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The Impact of Anion-Modulated Structural Variations on the Magnetic Coupling in Trinuclear Heterometallic Cu^{II}-Co^{II} Complexes Derived from a Salen-Type Schiff **Base Ligand**

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Three new trinuclear heterometallic [(Cu^{II}L)₂Co^{II}X₂] complexes $[H_2L = N, N'$ -bis(salicylidene)-1,3-propanediamine and X = thiocyanate (1), benzoate (2), or azide (3)] have been synthesized by reacting the metalloligand [CuL] with Co- $(ClO_4)_2 \cdot 6H_2O$ and the NH_4^+ or Na^+ salt of the corresponding anion in methanol. Structural characterization reveals that the central CoII ion is connected to two terminal metalloligands through $\mu_{1,1}$ -diphenoxido bridges in all three complexes. However, two monodentate thiocyanato ions, which are mutually *cis* coordinated to the Co atom in **1**, generate a "bent" structure, whereas the trans-coordinated syn-syn bridging benzoato $(1\kappa O: 2\kappa O')$ and the end-on bridging azido $(\mu_{1,1})$ coligands in **2** and **3**, respectively, produce linear struc-

Introduction

For decades, the combination of coordination chemistry and molecular magnetism has greatly inspired scientists to investigate the magnetic properties of isolated molecules, especially mixed-valence or heterometallic compounds that show low-temperature ferrimagnetic coupling.^[1] One of the primary goals of these studies is to explore the magnetostructural correlations of the exchange interactions between multiple nonequivalent spin-carrying centers, which may be ferro- or antiferromagnetically coupled.^[2] Such correlations can help to direct future synthetic strategies for the design of magnetic materials for efficient information storage, quantum information processing, solvatomagnetic

tures. The changes in the number and nature of the bridges with a shortening of the distances between the metal centers leads to a concomitant decrease of the average Cu^{II}-O-Co^{II} bridging angle from 99.3(2) to 97.1(4) and 91.5(1)° for 1, 2 and 3, respectively. Variable-temperature magnetic susceptibility measurements show the presence of a dominant antiferromagnetic coupling between the Cu-Co pairs in all three complexes. However, a steady decrease of the magnitude of the exchange coupling constant (J_{Cu-Co}) is observed from -33.4 (for 1) to -11.4 (for 2) and -2.15 cm⁻¹ (for 3). This trend suggests that larger Cu-O-Co angles are associated with stronger antiferromagnetic coupling.

sensing, and various spintronic devices.^[3] It should be noted that magnetostructural correlations have been drawn mostly between isotropic spins, and several groups have successfully determined the critical impact of the bridging angle on the nature and magnitude of exchange interactions.^[1,4] However, such attempts are rather scarce in complexes with heterospins, although the generation of large ground spin states with slow magnetic relaxation dynamics in heterometallic transition-metal complexes has become of paramount importance in the field of single-molecule magnets (SMMs).^[5]

Recently, we have been investigating trinuclear [(ML)₂- $M'X_n$ complexes (H₂L is a N₂O₂-donor salen-type Schiff base ligand, X⁻ is an anionic coligand, and M and M' are two different paramagnetic transition-metal ions).^[6] These complexes showed promising evidence of linear-bent conformational flexibility, which led to antiferro- or ferromagnetic switching of exchange interactions.^[7] We further proceeded to tune the bridging angle in heterometallic Cu^{II}₂-Mn^{II} complexes by using various coligands (X⁻) to determine their influence on the exchange coupling and the possible ferromagnetic to antiferromagnetic crossover angle.^[8] In the present study, we continue our quest to obtain a correlation between the bridging angle and magnetic coupling

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for trinuclear Cu^{II}₂Co^{II} complexes. Such systems are expected to have intricate magnetic properties as a result of a considerable orbital and spin-orbit coupling contribution to the effective magnetic moment arising from the intrinsic orbital angular momentum in the octahedral ground state of high-spin Co^{II} ions $[{}^{4}T_{1g}(F)]$.^[1,5b,9] Moreover, analogous Cu/Co/M'' (M'' = Cd^{II} and Pb^{II}) spin-coupled systems have shown strong geometrical dependence of exchange coupling.^[10] The anionic coligands have been chosen in such a way that a wide variation in the phenoxido bridging angle can be achieved by exploiting the differences in their mode of ligation.^[8] A large number of structurally and magnetically characterized heterometallic CuII/CoII molecular clusters constructed by diphenoxido bridges have been reported; however, they are mostly derived from acyclic or cyclic Schiff base ligands.[11] In those complexes, the diphenoxido-bridged dimetallic Cu^{II}/Co^{II} molecular clusters are rather rigid and, hence, do not allow a significant aniondependent variation of the Cu^{II}-O-Co^{II} angles.

Herein, we report the synthesis, characterization, crystal structures, and magnetic properties of three analogous $[(Cu^{II}L)_2Co^{II}X_2]$ complexes $[H_2L = N,N'$ -bis(salicylidene)-1,3-propanediamine and X = SCN⁻, OBz⁻, N₃⁻]. The conformational flexibility of the trinuclear $[(Cu^{II}L)_2Co^{II}]^{2+}$ coordination cluster permits different modes of ligation of the anions, which results in significant modulation of the Cu^{II}-O-Co^{II} angles and the relative positions of the Cu^{II}-Co^{II}-Cu^{II} atoms. These subtle structural changes give rise to clear differences in the magnitude of the antiferromagnetic exchange interactions in these complexes and, thus, emphasize the relevance of the distinct geometrical positions

of the spin-carrying centers and the bridging angle on the nature of the magnetic coupling in Cu^{II}/Co^{II} complexes. This anion-dependent variation of the oxido bridging angle for any heterometallic spin-coupled systems has rarely been observed.^[8]

Results and Discussion

Syntheses and Spectral Characterizations of the Complexes

Previously, we have synthesized several trinuclear complexes with [CuL] as a metalloligand and diamagnetic Na^I, Pb^{II}, Zn^{II}, Cd^{II}, and Hg^{II} or paramagnetic Ni^{II}, Mn^{II}, and Tb^{III} central metal ions.^[6,8a,12] In the present study, we have prepared three trinuclear complexes by reactions between [CuL], Co(ClO₄)₂·6H₂O, and the anionic coligands thiocyanate (SCN⁻), benzoate (PhCOO⁻), and azide (N₃⁻) in methanol (Scheme 1). As observed previously with related compounds, the pseudohalide SCN⁻ leads to an angular trinuclear complex (1), whereas the benzoate and azide ions yield linear trinuclear complexes (**2** and **3**, respectively).

