coupling values (*J*) of -4.7 cm⁻¹ for 3, -18.2 cm⁻¹ for 4, and -5.5 cm⁻¹ for 5. An in-depth evaluation of the metal geometry highlights the inefficient overlap of the magnetic *d*-orbitals through the bridging ligand, most likely leading to reduced delocalization and coupling.

Introduction

Of the various isomers of triazine, 1,3,5-triazine (or *s*-triazine) is the most prominent. Derivatives of this compound have many noteworthy applications, such as serving as herbicidal and antibacterial agents,¹ components of resins,² complexants in analytical chemistry³ and reagents in organic synthesis.⁴ Recently, triazine-based monomers and polymers have been used as physical building blocks or templates in crystal engineering,⁵ combinatorial chemistry⁶ and peptidomimetics.⁷ The opto-electronic properties of π -conjugated systems are attracting increased attention for their potential as components of diverse materials, including liquid crystals,⁸ OLEDs^{9,10} and advanced magnetic materials.¹¹

Unlike other coupled heterocyclic systems such as bipyridine (**A**, Chart 1) and bipyrimidine (**B**), which are commonplace, triazines containing two or more consecutive rings are rare.¹²⁻¹⁶ Several bi(1,2,4-triazines) have been reported,¹² including one



involved in the formation of an extended Cu(I) network.¹³ To date, however, the only structurally-characterized bi(1,3,5-triazines) in the literature are 4,4',6,6'-tetracyano-2,2'-bi(1,3,5-triazine) (**C**, **R** = CN),¹⁴ generated by reduction of 2,4,6-tricyano-1,3,5-triazine and isolated as a charge-transfer complex, and 4,4',6,6'-tetraphenyl-2,2'-bi(1,3,5-triazine) (**C**, **R** = C₆H₃),¹⁵ produced by metal-catalyzed coupling of 2-chloro-4,6-diphenyl-1,3,5-triazine. Syntheses involving Ni-¹⁵ or Cu-catalyzed¹⁶ self-coupling reactions of chloro- or iodotriazines have been reported, resulting in the isolation of bitriazines with conjugated substituents. A comprehensive investigation of the electronic

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[†] Electronic supplementary information (ESI) available: Crystallographic information files in the form of CIF files, pictorial depictions of NMR spectra of compound 1, models of various orientations of complexes 2–5, and tables of selected bond distances and angles of complexes 2–5. CCDC reference numbers 806769–806772. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt00018g

properties revealed improved electron-accepting abilities in the heterocycle upon coupling and conjugation to a second triazine ring,¹⁵ leading Ren *et al.* to explore the capabilities of these novel bitriazines as electron-transport layers for organic light-emitting diodes.⁹

To the best of our knowledge, there are no reported examples of transition metal complexes supported by bi(1,3,5-triazine) scaffolds. This is in contrast to the closely-related cases of 2,2'bipyridine and 2,2'-bipyrimidine, which have enjoyed widespread use as ligands in coordination chemistry.¹⁷ Although not as ubiquitous as bipyridine, bipyrimidine can nevertheless assemble multinuclear species by bridging two metal centers in a bisbidentate fashion. This behaviour has attracted attention as a way to form dinuclear species, coordination polymers and extended structures.¹⁸⁻²² In addition, bipyrimidine complexes display enhanced participation in certain photophysical processes in comparison to bipyridines. This can permit a higher degree of intramolecular energy/electron transfer between two bridged metal centers, making bipyrimidine complexes of interest in the areas of advanced magnetic materials and electro- and photocatalysis, and suggesting that bitriazine complexes may have similar useful behaviour.19

There are extensive references to transition metal complexes of pyridyl-substituted 1,3,5-triazines, such as 2,4,6-tris(2-pyridyl)-1,3,5-triazine (D), which may adopt bipyridine- or terpyridine-like coordination motifs to bind one, two or three metal centers.²³⁻²⁷ Available commercially as an analytical reagent for the detection of Fe, Ru and Co,³ compound D has been widely studied in coordination chemistry. These studies have revealed interesting spectroscopic properties and redox behaviours in the assembled transition metal systems, with potential applications in electroand photocatalytic reduction reactions.²³ However, in certain cases of metal coordination, ligand-to-metal o-donation enhances the electron deficiency of the triazine ring, thereby increasing its susceptibility towards hydrolysis by nucleophilic attack.23,27 Similar behaviour is witnessed in the coordination chemistry of the closely-related congener, 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (E),²⁸⁻³⁰ which has not yielded crystallographically characterized transition metal complexes.³¹ When this compound reacts with Cu salts, the triazine ring tends to undergo hydrolytic cleavage, leading to complexes derived from products of degradation.^{30,32}

