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Porphyrazines Peripherally Functionalized with Hybrid Ligands as Molecular Scaffolds for Bimetallic Metal-Ion Coordination

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We report the synthesis and physical characterization of a new family of peripherally functionalized porphyrazine (pz) compounds, denoted **1**[M[1], M[2]], where metal ion M[1] is incorporated into the pz core and metal ion M[2] is bound to a salicylidene/picolinamide "hybrid" chelate built onto two nitrogen atoms attached to the pz periphery. The complexes **1**[MnCl, Cu], **1**[VO, Cu], and **1**[Cu, Cu] have been prepared, and crystal structures show **1**[MnCl, Cu] and **1**[VO, Cu] to be isostructural. These complexes have been subjected to electron paramagnetic resonance and temperature-dependent magnetic susceptibility measurements. The variation of the ligand-mediated exchange splittings (Δ) in these complexes is striking: Δ/k_B values for **1**[MnCl, Cu] and **1**[VO, Cu] are 22 and 40 K, respectively, while Δ/k_B for **1**[Cu, Cu] is only 1 K. These coupling results are explained in terms of the relative orientation of the M[1] and M[2] orbitals and reflect the fact that the ligand set of M[2] in the periphery is rotated in-plane by 45° relative to the effectively coplanar pz ligand set of M[1]. The exchange couplings are essentially the same as those we determined for the Schiff base porphyrazines (pzs). Thus, the hybrid ligand has eliminated the dimerization found to occur when Cu(II) is bound to the periphery of bis(picolinamido) pzs and has created a more robust ligand system than the Schiff base pzs while retaining the ability they show to promote spin coupling between M[1] and M[2].

Introduction

Dimetallic systems are of great interest because of their applications in catalysis,[1,2] ligand mediated spin-coupling,[3] and biomimetic chemistry.[4] Their use to develop magneto-structural correlations for the interactions between metal ions further opens a way to ultrahigh-spin molecules.[5] Heterobimetallic compounds are especially important, as the types of interactions between two different metal ions within a molecular unit are much more diverse than those between like ions. However, the synthesis of heterobimetallic complexes is relatively more difficult than their homobimetallic counterparts, and most of them are synthesized with the "complex as ligand" approach.[6]

Recently we have shown that porphyrazines (pzs) can be used as convenient scaffolds on which to construct peripheral chelates, and this allows us to prepare heterobimetallic complexes that incorporate one metal ion in the porphyrazine (pz) core and bind another type of metal ion at the periphery. We first reported the synthesis of pzs with a peripherally appended Schiff base chelate[7−9] and subsequently with a bis(picolinamido) chelate.[10] Both systems exhibit spin coupling between core and peripherally bound metal ions. However, the peripheral ligands of the former system are not robust enough to permit binding of some metal ions, such as VO(II) and Fe(III), in the pz core. The latter chelate is much more stable, but the peripheral metalation is complicated in some cases by metal-ion-linked dimerization. We reasoned

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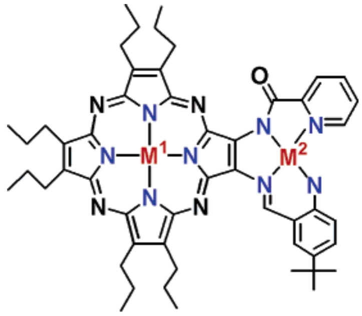
Chart 1



1[M^1, M^2]

that a hybrid of these two systems, which contains a salicylidene moiety and a picolinamide moiety (Chart 1), might combine the advantages of both systems, rather than their disadvantages. The mononuclear chelates of salicylidene/picolinamide hybrid ligands had been synthesized with metal ions such as VO(II), Mn(III), and Cu(II).[11−13] We here report that appending this chelate to the pz periphery indeed permits the synthesis of monomolecular, dimetallic complexes, **1**[M^1, M^2] (Chart 1). Compounds **1**[VO(II), Cu], **1**[Mn(III)Cl, Cu], and **1**[Cu(II), Cu(II)] have been synthesized and characterized, and the intramolecular metal−metal spin-coupling has been studied by electronic paramagnetic resonance (EPR) and temperature-dependent magnetic susceptibility measurements. We find that the coupling between VO(II) and Cu(II) and between Mn(III)Cl and Cu(II) is much stronger than that between Cu(II) and Cu(II), as with the Schiff base pzs, and this result again is explained by the relative orientation of the magnetic orbitals of the coupled metal ions.

Experimental Section

Materials and Methods. All starting materials were purchased from Aldrich Chemical and used as received, with the exception of picolinoyl chloride hydrochloride, which was purchased from TCI and used as received. All solvents were used as supplied. Chromatography was carried out on silica (eluants are given in parentheses). Compound pz **2**[Mg, Se] was prepared as previously reported.[14]

Electronic absorption spectra were recorded using a Hewlett-Packard HP8452A diode array spectrophotometer. Elemental analyses were performed by Quantitative Technologies Inc. (Whitehouse, NJ). Atmospheric phase chemical ionization mass spectra (APCI-MS) and electron spray ionization mass spectra (ESI-MS) were recorded using a Finnigan LCQ Advantage mass spectrometer; matrix-assisted laser desorption ionization time-of-flight mass spectra (MALDI-TOF-MS) were recorded on a PE Biosystems Voyager System 6050, using α-cyano-4-hydroxycinnamic acid as the matrix. EPR spectra were measured at 77 K with a modified Varian E-4X-band spectrometer. Solid-state magnetic susceptibility measurements were made by using a Quantum Design MPMS SQUID susceptometer operating in the temperature range 2−300 K and equipped with a 500 G field.