In addition to elemental analysis, all complexes have been primarily characterized by IR spectroscopy. The Schiff base moiety shows strong and sharp IR absorption bands at 1619, 1624, and 1613 cm⁻¹ for **1**, **2** and **3**, respectively. The precursor metalloligand [CuL] is neutral and, therefore, has no counteranion. The anionic coligands in these three complexes show characteristic IR absorption bands at 2044, 1561, and 2062 cm⁻¹ for SCN⁻, PhCOO⁻, and N₃⁻, respectively.^[13]



Scheme 1. Formation of the precursor metalloligand and 1, 2, and 3.

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All three complexes and the free metalloligand have been characterized by UV/Vis/NIR spectroscopy in methanol as well as in the solid state. In solution, all compounds display very similar UV/Vis spectra with intense bands at ca. 595 (Cu^{II} d–d transition; Figure S1, upper right, Supporting Information), 360 (ligand-to-metal charge-transfer transition of [CuL]), and 274 nm (intraligand π – π * transition of [CuL]), which are similar to those of the free metalloligand (Figure S1, upper left). The solid-state electronic spectra exhibit the expected bathochromic as well as hypochromic shifts of the d–d transition bands of the metalloligand, as a result of its complexation with the Co^{II} center (Figure S1, bottom left). Hence, the corresponding band at 595 nm for the free [CuL] moiety is observed at 619 (1), 617 (2), and 609 nm (3). The metalloligand [CuL] has no characteristic

absorption maxima in the region 800–1400 nm, but the octahedral high-spin d⁷ Co^{II} ions are expected to exhibit absorption bands in the NIR region that correspond to the spin-allowed d–d transitions. Accordingly, the bands at 1310, 1290, and 1281 nm are assignable to the characteristic $[{}^{4}T_{1g}(P) \leftarrow {}^{4}T_{1g}(F)]$ transitions of the octahedral Co^{II} centers in **1**, **2**, and **3**, respectively (Figure S1, bottom right).^[14]

Description of the Structures

The X-ray crystal structure of 1 consists of a "bent"^[15] trinuclear asymmetric unit, viz., $[(CuL)_2Co(NCS)_2]$ (Figure 1). Selected coordination bonds and angles are listed in Table 1.



Figure 1. Representation of the molecular structure of **1** with partial atom-numbering scheme. Atom color scheme: grey C, blue N, red O, yellow S, green Cu, pink Co. Hydrogen atoms are omitted for clarity.

The structure contains a hexacoordinate central cobalt atom in a CoN_2O_4 octahedral environment together with two tetracoordinate square-planar copper atoms from two [CuL] metalloligands. The equatorial plane of the octahedral coordination sphere comprises two *cis*-coordinated thiocyanato N atoms [N(5) and N(6)] and two phenoxido O atoms [O(1) and O(4)] from two different [CuL] ligands. The remaining two phenoxido O atoms [O(2) and O(3)] of the two [CuL] moieties occupy the axial positions. The equatorial Co–O bond lengths [2.164(2) and 2.236(2) Å] are FULL PAPER

significantly longer than the Co–N_{NCS} bond lengths [2.028(3) and 2.068(2) Å], whereas the axial Co–O bond lengths [2.102(2) and 2.085(2) Å] are intermediate; all of them are typical of high-spin Co^{II} ions.^[16] The equatorial N–Co–N bond angle involving the two *cis*-thiocyanato groups [101.27(9)°] and those involving the oxygen atoms of each chelating [CuL] ligand [70.17(7) and 68.90(7)°] deviate significantly from the ideal value (90°). In addition, the axial O–Co–O bond angle [163.13(7)°] is also far from that of an ideal octahedron (180°). All these metric parameters characterize a highly distorted octahedral Co^{II} environment, which is very similar to those found in related structures.^[7,16]

Each of the two terminal copper atoms of the trinuclear $(Cu^{II}L)_2Co^{II}$ core is bonded to four donor atoms [O(1), O(2), N(1), N(2) for Cu(1) and O(3), O(4), N(3), N(4) for Cu(2)] of one tetradentate L²⁻ ligand to generate a squareplanar geometry. The Cu-O and Cu-N bond lengths are in the ranges 1.921(2)-1.937(2) and 1.955(2)-1.973(2) Å, respectively. This geometry is also confirmed by the socalled τ_4 index.^[17] This value measures the distortion between a perfect tetrahedron ($\tau_4 = 1$) and a perfect square plane ($\tau_4 = 0$) and can be calculated with the formula $\tau_4 =$ $[360^{\circ} - (a + \beta)]/141^{\circ}$; a and β (in °) are the two largest angles around the metal center in the complex. The τ_4 values of 0.137 and 0.164 for Cu(1) and Cu(2), respectively, confirm their slightly distorted square-planar geometries. The rootmean-square (r.m.s.) deviations from the mean plane passing through the four atoms coordinated to the copper ions are 0.027 and 0.107 Å for Cu(1) and Cu(2), respectively, and the metal atoms are located 0.017(1) [Cu(1)] and 0.013(1) Å [Cu(2)] away from this plane. The metal...metal separations and the angle between the metal centers in the angular (CuL)₂Co unit are Cu(1)···Co(1) 3.122(1) Å, Cu(2)···Co(1) 3.091(1) Å, Cu(1)···Cu(2) 4.403(1) Å, and Cu(1)····Co(1)····Cu(2) 90.24(1)°.