Herein, we describe the preparation of novel aminofunctionalized bi(1,3,5-triazine) **1** (Btzn, Chart 2). Btzn bears resemblance to **2-appt** (2-appt = 2-amino-4-phenylamino-6-(2pyridyl)-1,3,5-triazine, Chart 2),³³ which has been studied in crystal engineering for its ability to associate by hydrogen bonds and π - π interactions.³⁴ The donor-acceptor-donor motif of the aminefunctionalized triazine has been shown to help Ru complexes bind to the minor groove of DNA as potential metal-based therapeutic agents.³⁵



In this report, we present the first examples of a transition metal complex supported by a novel amino-functionalized bi(1,3,5-triazine), which has proven to be a novel bridging ligand for the assembly of metallic dimers of Co, Ni and Cu. Structural characterization of the resulting complexes is presented, as well as an analysis of their magnetic properties.

Results and discussion

Unlike previously reported bi(1,3,5-triazines), which have been prepared by coupling reactions of preformed triazines, the novel amino-functionalized bitriazine scaffold, **1**, was synthesized by constructing the triazine rings using a procedure similar to that described by Shapiro and Overberger.³⁶ Condensation of dimethyl oxalate with 2 equiv of phenylbiguanide (Scheme 1) gave ligand **1** as a colourless solid in good yield. Its ¹H NMR spectrum displays the expected peaks, with the aminophenyl proton shifted downfield to 9.73 ppm. The ¹³C NMR spectrum includes the 2,2'-C peak at 170.7 ppm, with the other two carbon atoms of the triazine ring at 167.5 and 164.9 ppm.

The coordinating abilities of compound 1 were explored with several first-row transition metal salts. Notably, under the circumstances presented herein, the ligand does not undergo hydrolytic cleavage upon coordination such as that observed in electron-deficient tris(pyrimidyl)triazine systems.^{30,32} Complexes 2–5 were synthesized by the reaction of 2 equiv of the transition metal salt with 1 equiv of the ligand to obtain homodinuclear species, in which the ligand bridges two metal centers in a bis-bidentate fashion.

Complex 2 was produced *via* the reaction of Co(NCS)₂, generated *in situ*, with ligand 1 in DMF/EtOH. Bright orange paramagnetic crystals of complex 2 were grown from a concentrated solution in EtOH and the structure was elucidated by X-ray diffraction (Fig. 1). The molecular unit consists of a symmetrygenerated dimer, in which the ligand bridges two Co centers in a bis-bidentate nature *via* the adjacent nitrogen atoms of the triazine rings [Co–N1 = 2.188(4) Å, Co–N3 = 2.180(4) Å, N1–Co–N3 = 75.48(13)°]. Two of the six coordination sites on each cobalt are occupied by the ligand, and the coordination is completed by two nitrogen-bound thiocyanate anions [Co–N7 = 2.056(5) Å,



Scheme 1

	2	3	4	5
formula	$C_{36}H_{54}Co_2N_{16}O_6S_4$	$C_{28}H_{46}N_{16}Ni_2O_{18}$	$C_{26}H_{38}Cl_4Cu_2N_{12}O_4$	$C_{26}H_{37}Cu_2N_{17}O_{16}$
Mw	1053.05	1012.23	851.56	970.81
crystal system	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_{1}/c$	$P\bar{1}$	$P\overline{1}$	C2/c
a(Å)	9.8096(18)	9.10730(10)	10.3414(2)	25.2640(4)
$b(\mathbf{A})$	17.481(3)	9.48280(10)	10.4430(2)	10.8761(2)
$c(\dot{A})$	14.825(3)	13.0297(2)	10.5451(2)	19.8923(6)
α (°)	90	106.2700(10)	66.8280(10)	90
β(°)	96.962(3)	92.7070(10)	89.8480(10)	127.5490(10)
γ (°)	90	93.2830(10)	62.3640(10)	90
$V(Å^3)$	2523.5(8)	1076.09(2)	904.60(3)	4333.53(17)
Z	2	1	1	4
radiation (K_{α} , Å)	0.71073	0.71073	0.71073	0.71073
<i>T</i> (K)	223(2)	223(2)	296(2)	296(2)
D_{calcd} (g cm ⁻³)	1.386	1.562	1.563	1.488
$\mu_{\text{calcd}} (\text{mm}^{-1})$	0.880	0.965	1.521	1.065
F_{000}	1096	526	436	1992
R, wR^{2a}	0.0590, 0.1353	0.0278, 0.0707	0.0270, 0.0712	0.0456, 0.1309
GoF	0.987	1.038	1.043	1.024

 Table 1
 Crystal data and structure analysis results for complexes 2–5



Fig. 1 Thermal ellipsoid plot for complex **2** with the ellipsoids drawn at the 50% probability level. Hydrogen atoms and amine substituents have been removed for clarity.

