m, 1232 m, 1171 vs, 1139 vs, 1093 vs, 1055 s, 1021 m, 982 s, 955 vs, 921 m, 881 m, 834 s, 802 w, 734 m, 675 vs, 615 s, 586 m, 529 m, 509 m, 465 w, 454 w cm^{-1}; elemental analyses (THF and toluene were removed by drying **1** under vacuum) calcd for $C_{44}H_{102}O_{25}P_8Zn_{12}$ (2063.51): C 25.61, H 4.98; found: C 25.86, H 5.25.

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[19] Crystal data for **1**: $C_{62.5}H_{130}O_{27}P_8Zn_{12}$ ($\mathbf{1}\cdot 1.5\,C_7H_8$), $M_r = 2345.86$, triclinic, space group $P\bar{1}$, $a = 15.049(10)$, $b = 15.178(10)$, $c = 24.89(2)$ Å, $\alpha = 72.89(2)$, $\beta = 75.54(3)$, $\gamma = 62.51(4)^\circ$, $V = 4777(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.631\ g\,cm^{-3}$, $F(000) = 2402$, $\lambda = 0.71073$ Å, $T = 150$ K, $\mu(Mo_{K\alpha}) = 31.51\ cm^{-1}$, min./max transmission 0.1871/0.3654, crystal dimensions 0.80 × 0.50 × 0.40 mm, $3.59 < \Theta < 25.13^\circ$; 16331 data were collected of which 13156 were independent ($R_{int} = 0.0753$). For the final refinement of 1023 parameters no restraints were used. The *R* values were: $R1 = \Sigma|F_o - F_c|/\Sigma F_o = 0.0467$ for $I > 2\sigma(I)$, and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^4]^{1/2} = 0.1292$ for all data; max/min. residual electron density: 0.990/ − 0.782 e Å^{-3}. The unit cell contains two molecules of **1** and three molecules of toluene of crystallization, one of them disordered about the inversion center. Intensity data of **1** were collected on a Siemens–Stoe AED-2 four-circle diffractometer. The crystal was transferred in an inert oil and then flash-cooled in a nitrogen stream.[22] The structure of **1** was solved with direct methods (SHELXS-97)[23] and was refined against F^2.[24] An empirical absorption correction was employed.[25] All non-hydrogen atoms were refined anisotropically and the riding model was used for the hydrogen atoms. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102564. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Hydrogen-Bonding Cavities about Metal Ions: A Redox Pair of Coordinatively Unsaturated Paramagnetic Co–OH Complexes[**]

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Described herein is a synthetic system that uses hydrogen bonds to regulate the chemistry at a coordinatively unsaturated metal center. These regulatory properties are illustrated by the isolation and characterization of monomeric Co–OH complexes, including a five-coordinate paramagnetic Co^{III}–OH complex which, to our knowledge, has not been observed

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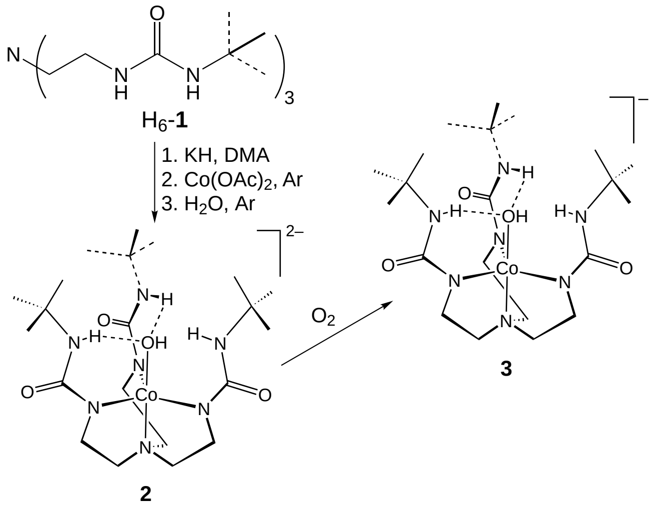
previously. To accomplish this chemistry the new tripodal ligand $[H_3\text{-}\mathbf{1}]^{3-}$ (see Scheme 1) was synthesized. Metal ion binding to $[H_3\text{-}\mathbf{1}]^{3-}$ yields a cavity structure that can provide up to three intramolecular hydrogen bonds to an external donor atom coordinated to the metal center. To ensure intramolecular hydrogen bonds in these metal complexes, $[H_3\text{-}\mathbf{1}]^{3-}$ is designed so that thermodynamically favored six-membered rings are formed during formation of the hydrogen bonds.[1]