In contrast to 1, both 2 and 3 consist of centrosymmetric linear trinuclear units^[15] of formulae $[(CuL)_2Co(O_2CPh)_2]$ and $[(CuL)_2Co(N_3)_2]$, respectively. The corresponding molecular structures are depicted in Figure 2, and selected bond lengths and angles are listed in Table 1.

The structures of both complexes consist of a hexacoordinate central cobalt atom in an octahedral geometry together with two pentacoordinate square-planar copper atoms. The phenoxido oxygen atoms O(1) and O(2) and their symmetry related ones (O1a and O2a) from each [CuL] metalloligand form the equatorial plane of the octahedral coordination sphere of the CoII centers with bond lengths of 2.084(6)-2.163(2) Å for the two complexes. The axial positions are occupied by oxygen atoms O(3) of the syn-syn bridging benzoate ligand $(1\kappa O: 2\kappa O')$ and the nitrogen atom N(3) of the end-on bridging azide ligand ($\mu_{1,1}$) with bond lengths of 2.065(8) and 2.075(2) Å for 2 and 3, respectively. The bond lengths of the ligating atoms to the Co^{II} center are comparable for the CoO_6 and the CoO_4N_2 octahedra in 2 and 3, respectively, and show weak Jahn-Teller distortion, which is a typical feature for high-spin Co^{II} ions. Owing to the presence of centers of inversion in



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Table 1. Selected bond	l lengths [.	Å] and	angles	[°] for	1–3.
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	1		2	3
$\overline{Cu(1)-O(1)}$	1.926(2)	Cu(1)–O(1)	1.951(7)	1.941(2)
Cu(1) - O(2)	1.928(2)	Cu(1) - O(2)	1.969(7)	1.926(2)
Cu(1) = N(1)	1.960(2)	Cu(1) = N(1)	1 989(9)	1 937(2)
Cu(1) = N(2)	1.970(2)	Cu(1) - N(2)	1.958(9)	1.968(2)
Cu(1) = U(2) Cu(2) = O(3)	1.970(2)	$Cu(1) \Omega(4)*/N(3a)#[a]$	2.218(8)	2.572(3)
Cu(2) = O(3)	1.921(2) 1.027(2)	Cu(1) = O(4) / In(5a) + 1	2.210(0)	2.372(3)
Cu(2) = O(4)	1.937(2)			
Cu(2)-N(3)	1.9/3(2)			
Cu(2) - N(4)	1.955(2)			
Co(1) - O(1)	2.164(2)	Co(1)-O(1)	2.084(6)	2.163(2)
Co(1)–O(2)	2.102(2)	Co(1)–O(2)	2.110(6)	2.102(2)
Co(1)–O(3)	2.085(2)	Co(1)–O(3)*/N(3)#	2.065(8)	2.075(2)
Co(1) - O(4)	2.236(2)			
$C_0(1) = N(5)$	2.028(3)			
$C_0(1) = N(6)$	2.068(2)			
$C_{0}(1) C_{1}(1)$	3 122(1)	$C_{0}(1)$ $C_{1}(1)$	3.041(1)	2 916(1)
$C_0(1) - C_0(1)$	3.122(1)	$\operatorname{CO}(1)$ - $\operatorname{Cu}(1)$	5.041(1)	2.910(1)
Co(1) = Cu(2)	5.091(1)	$C_{22}(1)$ $C_{22}(1_2)/C_{22}(1_2)$	(0.000(0))	5.021(2)
Cu(1)– $Cu(2)$	4.403(1)	Cu(1)- $Cu(1a)/Cu(1b)$	6.082(2)	5.831(2)
O(1)-Cu(1)-O(2)	79.05(7)	O(1)–Cu(1)–O(2)	81.4(3)	80.89(8)
O(1) - Cu(1) - N(1)	91.96(8)	O(1)-Cu(1)-N(1)	89.8(3)	92.36(8)
O(1) = Cu(1) = N(2)	170 13(8)	O(1) - Cu(1) - N(2)	163 3(3)	160 36(8)
O(2)-Cu(1)-N(1)	170.61(8)	O(1) - Cu(1) - O(4) * / N(3a) #	98 1(3)	76 65(8)
O(2) Cu(1) N(2)	01 11(8)	O(2) Cu(1) N(1)	170.5(3)	165 95(8)
N(1) Cu(1) N(2)	07.01(0)	O(2) - Cu(1) - N(1) O(2) - Cu(1) - N(2)	170.3(3)	103.75(0)
N(1) = Cu(1) = N(2)	97.91(9)	O(2) = Cu(1) = N(2) O(2) = Cr(1) = O(4) * / N(2r) #	90.7(3)	92.24(9)
O(3) = Cu(2) = O(4)	/8./6(/)	O(2)=Cu(1)=O(4)*/N(3a)#	94.0(3)	/3.45(8)
O(3) - Cu(2) - N(3)	91.35(8)	N(1)-Cu(1)-N(2)	96.9(3)	97.93(9)
O(3)-Cu(2)-N(4)	168.59(9)	N(1)-Cu(1)-O(4)*/N(3a)#	90.8(3)	93.06(8)
O(4)-Cu(2)-N(3)	168.30(8)	N(2)-Cu(1)-O(4)*/N(3a)#	97.2(3)	119.18(8)
O(4)-Cu(2)-N(4)	92.70(8)			
N(3)-Cu(2)-N(4)	97.90(9)	O(1)-Co(1)-O(2)	75.1(3)	72.03(7)
O(1)-Co(1)-O(2)	70.17(7)	O(1)-Co(1)-O(3)*/N(3)#	89.4(3)	95.80(9)
$O(1) - C_0(1) - O(3)$	95.62(6)	O(1) - Co(1) - O(1a)	180.00	180.00
$O(1) = C_0(1) = O(4)$	76 61(7)	O(1) = Co(1) = O(2a)	104 9(3)	107 97(7)
O(1) - Co(1) - N(5)	96.04(8)	$O(1) - C_0(1) - O(3b) * / N(3a) #$	90 6(3)	84 20(9)
O(1) Co(1) N(6)	15754(8)	$O(2)$ $C_{0}(1)$ $O(3)*/N(3)#$	00.2(3)	09.06(0)
O(1) = CO(1) = N(0)	157.54(8) 162.12(7)	O(2) = Co(1) = O(3) / N(3) #	$\frac{90.2(3)}{180.00}$	180.00(9)
O(2) = CO(1) = O(3)	103.13(7)	O(2) = CO(1) = O(2a)	180.00	180.00
O(2) = Co(1) = O(4)	98.14(7)	$O(2) - Co(1) - O(3b)^* / N(3a) #$	89.8(3)	81.94(9)
O(2)-Co(1)-N(5)	95.61(8)	O(3)*/N(3)#-Co(1)-O(3b)*/N(3a)#	180.00	180.00
O(2)-Co(1)-N(6)	93.82(8)			
O(3)–Co(1)–O(4)	68.90(7)			
O(3)-Co(1)-N(5)	94.90(8)			
O(3)-Co(1)-N(6)	97.02(8)			
O(4)-Co(1)-N(5)	161.06(8)			
O(4) - Co(1) - N(6)	90.77(8)			
$N(5)-C_0(1)-N(6)$	101 27(9)			
$C_{11}(1) = C_{01}(1) = C_{11}(2)$	90 24(1)	Cu(1) = Co(1) = Cu(1a)/Cu(1b)	180	180
	JU.27(1)		100	100

