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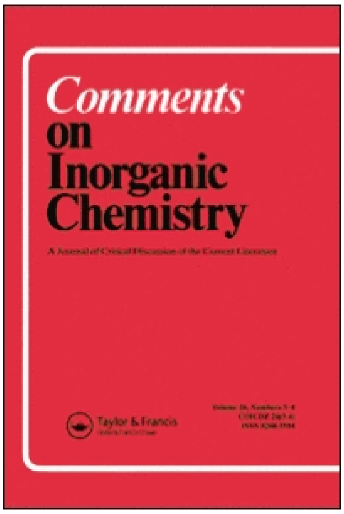

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Azide Bridged Dicopper and Dinickel Complexes: Structure and Magnetism

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Azide Bridged Dicopper and Dinickel Complexes: Structure and Magnetism

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The quest for coordination complexes with novel magnetic properties, which may have potentially useful applications in materials science, has focussed attention on superexchange bridges with the ability to propagate ferromagnetic coupling between paramagnetic transition metal centers. The flexi-dentate azide ligand can bridge two metal centers in two ways, in the μ_2-1,1- or μ_2-1,3- fashion. In the 1,3-mode superexchange is exclusively antiferromagnetic in nature, whereas in the 1,1-mode the magnetic role of the azide bridge depends in large measure on the angle it subtends at the two metal centers. For dicopper(II) systems with small angles (<108°) ferromagnetic coupling dominates, while at larger angles the azide has been shown to propagate antiferromagnetic exchange. Control of the molecular dimensions, which in turn can influence the geometry at the azide, can lead to control of the magnetic properties. Examples of dicopper(II) and dinickel(II) complexes illustrating the ferromagnetic and antiferromagnetic realms of the azide bridge will be discussed, in addition to the design features of the dinucleating ligands required to bring the two metal centers into juxtaposition in a controlled fashion.

Key Words: *ferromagnetism, antiferromagnetism, magnetic exchange, azide, copper, nickel*

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INTRODUCTION

Simple anionic ligands, e.g., hydroxide, can bridge two transition metal centers (e.g., Cu(II) ions) without the constraining influence of a primary dinucleating ligand, which would normally bring the two metal centers into juxtaposition. The classic dihydroxo-bridged copper(II) systems discussed by Hatfield[1] have provided an excellent example of this situation, and the resulting magnetostructural correlation demonstrated in an elegant way the role of the bridge, and in particular the Cu–OH–Cu angle, in controlling the exchange process. The bridge angles ranged from 95.6° to 104.1°, and the magnetic properties changed from ferromagnetic at angles <97.5° to antiferromagnetic at larger angles. The angle subtended at a bridging group connecting two metal centers depends on the distance of separation of the metals, which in turn is controlled in large measure by the geometrical properties of the primary dinucleating ligand. However, in the Hatfield systems it is not clear that the terminal, bidentate N_2 ligands had any significant primary influence on geometry, and in large measure the resulting complexes were produced by chance.

In this Comment we examine the magnetic role of the azide bridge, in particular the μ_2-1,1-azide, in a variety of dicopper(II) and dinickel(II) complexes. Geometrical control of the dinuclear center dimensions, by the selective use of a primary dinucleating ligand, and hence control over the magnetic properties of the system will be discussed. In contrast, in previous literature examples, particularly those involving μ_2-1,1-azides, such control of the geometry of the dinuclear center was left largely to nature to decide. Early studies in the area of dicopper(II) azide complexes[2–4] focussed on the remarkable property of the μ_2-1,1-azide to generate ferromagnetic systems, with Cu–N_3–Cu angles in the range 95.7–105.5°, and antiferromagnetic complexes with the azide bridging in the μ_2-1,3-mode. Although only three complexes were discussed, the ability of the μ_2-1,1-azide to cause ferromagnetic exchange was attributed to a *spin polarization* effect involving an interaction between the two copper d_{xy} metallic orbitals and the π_g MO on the azide.[3] The rationale for this explanation rested with the fact that in this angle range the splitting between the two molecular orbitals constructed from the d_{xy} magnetic orbitals in the triplet state, and appropriate symmetry orbitals on the bridging ligands (Δ), according to extended Hückel calculations,[2] was considered to be very weak, and so any antiferromagnetic contribution would be unlikely to compensate any inherent ferromagnetic term, leading to systems that would always be ferromagnetic. The net exchange for a system with the two spin levels thermally populated at room temperature can be expressed as

$$J = J_{AF} + J_F, \quad J_{AF} = -2\Delta S, \quad J_F = 2C \qquad (1)$$

where S is the overlap integral and C the two-electron exchange integral.[3]

The antiferromagnetic realm for the μ_2-1,1-azide bridge remained elusive for a number of years, and examples of small angle ferromagnetic systems were attributed to the *spin polarization* effect. Our recent studies with dinucleating N_4 diazine ligands (pyridazines, phthalazines, thiadiazoles) have shown that by using variable ligand "bite size", which involves a combination of chelate ring size and diazine ring size effects, a very large range of azide bridge angles can be generated (98.3–124.1°), and that antiferromagnetic μ_2-1,1-azide bridged dicopper complexes can be produced, some with very strong coupling ($-2J > 900$ cm^{-1}),[5,6] in which the azide bridge has entered an antiferromagnetic realm.

Readers may wish to consult the Table of Chemical Abbreviations in the Appendix.

DICOPPER(II) AND DINICKEL(II) COMPLEXES WITH μ_2-1,1- AND μ_2-1,3-AZIDE BRIDGES

1. 1,1- or 1,3-Azide Bridges?