Hydrogen-bonding interactions are important in influencing the structural and functional properties of metalloproteins.[2, 3] In several metalloproteins, hydrogen bonds are used in conjuction with metal–ligand covalent bonds to stabilize or control the chemistry of reactive species. This combination of bonding modes is typified by the structure of the active site in oxyhemoglobin, which has, in addition to a covalent Fe–O bond, a hydrogen bond between the distal imidazolyl residue of histidine and the coordinated O_2 molecule.[4] To model these desirable effects, several synthetic systems have been reported that combined intramolecular covalent and hydrogen bonds to selectively bind and stabilize metal–ligand adducts.[5] However, few of these systems are structurally characterized to conclusively show that multimode binding is present.[5e–g,k,l] We have examined how the structures of C_3-symmetric cavities direct the chemistry of trigonal mono- and bipyramidal complexes.[6] We now extend our studies to include C_3-symmetric hydrogen-bonding cavities. X-ray diffraction results confirm that these cavities organize such that hydrogen bonds can form to Co–OH moieties in trigonal-bipyramidal complexes.

$K_2[CoH_3\text{-}\mathbf{1}(OH)]$ (K_2-**2**) was isolated by a two-step synthesis as shown in Scheme 1. Compound **2** has a quasi-reversible one-electron redox couple at −740 mV (vs. SCE) and can be readily oxidized by O_2 to form $[CoH_3\text{-}\mathbf{1}(OH)]^-$ (**3**).[7] Labeling studies confirm that water is the source of the OH^- ion in **3**, as no change was observed in the frequency of the $\tilde{\nu}(OH)$ band when $^{18}O_2$ was used as the oxidant. Moreover, the use of $H_2{}^{18}O$ in the reaction affords $[^{18}O]$-**3** (IR: $\tilde{\nu}(^{16}OH) = 3616$, $3594\ cm^{-1}$; $\tilde{\nu}(^{18}OH) = 3606$, $3582\ cm^{-1}$; $\tilde{\nu}(^{16}OH)/\tilde{\nu}(^{18}OH) = 1.003$ and 1.003, respectively, calcd 1.003).



Scheme 1. Synthesis of **2** and **3**.

The molecular structures of K_2-**2** and K-**3** were determined by X-ray diffraction methods. The overall structures of **2** and **3** are similar (shown in Figure 1 for **3**), with both complexes having a trigonal-bipyramidal coordination geometry around their cobalt centers.[8] In **3** the three deprotonated urea nitrogen atoms define the trigonal plane with an average $Co1-N_{urea}$ bond length of 1.957(2) Å. The terminal hydroxo ligand is positioned nearly *trans* to the apical amine nitrogen atom N1; the Co1–O1 and Co1–N1 distances are 1.894(2) and 1.945(3) Å, and the O1-Co1-N1 angle is 175.94(11) Å. The O1–H1A vector is located between the urea arms containing N2 and N6: To accommodate this disposition of the hydroxo ligand the N2-Co1-N6 angle is significantly increased to 132.35(11)° from that expected for trigonal-bipyramidal geometry (120°).