[a] * and # are for 2 and 3, respectively. Symmetry codes: a = -x, -y, -z and b = -x + 1/2, -y + 1/2, -z.



Figure 2. Representations of the molecular structures of 2 (left) and 3 (right) with partial atom-numbering schemes; a = -x + 1/2, -y + 1/2, -z and -x, -y, -z for 2 and 3, respectively. Atom color scheme: grey C, blue N, red O, green Cu, Pink Co. Hydrogen atoms are omitted for clarity.

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both 2 and 3, all of the trans angles are ideal (180°), but the cis angles in the equatorial plane [75.1(3) and 104.9(3)° for 2 and 72.03(7) and 107.97(7)° for 3] and the cis angles with the axially coordinated atoms $[89.4(3)-90.6(3)^{\circ}$ for 2 and 81.94(9)-98.06(9)° for 3] deviate considerably from the perfect value (90°). The range of values also indicates that the distortion is higher in 3 than it is in 2. The basal planes of each of the two terminal copper atoms of the trinuclear (Cu^{II}L)₂Co^{II} cores of **2** and **3** contain four donor atoms of the Schiff base, namely, two imine N atoms [N(1) and N(2)] with Cu-N bond lengths in the range 1.937(2)-1.989(9) Å and two phenoxido O atoms [O(1) and O(2)] with Cu-O bond lengths in the range 1.926(2)–1.969(7) Å. The bridging benzoate and the azide ions occupy the axial positions of the square pyramids with Cu(1)-O(4) and Cu(1)-N(3)distances of 2.218(8) and 2.572(3) Å, respectively. Thus, the axial interactions of the bridging coligands with the Cu^{II} centers are much weakened in 3 compared to those in 2. Moreover, the angles between the axially and equatorially coordinated atoms vary within a narrow range of 90.8(3)-98.1(3)° in 2, but those in 3 cover a wide range [73.45(8)-119.18(8)°]. The so-called Addison parameter (τ_5) amounts to 0.120 and 0.093 for 2 and 3, respectively, and, hence, confirms the slightly distorted square-pyramidal geometry for the copper(II) ions (τ_5 is 0 for a perfect square pyramid, whereas it is 1 for a trigonal bipyramid).^[18] The r.m.s. deviation of the four basally coordinated atoms from the mean plane passing through them is much less (0.087 Å) in 2 that it is in 3 (0.241 Å), and the metal atoms are 0.169(1) and 0.056(1) Å away from this plane toward the axially coordinated oxygen atoms. The Co…Cu distances in 2 and 3 [3.041(1) and 2.916(1) Å] are slightly shorter than those in 1, but the Cu···Cu separations [6.082(2) and 5.831(2) Å] are much longer than that of 1 as a consequence of the linear structure with triply bridged metal centers. Another significant structural difference arising from the different bridges in 2 and 3 is the relative position of the terminal Cu^{II} ions with respect to the equatorial CoO₄ plane. The perpendicular distances of the copper atoms from the said plane are ca. 0.743 and 1.102 Å in 2 and 3, respectively. Although the heterometallic coordination clusters of both 2 and 3 comprise one Co octahedron and two Cu square pyramids, they are joined together through two monoatomic bridges in an edge-sharing manner in 2, whereas they share common faces through three monoatomic bridges in 3 (Figure S2).