Co-N8 = 2.071(4) Å, one molecule of DMF [Co-O1 = 2.158(3) Å] and a molecule of ethanol [Co-O2 = 2.058(4) Å] in a distorted octahedral geometry. The thiocyanate anions are located cis to each other $[N7-Co-N8 = 93.57(17)^{\circ}]$ and have slightly different bond distances and angles [N7-C15 = 1.142(6) Å vs. N8-C16 =1.159(6) Å, C15-S1 = 1.630(6) Å vs. C16-S2 = 1.592(6) Å, Co- $N7-C15 = 164.9(4)^{\circ}$ vs. Co-N8-C16 = 157.9(4)°, N7-C15-S1 = $177.3(5)^{\circ}$ vs. N8–C16–S2 = 179.0(5)°] as well as CN stretching frequencies in the IR spectrum [$v_{(CN)} = 2110$, 2058 cm⁻¹]. One molecule of ethanol per Co center can be found in the lattice. The two triazine rings of the ligand are co-planar and joined by a C–C single bond [C3–C3A = 1.521(9) Å] and the other bond distances and angles of the triazine rings are as expected. The two Co centers are separated by 5.828 Å across the ligand and lie alternately 0.135 Å above and below the plane of the ligand. Crystallographic parameters can be found in Table 1, and selected bond distances and angles can be found in the ESI.[†]

Reaction of 2 equiv of Ni(NO₃)₂·6H₂O with bitriazine, 1, led to the formation of complex 3 as a bright emerald-green solid. Crystals suitable for X-ray diffraction were grown by the slow evaporation of a methanol solution, and a model of the determined structure appears in Fig. 2. The structure is composed of a symmetry-generated dimer in which the ligand bridges two Ni centers. The geometry about each Ni center is distorted octahedral, completed by the ligand system [Ni1-N1 = 2.1231(13) Å, Ni-N2 = 2.0992(14) Å], an oxygen atom from a molecule of DMF [Ni1-O3 = 2.0462(12) Å], two molecules of methanol located *trans* to each other [Ni1–O1 = 2.0561(15) Å, Ni1–O2 = 2.0603(14) Å, O1-Ni1-O2 = 173.50(6) Å], and an oxygen-bound monodentate nitrate moiety [Ni–O4 = 2.0943(13) Å], which displays a noncoplanar arrangement with the metal center [Ni1-O4-N7-O5 = $101.39(19)^{\circ}$]. The ligand has a bite angle of $78.39(5)^{\circ}$ and separates the two Ni centers by 5.645 Å. The distance between the two carbon atoms joining the triazine rings is slightly shorter than that seen in compound 2 [C1–C1A = 1.500(3) Å], and the nickel atoms are located approximately 0.095 Å above and below the plane of the ligand. Charge balance is maintained by the presence of two additional nitrate ions per molecule, located above



Fig. 2 Thermal ellipsoid plot of complex 3 with the ellipsoids drawn at the 50% probability level. Hydrogen atoms and amine substituents have been removed for clarity.

and below the plane of the ligand and stabilized by hydrogen bonding with neighbouring metal-bound methanol groups [H2H– O9" = 1.985 Å, H2H–O8" = 2.606 Å, H1H–O7 = 2.196 Å, H1H–O8 = 2.502 Å]. One oxygen atom of the nitrate anion is also hydrogen-bonded to an amine group from a separate ligand [O9– H4NA = 2.135 Å], assembling a zig-zag chain structure in which the ligand planes are parallel, but staggered from one another. The distance between layered planes is 3.454 Å, leading to the shortest intermolecular Ni–Ni distance of 9.107 Å.