[7,8,12,13,17,18-Hexapropyl-2-(amino)-3-(picolinamido)]porphyrazine {3[2H, NH$_2$]} {H$_2$[pz(A;B$_3$)]; A = 2-Amino-3-picolinamido, B = (*n*-Propyl)$_2$}. H_2S was bubbled through pz **2**[Mg, Se] (100 mg, 0.144 mmol) in pyridine (50 mL) for 8 min, during which time the solution changed color from blue to violet. Picolinoyl chloride hydrochloride (77.0 mg, 0.432 mmol, 1.5 equiv) was added under nitrogen, and the mixture was allowed to stir at room temperature overnight. The solvent was removed by rotary evaporation, and the residue was dissolved in $CHCl_3$ (50 mL) and stirred with saturated aqueous $NaHCO_3$ (20 mL) for 0.5 h. The organic phase was separated and washed with water (3 × 50 mL). The solvent was removed, and the pz was chromatographed (CH_3OH/CH_2Cl_2 1:200) to provide pz **3**[2H, NH$_2$] (85 mg, 84%) as a purple solid: UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 343 (4.78), 553 (4.36), 636 (4.26) nm. APCI-MS: *m*/*z* 702.5 (M + H)$^+$, calcd $C_{40}H_{52}N_{11}O$ 702.4.

***N*,*O*-Copper(II)-[7,8,12,13,17,18-hexapropyl-2-(5-*tert*-butylsalicylidenimino)-3-(picolinamido)porphyrazinato]copper(II) {1-[Cu, Cu]} {Cu[pz(A;B$_3$)]; A = Cu(II)-2-(5-*tert*-butylsalicylidenimino)-3-picolinamido, B = (*n*-Propyl)$_2$}.** 5-*tert*-Butyl-2-hydroxybenzaldehyde (0.06 mL, 0.36 mmol, 10 equiv) was added to pz **3**[2H, NH$_2$] (25 mg, 0.036 mmol) in pyridine (40 mL). The mixture was stirred at room temperature overnight, after which time the solvent was removed by rotary evaporation. The crude ligand **1**[2H, 2H] and $(CF_3SO_3)_2Cu$ (130 mg, 0.36 mmol, 10 equiv) in MeOH and $CHCl_3$ (1:1; 40 mL) were heated to reflux (bath temperature 70−80 °C) with stirring for 2 h. The solvents were removed by rotary evaporation and the pz was chromatographed (CH_3OH/$CHCl_3$ 1:50) to provide pz **1**[Cu, Cu] (33 mg, 92%) as a blue solid: IR (film) 1731, 1594, 1462, 1260, 1099, 1022 cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 344 (4.75), 607 (4.54), 640 (4.60) nm. MALDI-TOF-MS: *m*/*z* 984.4 (M + H)$^+$, calcd $C_{51}H_{60}Cu_2N_{11}O_2$ 984.4.

[7,8,12,13,17,18-Hexapropyl-2-(amino)-3-(picolinamido)porphyrazinato]manganese(III) Chloride {3[MnCl, NH$_2$]} {MnCl-[pz(A;B$_3$)]; A = 2-Amino-3-picolinamido, B = (*n*-Propyl)$_2$}. A mixture of pz **3**[2H, NH$_2$] (43.5 mg, 0.062 mmol), MnI_2 (190 mg, 0.62 mmol, 10 equiv), and 2,6-lutidine (2 mL) in THF and PhMe (1:1; 50 mL) were heated to reflux (bath temperature 95−100 °C) with stirring for 20 h, after which time core metalation was complete. After rotary evaporation, the residue in CH_2Cl_2 (40 mL) was stirred with brine (20 mL) for 0.5 h under open air. The organic phase was separated, rotary evaporated, and chromatographed (CH_3OH/CH_2Cl_2 1:50) to provide pz **3**[MnCl, NH$_2$] (40 mg, 82%) as a green solid: IR (film) 3277, 1661, 1632, 1528, 1148 cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 366 (4.52), 557 (4.16), 627 (4.19) nm. ESI-MS: *m*/*z* 754.6 (M − Cl)$^+$, calcd $C_{40}H_{49}MnN_{11}O$ 754.4.

[7,8,12,13,17,18-Hexapropyl-2-(amino)-3-(picolinamido)porphyrazinato]oxovanadium(II) {3[VO, NH$_2$]} {VO[pz(A;B$_3$)]; A = 2-Amino-3-picolinamido, B = (*n*-Propyl)$_2$}. A mixture of pz **3**[2H, NH$_2$] (36.5 mg, 0.052 mmol), $VOSO_4$ (85 mg, 0.52 mmol, 10 equiv), and 2,6-lutidine (2 mL) in DMF and 1,2-dichlorobenzene (1:1; 50 mL) were heated to reflux (bath temperature 160−170 °C) with stirring for 36 h. The solvents were removed under high vacuum, and the residue was chromatographed (EtOAc/CH_2Cl_2 1:100) to provide pz **3**[VO, NH$_2$] (5.6 mg, 14%) as a blue-green solid: UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 343 (4.61), 555 (4.23), 605

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(4.29) nm. ESI-MS: *m/z* 767.6 (M + H)$^+$, calcd $C_{40}H_{50}N_{11}O_2V$ 767.4.