As all three complexes possess a $\mu_{1,1}$ -diphenoxidobridged (Cu^{II}L)₂Co^{II} unit, they can be compared through their respective bridging angles (Table 2). For 1, the trinuclear unit is formed only by diphenoxido bridges, which connect the central Co^{II} ion (bound to two terminal thiocyanato coligands) to two terminal Cu^{II} ions, and the bridging angles range from 95.34(8) to 101.47(8)° with an average value of 99.3(2)° (Scheme 2). For **2**, the trinuclear unit includes an additional $\mu_{1,3}$ -carboxylato bridge between the terminal Cu^{II} centers and the central Co^{II} ion, which brings them closer, and there is a concomitant decrease of the average phenoxido bridging angles to 97.1(4)°. In **3**, the additional $\mu_{1,1}$ -azido bridge shortens the Cu^{II}···Co^{II} separa-

tion further. Consequently, the phenoxido bridging angle decreases to an average value of $91.5(1)^{\circ}$.

Table 2. List of $\mu_{1,1}$ bridging angles for 1–3.

.,							
$\mu_{1,1}$ Bridging angle	1	2	3				
Cu(1)–O(1)–Co(1)	99.37(8)	97.8(3)	90.39(7)	-			
Cu(1) - O(2) - Co(1)	101.47(8)	96.4(3)	92.63(8)				
Cu(2)–O(3)–Co(1)	100.94(8)	_	_				
Cu(2) - O(4) - Co(1)	95.34(8)	_	_				
$Cu(1^{a})-N(3)-Co(1)$	_	_	76.90(8)				



Scheme 2. The average phenoxido bridging angles of the $Cu(\mu_{1,1}-O)_2Co$ units in 1–3 (from left to right, respectively).

Magnetic Properties

The study of the magnetic properties of heterometallic complexes comprising exchange-coupled copper and highspin octahedral cobalt(II) involves difficulties derived from the nonquenched orbital angular momentum of the latter ions. This has been done in a number of different ways. One approach, for instance, is to consider only a lower range of temperatures, at which the lowest J multiplet of the Co^{II} ${}^{4}T_{1}$ term is mainly populated (J = 1/2) and to treat it as an effective S = 1/2 and use a spin-only model for the whole problem.^[19] Sometimes, the lowest two J multiplets have been included as effective S = 1/2 and S = 3/2 spin moments with the splitting at zero field between both states modeled as the result of magnetoanisotropy.^[10,20] Ideally, however, the model should include the effect of the orbital angular momentum of the Co^{II} ion (L = 1), as it couples with the electronic spin (S = 3/2), and also the effect of its interaction with an external magnetic field. Unfortunately, the problem does not allow for an analytical solution to the wave equation from the resulting Hamiltonian;^[21] therefore, to simulate the magnetic properties in these systems, it is necessary to employ matrix diagonalization procedures (see below).

Molar paramagnetic susceptibility (χ_M) measurements in the 2–300 K temperature range were performed on powdered polycrystalline samples of **1**, **2**, and **3** under a constant magnetic field of 0.5 T. The results are shown in Figure 3 as $\chi_M T$ versus T plots. To simulate these data, the coupling between the orbital and the spin magnetic moments (L = 1 and S = 3/2) of the octahedral high-spin Co^{II} ion was taken into consideration. To this, the exchange between the magnetic moments of the Co^{II} and Cu^{II} ions was also added by following the treatment of Lines,^[22] which considers only the coupling between true spins (S = 3/2 and 1/2 for Co^{II} and Cu^{II} ions, respectively). In addition, the

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effect of the magnetic field on the various magnetic moments resulting from these interactions (the Zeeman effect) was included. Thus, the Hamiltonian employed is that in Equation (1).

$$\hat{H} = \lambda \sigma \hat{L}_1 \hat{S}_1 - 2J (\hat{S}_1 \hat{S}_2 + \hat{S}_1 \hat{S}_3) + \mu_B (\sigma \hat{L}_1 + g_1 \hat{S}_1 + g_2 \hat{S}_2 + g_3 \hat{S}_3) \vec{B}$$
(1)



Figure 3. Plots of $\chi_M T$ vs. *T* for 1, 2, and 3. The solid lines are fits to the experimental data (see text for details).