Dinuclear copper complexes 4 and 5 were synthesized via reaction of ligand 1 with 2 equiv of the hydrated copper salts, CuCl₂ and Cu(NO₃)₂, respectively. Yellow crystals of complex 4 were grown from a MeOH-layered DMF solution at room temperature, and the molecular unit can be seen in Fig. 3. Compound 4 consists of two identical 5-coordinate Cu centers bridged by the bisbidentate ligand system. The dimer is symmetry-generated, with a center of inversion located in the middle of the C-C bond between the two triazine rings. The geometry of each Cu center can best be described as a distorted trigonal bipyramid ($\tau = 0.74$),³⁷ in which the chloride ions [Cu-Cl1 = 2.3214(6) Å, Cu-Cl2 = 2.2907(7) Å] and one nitrogen donor of the ligand [Cu-N2 = 2.1805(15) Å]occupy the equatorial plane. The adjacent N-donor atom of the ligand [Cu–N1 = 2.0163(16) Å, N1–Cu–N2 = $78.38(6)^{\circ}$] and an oxygen-bound molecule of DMF [Cu–O1 = 1.9607(15) Å] occupy the axial positions. Spanning the axial and equatorial positions, the ligand-metal bond distances are notably different, resulting in an axially-compressed distortion to the trigonal bipyramidal geometry. Alternatively (and on the other extreme), the geometry of Cu may be described as a "4 + 1" apically-elongated square pyramid, in which the nitrogen atom of the ligand with the longest ligand-metal bond occupies the apical position and all other atoms are basally located. Due to the geometrical constraints enforced by the ligand coordination, the most accurate description lies somewhere between the two, closer to the former, but with a small, but not insignificant, contribution from the latter. The bond distances and angles of the ligand are within expected values and the C-C distance between the two triazine rings is 1.500(4) Å. Two disordered molecules of methanol per molecular unit can

be found in the lattice. A striking feature of the complex, not found in others described herein, is the degree of non-coplanarity of the metal centers with the ligand backbone. The Cu atoms in complex **4** are oriented above and below the plane by 13.32° (or by a distance of 0.374 Å), leading to a separation of 5.584 Å between the two Cu centers. The molecules are arranged in planes and the intermolecular distance between Cu centers is 6.757 Å.

The solid-state structure of complex 5 was solved by X-ray diffraction, using crystals grown from a concentrated DMF solution layered with acetonitrile. The structure (Fig. 4) shows two identical hexa-coordinate Cu centers bridged across the bisbidentate bitriazine ligand [Cu-N1 = 2.2086(19) Å, Cu-N2 = 2.0129(19) Å, N1–Cu–N2 = $78.22(7)^{\circ}$]. The distorted octahedral geometry is completed by the presence of a molecule of water [Cu-O5 = 1.9739(17) Å], an oxygen-bound molecule of DMF [Cu-O4 = 2.0117(18) Å] and a nitrate anion that is asymmetrically bidentate [Cu-O1 = 2.429(4) Å, Cu-O2 = 2.071(3) Å, O1-Cu-O2 = 55.43(10)°]. The longer Cu–O1 distance reflects participation in weak off-axis semi-coordination with the metal center.³⁸ Elongation of the Cu-N bond trans to the elongated Cu-O bond [O1- $Cu-N1 = 160.22(8)^{\circ}$ results in an axially-elongated "4 + 2"-type geometry. Two nitrate anions are held in proximity to the molecule *via* short hydrogen bonds to the coordinated water [O8''-H5C =1.653 Å]. The other hydrogen atom of water binds a second anion of nitrate [O6-H5D = 1.811 Å], thereby assembling a network of molecules in which the shortest intermolecular Cu-Cu distance is 6.357 Å. The two triazine rings are not perfectly coplanar and are both bent down by approximately 2° and held together by a carbon-carbon bond of 1.497(4) Å. The molecular unit can best be described as having a C2 axis located equidistant between the two carbon atoms joining the two triazine rings and perpendicular to the idealized ligand plane (in contrast to the other complexes described herein, which contain an inversion center midway between the two C atoms). As a result of this symmetry, the Cu centers are both located about 0.15 Å above the idealized plane of the ligand and separated by 5.634 Å. In addition, the bidentate nitrate moieties are both located on the same side of the ligand plane and canted by 57.49° from each other, and both molecules of DMF are located on the opposite side. One molecule of acetonitrile per ligand completes the lattice.



Fig. 3 Thermal ellipsoid plot of complex **4** with the ellipsoids drawn at the 50% probability level. Hydrogen atoms have been removed for clarity.



Fig. 4 Thermal ellipsoid plot of complex **5** with the ellipsoids drawn at the 50% probability level. Selected hydrogen atoms and the amine substituents of the ligand have been removed for clarity.