***N,O*-Copper(II)-[7,8,12,13,17,18-hexapropyl-2-(5-*tert*-butylsalicylidenimino)-3-(picolinamido)porphyrazinato]manganese(III) Chloride {1[MnCl, Cu]} {MnCl[pz(A;B$_3$)]; A = Cu(II)-2-(5-*tert*-butylsalicylidenimino)-3-picolinamido, B = (*n*-Propyl)$_2$}.** 5-*tert*-Butyl-2-hydroxybenzaldehyde (0.07 mL, 0.38 mmol, 10 equiv) was added to pz **3**[MnCl, NH$_2$] (30 mg, 0.038 mmol) in pyridine (40 mL). The mixture was stirred at room temperature overnight, after which time the solvent was removed by rotary evaporation. Without further purification, the crude ligand **1**[MnCl, 2H] was dissolved in EtOH and $CHCl_3$ (1:1; 40 mL) and stirred with $(CF_3SO_3)_2Cu$ (138 mg, 0.38 mmol, 10 equiv) at room temperature overnight. The solvents were removed by rotary evaporation, and the residue was chromatographed (CH_3OH/CH_2Cl_2 1:25) to provide pz **1**[MnCl, Cu] (33 mg, 90%) as a green solid: IR (film) 1729, 1647, 1572, 1512, 1459, 1159, 1028 cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 366 (4.56), 595 (4.43), 637 (4.42) nm. ESI-MS: *m/z* 975.7 (M − Cl)$^+$, calcd $C_{51}H_{59}CuMnN_{11}O_2$ 975.4. Anal. Calcd for $C_{53}H_{59}ClCuMnN_{11}O_2$·EtOH: C, 60.16; H, 6.19; N, 14.56. Found: C, 60.32; H, 5.98; N, 14.41. Recrystallization by the solvent layering method using (Et_2O + MeCN)/(PhMe + CH_2Cl_2) gave dark blocks suitable for an X-ray structure determination.

***N,O*-Copper(II)-[7,8,12,13,17,18-hexapropyl-2-(5-*tert*-butylsalicylidenimino)-3-(picolinamido)porphyrazinato]oxovanadium(II) {1[VO, Cu]} {VO[pz(A;B$_3$)]; A = Cu(II)-2-(5-*tert*-butylsalicylidenimino)-3-picolinamido, B = (*n*-Propyl)$_2$}.** This compound was synthesized using the same strategy as **1**[MnCl, Cu], and the product was chromatographed (EtOAc/CH_2Cl_2 1:19) to provide pz **1**[VO, Cu] (12 mg, 90%) as a blue solid: IR (film) 1726, 1597, 1462, 1260, 1155 cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 347 (4.80), 566 (4.47), 634 (4.52) nm. ESI-MS: *m/z* 988.6 (M + H)$^+$, calcd $C_{51}H_{60}CuN_{11}O_3V$ 988.4. Recrystallization by the solvent layering method using $CH_3OH/CHCl_3$ gave dark plates suitable for an X-ray structure determination.

X-ray Structure Determination. All measurements were made on a CCD area detector with graphite-monochromated Mo Kα radiation. Summaries of the crystal data and structure refinement parameters for compounds **1**[VO, Cu] and **1**[MnCl, Cu] are provided in Table 1. Both structures were solved by direct methods and expanded using Fourier techniques and were refined by full matrix least-squares based on F^2. All of the non-hydrogen atoms of both complexes were refined anisotropically. Hydrogen atoms were included but not refined. For compound **1**[VO, Cu], the proposed structure was refined with contributions from $^3/_4$ of a chloroform molecule in the asymmetric unit removed from the diffraction data using the bypass procedure in PLATON (Spek, 1990), The electron count from the "squeeze" model converged to about 1.5 chloroform molecules. The "squeeze" data are reported here. The total potential solvent accessible area volume is 330.1 Å^3; the electron count/cell is 85.

Result and Discussion

Synthetic Scheme. The two synthetic routes employed to prepare bimetallic complexes **1**[M^1, M^2] are shown in Schemes 1 and 2. Both involve the in situ formation of a diamino pz through reductive deselenation of pz **2**[Mg, Se] in pyridine by hydrogen sulfide.[9,14,15] The direct route to a homobimetallic complex, Scheme 1, involved subsequent reaction of the porphyrazinediamine with 1 equiv of picolinoyl chloride hydrochloride to form **3**[2H, NH$_2$], followed by addition of 5-*tert*-butyl-2-hydroxybenzaldehyde to generate the dinucleating ligand **1**[2H, 2H]. Reaction with 2 equiv of Cu(II) gave pz **1**[Cu, Cu] in one step with high yield. To prepare heterobimetallic complexes, we employed Scheme 2, in which **3**[2H, NH$_2$] was allowed to react with a salt of M^1 and the product was allowed to react with 1 equiv of 5-*tert*-butyl-2-hydroxybenzaldehyde to give the hybrid ligand **1**[M^1, 2H]. Although this compound was unstable toward purification, the crude **1**[M^1, 2H] could be reacted with a salt of M^2 without further purification to form **1**[M^1, M^2].