The ability of the azide ligand to function in two bridging environments, via two nitrogen atoms at the extremities of the ion (μ_2-1,3-N_3; Fig. 1a) or via a single nitrogen atom (μ_2-1,1-N_3; Fig. 1b) creates an ideal opportunity to exploit the magnetic properties of these two bridging modes, if appropriate geometrical constraints can be brought to bear in a dinuclear complex. However, without some restraining geometrical influence on the part of a primary bridging ligand (B, Fig. 1c,d), the role of the azide is largely left to the whims of nature. The complex [Cu_2(24-ane-N_2S_4)(μ_2-1,3-N_3)$_2$(N_3)$_2$] contains a large 24-membered macrocyclic N_2S_4 ligand, which creates a large cavity within which two μ_2-1,3-azide bridges link two d_{xy} ground state copper(II) centers equatorially, with a Cu–Cu separation of 5.145(1) Å (Fig. 1a). Variable temperature magnetism indicates very strong antiferromagnetic coupling, with essentially diamagnetic behaviour in the range 1.9–390 K.[7] In another example involving a related

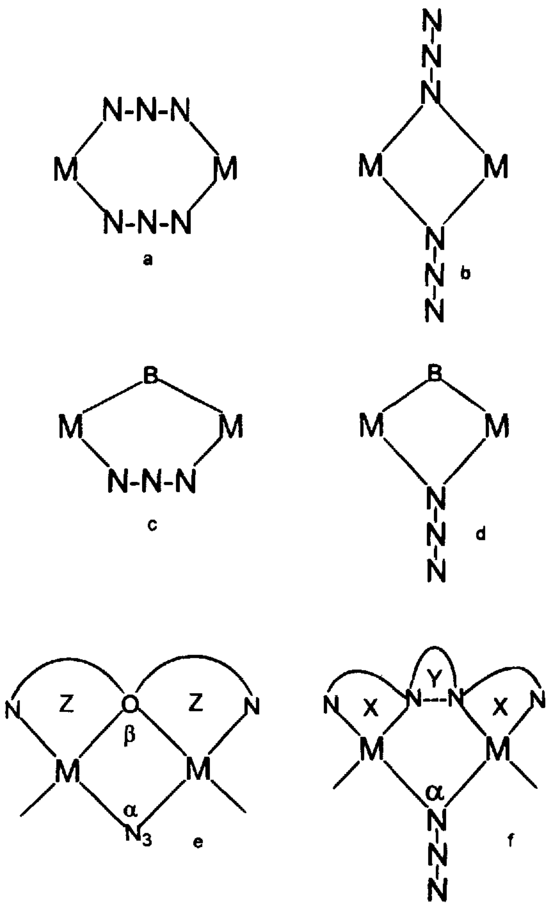

FIGURE 1 Azide bridging modes and the geometrical influence of primary dinucleating ligands.

24-membered N_6 macrocyclic ligand, $[Cu_2(24\text{-ane-}N_2O_6)(\mu_2\text{-}1,1\text{-}N_3)_2(N_3)_2]$, the two d_{xy} ground state copper centers are bridged equatorially by two μ_2-1,1-azides (Fig. 1b), with a Cu–Cu separation of 3.162 Å. This compound exhibits strong ferromagnetic coupling ($2J = 70 \pm 20$ cm^{-1}).[2] It is not clear from the structures of these two compounds why two such dramatically different azide bonding modes can occur, given the similarity in the ligand structural constraints. The complex

$[Cu_2(Me_5dien)_2(\mu_2\text{-}1,3\text{-}N_3)_2](BPh_4)_2$ also has a large Cu–Cu separation (5.2276(7) Å), but with a different bridging arrangement in which two μ_2-1,3-azides connect the two $d_{x^2-y^2}$ copper centers via alternating axial and equatorial contacts. This resulting orthogonal bonding situation leads to very weak net antiferromagnetism ($-2J = 13\ cm^{-1}$).[8]

Examples of dinuclear nickel complexes exist with both μ_2-1,3- and μ_2-1,1-azide bridges, and are not dependent on the primary influence of a specific dinucleating ligand. The complex $[Ni_2(tren)_2(\mu_2\text{-}1,3\text{-}N_3)_2](BPh_4)_2$ contains a tetradentate ligand which occupies four contiguous coordination sites around each nickel center, leaving two cis-coordination sites per metal available for exogenous ligand bonding. This results in an asymmetric bridging arrangement of two 1,3-azide bridges, with a large (5.220(2) Å) Ni–Ni separation, and as expected the complex exhibits strong antiferromagnetic coupling ($J = -35.1\ cm^{-1}$).[9] In a related system with three μ_2-1,3-azide bridges, $[LNi(\mu_2\text{-}1,3\text{-}N_3)_3NiL](ClO_4)$ (L = N, N′, N″-trimethyl-1,4,7-triazacyclononane), much stronger exchange was observed ($J = -71\ cm^{-1}$).[10]

Other dinickel complexes with non-bridging, primary tridentate and tetradentate ligands produce μ_2-1,1-azide bridged complexes, but these ligands appear to have little control over the reaction outcome in terms of how the azide bonds. The complex $[Ni(en)_2(\mu_2\text{-}1,1\text{-}N_3)]_2(ClO_4)_2$ has a six-coordinate structure with a much smaller metal–metal separation (3.369(1) Å), leading to the formation of a 1,1-azide bridge with an azide bridge angle of 104.3(2)°. Ferromagnetic coupling was observed, in agreement with the dicopper cases of comparable dimensions ($J = 21.7\ cm^{-1}$).[11] Other similar examples include $[Ni(terpy)(\mu_2\text{-}1,1\text{-}N_3)(N_3)]_2.2H_2O$ (Ni–Ni 3.276(1) Å; Ni–N_3–Ni 101.3(3)°; $J = 20.1\ cm^{-1}$),[12] $[Ni(pepci)(\mu_2\text{-}1,1\text{-}N_3)(N_3)]_2$ (Ni–Ni 3.297(1) Å; Ni–N_3–Ni 101.0(2)°, 102.2(2)°; $J = 36.3\ cm^{-1}$),[13] $[Ni(Me_3[12]N_3)(\mu_2\text{-}1,1\text{-}N_3)]_2(ClO_4)_2.2H_2O$ ($Me_3[12]N_3$ = 2,4,4-trimethyl-1,5,9-triazacyclodec-1-ene) (Ni–Ni 3.273(1) Å; Ni–N_3–Ni 103.8(3)°; $J = 43.9\ cm^{-1}$),[14] and $[Ni(232\text{-}N_4)(\mu_2\text{-}1,1\text{-}N_3)]_2(ClO_4)_2$ (232-N_4 = N,N′-bis(2-aminoethyl)-1,3-propanediamine) (Ni–Ni 3.434(1) Å; Ni–N_3–Ni 104.9(2)°; $J = 33.8\ cm^{-1}$).[14]

2. The Geometrical Influence of a *Primary* Bridging Ligand

When azide is the only bridge it is clear that its role cannot be influenced to any significant extent by terminal, non-bridging ligands. However, with a variable primary ligand bridge (B; Fig. 1c,d), not only can the role of the azide be controlled (i.e., 1,1- or 1,3-bridging), but by virtue of the size and bite of B significant control can be exerted over the angle at the 1,1-azide bridge (Fig. 1d,e), resulting in the ability to "tune" magnetic properties and, in the case of ligands with appropriate bite, to specifically generate systems in which the 1,1-azide propagates ferromagnetic exchange. If B can be engineered to provide a large (>≈ 3.5 Å) separation between the metal centers, a 1,3-azide will fit nicely, but a 1,1-azide will not. Conversely, if B creates a smaller metal–metal separation (≈3.0–3.4 Å), the 1,1-azide will fit, but the 1,3-azide will not.