Various structural features of ligand 1 in its coordination complexes deserve attention. In particular, the triazine rings are largely coplanar with respect to each other and separated by a normal single C-C bond, ranging from 1.521(9) Å in complex 2 to 1.497(4) Å in complex 5. The degree of non-coplanarity of the metal centers with the ligand backbone varies between the complexes, as highlighted in Fig. S3-6 in the ESI,† in which the complexes are displayed in two different orientations (along the C-C bond of the ligand and along the line connecting the two metal centers). The amine substituents are strongly conjugated with the rings, as suggested not only by the short exocyclic N-C bond distances (shorter than the majority of the endocyclic C-N bonds) but also by the planar sp^2 hybridization of the amino nitrogen atoms, based on the positions of hydrogen atoms located from difference Fourier maps. In addition, the aromatic planes of the -NHPh substituents are close to the plane of the triazine rings (tilting of 9.11°-16.85°). Both -NH₂ and -NHPh hydrogen atoms are involved in hydrogen bonding with *cis*-coordinated groups. Notably, in the majority of cases, DMF is bound in a meridional position with respect to ligand 1, highlighting the previously reported substrate-directing capabilities of pendant amino groups.39

Magnetic measurements

Variable temperature dc magnetic susceptibility data were collected on freshly filtered crystalline samples of complexes 2–5. The dc magnetic susceptibility (χ) data were collected in the temperature range of 1.8–300 K in a 1000 Oe magnetic field and are plotted as $\chi T vs. T$ in Fig. 5.

For each sample, the product of χT decreases with decreasing temperature to a value close to zero at 1.8 K, indicating a ground state configuration of S = 0 and displaying behaviour characteristic of antiferromagnetic exchange between the spin carriers. In each case, the room temperature values of γT are in agreement with those expected for two uncoupled divalent metal ions (Table 2). For complex 2, a definitive interpretation of the negative deviation of γT is complicated by the presence of spinorbit coupling of Co(II) and may not necessarily be the result of antiferromagnetic exchange, but rather magnetic anisotropy, depopulation of low-lying excited states or a combination of all three factors. Due to the complexity of Co(II) magnetism, it is difficult to evaluate the strength of the magnetic interaction. For complexes 3–5, the application of the van Vleck equation⁴⁰ to Kambe's vector coupling method⁴¹ enabled the fitting of the susceptibility data to determine the exchange interaction parameter (J) between the metal centers. The spin Hamiltonian



Fig. 5 Temperature dependence of χT at 0.1 T (with $\chi = M/H$ normalized per mol) for complexes 2–5. Solid lines represent the fitted curves (see text for details).

describing the exchange interactions for a dinuclear system can be written as $H = -2J(S_1S_2)$, where $S_1 = S_2 = 1$ for complex **3** and $S_1 = S_2 = \frac{1}{2}$ for complexes **4** and **5**. The χT equation can

be written as:
$$\chi_M T = \frac{2Ng^2\beta^2}{k} \left| \frac{\exp\left(\frac{2J}{kT}\right) + 5\exp\left(\frac{6J}{kT}\right)}{1 + 3\exp\left(\frac{2J}{kT}\right) + 5\exp\left(\frac{6J}{kT}\right)} \right| + \text{TIP for}$$

a dinuclear Ni system with $S_1 = S_2 = 1$ (Temperature-Independent Paramagnetism (TIP) = 200×10^{-6} cm³ mol⁻¹), and

as:
$$\chi_M T = \frac{2Ng^2\beta^2}{k} \left| \frac{\exp\left(\frac{2J}{kT}\right)}{1+3\exp\left(\frac{2J}{kT}\right)} \right| + \text{TIP for a dinuclear Cu system}$$

with $S_1 = S_2 = \frac{1}{2}$ (TIP = 120×10^{-6} cm³ mol⁻¹). The best set of fitting parameters obtained is given in Table 2.