Table 1. Crystallographic Data for **1**[MnCl, Cu] and **1**[VO, Cu]

	1[MnCl, Cu]	**1**[VO, Cu]
formula	$C_{51}H_{59}N_{11}O_2ClMnCu$	$C_{51.75}H_{59.75}N_{11}O_3Cl_{12.25}CuV$
fw	1012.02	1078.10
color, habit	dark, block	dark, plate
cryst size (mm)	0.430 × 0.136 × 0.112	0.680 × 0.412 × 0.096
lattice type	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.0989(12)	10.2066(8)
b (Å)	16.4065(19)	14.4351(11)
c (Å)	18.618(2)	19.0479(14)
α (deg)	65.0239(17)	75.9010(10)
β (deg)	88.1190(19)	75.2880(10)
γ (deg)	75.6332(18)	79.0280(10)
V (Å^3)	2699.7(5)	2607.8(3)
Z	2	2
D_c (g cm^{-3})	1.245	1.373
F(000)	1058	1123
T (K)	153(2)	153(2)
$2\theta_{max}$ (deg)	57.76	57.74
no. of total data	24 891	24 489
no. of unique data	12 596	12 253
no. of params	590	618
R1[a]	0.0595	0.0536
wR2[b]	0.1502	0.1535

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$.

Description of the Structures. **1**[VO, Cu] and **1**[MnCl, Cu] crystals were obtained, and their X-ray structures were solved as described above. The ORTEP diagrams of these two complexes are shown in Figure 1. These structures show that the mixed peripheral ligand of **3**[M^1, Cu] forms a single peripheral chelate with Cu(II) to form the monomeric heterobimetallic compound, like the Schiff base pz compounds,[7,9] rather than forming a dimeric structure like the bis(picolinamido) pz.[10] As compounds **1**[VO, Cu] and **1**[MnCl, Cu] are isostructural, we discuss the structure of **1**[VO, Cu] only; selected bond distances and angles for both compounds are listed in Table 2. The VO(II) ion of the pz core adopts a square pyramid with the oxo ligand in the apical position and the four inner pyrrolic nitrogen atoms in the basal plane. The four basal atoms are within 0.01 Å of the mean plane with the vanadium atom 0.58 Å above this plane. The V−N distances do not differ significantly and are in the range of 2.01−2.02 Å. The V═O bond length is 1.60 Å, in the range of 1.56−1.63 Å reported for other square pyramidal oxovanadium(IV) complexes.[16]

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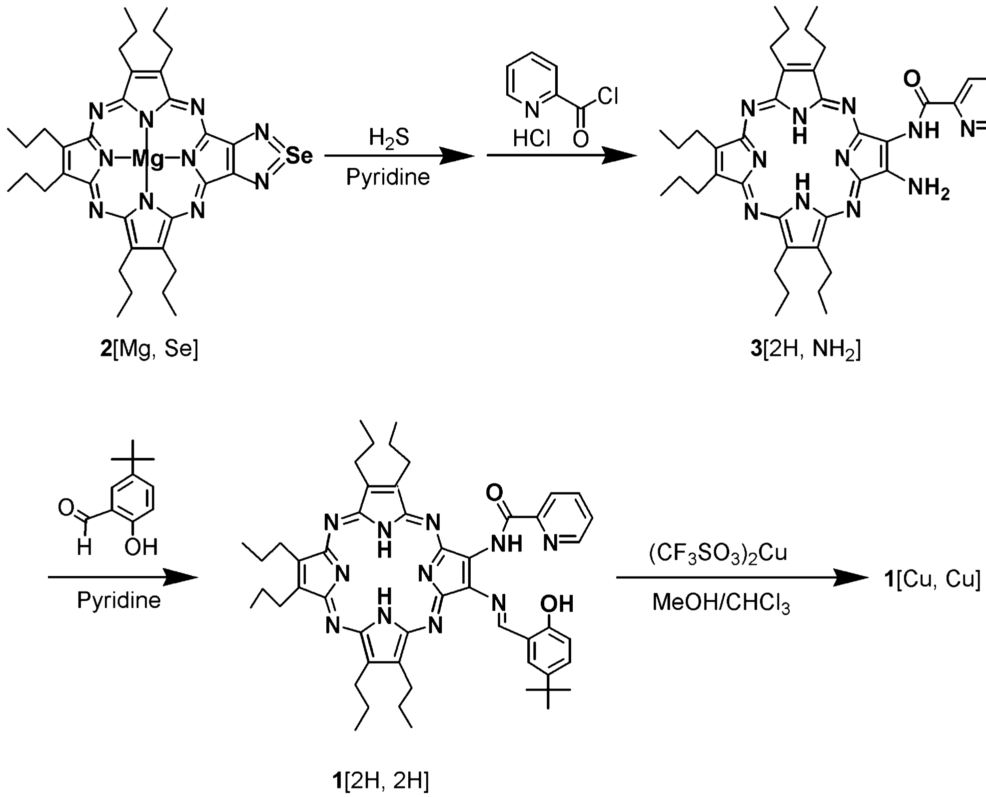
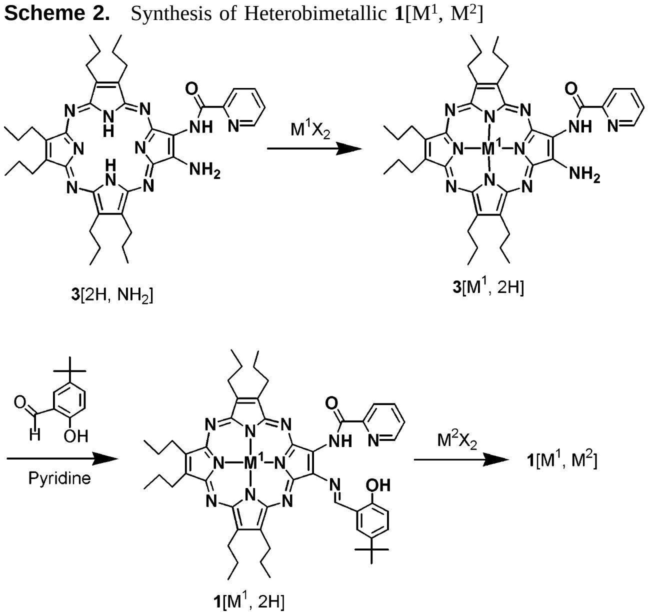
Scheme 1. Synthesis of Homobimetallic **1**[Cu, Cu]