Hemocyanin model studies provided an opportunity for the creation of novel dinuclear copper(II) complexes with Cu–Cu separations in the range 3–3.6 Å, and the early target ligands were based on alkoxide or phenoxide derivatives, in which a single oxygen center coordinated the two copper(II) ions in a dinuclear arrangement.[15,16] With ligands derived from 1,3-diamino-2-hydroxypropane[15] and 2,6-diamino-p-cresol[16] azide bridged models were synthesized for metazidohemocyanin (metHc(N_3)) and were found to contain 1,3-azide bridges with Cu–Cu separations >3.5 Å (Fig. 1e; $Z = 5$). Very strong antiferromagnetic coupling typified this bridging mode and also suggested a similar bonding situation in metHc(N_3) itself.

If the distance of separation between the metals is reduced by increasing the chelate ring size (Fig. 1e; $Z = 6$) in, e.g., 2,6-diaminomethylphenol derivatives, the role of the azide bridge switches to 1,1-bonding. In the complex $[Cu_2(L)(\mu_2\text{-}1,1\text{-}N_3)](PF_6)_2$ (L = 2,6-bis-(bis-(2-pyridylethyl)aminomethyl)phenol),[17] containing distorted square-pyramidal copper(II) centers, the Cu–N_3–Cu angle (103.6(5)°[α]) and the Cu–O(Ph)–Cu angle (107.9(3)°[β]) place these bridges in opposing magnetic realms. The phenoxide bridge would be expected to propagate strong antiferromagnetic coupling,[18] while the small azide bridge angle would implicate ferromagnetic exchange. The measured exchange is in fact antiferromagnetic ($-2J = 440$ cm^{-1}), but the coupling constant ($-2J$) is much smaller than expected, in keeping with a ferromagnetic azide contribution.[19] Other comparable examples[19–23] with identical combinations of μ_2-1,1-azide and phenoxide with Cu–N_3–Cu angles in the range 99.7–106.1°[α] and Cu–O(Ph)–Cu angles in the range 98.4–106.0°[β] all exhibit net antiferromagnetic exchange with small $-2J$ values in the range 86.5–428 cm^{-1}. Reduced antiferromagnetism in all cases is again evidence of ferromagnetic contributions associated with azide bridge angles in this range.[19]

3. Influencing the Dinuclear Center Dimensions

Tetradentate N_4 ligands based on a dinucleating diazine fragment, e.g., pyridazine, phthalazine, thiadiazole, etc. (Fig. 1f, Fig. 2), can be synthesized with variable diazine ring size ($Y = 5,6$) and chelate ring size ($X = 5,6,7$). As both X and Y change in size the resulting geometric constraints would reasonably allow a systematic variation in α, the μ_2-1,1-N_3 bridge angle. Also, because of the angles subtended by the M–N (diazine) bonds, it is impossible for the azide to bridge successfully in the 1,3-mode. A series of typical N_4 diazine ligands is shown in Figs. 2a,b, and ligands of this sort have been used successfully to generate a series of five-coordinate, square-pyramidal hydroxo-bridged dicopper(II) complexes, with a very large bridge angle range 100.1–126.3° (Fig. 2b; C=OH).[24] With 6,6,6 (X,Y,X) ligands, e.g., PAPR (Fig. 2a), Cu–OH–Cu angles varied from 100.1 to 111.6°, with small, single atom axial bridge groups (Fig. 2b; D = Cl, Br) (Cu–Cu <3.15 Å). Replacing D with bidentate bridging anions, e.g., NO_3, SO_4, IO_3, e.g., in the complex $[Cu_2(PAPH)(\mu_2$-$OH)Cl(\mu_2$-

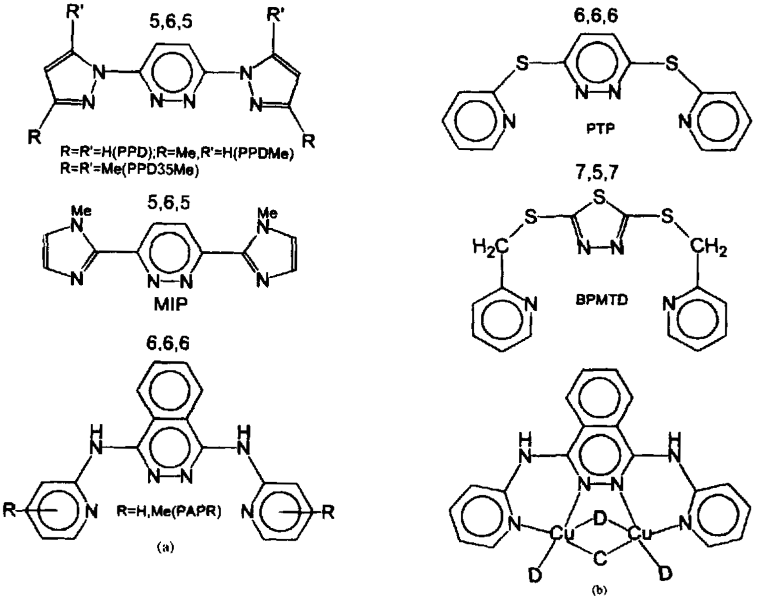

FIGURE 2 Tetradentate N_4 diazine ligands.