In complexes 2–5, the metal centers interact antiferromagnetically across the bitriazine ligand, albeit to varying extents. As shown above, the ligand features in each complex are very similar, with the triazine rings connected by normal single C–C bonds. The clear presence of a C–C single bond in this position suggests a lack of delocalization between the triazine rings, contrary to the related dinuclear complexes of bipyrimidine,²⁰ in which the C–C bond decreases in length by approximately

TABLE 2 SCIECTER TATA TOTILITASTICUE SUSCEDUDINEV INCASULEINE	Table 2	Selected d	data from	magnetic susce	ptibility	v measuremen
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Complex	M-M (Å)	Room temperature magnetic susceptibility (cm ³ K mol ⁻¹)		Calculated parameters	
		Expected	Experimental	$-J (\mathrm{cm}^{-1})$	g
2	5.828	5.40	5.53	_	
3	5.645	2.46	2.418	4.7(1)	2.22(1)
4	5.584	0.77	0.73	18.2(2)	2.03(1)
5	5.634	0.77	0.77	5.5(1)	2.03(1)

0.08 Å from that observed in the free ligand. The extent of magnetic interaction correlates well with the distance between the metal centers, with the shortest distance (4) displaying the largest coupling constant. The calculated exchange constant J for complex 3 is similar to previously reported values for dinuclear Ni complexes of bipyrimidine.²¹ However, bipyrimidine-bridged Cu complexes commonly display coupling constants much greater than those reported here (>100 cm⁻¹).^{20,22} Although neither of the calculated values for complexes 4 and 5 can be considered strong, the value of -18.2 cm⁻¹ for 4 is still significant. It is common for Cu complexes to display greater exchange than that shown by other first-row transition metal bivalent ions due to the shorter metal-ligand bond distances and the lower energy dorbitals. Consequently, the enhanced spin-density delocalization throughout the bridge facilitates the magnetic interaction between the two metal centers. However, the magnitude of J is controlled in part by the orientation of the metal center and its d-orbitals with respect to the bridging ligand. Stronger couplings are observed when the ligand is located in the equatorial position and co-planar with the metal, thereby achieving good overlap of the $d(x^2 - y^2)$ orbitals and enhancing the σ in-plane exchange pathway.²⁰ The non-coplanarity of the metal centers with the ligand plane in complex 4 may therefore help explain why the exchange values for Cu are lower than expected.^{20,22} However, the Cu complex displaying the largest degree of non-coplanarity of the metal (see ESI[†]) is also the complex with the greatest exchange. The decreased antiferromagnetic coupling between the Cu centers in complexes 4 and 5 may therefore be clarified by an in-depth exploration of the stereochemistry of the metal centers.

The geometry about copper in complex 4 is best represented as an axially-compressed trigonal bipyramid with a degree of square-pyramidal distortion in which the ligand system spans axial and equatorial positions. The asymmetric binding of the ligand therefore ensures that the $d(z^2)$ ground state overlaps at only one site on the ligand, that site being opposite and located on the other triazine ring in the second Cu center due to the C_i symmetry of the molecule. Similarly, the ligand system in complex 5 also spans the axial and equatorial sites on the axially-elongated distorted octahedral Cu center. As such, the overlap between the orbitals of the Cu centers is once again not ideal due to the fact that the $d(x^2 - y^2)$ ground states are opposite and overlap with separate triazine rings of the ligand (C_2 symmetry). Given that overlap is not ideal for complexes 4 and 5, the greater exchange interaction observed in 4 may in fact be due to the shorter $Cu \cdots Cu$ and Cu-Nbond distances, most likely imposed by the reduced coordination number.

Conclusions

In summary, the novel bitriazine ligand, 1, has been synthesized, and its transition metal complexes have been prepared and characterized. Variable temperature magnetic susceptibility data display small, but significant, degrees of antiferromagnetic exchange between the spin carriers. Due to the geometrical distortion about the metal centers and the decreased overlap of the ligand with the ground state *d*-orbitals, conditions do not favour an overly coupled system. Work is in progress on the preparation of additional transition metal complexes and attempts are being made to constrain the final geometry of the metal center using a variety of supplemental ligands and anions.

Experimental section

General considerations

 $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ were purchased from Fisher Scientific Company, Cu(NO₃)₂·2.5H₂O was purchased from Caledon Laboratory Chemicals, KSCN was purchased from BDH Chemicals and dimethyl oxalate was purchased from Sigma Aldrich. All of these materials were used without further purification. Phenylbiguanide was prepared following published procedures.⁴² All operations were conducted under standard conditions. NMR spectra were recorded at 20 °C with a 300 MHz Mercury plus Varian Instrument with an Oxford magnet. Elemental analyses were performed on an EAS 1108 apparatus from Fisons Instruments SPA. The IR spectra were recorded in Nujol mulls with a Perkin Elmer FT-IR System Spectrum GX spectrometer (4000–600 cm⁻¹).

Preparation of 4,4'-(NH₂)₂-6,6'-(NHC₆H₅)₂-2,2'-(1,3,5-C₃N₃)₂ (Btzn) [1].