Scheme 2. Synthesis of Heterobimetallic **1**[M[1], M[2]]



The peripheral site consists of an equatorial tetradentate ligand that provides pyridyl, amido, imino, and phenolato coordination to the Cu(II) ion. The overall geometry is best described as distorted square-planar. Within the ligand−metal fragment, the four adjacent bond angles around the Cu center are unevenly distributed from the ideal 90°. The N_{py}−Cu−N_{amino} bond angle in five-membered rings is 82.33(8)°, which is in the range of 79−84° found in other similar five-membered rings.[17,18] However, the N_{imino}−Cu−O bond angle is 94.84(8)° within the six-membered Schiff base ring, whose value is slightly larger: those angles in complexes [Cu(salen)][19] and [Cu(saltn)][20] have been found in the range of

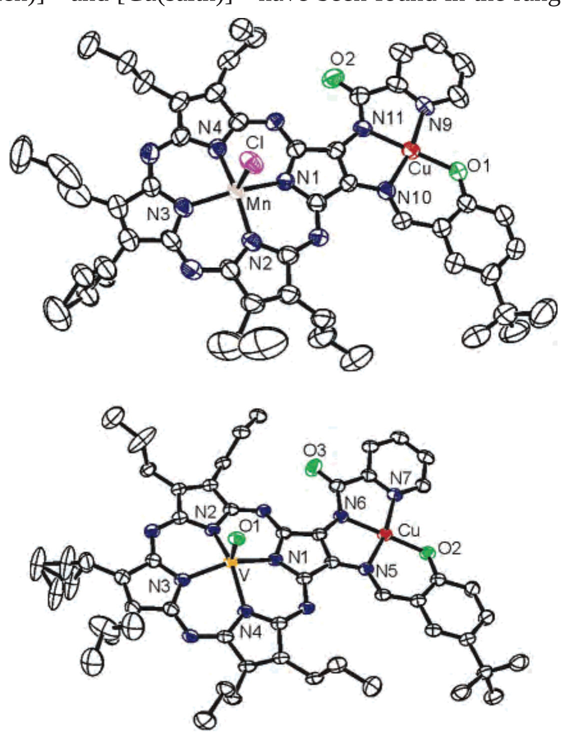


Figure 1. Molecular structure of **1**[MnCl, Cu] (upper) and **1**[VO, Cu] (lower).

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Table 2. Important Bond Lengths (Å) and Angles (deg) for **1**[MnCl, Cu] and **1**[VO, Cu]

1[MnCl, Cu]		**1**[VO, Cu]	
Mn−N1	1.955(2)	V−N1	2.020(2)
Mn−N2	1.945(3)	V−N2	2.007(2)
Mn−N3	1.958(3)	V−N3	2.018(2)
Mn−N4	1.927(3)	V−N4	2.008(2)
Mn−Cl	2.3794(10)	V−O1	1.6035(18)
Cu−O1	1.877(2)	Cu−O2	1.8695(18)
Cu−N9	1.980(3)	Cu−N5	1.966(2)
Cu−N10	1.946(3)	Cu−N6	1.925(2)
Cu−N11	1.940(3)	Cu−N7	2.001(2)
Mn−Cu	6.75	V−Cu	6.82
N1−Mn−N3	161.44(11)	N2−V−N1	86.24(8)
N2−Mn−N1	89.23(11)	N3−V−N1	146.95(9)
N2−Mn−N3	87.62(12)	N4−V−N1	84.87(8)
N4−Mn−N1	88.71(11)	N2−V−N3	84.10(9)
N4−Mn−N2	160.51(11)	N2−V−N4	145.93(9)
N4−Mn−N3	88.20(12)	N4−V−N3	85.67(8)
O1−Cu−N9	97.36(11)	O2−Cu−N5	94.84(8)
O1−Cu−N10	94.59(11)	O2−Cu−N6	177.68(8)
O1−Cu−N11	179.61(11)	O2−Cu−N7	97.31(8)
N10−Cu−N9	168.05(12)	N6−Cu−N5	85.71(8)
N11−Cu−N9	82.26(11)	N5−Cu−N7	167.08(9)
N11−Cu−N10	85.79(11)	N6−Cu−N7	82.33(8)

91−93.5°. The Cu−N_{amido} distance of 1.925(2) Å suggests that the amide nitrogen is a slightly better donor than the imine and pyridyl nitrogen (Cu−N_{imine} = 1.966(2) Å and Cu−$N_{pyridyl}$ = 2.001(2) Å) in this complex. The Schiff base moiety of the ligand in **1**[VO, Cu] is planar, indicating significant conjugation within this unit. This planar structure also prevents the formation of a dimer, as has been observed with bis(picolinamido) ligands.[10] The intramolecular V−Cu separation for **1**[VO, Cu] is 6.82 Å.