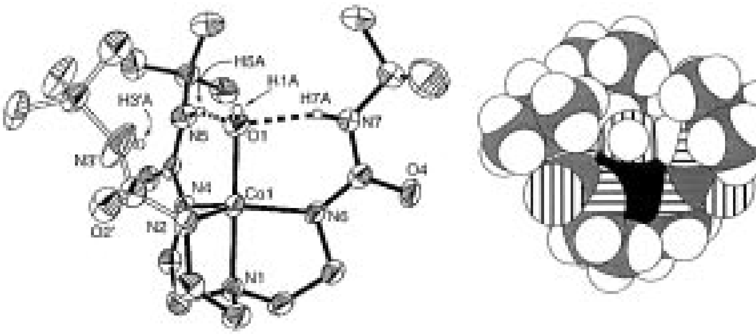


Figure 1. Thermal ellipsoid diagram (left) and a space-filling representation (right) of the structure of **3**. The ellipsoids are drawn at the 50 % probability level, and only the urea and hydroxo hydrogen atoms are shown. Only one of the disordered fragments for the arm containing N2 is shown. Selected bond lengths [Å] and angles [°] for **3** (**2**): Co1–N1 1.945(3) (2.190(3)), Co1–N2 1.957(3) (2.042(3)), Co1–N4 1.974(3) (2.090(3)), Co1–N6 1.939(3) (2.085(3)), Co1–O1 1.894(2) (2.072(2)); N2-Co1-N4 108.16(11) (118.34(10)), N2-Co1-N6 132.35(11) (115.92(10)), N4-Co1-N6 116.36(11) (117.70(11), O1-Co1-N1 175.94(11) (172.67(10)).

In addition to the covalent Co–OH bond in **2** and **3**, two intramolecular hydrogen bonds to the hydroxo ligand are present between the hydroxo oxygen atom and the urea NH groups. For **3** the heavy atom O1 ⋯ N5 and O1 ⋯ N7 distances of 2.748(4) and 2.680(4) Å and the O1-H5A-N5 and O1-H7A-N7 angles of 161(4) and 163(4)° are indicative of strong hydrogen bonds. Similar metrical features are found in **2**.[9] The NH group of the remaining arm in both complexes is not involved in hydrogen bonding, as it is canted such that the N–H vector is directed away from O1.[9] In **3**, O2, N3, and C4 exhibit a high degree of anisotropic disorder, causing this portion of the arm to be refined as two fragments, one of which is shown in Figure 1. The presence of distinct urea NH groups in K_2-**2** and K-**3** is supported by solid-state FT-IR studies that show multiple $\tilde{\nu}(NH)$ bands.

The molecular structures of **2** and **3** resemble the structure of a Cu^{II}–OH complex recently reported by Tolman et al. that also has two hydrogen bonds to the hydroxo oxygen atom. However, there are no examples of cobalt complexes where a redox pair has been isolated having the same trigonal-bipyramidal stereochemistry as shown here for **2** and **3**. Moreover, while Co–OH complexes are known, many are polynuclear species containing bridging hydroxo ligands.[10] In fact, there are just two reports of structurally characterized monomeric Co–OH complexes:[11] a low-spin square-pyramidal Co^{II}–OH complex[12] and the six-coordinate [Co(terpy)(η^2-CO_3)(OH)] complex (terpy = 2,2′:6′,2″-terpyridine).[13] Additionally, Co^{III} complexes are normally diamagnetic, yet **2** and **3** are paramagnetic.[14] Compound **2** is a high-spin ($S = 3/2$) complex with a room-temperature magnetic moment μ_{eff} of 4.49 μ_B and an X-band EPR signal at $g = 3.87$ (77 K). Compound **3** has a room-temperature μ_{eff} value of 3.28(6) μ_B, which is consistent with an $S = 1$ ground state.[15] The unusual spin state in **3** is achieved because the trigonal symmetry around the Co^{III} mandates an intermediate spin ground state for a d^6 ion. This trigonal-bipyramidal stereochemistry is enforced by the protective hydrogen-bonding cavity of $[H_3\text{-}\mathbf{1}]^{3-}$, preventing the binding of any additional ligands that would lead to a more common six-coordinate $S = 0$ complex.

The results obtained in this study are reminiscent of the regulatory properties provided by active-site structures in metalloproteins.[16] The threefold symmetric hydrogen-bonding cavities formed in metal complexes of $[H_3\text{-}\mathbf{1}]^{3-}$ can control the binding and stabilization of metal–ligand adducts, as demonstrated by the isolation of a unique redox pair of Co–OH complexes.