Dimethyl oxalate (3.33 g, 28.2 mmol) was added to a suspension of phenylbiguanide (10.0 g, 56.4 mmol) in MeOH (350 mL) and the mixture was heated at reflux for two days. The mixture was filtered and the solid was subsequently dissolved in DMF. The resulting yellowish solution was filtered prior to the addition of distilled water (350 mL). The cloudy off-white suspension was stirred overnight and filtered to give a solid that was dried overnight at 115 °C. Compound 1 was obtained as a colourless solid (7.24 g, 19.4 mmol, 69% yield). Anal. Calcd (found) for $C_{18}H_{16}N_{10}$ (%): C, 58.05 (57.99); H, 4.33 (4.28); N, 37.61 (37.65); melting point: 348.5 °C; ¹H NMR (20 °C, 300 MHz, (CD₃)₂SO): δ 9.73 (s, 2H, NH), 7.81 (d, 4H, C₆H₅), 7.22 (t, 2H, C₆H₅ & t, 4H, NH₂), 6.93 (t, 2H, C₆H₅); ¹³C NMR (20 °C, 75 MHz, (CD₃)₂SO): δ 170.68 (2,2'-C), 167.52 $(4,6'-CNH_2)$, 164.92 $(4',6-C(NHC_6H_5))$, 140.20, 128.87, 122.58, 120.33 (C_6H_5) (ESI[†]); IR (Nujol mull, cm⁻¹): v 3394, 3289, 3191, 2926, 1640, 1599, 1223, 979, 817, 752.

Preparation of {(Btzn)[Co(NCS)2(EtOH)(Me2NCHO)]2}-2EtOH [2]

A solution of KSCN (0.10 g, 1.03 mmol) in warm EtOH (15 mL) was added dropwise to a stirred solution of Co(NO₃)₂·6H₂O (0.15 g, 0.51 mmol) in EtOH (15 mL). The mixture became deep cobalt blue and a solid separated. The suspension was centrifuged to remove the solid, and a solution of ligand 1 (0.10 g, 0.27 mmol) in DMF (10 mL) was added dropwise to the stirring supernatant, turning it brownish yellow. Stirring was continued for 4 h, the solution was evaporated to dryness, and the residue was re-dissolved in EtOH to give a greenish-yellow solution. Orange crystals of 2 grew overnight when this mixture was left at room temperature (0.20 g, 0.19 mmol, 71% yield). Anal. Calcd (found) for C₃₆H₃₈Co₂N₁₆O₆S₄ (%): C, 41.06 (40.77); H, 5.16 (4.85); N, 21.29 (21.63); S, 12.18 (12.48); IR (Nujol mull, cm⁻¹) v 3292, 3150, 2110, 2058, 1606, 1583, 1562, 1488, 1451, 1405, 1377, 1262, 1227, 1114, 1040, 1009, 803, 760, 679, 622.

Preparation of $\{(Btzn)[Ni(\eta^1-ONO_2)(MeOH)_2(Me_2NCHO)]_2\}$ · 2[NO₃] [3]

A solution of ligand 1 (0.20 g, 0.54 mmol) in DMF (10 mL) was added dropwise to a stirred solution of Ni(NO₃)₂·6H₂O (0.32 g, 1.10 mmol) in EtOH (30 mL), and the resulting emerald–lime green solution was stirred overnight. After evaporation of the solvent, the residual solid was dissolved in a minimal amount of MeOH and the solution was allowed to stand at room temperature. Green crystals of **3** grew by slow evaporation of the solution (0.39 g, 0.38 mmol, 71% yield). Anal. Calcd (found) for $C_{28}H_{46}Ni_2N_{16}O_{18}$ (%): C, 33.22 (32.87); H, 4.58 (4.19); N, 22.15 (22.44); IR (Nujol mull, cm⁻¹) v 3312, 3251, 3214, 3108, 1667, 1615, 1590, 1570, 1491, 1453, 1409, 1379, 1336, 1294, 1018, 800, 764, 690.