UV−Visible Spectra. The UV−vis spectra of **3**[2H, NH_2], **3**[VO, NH_2], **3**[MnCl, NH_2], **1**[Cu, Cu], **1**[VO, Cu], and **1**[MnCl, Cu] are shown in Figure 2. These pzs all have less than 4-fold symmetry and display split Q-bands in the 500−700 nm range.[21,22] The spectrum of **3**[2H, NH_2] is similar to that of a pz with bis(picolinamido) substituents in Q-band peak positions (λ_{max} of 553 and 636 vs 572, 631 nm).[10] The additional breadth of the Q-band is attributed to a coupling of the lone-pair orbital of the NH_2 group to the pz π system.[23] In compounds **3**[VO, NH_2] and **3**[MnCl, NH_2], core metalation does not cause the Q-band to coalesce to a single peak, as reported previously for pzs with bis(dimethylamino) or bis(picolinamido) substituents,[10,24] a result of the desymmetrizing influence of the NH_2 on the periphery. Compounds **1**[MnCl, Cu] and **3**[MnCl, NH_2] show a less intense shoulder at λ_{max} of 440 and 426 nm, respectively. Those absorptions are not amenable to simple interpretation, as they reflect the well-known complexity of the absorption spectra of Mn(III) porphyrin compounds.[25,26] As we observed previously, the peripheral metalation red-shifts the Q-band (ca. 20 nm for both **1**[MnCl, Cu] and **1**[VO, Cu]), probably the result of an extension of the conjugated system.[7]

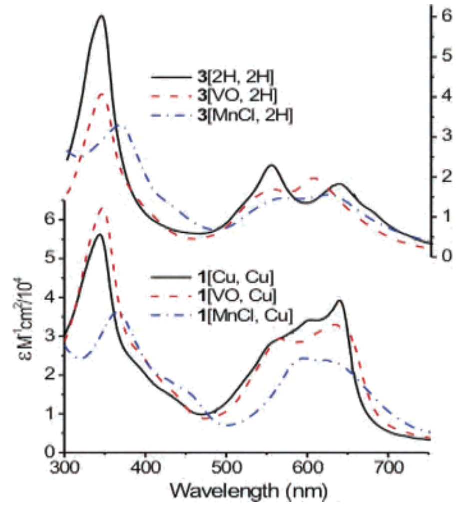

Figure 2. UV−vis spectra for pzs **3**[2H, NH_2], **3**[VO, NH_2], **3**[MnCl, NH_2], **1**[Cu, Cu], **1**[VO, Cu], and **1**[MnCl, Cu] in CH_2Cl_2.

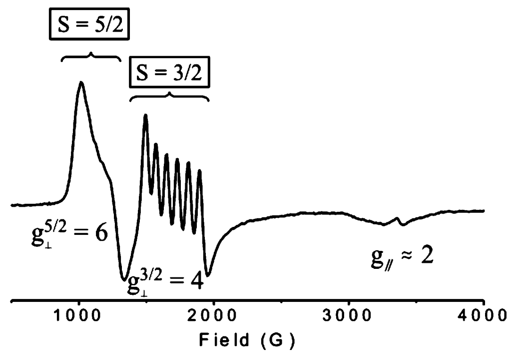

Figure 3. Frozen-solution X-band EPR spectra of **1**[MnCl, Cu] dissolved in chloroform/dichloromethane (1/9) (77 K).

Magnetic and EPR Studies. Figure 3 displays a frozen-solution X-band EPR spectrum of **1**[MnCl, Cu] taken at 77 K. As with Schiff base pzs,[7,8] Heisenberg exchange coupling ($H = JS_1S_2$) between the Mn(III) ($S = 2$) and Cu(II) ($S = {}^1/_2$) produces two total spin manifolds separated in energy by $\Delta = 5J = 0$ with $S = {}^3/_2$ lower in energy and $S = {}^5/_2$ higher. The spectrum shows two overlapping "perpendicular" features: $g_\perp \approx 6$ from the $S = {}^5/_2$ manifold; $g_\perp \approx 4$ from the $S = {}^3/_2$ manifold. The latter displays a well resolved sextet splitting from interaction with the ^{55}Mn ion ($I = {}^5/_2$), $A^{3/2} =$ 80 G; the former shows a poorly resolved sextet with a smaller coupling, $A^{5/2} = 52$ G. These two values are almost the same as we found in the Schiff base pz,[7] which unsurprisingly means that altering the peripheral chelate did not change the intrinsic electronic properties of the core Mn(III) ion. As we discussed in regard to the Schiff base pzs, these values can be interpreted in terms of the coupling for the isolated Mn(III) ions, $A_{Mn}/A_{Mn}^{3/2} = ({}^6/_5)A_{Mn}$ and $A_{Mn}^{5/2}$

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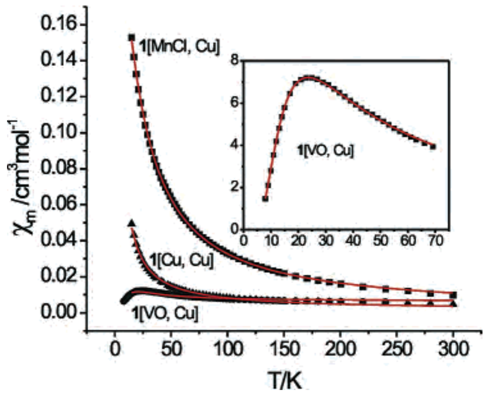

Figure 4. Plot of the molar magnetic susceptibility of a powder sample of **1**[MnCl, Cu], **1**[VO, Cu], and **1**[Cu, Cu] versus temperature. Inset is ×100 expansion of **1**[VO, Cu]. The solid line is a fit to the data by eq 1 for M^1 = Mn and eq 2 for the other two. The best fit parameters are $\theta = -2.2$ K, $g = 2.06$, $D^{3/2} = (^3/_5)D^{Mn} = -1.98$ K, and $\Delta/k_B = 5J/k_B = 22$ K for **1**[MnCl, Cu]; $g = 1.95$, $\Delta/k_B = J/k_B = 40$ K, $\rho = 0.01$, $\theta = -1.5$ K, and $N\alpha = -0.005$ cm^3 mol^{-1} for **1**[VO, Cu]; $g = 2.02$ and $\Delta/k_B = J/k_B = 1.1$ K for **1**[Cu, Cu].