SO_4)].$2H_2O$, leads to a significant increase in the dinuclear center dimensions, as a result of the triatomic bridging groups forcing the metal centers apart. Cu–Cu separations are found in the range 3.13–3.21 Å, with Cu–OH–Cu angles in the range 113.7–115.5°. Using 5,6,5 ligands, e.g., PPD, PPDMe, MIP (Fig. 2a), caused a marked expansion of the dinuclear centers, too much to allow the formation of an axial bridge, and very large Cu–Cu separations (3.3–3.45 Å) and Cu–OH–Cu angles (116.4–126.3°) were observed, e.g., in the complex $[Cu_2(MIP)(\mu_2\text{-}OH)Cl_3(H_2O)].H_2O$ (Cu–OH–Cu 126.3°).[24] A magnetostructural correlation revealed a gradual increase in antiferromagnetic exchange ($-2J = 190\text{–}1300\ cm^{-1}$) over the range of hydroxide bridge angles studied, and a linear relationship between exchange integral and bridge angle in the range 100–116°,[24] associated primarily with the varying Cu–OH–Cu angle. This was entirely consistent with the correlation described by Hatfield for the dihydroxo-bridged dicopper(II) complexes.[1]

4. Antiferromagnetic μ_2-1,1-azide Complexes

The same geometrical consequences resulted when the bridging hydroxide was replaced by 1,1-azide, either by simple metathesis reactions or by adding azide to a solution of the appropriate ligand and metal salt. With 6,6,6 PAPR ligands, complexes containing the $[Cu_2(L)(\mu_2\text{-}1,1\text{-}N_3)]$ core are obtained, with Cu–Cu separations in the range 3.16–3.22 Å and Cu–N_3–Cu angles in the range 107.9–111.7°.[5,6] Structures of the complexes $[Cu_2(PAPH)(\mu_2\text{-}1,1\text{-}N_3)Cl_3].CH_2Cl_2$ (**1**) (Cu–N_3–Cu 107.9(2)°), $[Cu_4(PAPH)_2(\mu_2\text{-}1,1\text{-}N_3)_2(\mu_2\text{-}1,3\text{-}N_3)_2(\mu_2\text{-}CH_3OH)_2(N_3)_4]$[25] (**2**) (Cu–$N_3$–Cu 107.9(5)°) and $[Cu_2(PAP6Me)(\mu_2\text{-}1,1\text{-}N_3)(\mu_2\text{-}H_2O)(NO_3)_2]NO_3.0.75\ CH_3OH$ (**3**) (Cu–N_3–Cu 111.7(5)°) are illustrated in Figs. 3, 4 and 5, respectively. In some cases weak axial bridge groups exist (e.g., H_2O in **3**). For **2** a weakly bound axial methanol bridges the two copper centers in addition to the diazine and azide bridges, but another pair of μ_2-1,3-azides bridge two dinuclear units in a most unusual structure to form a tetranuclear cluster.[25] In this complex the intermolecular 1,3-azide bridges and the methanol bridges link the copper pairs via axial interactions (orthogonal to the magnetic plane), and so do not contribute to antiferromagnetic exchange. In all cases these complexes exhibit variable temperature magnetism which is consistent with net antiferromagnetic exchange, with maxima in the susceptibility/temperature plots at 30 K (**1**), 80 K (**2**) and 240 K (**3**). While the variable temperature magnetic data for **3** could be fitted to the Bleaney–Bowers equation[26] ($g = 2.10(8)$,

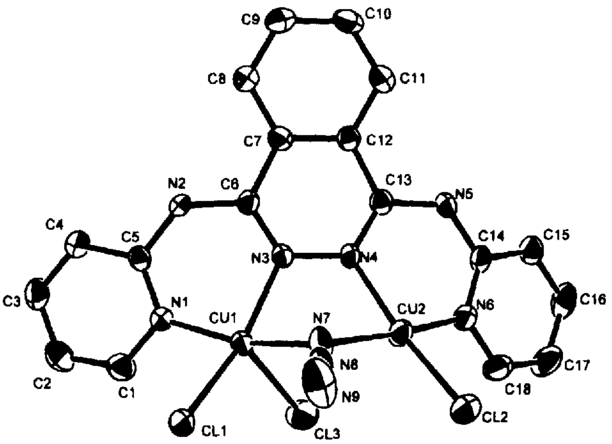

FIGURE 3 Structural representation of $[Cu_2(PAP)(\mu_2\text{-}1,1\text{-}N_3)Cl_3].CH_2Cl_2$ (**1**).

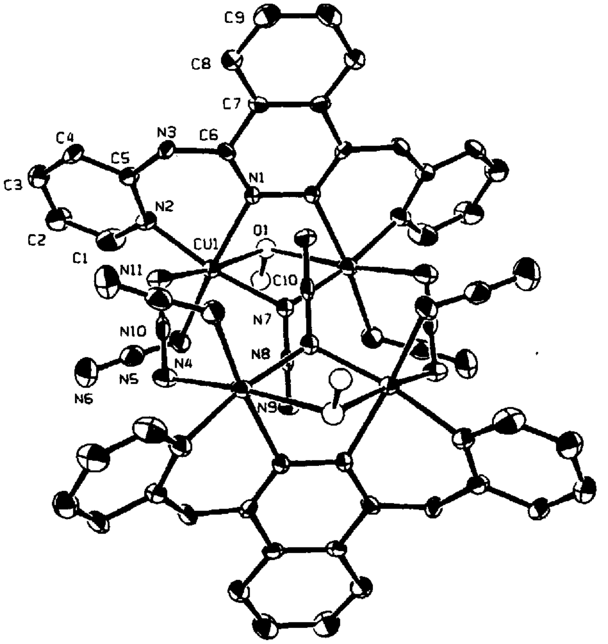

FIGURE 4 Structural representation of $[Cu_4(PAP)_2(\mu_2\text{-}1,1\text{-}N_3)_2(\mu_2\text{-}1,3\text{-}N_3)_2(\mu_2\text{-}CH_3OH)_2(N_3)_4]$ (**2**).

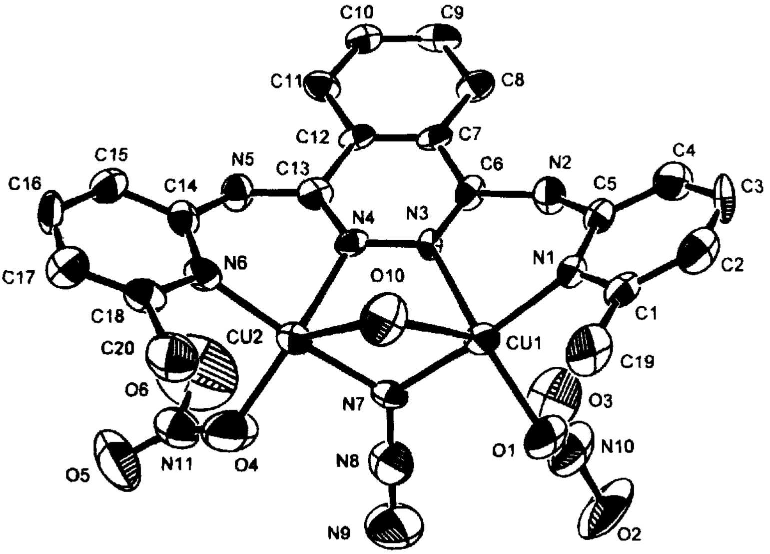

FIGURE 5 Structural representation of $[Cu_2(PAP6Me)(\mu_2\text{-}1,1\text{-}N_3)(\mu_2\text{-}H_2O)(NO_3)_2](NO_3).0.75CH_3OH$ (3).