In this Hamiltonian, $L[and]_1$ and \hat{S}_1 are the orbital and spin angular moments of the Co^{II} ion, and \hat{S}_2 and \hat{S}_3 are the spin operators of each copper ion. Likewise, g_1 , g_2 , and g_3 are the isotropic gyromagnetic ratios of the Co^{II} and both Cu^{II} centers, respectively. The terms J, λ , and σ correspond to the exchange coupling constant between Co and Cu, the spin-orbit coupling constant of Co, and a combined orbital reduction parameter of this metal, respectively; $^{[21]}\mu_{B}$ and B have the usual meanings. The program PHI^[23] was employed for the diagonalization of the matrix arising from this Hamiltonian and to obtain the parameters that best fit the experimental data. To avoid the overparameterization of the problem, the values of g_1 and $g_2 = g_3$ were fixed to reasonable values of 2.0 and 2.2, respectively. Additionally, the data could only be fitted satisfactorily if the contribution of a small amount of a Co^{II} paramagnetic impurity was considered (amounting to molar fractions of 0.1, 0.1, and 0.05 in 1, 2, and 3, respectively). The best solutions were obtained for J, λ , and σ values of (in the 1/2/3 format) -33.4/-11.4/-2.15 cm⁻¹, -180/-170/-165 cm⁻¹, and -1.30/-1.16/-0.99, respectively, and the ensuing simulations are represented as solid lines in Figure 3. Of these results, the most salient feature is the gradation in the strength of the magnetic exchange between the Cu^{II} and Co^{II} ions from 1 to 3. Thus, it is tempting to search for a correlation between the magnitude of this coupling and some structural parameter. In this context, a very common occurrence is a correlation between the M-X-M angle ("X" is a monoatomic bridge) and the exchange coupling constant.^[24] However, such correlations can only be performed when the remaining structural parameters or the chemical nature of the systems compared remain constant. In this case, the systems may not be directly comparable as 2 and 3 exhibit, in addition to the phenoxide bridges, syn-syn carboxylato or end-on azido bridging ligands, respectively, which are known to be active as magnetic couplers.^[25] Nevertheless, as these ligands are bound to the Cu^{II} ions through the long axial positions, their interaction with the $d_{x^2-y^2}$ magnetic orbitals of the Cu^{II} ions and, thus, their contribution to the magnetic coupling is expected to be negligible. In the present system, a trend seems to emerge that suggests that the larger Cu–O–Co angles (involving the phenolate bridges) are conducive to stronger antiferromagnetic couplings (Figure S3). This observation is reminiscent of the many previously established correlations in which [Cu₂] complexes with wider Cu-O-Cu angles involving equatorial bonding positions cause stronger antiferromagnetic interactions.^[26] We have similarly examined a possible relationship between the Co-O or the Cu-O bond lengths (Figures S4 and S5) and the extent of the magnetic coupling. The bond lengths to the Co center seem to be unrelated to the coupling, whereas longer average Cu-O bond lengths are accompanied by an increase of the coupling. This observation seems contradictory if the coupling is understood in part as a measure of the overlap between the magnetic orbitals of the metal ions and the orbitals from the ligands that facilitating the superexchange, unless the slight elongation is more detrimental to potential ferromagnetic pathways than antiferromagnetic ones, as was previously suggested for a related system.^[19] It could also be that this correlation is accidental and that the true parameter related to the coupling is indeed the bonding angle. In view of these observations, it was deemed appropriate to examine in more detail all the previously reported compounds that feature Co-Cu heterometallic fragments with both metals exhibiting two monoatomic oxygen bridges. The Cambridge Structural Database (February 2014 update) yields 56 hits involving this moiety. We summarize the systems for which magnetic data have been modeled in Table 3, together with the magnitude of the coupling constants reported as well as their most relevant structural parameters. Analysis of these data reveals an approximate correlation between the average Cu-O–Co angle and J (Figure 4). This correlation is exceptionally good if one considers the following aspects: (1) the magnetic data have been simulated by using a large variety of different models (see above) for the various systems, (2) the coordination geometries and even the coordination numbers of the Co^{II} ions change significantly from compound to compound and, thus, they have different degrees of influence of the orbital angular momentum on the magnetic properties, (3) other parameters, which are known to influence the magnetic coupling, such as the planarity of the $[Cu(\mu-O)_2Co]$ core, the M–O bond angles, and the C– O…O angles, vary from complex to complex. Taking these and other aspects into consideration, it can be concluded that the bridging Cu-O-Co angle must indeed be considered as a very relevant parameter in defining the extent of the magnetic exchange. It is very likely that if the data for all these compounds were treated by the same model, a much better correlation would be obtained. A possible relationship between the average Cu-O and Co-O bond lengths

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Table 3. List of all complexes from the literature containing the $Co(\mu-O)_2Cu$ moiety for which the magnetic data have been analyzed, together with the *J* constants determined for them and relevant metric parameters.

Complex	Cu–O–Co [°] ^[a]	Cu–O [Å] ^[a]	Co–O [Å] ^[a]	$J [{ m cm}^{-1}]^{[{ m b}]}$	Ref.
$\overline{[CuCo_{3}(MeDea)_{3}Cl_{3}(CH_{3}OH)_{0.55}(H_{2}O)_{0.45}]^{[c]}}$	93.74	2.171	2.130	-2.38	[9c]
$[Cu_2Co(NCS)_3(N(CH_3)_2C_2H_4O)_3]$	101.04	1.941	2.095	-20.05	[27]
$[Cu_2Co(OH)I_2(N(CH_3)_2C_2H_4O)_3]_2$	99.145	1.958	2.128	-24.35	[27]
$[Cu_2Co_2(L1)_2(H_2O)_2]_n^{[d]}$	98.54	1.909	2.082	-12.5	[11i]
$[CuCo(prp2en)(hfa)_2]^{[e]}$	96.7	1.892	2.122	-16.3	[19]
$[Cu_2CoPbCl_4(L2)_4]_2^{[f]}$	100.34	1.947	2.088	-19	[10]
$[Cu_2CoCd_2Cl_6(L2)_4(MeHO)_2]^{[f]}$	95.3	1.99	2.046	+1.6	[10]
$[(CuL3)_2(CuCoL3(H_2O)_3)](ClO_4)_2^{[g]}$	102.6	1.884	2.124	-8.0	[20]
$[CuCo(prp2pr)(hfa)_2]^{[e,h]}$	100.07	1.904	2.041	-15	[11a]
$[CuCo(L4)(hfa)]_{2}^{[e,i]}$	100.11	1.902	2.103	-20.2	[11k]
$[Cu_2Co(L5)_2(H_2O)]^{[j]}$	98.48	1.935	2.016	-26.2	[28]
[CuCo(salen)Cl ₂] ^[k]	98.99	1.912	2.004	-51	[29]
$[CuCo(L6)(NCS)_2]^{[1]}$	104.77	1.955	2.021	-50.6	[11d]
$[CoCu(L7)](ClO_4)_2^{[m]}$	97.74	1.921	2.097	-8.0	[11c]
$[CoCu(L8)(MeCN)(PrOH)](ClO_4)_2^{[n]}$	101.14	1.955	1.993	-38	[11c]