$= (^4/_5)A_{Mn}$. The resulting prediction that $A_{Mn}{}^{3/2}/A_{Mn}{}^{5/2} = {}^3/_2$ clearly matches the ratio of observed couplings, $A_{Mn}{}^{3/2}/A_{Mn}{}^{5/2}$ = 80 G/52 G = 1.54; the resulting hyperfine interaction for the uncoupled Mn(III), A_{Mn} = 66 G, is typical for such ions.[27]

The magnetic susceptibility of **1**[MnCl, Cu] was measured between temperatures of 2 and 300 K using a SQUID magnetometer to determine the value of Δ. A plot of molar susceptibility versus temperature for **1**[MnCl, Cu] is illustrated in Figure 4. The measured χ_m was fitted to the theoretical expression, eq 1,[28]

$$\chi^{3/2} = C\left[\frac{1}{3}\frac{1 + (9\exp[-2D^{3/2}/(k_BT)])}{4\{1 + \exp[-2D^{3/2}/(k_BT)]\}} + \frac{2}{3}\frac{4 + \frac{3k_BT}{D^{3/2}}\{1 - \exp[-2D^{3/2}/(k_BT)]\}}{4\{1 + \exp[-2D^{3/2}/(k_BT)]\}}\right]$$

$$\chi = \chi^{3/2}\frac{2}{2 + \{3\exp[-\Delta/(k_BT)]\}} + (C/4)\frac{35\exp[-\Delta/(k_BT)]}{2 + \{3\exp[-\Delta/(k_BT)]\}} \quad (1)$$

where $C = N\mu_B{}^2g^2/[k_B(T - \theta)]$ and the other symbols have their usual meanings; the function $\chi^{3/2}$ is associated with the $S = {}^3/_2$ manifold and incorporates the effects of the zero-field splitting, $D^{3/2} = (^3/_5)D^{Mn}$, $D^{Mn} = -2.3$ cm^{-1}.[26] The fit gives $g = 2.06$ and $\Delta/k_B = 22$ K.

The EPR spectrum of **1**[VO, Cu] is unresolved (not shown) exhibiting neither the typical, well-resolved spectra expected for the core VO(II) or peripheral Cu(II) chelates nor the features of a triplet spectrum expected for an $S = 1$ spin state formed by exchange-coupling of the two $S = {}^1/_2$ ions. The temperature-dependent susceptibility was measured to determine the exchange coupling of the two spin centers. However, the temperature dependence of the molar susceptibility of **1**[VO, Cu], Figure 4, demonstrates that these two ions are exchange-coupled. It exhibits a maximum around 25 K that is characteristic of an antiferromagnetic interaction between VO(II) and Cu(II) metal ions, both $S = {}^1/_2$. These data were fit to the Bleaney−Bowers equation, eq 2,[29] by use of the exchange Hamiltonian given above for two interacting $S = {}^1/_2$ centers, where $\Delta = J$ is the singlet−triplet splitting, χ_m is the susceptibility per mole of metal ions,

$$\chi_m = \frac{N\beta^2g^2}{3k_B(T - \Theta)}\left[1 + \frac{1}{3}\exp(\Delta/(k_BT))\right]^{-1}(1 - \rho) + \frac{[N\beta^2g^2]\rho}{4k_BT} + N\alpha \quad (2)$$

ρ is the molar fraction of mononuclear impurity, Θ reflects for intermolecular interactions, $N\alpha$ represents the temperature-independent paramagnetism, and the other symbols have their usual meaning. Data were satisfactorily fit by eq 2 with $g = 1.95$ and $\Delta/k_B = 40$ K.

A plot of molar susceptibility versus temperature for **1**[Cu, Cu] is shown in Figure 4. The susceptibility was analyzed according to eq 2 with ρ and Θ set to 0. As shown in Figure 4, a good fit to the experimental data was attained with $g = 2.02$ and $\Delta/k_B = 1.1$ K. These values are essentially the same as those we determined for the Schiff base pzs.

Mechanism of the Exchange Coupling. We have seen that when an M^1 = Mn(III) or VO(II) is in the pz core, the coupling with an M^2 = Cu(II) ion at the periphery is much stronger than when an M^1 = Cu(II) is in the pz core. These results can be explained by assuming that the exchange coupling involves the d_σ orbitals ϕ_{M^1} and ϕ_{M^2} (Figure 5), which contain the single unpaired electron of the $S = {}^1/_2$ Cu(II) and VO(II) ions and the single d_σ orbital of the $S = 2$ Mn(III) ion.