$-2J = 234(10)\ cm^{-1}$),[6] a poor data fit was obtained. However, no sensible data fit could be obtained for **1** and **2** (see Section 5).

The 5,6,5 ligands PPD, PPDMe, PPD35Me (Fig. 2a) form dinuclear 1,1-azide bridged complexes with much larger dinuclear centers (Cu–Cu 3.40–3.51 Å; $Cu\text{-}N_3\text{-}Cu$ angles 119.8–124.1°). The angle of 124.1° found in the complex $[Cu_2(PPDMe)(\mu_2\text{-}1,1\text{-}N_3)Cl_3(H_2O)_{1.5}]$[5] (4) (Fig. 6) is the largest known angle for a 1,1-azide bridge, and clearly results from the geometrical consequences of the ligand itself. The two $d_{x^2-y^2}$ copper centers are bridged in an essentially flat structure by just the pyridazine and the 1,1-azide with a Cu–Cu separation of 3.510(1) Å. This complex exhibits very strong net antiferromagnetic exchange ($-2J = 778(6)\ cm^{-1}$). Examples of dicopper(II) complexes containing just pyridazine bridges are rare, but in the planar complex $[Cu_2(L)_2(ClO_4)_2(H_2O)_2]$ (L = pyridazine-3,6-dicarbaldehyde dioxime), in plane coordination of two bridging pyridazines to two $d_{x^2-y^2}$ ground state copper(II) centers generates quite strong antiferromagnetic coupling ($-2J = 536\ cm^{-1}$).[27] The Cu–Cu separation is very large (3.760(2) Å), and the Cu–N–N (pyridazine) angles are on average 127.1°. The complex

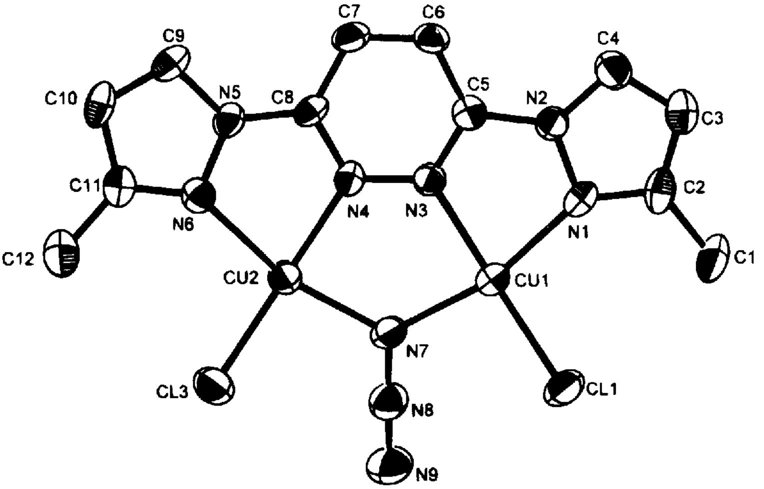

FIGURE 6 Structural representation of $[Cu_2(PPDMe)(\mu_2\text{-}1,1\text{-}N_3)Cl_3(H_2O)_{1.5}]$ (4) (disordered axial chlorine/water omitted).

$[Cu_2(PTP)Cl_4]$(PTP = 3,6-bis-(2′-pyridylthio)pyridazine; Fig. 2b) contains two square-pyramidal copper(II) centers bridged equatorially by *one* pyridazine, but axially by two chlorines in an axial/equatorial orthogonal arrangement. The experimentally observed exchange integral ($-2J = 131$ cm^{-1}) can, therefore, be assigned to the pyridazine bridge.[28] The Cu–Cu separation is 3.198(1) Å, with Cu–N–N$_{\text{(pyridazine)}}$ angles of 116.0(5)° and 118.0(5)°. **4** has comparable Cu–N–N$_{\text{(pyridazine)}}$ angles (ave. 116.4°) and only *one* pyridazine bridge, and so although the pyridazine bridge in **4** would be expected to provide an antiferromagnetic contribution, it is expected to be small and is clearly acting in a complementary manner to the antiferromagnetic azide. Other examples of similar antiferromagnetic complexes include $[Cu_2(PPD35Me)(\mu_2\text{-}1,1\text{-}N_3)Br_3(CH_3OH)]$[6] (**5**) (Cu–Cu 3.487(2) Å; Cu–N$_3$–Cu 122.5(5)°; $-2J = 921(9)$ cm^{-1}) (Fig. 7) and $[Cu_2(PPD)(\mu_2\text{-}1,1\text{-}N_3)(N_3)_2(ClO_4)]$[29] (**6**) (Cu–Cu 3.409(2) Å; Cu–N$_3$–Cu 123.2(2)°; $-2J = 829(11)$ cm^{-1} (Fig. 8). Cu–N–N (pyridazine) angles (122.35°$_{\text{ave.}}$ (**5**); 122.15°$_{\text{ave.}}$ (**6**)) for these compounds are comparable with **4**, again indicating a very significant antiferromagnetic azide contribution to total exchange. $-2J$ values for this class of compounds fall in the range 468–1100 cm^{-1}, placing these azide complexes in a magnetic realm comparable with that of the hydroxide complexes.[5,6,24] A plot of ex-

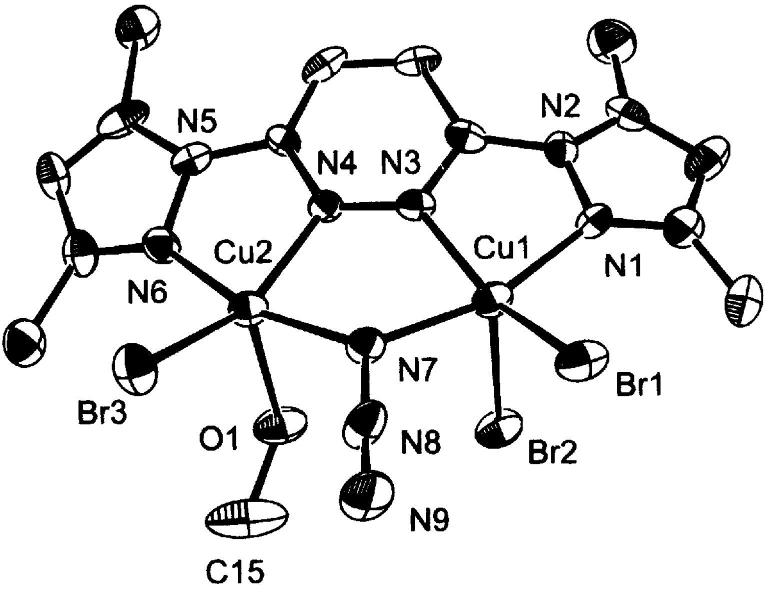

FIGURE 7 Structural representation of [Cu_2(PPD35Me)(μ_2-1,1-N_3)Br_3(CH_3OH)] (5).