[a] Average values. [b] The Hamiltonian convention employed is $H = -2JS_1S_2$. [c] H₂MeDea = *N*-methyldiethanolamine. [d] H₄L1 = 2-hydroxy-3-[(*E*)-({2-[(2-hydroxybenzoyl)amino]ethyl}imino)methyl]benzoic acid. [e] H₂prp2en = *N*,*N'*-ethylenebis(2-hydroxypropiophenoneimine); hfa⁻ = hexafluoroacetylacetonato. [f] HL2 = 2-(dimethylamino)ethanol. [g] H₂L3 = *N*,*N'*-ethylenebis(3-ethoxysalicylaldimine). [h] H₂L4 = *N*,*N'*-propylenebis(2-hydroxypropiophenoneimine). [i] H₃L4 = 1-(2-hydroxybenzamido)-2-[(2-hydroxy-3-methoxybenzylidene) amino]ethane. [j] H₃L5 = *N*-3-carboxylsalicylidene-*N'*-salicylaldehyde-1,2-diaminoethane. [k] H₂salen = *N*,*N'*-ethylenebis(salicyliden-imine). [l] H₂L6 = *N*,*N'*-propylenebis(3-methoxysalicylideneimine). [m] H₂L7 = two 2-[(methylamino)methyl]-6-(iminomethyl)-4-bromophenol units linked at both ends by a $-(CH_2)_2$ - chain at one end and a $-(CH_2)_3$ - chain at the other.

with J was also investigated. For the former parameter, and contrary to what the same analysis for only 1, 2, and 3 suggested (see above), almost no correlation was observed (Figure S6). As for the dependence of J with the average Co–O bond lengths, an inverse relationship could be inferred, although of a much lower quality (Figure S7, Supporting Information).



Figure 4. Plot of -J vs. Cu–O–Co angle (*a*) for 1–3 and the compounds from Table 3. The red line is a linear regression, which produced a best fit for -J = -286 + 3.1a.

Conclusions

To assess the magnetic coupling in phenoxido-bridged Cu^{II} -Co^{II} entities and to find the antiferromagnetic-to-ferromagnetic crossover angle, three trinuclear Cu-Co complexes have been prepared by utilizing a copper metalloligand derived from a N₂O₂-donor salen-type Schiff base and different anionic coligands. The complexes obtained exhibit linear or bent arrangements of the metal centers associated with a wide range of phenoxido bridging angles within the $Cu(\mu_{1,1}-O)_2Co(\mu_{1,1}-O)_2Cu$ core, depending upon the coordination modes of the anionic coligands. The average Cu-O-Co angle of 91.5(1)° in 3 appears to be the lowest reported to date for a diphenoxido-bridged Cu^{II}-Co^{II} compound. All of these complexes are overall antiferromagnetic and lead to final ground states with effective spins of 1/2 at low temperature; hence, the crossover angle is yet to be achieved. However, a trend is clearly observed as the antiferromagnetic interaction, which has the highest value for 1 with the largest bridging angle, decreases as the phenoxido bridging angle decreases. Thus, the present study validates the strategy of using metalloligands to synthesize heterometallic spin-coupled systems with a predetermined nuclearity in an easy and effective manner. In addition, the inherent flexibility of the basic structural unit allows the modulation of the bridging angles through the judicious choice of anion, which make these groups of complexes extremely valuable for investigations of the influence of the bridging angle on magnetic exchange interactions between heterometallic centers.

Experimental Section

Starting Materials: Reagent grade salicylaldehyde and 1,3-propanediamine were purchased from Lancaster and used as received. The reagents and solvents used were of commercially available reagent quality, unless otherwise stated.

Caution! Perchlorate and azide salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and it should be handled with care.

Schiff Base Ligands H_2L and the Metalloligand [CuL]: The Schiff base ligand H_2L was prepared by following reported methods.^[30]

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Briefly, 1,3-propanediamine (0.42 mL, 5 mmol) was mixed with salicylaldehyde (1.0 mL, 10 mmol) in methanol (20 mL). The resulting solution was heated to reflux for ca. 2 h and then cooled to room temperature. The yellow methanolic solution was used directly for complex formation. To a methanolic solution (20 mL) of Cu(ClO₄)₂· $6H_2O$ (1.852 g, 5 mmol), a methanolic solution of H_2L (5 mmol, 20 mL) and triethylamine (1.4 mL, 10 mmol) were added to prepare the precursor metalloligand [CuL], as reported previously.^[30]

Complexes [(CuL)₂Co(NCS)₂] (1), [(CuL)₂Co(O₂CPh)₂] (2), and $[(CuL)_2Co(N_3)_2]$ (3): To a methanolic solution (20 mL) of the precursor complex [CuL] (0.718 g, 2 mmol), a solution of Co(ClO₄)₂· $6H_2O$ (0.367 g, 1 mmol) in methanol (2 mL) was added, followed by an aqueous solution of ammonium thiocyanate (0.159 g, 2.0 mmol, 2 mL), sodium benzoate (0.288 g, 2.0 mmol, 4 mL), or sodium azide (0.130 g, 2.0 mmol, 2 mL) for 1, 2, and 3, respectively. In all cases, green microcrystalline products started to separate rapidly. The stirring was continued for 1 h, and then the solid compound was collected by filtration, washed with methanol, and dried in a vacuum desiccator containing anhydrous CaCl₂. The filtrate was allowed to stand overnight at room temperature, and single crystals of X-ray quality appeared at the bottom of the vessel of each solution. The crystals were washed with a methanol-water mixture, dried in a desiccator containing anhydrous CaCl₂, and subsequently characterized by elemental analysis, spectroscopic methods, and X-ray diffraction.

Complex 1: Yield 0.561 g, 65%. $C_{36}H_{32}CoCu_2N_6O_4S_2$ (862.81): calcd. C 50.11, H 3.74, N 9.74; found C 50.34, H 3.87, N 9.54. UV/Vis: λ_{max} (MeOH, absorbance) = 596, 360, 274 nm; λ_{max} (solid, reflectance) = 1310, 867, 619, 356 nm. IR: $\tilde{v} = 2044$ [v(N=C=S⁻)], 1619 [v(C=N)] cm⁻¹.