For compound **1**[Cu, Cu], the "magnetic orbital" ϕ_{Cu^1} of the Cu(II) (configuration d^9) in the pz core is $d_\sigma = d_{x^2-y^2}$, which points from Cu(II) toward the four nitrogen atoms of the pz core in an antibonding fashion. This orbital is symmetric with regard to the *xz* mirror plane of the dimetallic pz (Figure 5). The magnetic orbital ϕ_{Cu^2} of the Cu(II) (configuration d^9) in the pz periphery is $d'_\sigma = d'_{x^2-y^2}$, as defined relative to its ligand atoms. However, the peripheral ligand environment is rotated by 45° relative to that of the pz core, so the magnetic orbital ϕ_{Cu^2} is $d_\sigma = d_{xy}$ in the coordinate frame of the pz, and this is antisymmetric with regard to the *xz* mirror plane of the pz. As a result, ϕ_{Cu^1} and ϕ_{Cu^2} are orthogonal, and the exchange parameter J for the Cu^1−Cu^2 pair, which would be proportional to the overlap integral, $\langle\phi_{Cu^1}|\phi_{Cu^2}\rangle$, should vanish as observed. In contrast, for compound **1**[VO, Cu], the ϕ_{VO} magnetic orbital of VO(II) (configuration d^1) is $d_\sigma = d_{xy}$, which also is antisymmetric with regard to the *xz* mirror plane of the pz. Thus, while the overlap integral $\langle\phi_{Cu^1}|\phi_{Cu^2}\rangle$ is identically zero by symmetry

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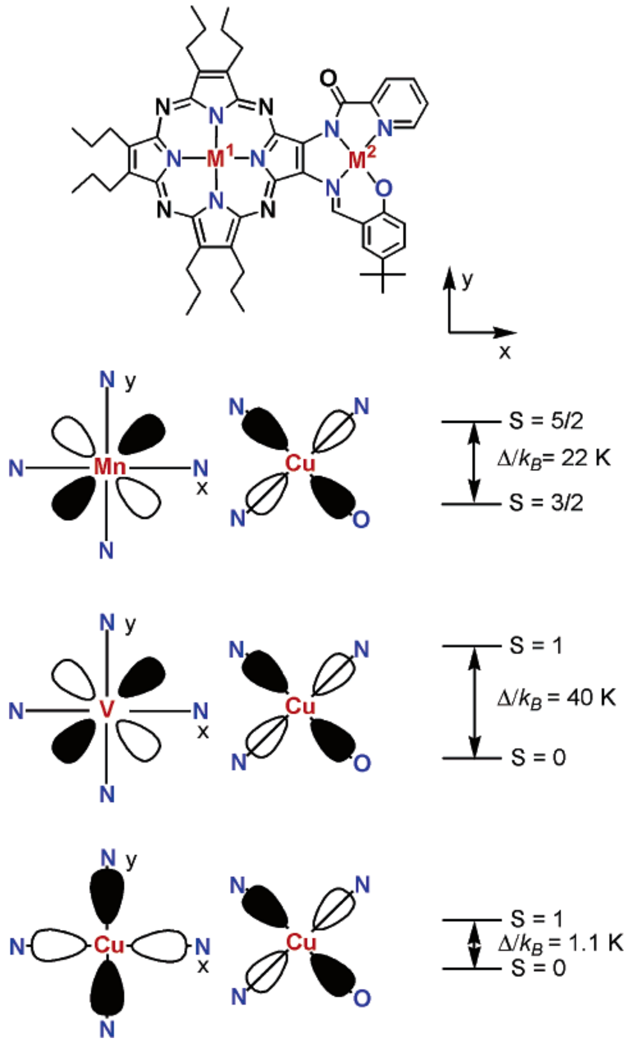

Figure 5. Magnetic orbitals and exchange coupling of the compounds **1**[MnCl, Cu], **1**[VO, Cu], and **1**[Cu, Cu].

for the Cu^1-Cu^2 pair, the magnetic orbitals of the $VO-Cu^2$ pair are of the same symmetry and interact antiferromagnetically through intervening atoms. The Mn(III)Cl of the compound **1**[Mn, Cu] has a high-spin d^4 configuration with the four unpaired electrons occupying three d_π orbitals, d_{xz}, d_{yz}, and d_{z^2}, and $d_\sigma = d_{xy}$. This last orbital is in-plane with, and has the same symmetry as, the magnetic orbital of the Cu^2 in the peripheral site (Figure 5), allowing for effective exchange coupling. This difference in magnetic symmetry between the dimetallic pzs clearly explains why exchange coupling between $VO-Cu^2$ and $MnCl-Cu^2$ is much stronger than Cu^1-Cu^2 coupling.

Conclusion

In summary, the ligand system **1**[2H, 2H], which has a salicylidene/picolinamide "hybrid" chelate appended to the pz periphery, has been synthesized and used to prepare a series of bimetallic complexes **1**[MnCl, Cu], **1**[VO, Cu], and **1**[Cu, Cu]. X-ray structures have been determined for **1**[MnCl, Cu] and **1**[VO, Cu]. Magnetic studies showed that the exchange coupling for the metal ion pairs, Mn(III)Cl−Cu(II) and VO(II)−Cu(II), is much stronger than for Cu-(II)−Cu(II). The exchange couplings are essentially the same as those we determined for the Schiff base pzs. Thus, the hybrid ligand has eliminated the dimerization found to occur when Cu(II) is bound to the periphery of the bis(picolinamido) pzs and has created a more robust ligand system than the Schiff base pzs while retaining the ability they show to promote spin coupling between M^1 and M^2. These results further support the conclusion that the exchange coupling is mediated by the pz macrocycle but is rigorously controlled by the symmetries of the singly occupied d_σ orbitals on the metal ions. Other combinations of metal ions in this system will be reported in due course.

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Supporting Information Available: X-ray crystallographic files in CIF format for compounds **1**[MnCl, Cu] and **1**[VO, Cu]. This material is available free of charge via the Internet at http://pubs.acs.org.

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