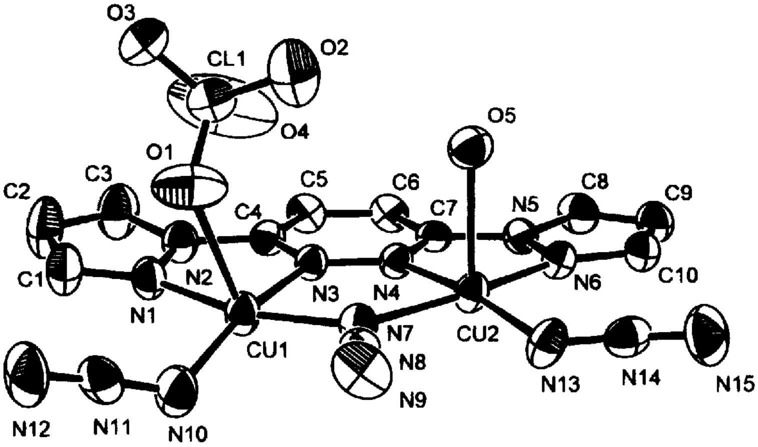

FIGURE 8 Structural representation of [Cu_2(PPD)(μ_2-1,1-N_3)(N_3)$_2$(ClO_4)] (6).

perimental (χ_m vs. Temp.) data for **5** and the theoretical line for $g = 2.21(2)$, $-2J = 921(9)$ cm^{-1}, TIP = 61 × 10^{-6} emu, $\theta = 1$ K and corrected for 0.41% paramagnetic impurity is shown in Fig. 9. A general observation is that for comparable bridge angles, $-2J$ values are slightly lower for the azide complexes than for similar hydroxide complexes.

5. Anomalous Magnetic Behavior at Cu–N3–Cu Bridge Angles Close to 108°

Some of the complexes with azide bridge angles close to 108°, e.g., **1** and **2**, have susceptibility versus temperature profiles with maxima in the range 30–80 K, but do not give acceptable fits to the Bleaney–Bowers equation[26] (Eq. (2), Fig. 9). These low $T_{\chi\max}$ values are clearly indicative of *small* net antiferromagnetic exchange terms, but are not considered to be the sum of two antagonistic exchange effects, since the presence of a ferromagnetic and a stronger antiferromagnetic exchange bridge in the same mol-

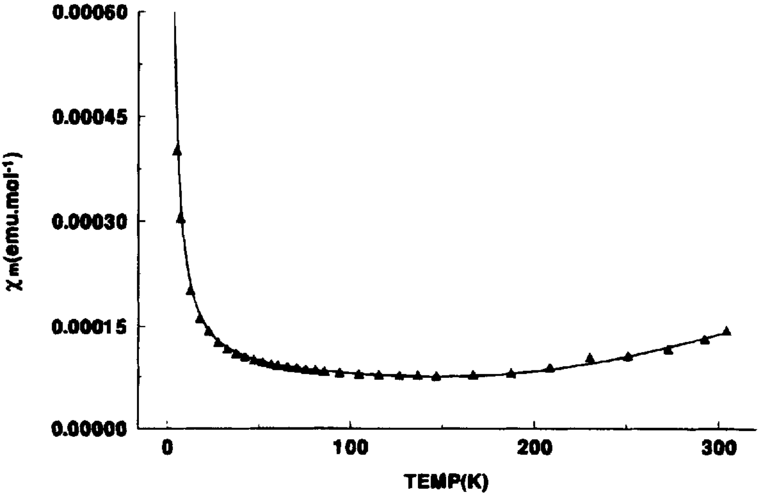

FIGURE 9 Variable temperature susceptibility data for **5**. The solid line was calculated from the Bleaney–Bowers equation (Eq. (2)) (Ref. 26) with $g = 2.21$ (2), $-2J = 921(9)$ cm^{-1},

$$\chi_m = \frac{N\beta^2 g^2}{3k(T-\theta)}[1 + 1/3\exp(-2J/kT)]^{-1}(1-\rho) + \frac{[N\beta^2 g^2]\rho}{4kT} + N\alpha \qquad (2)$$

TIP = 61 × 10^{-6} emu, $\theta = 1$ K (corrected for 0.41% paramagnetic impurity).

ecule would be expected to give net antiferromagnetism, and would be consistent with the Bleaney–Bowers equation.[19,26] Rather, the situation appears to be the result of a peculiar combination of two antiferromagnetic terms, one *quite small*, associated with the azide, and the other somewhat larger, associated with the diazine. The variable temperature susceptibility data are numerically suppressed, in some cases by as much as 50%, when compared with *normal* spin coupled dinuclear copper(II) systems with comparable $T_\chi$max values. Preliminary studies indicate that this may be due to a situation where, as a result of changing molecular dimensions, e.g., shrinkage of the unit cell and concomitant decrease in the azide bridge angle and copper–copper separation as temperature is lowered, the exchange integral ($-2J$) associated with the azide bridge decreases throughout the 300–4 K temperature range used. Successful data fits to the Bleaney–Bowers equation have been obtained for these compounds using both linear and curved expressions for $-2J$.[6,30]