Complex 2: Yield 0.613 g, 62%. $C_{48}H_{42}CoCu_2N_4O_8$ (988.89): calcd. C 58.30, H 4.28, N 5.67; found C 58.46, H 4.12, N 5.85. UV/Vis: λ_{max} (MeOH, absorbance) = 598, 360, 274 nm; λ_{max} (solid, reflectance) = 1290, 617, 356 nm. IR: \tilde{v} = 1598, 1561 [$v_{s+as}(COO^{-})$], [1624 v(C=N)] cm⁻¹.

Complex 3: Yield 0.573 g, 69%. $C_{34}H_{32}CoCu_2N_{10}O_4$ (830.73): calcd. C 49.16, H 3.88, N 16.86; found C 49.25, H 4.05, N 16.98. UV/Vis: λ_{max} (MeOH, absorbance) = 593, 360, 274 nm; λ_{max} (solid, reflectance) = 1281, 609, 356 nm. IR: $\tilde{v} = 2062 [v(N_3^{-})]$, 1613 $[v(C=N)] \text{ cm}^{-1}$.

Physical Measurements: Elemental analyses (C, H, and N) were performed by using a Perkin–Elmer 2400 series II CHN analyzer. IR spectra (4000–500 cm⁻¹) of samples as KBr pellets were recorded by using a Perkin–Elmer RXI FTIR spectrophotometer. All solutions were prepared with spectroscopic grade solvents. Electronic spectra were recorded with samples in methanol (800–200 nm) in a 1 cm optical glass cuvette as well as in the solid state (1400–300 nm) with a Hitachi U-3501 spectrophotometer. The variable-temperature magnetic susceptibility data of crystalline samples of 1–3 were collected with a Quantum Design superconducting quantum interference device (SQUID) magnetometer at the Serveis Cientificotècnics of the Universitat de Barcelona. Pascal's constants were used to estimate diamagnetic corrections to the molar paramagnetic susceptibility, and a correction was applied for the sample holder.

Crystallographic Data Collection and Refinement: Suitable single crystals of each of the three complexes were mounted in a Bruker AXS SMART APEX II diffractometer equipped with a graphite monochromator and Mo- K_{α} ($\lambda = 0.71073$ Å) radiation. The crystals were positioned 60 mm from the CCD. 360 frames were measured with a counting time of 5 s. The structures were solved by

the Patterson method by using SHELXS 97. Subsequent difference Fourier syntheses and least-squares refinements revealed the positions of the remaining non-hydrogen atoms, which were refined with independent anisotropic displacement parameters. However, for 1, the disordered carbon atom C(26) was refined isotropically. Hydrogen atoms were placed in idealized positions, and their displacement parameters were fixed to be 1.2 times those of the attached non-hydrogen atom. Successful convergence was indicated by maximum shift/errors of 0.001 for the last cycle of the leastsquares refinement. Owing to the intrinsic nature of the crystal, the data for 2 were not ideal. Absorption corrections were applied by using the SADABS program.^[31] All calculations were performed by using SHELXS 97,^[32] SHELXL 97,^[33] PLATON 99,^[34] OR-TEP-32,^[35] and WinGX system version1.64.^[36] The data collection and structure refinement parameters and crystallographic data for the three complexes are given in Table 4.

Table 4. Parameters for data collection and structure refinement for 1-3.

	1	2	3
Formula	C ₃₆ H ₃₂ N ₆ O ₄ -	C48H42N4O8-	C ₃₄ H ₃₂ N ₁₀ O ₄ -
	S ₂ Cu ₂ Co	Cu ₂ Co	Cu ₂ Co
Formula weight	862.81	988.89	830.73
Space group	monoclinic	monoclinic	monoclinic
Crystal system	$P2_1/c$	C2/c	$P2_1/c$
a /Å	12.267(5)	25.577(5)	9.366(5)
b /Å	10.089(5)	10.524(5)	11.135(5)
<i>c</i> /Å	28.578(5)	17.594(5)	16.009(5)
β /°	101.597(5)	96.308(5)	102.556(5)
$V/Å^3$	3465(2)	4707(3)	1629.7(12)
Ζ	4	4	2
$D_{\rm calcd.}/{\rm gcm^{-3}}$	1.654	1.395	1.693
μ /mm ⁻¹	1.861	1.299	1.854
F(000)	1756	2028	846
R _{int}	0.0267	0.1425	0.0269
θ range /°	1.5-25.3	1.6-25.1	2.3-25.3
Total reflections	23596	21680	11159
Unique reflections	6237	4200	2918
Data with $I > 2\sigma(I)$	5328	2858	2402
R_1 on $I > 2\sigma(I)$	0.0290	0.0912	0.0290
$wR_2 [I > 2\sigma(I)]$	0.0710	0.2581	0.0723
GOF on F^2	1.020	1.138	1.025
Temperature /K	293	293	293

CCDC-988253 (for 1), -988254 (for 2), and -988255 (for 3) contain 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.

Supporting Information (see footnote on the first page of this article): Electronic absorption and reflectance spectra of the complexes, schematic differences between 2 and 3, plot of -J vs. Cu–O–Co angle, average Cu–O and Co–O bond lengths in 1–3, plot of -J vs. average Cu–O and Co–O bond lengths in the complexes listed in Table 3.

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Magnetic Properties

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The Impact of Anion-Modulated Structural Variations on the Magnetic Coupling in Trinuclear Heterometallic Cu^{II}–Co^{II} Complexes Derived from a Salen-Type Schiff Base Ligand

Keywords: Metalloligands / Copper / Cobalt / Bridging ligands / Schiff bases / Magnetic properties / Magnetostructural correlations



Anion-mediated geometrical variations generate three heterometallic complexes with distinct trinuclear Cu_2Co cores as a result of different diphenoxido bridging angles between the Cu^{II} and Co^{II} ions. Magnetic studies reveal decreased antiferromagnetic exchange interactions associated with a decrease of this bridging angle.