Preparation of {(Btzn)[CuCl₂(Me₂NCHO)]₂}·2MeOH [4]

A solution of ligand **1** (0.131 g, 0.352 mmol) in DMF (10 mL) was added to a stirred solution of CuCl₂·2H₂O (0.120 g, 0.704 mmol) in EtOH (15 mL). After the orange solution was evaporated to dryness, the residue was dissolved in hot DMF and the extracts were centrifuged and layered with MeOH. Orange crystals of compound **4** grew when the mixture was kept for several days at room temperature (0.162 g, 0.190 mmol, 54% yield). Anal. Calcd (found) for C₂₆H₃₈Cl₄Cu₂N₁₂O₄ (%): C, 36.67 (36.37); H, 4.50 (4.60); N, 19.74 (19.72); IR (Nujol mull, cm⁻¹) ν 3374, 3088, 2954, 2923, 2853, 1660, 1607, 1585, 1567, 1543, 1488, 1319, 1307, 1014, 766, 694, 627, 621, 605.

$$\label{eq:constraint} \begin{split} Preparation of $$ (Btzn)[Cu(\eta^2-O_2NO)(OH_2)(Me_2NCHO)]_2$$ \\ $$ 2[NO_3]$ \cdot CH_3CN [5]$ \end{split}$$

A solution of ligand 1 (0.148 g, 0.397 mmol) in DMF (10 mL) was added to a stirred solution of Cu(NO₃)₂·2.5H₂O (0.188 g, 0.808 mmol) in EtOH (15 mL), and the resulting green solution was stirred for 3 h. After the mixture was evaporated to dryness, the residue was dissolved in a minimal amount of DMF. The extracts were centrifuged and layered with MeCN. Olive green crystals of compound 5 grew after several days at room temperature (0.286 g, 0.274 mmol, 69% yield). Anal. Calcd (found) for $C_{29}H_{44}N_{18}Cu_2O_{17}$ (due to the difficulty of removing DMF associated with the observed heat-sensitivity of this compound, the experimental analytical values obtained with several samples suggested contamination by 1 equiv of DMF per ligand, and this has been taken into consideration when calculating the theoretical values and percent yield) (%): C, 33.46 (33.42); H, 4.26 (4.22); N, 24.23 (23.95); IR (Nujol mull, cm⁻¹) v 3402, 3302, 3201, 3109, 2903, 1664, 1649, 1615, 1690, 1570, 1490, 1454, 1437, 1392, 1377, 1338, 1294, 1263, 1045, 1007, 772, 694.

Single crystal X-ray diffraction studies

Data used to solve the structures of complexes 2–5 were the best sets obtained in several trials for each sample. Crystals were mounted on thin glass fibers using paraffin oil and either cooled to 223 K (2 and 3) or left at room temperature (4 and 5). Data were collected on a Bruker SMART APEX II X-ray diffractometer with graphite-monochromated Mo K_{α} radiation ($\lambda = 0.71073$ Å) and on a Bruker AXS KAPPA single-crystal diffractometer equipped with a sealed Mo tube source (λ = 0.71073 Å) and an APEX II CCD detector.43 Data for all samples were collected with a sequence of $0.5^{\circ} \omega$ scans at 0, 120, and 240° in φ . Initial unit cell parameters were determined from 60 data frames collected at the different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied.44 Systematic absences in the diffraction data and unit-cell parameters were consistent with monoclinic $P2_1/c$ for 2, triclinic $P\overline{1}$ for 3 and 4, and monoclinic C2/c for 5. Solutions in the centro-symmetric space groups for compounds 2-5 yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with fullmatrix least-squares procedures based on F^2 . All structures 2–5 exhibit dimeric molecular motifs located on the inversion center element of symmetry for 2-4 and the C₂ axis for 5.

With the exceptions noted below, hydrogen atoms were treated as idealized. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being v.6.12.⁴⁵ For compound **2**: The two hydroxyl -H atoms of the two EtOH molecules were located from difference Fourier maps. The coordinated EtOH and the NH₂ group are disordered. SHELX commands, SADI, EADP, DFIX and PART were used to resolve the disorder. For compound **3**: the H atoms on –OH and –NH were located from difference Fourier maps. For compound **4**: one molecule of methanol per unit cell is disordered in the lattice. For compound **5**: one CH₃ group on the coordinated DMF molecule is disordered and there is one half-equivalent of CH₃CN per unit cell in the lattice.

Crystallographic data are reported in Table 1, and relevant bond distances and angles are reported in Tables S1–S4 in the ESI.†

Magnetic measurements

Variable-temperature dc magnetic susceptibility data were obtained using polycrystalline samples wrapped in a polyethylene membrane and collected using a Quantum Design MPMS-XL7 SQUID magnetometer operating between 1.8 and 300 K for a dcapplied field of 0.1 T. Experimental data were corrected for the sample holder and for diamagnetic contributions calculated from Pascal constants.⁴⁶

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