6. Ferromagnetic μ_2-1,1-azide Complexes

To test the notion that at angles below ≈108° the azide might enter its ferromagnetic realm, in keeping with earlier studies, complexes of the 7,5,7 ligand BPMTD (Fig. 2b) were synthesized. The isostructural complexes $[Cu_2(BPMTD)(\mu_2\text{-}1,1\text{-}N_3)(\mu_2\text{-}X)X_2].CH_3CN$ (X = Cl(**7**), Br(**8**))[5] contain square-pyramidal copper(II) centers bridged equatorially by the thiadiazole and the azide and axially by the halogen. The structure of **7** is illustrated in Fig. 10. Cu–Cu distances (3.1215(7) Å (**7**), 3.138(3) Å (**8**)) are quite short, and Cu–N_3–Cu angles (105.9(1)° (**7**), 105.0(8)° (**8**)) are much smaller than those observed for complexes of the 6,6,6 ligands. Cu–N–N (thiadiazole) angles are quite small (<114°), and so the thiadiazole contribution to exchange might be expected to be small. Both complexes exhibit strong ferromagnetic coupling ($2J = 168(3)$ cm^{-1}(**7**), 118(3) cm^{-1}(**8**)), with excellent data fits to the Bleaney–Bowers equation. The complex $[Cu_2(BPMTD)(\mu_2\text{-}Cl)_2Cl_2]$ (**9**) (Fig. 11) has a square-pyramidal structure with an equatorial thiadiazole bridge and two chlorine bridges, which make alternating axial and equatorial contacts to each copper center, thus creating an orthogonal chlorine bridging network.[31] In other respects, dimensions in **9** are comparable to those in **7** and **8** (e.g., Cu–N–N_{ave} 114°). This complex exhibits weak antiferromagnetic coupling ($-2J = 59.3$ cm^{-1}), and so this exchange term can be assigned to the thiadiazole bridge itself. Therefore the ferromagnetic exchange term associated with the azide bridges in **7** and **8** is substantially larger than the actual measured values.[19]

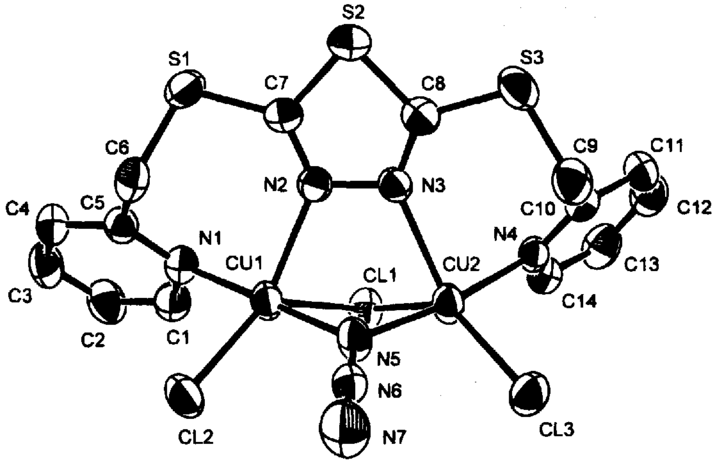

FIGURE 10 Structural representation of $[Cu_2(BPMTD)(\mu_2\text{-}1,1\text{-}N_3)(\mu_2\text{-}Cl)Cl_2].CH_3CN$ (**7**).

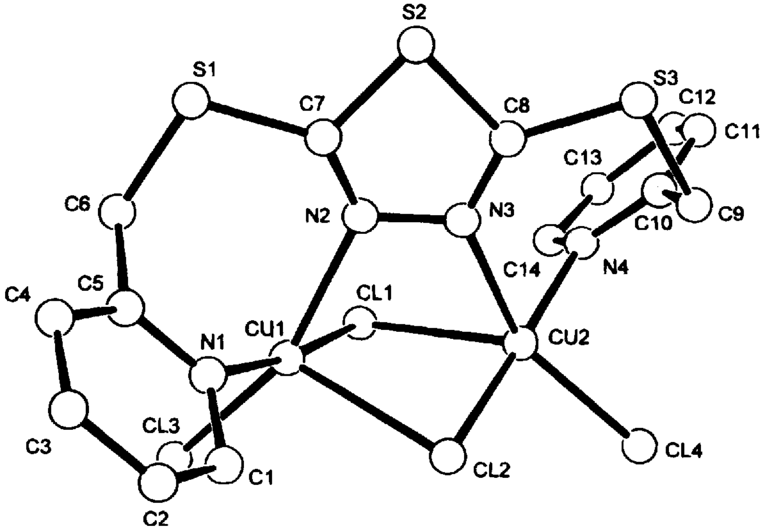

FIGURE 11 Structural representation of $[Cu_2(BPMTD)(\mu_2\text{-}Cl)_2Cl_2]$ (**9**).

The complex $[Cu_2(BPMTD)(\mu_2\text{-}1,1\text{-}N_3)_2(N_3)_2]$[5] **(11)** (Fig. 12) involves two 1,1-azide bridges and two terminal azides in an essentially square planar structure with two terminal pyridine nitrogens completing the square-plane. The axial thiadiazole lies above the copper planes with very long $Cu\text{–}N_{thiadiazole}$ contacts (2.538(8) Å, 2.680(8) Å) in complete contrast to **7** and **8**. The weakly bonding thiadiazole (seven-membered chelate ring) is displaced by the additional azides, and the complex adopts the more favored arrangement with the stronger azide ligands in the equatorial plane. The resulting short Cu–Cu separation (3.076(2) Å) and small $Cu\text{–}N_3\text{–}Cu$ angles (98.3(4)°, 101.8(4)°) are consistent with the bis μ_2-1,1-azide complexes reported earlier.[2,4] **11** is very strongly ferromagnetically coupled and a plot of experimental ($\chi_m \times T$ vs. Temp.) data and the theoretical line for $g = 2.146(1)$, $2J = 170(2)$ cm^{-1}, and TIP = $50*10^{-6}$ emu is shown in Fig. 13.

The μ_2-1,1-N_3 bridged dicopper(II) diazine complexes exhibit a similar magnetostructural correlation to the hydroxide bridged systems, with a reasonable straight line relationship between $2J$ and $Cu\text{–}N_3\text{–}Cu$ angle

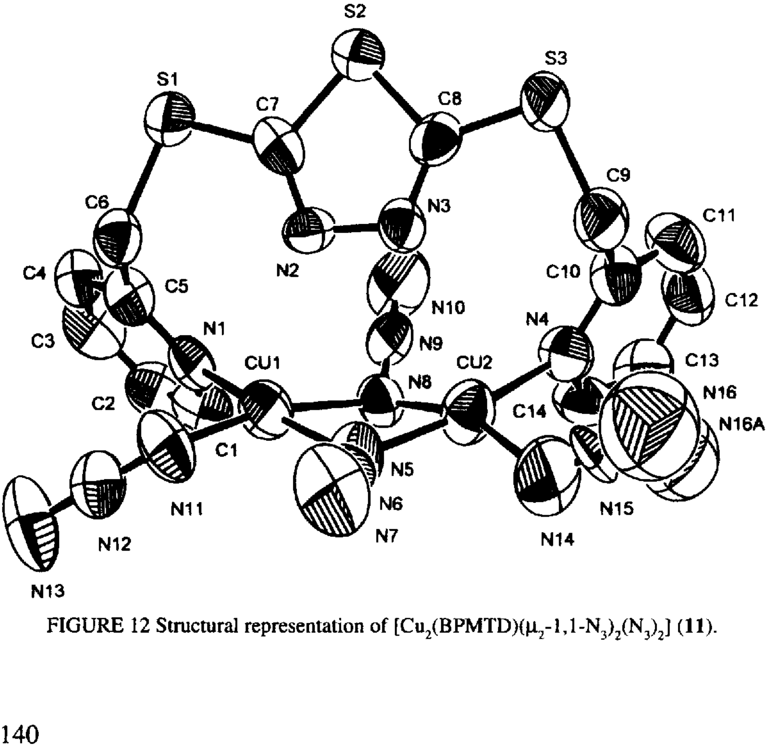

FIGURE 12 Structural representation of $[Cu_2(BPMTD)(\mu_2\text{-}1,1\text{-}N_3)_2(N_3)_2]$ (**11**).

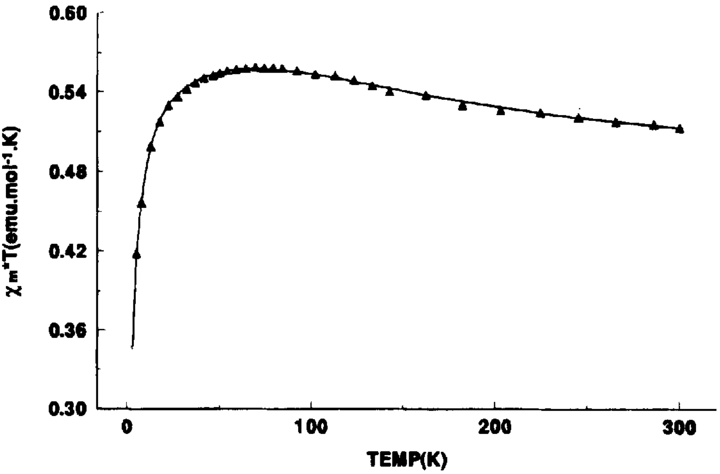

FIGURE 13 Variable temperature magnetic data ($\chi_m T$ vs. T) for (**11**). The solid line was calculated from the Bleaney–Bowers equation (Eq. (2)) with $g = 2.146(1)$, $2J = 170(2)\ \mathrm{cm}^{-1}$, TIP = 50×10^{-6} emu, $\rho = 0$, $\theta = 2$ K.

over an angle range of ≈ 125°. The experimental angle at which the μ_2-1,1-azide bridge changes its magnetic characteristics occurs at ≈ 108° in this series of complexes.[6] Given the fact that the experimental angle for crossover of magnetic behaviour for hydroxide (F ↔ AF) occurs at 97.5°,[1] whereas the calculated angle of accidental orthogonality is 92°, according to extended Hückel calculations,[2] this angle is entirely consistent with theory, which predicts the angle of accidental orthogonality for the μ_2-1,1-azide bridge to be 103°.[2]

CONCLUSIONS

The bridging azide ligand possesses special magnetic attributes, depending upon its mode of bonding, which can be influenced by exerting geometrical control over the dimensions of the dinuclear center. Left to itself, in the absence of the direction of a primary, dinucleating ligand, it forms either ferromagnetic 1,1- or antiferromagnetic 1,3-azide bridged dinickel complexes. Under similar circumstances with copper systems there appears to be a preference for ferromagnetic 1,1-bridged situations, but when the dinuclear center dimensions are enlarged sufficiently, by the external influence of a primary ligand, 1,3-bridging occurs and the systems are antiferromagnetic. A clear-cut demarcation in magnetic properties of these two bridging types persisted until the recent discovery that the 1,1-azide bridge angle could be controlled by the use of the bite and size of a primary dinucleating ligand, and the new antiferromagnetic realm of the 1,1-azide bridge in dicopper(II) chemistry was found to be accessible at bridge angles in the range 108–124.1°. Attempts to increase the bridge angle limit for the μ_2-1,1-azide by the use of, e.g., 5,5,5 ligands (Fig. 1) has so far not been successful, and 124.1° may be close to the maximum value. While extended Hückel calculations indicate that in the 1,1-azide bridge angle range 90–110° Δ is small,[2] so that J_{AF} may not predominate (Eq. (1)), beyond this range, at least for the 1,1-azide bridged dicopper(II) complexes of the N_4 diazine ligands, the azide acts as an antiferromagnetic bridge.

The question of an antiferromagnetic realm for the 1,1-azide bridge in dinickel(II) chemistry still remains. All cases with which we are familiar exhibit ferromagnetic coupling, with small bridge angles (<105°), and there are no examples where the constraining influence of a primary ligand has been used to control the bridging geometry and produce large bridge angles. Preliminary studies in our laboratory with the hexadentate dinucleating hydrazinophthalazone ligand PHP6Me (1,4-bis((6-methylpyridine-2-carboxaldimino)amino)phthalazine) show that the complex $[Ni_2(PHP6Me\text{-}H)(\mu_2\text{-}N_3)(N_3)_2(CH_3OH)_2]$[29] contains an azide bridge, and infrared studies suggest that it is a 1,1-azide bridge. This complex exhibits very strong antiferromagnetic coupling, with an unprecedented coupling constant ($J = 75.0(7)$ cm^{-1}) for a dinuclear nickel complex that appears to have just one azide bridge. We are actively exploring systems of this sort to document the antiferromagnetic realm of the μ_2-1,1-azide bridge in dinickel(II) chemistry and establish the angle at which magnetic crossover occurs in such systems.

APPENDIX

Exchange Hamiltonian

The isotropic exchange Hamiltonian for a dicopper(II) system is defined as $H = -2Js_1.s_2$, and exchange integrals are quoted accordingly. For nickel(II) systems, exchange integrals based on the same effective

Hamiltonian, adapted for single-ion zero-field splitting and interdimer exchange effects, are quoted, in as far as the references have allowed.

Table of Chemical Abbreviations

Me5dien	1,1,4,7,7-pentamethyldiethylenetriamine
tren	2,2′,2″-triaminotriethylamine
en	1,2-diaminoethane
bipy	2,2′-dipyridyl
terpy	2,2′:6,2″-terpyridine
pepci	N′-(2-pyridin-2-ylethyl)pyridine-2-carbaldimine

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