Experimental Section

K_2-**2**: A solution of H_6-**1** (0.11 g, 0.24 mmol) in anhydrous *N,N*-dimethylacetamine (DMA, 4 mL) was treated with solid KH (0.028, 0.72 mmol) under an Ar atmosphere. After H_2 evolution had ceased, solid $Co(OAc)_2$ (0.043 g, 0.24 mmol) was added. The resulting solution was stirred for 0.5 h and filtered to remove a small amount of insoluble material (KOAc), which was discarded. H_2O (0.0090 g, 0.48 mmol) was added to this filtrate, which caused an immediate color change from blue to violet. The reaction mixture was stirred for 1 h and then filtered. Diethyl ether vapor was allowed to diffuse into the violet filtrate to provide crystalline K_2-**2** (0.068 g, 40% yield). Elemental analysis calcd (found) for K_2-**2** · 0.75 DMA ($C_{24}H_{49.75}CoK_2N_{7.75}O_{4.75}$): C 43.67 (43.24), H 7.60 (7.86), N 16.45 (16.30). The presence of DMA was corroborated by IR spectroscopy); IR (Nujol): $\tilde{\nu} = 3227$, 3138 (N–H), 1587 cm^{-1} (C=O); EPR (X-band, DMA, 77 K): $g = 3.87$; UV/Vis (DMA): $\lambda_{max}(\varepsilon) = 395$ (sh), 474 (sh), 514 (52), 596 (sh), 618 (sh), 681 nm (24); cyclic voltammetry (DMF, 0.1 V s^{-1}): $E_{1/2} = -0.74$ V, $E_{p,c} = 0.39$, 0.82 V; $\mu_{eff} = 4.49$ μ_B (solid, 298 K).

X-ray structure anaylsis for K_2-**2** · CH_3CN · DMA (crystals used for X-ray diffraction were grown by diffusing diethyl ether into a DMA/MeCN solution): crystal dimensions, 0.35 × 0.34 × 0.12 mm, monoclinic, space group *C*2/c, $a = 33.5148(4)$, $b = 12.8140(4)$, $c = 23.2786(4)$ Å; $\beta = 132.464(1)°$; $V = 7374.9(2)$ Å^3, $\rho_{calcd} = 1.302$ Mg m^{-3}, $Z = 8$, $3.30 \le 2\theta \le 50.00°$; $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $F(000) = 3080$, $T = 173$ K; of a total of 17622 reflections collected on a Siemens SMART Platform CCD diffractometer, 6418 were independent ($R_{int} = 0.0358$), refection/parameter ratio 6418/453; absorption correction: SADABS (Sheldrick, 1996), max./min. transmission factor 1.000/0.888; structure solution by direct methods (SHELXTL-V5.0), all urea and hydroxo hydrogen atoms were found in the Fourier difference map and refined positionally while holding the U_{eq} values at relative values; refinement by full-matrix least squares on F^2, $R1 = 0.0513$, $wR2 = 0.0917$ ($I > 2\sigma(I)$), GOF = 1.048, min./max. residual electron density 0.261/−0.301 e Å^{-3}.

K-**3**: A solution of K_2-**2** (0.24 mmol) in anhydrous DMA (4 mL) was treated with dry O_2 (0.48 mmol), which caused an immediate color change from violet to dark red. The mixture was stirred for 1 h and evacuated to remove excess O_2. The resulting solution was filtered, and volatile components were removed under reduced pressure. The complex was crystallized by vapor diffusion of diethyl ether into a solution of K-**3** in DMF (0.64 g, 47% yield). Elemental analysis calcd (found) for K-**3** ($C_{21}H_{43}CoKN_7O_4$): C 45.38 (44.93), H 7.81 (7.86), N 17.64 (17.24); IR: $\tilde{\nu} = 3616$, 3594 (O–H), 3366, 3251, 3161 (N–H), 1599, 1581, 1522 cm^{-1} (C=O); UV/Vis: $\lambda_{max}(\varepsilon) = 288$ (6600), 389 (sh), 474 (3900), 793 nm (480); $\mu_{eff} = 3.28(6)$ μ_B.

X-ray structure anaylsis for K-**3**: crystal dimensions, 0.30 × 0.15 × 0.06 mm, triclinic, space group $P\bar{1}$, $a = 10.7774(3)$, $b = 11.3017(3)$, $c = 11.7250(2)$ Å, $\alpha = 94.319$, $\beta = 95.146(1)$, $\gamma = 98.003(1)°$; $V = 1402.94(6)$ Å^3, $\rho_{calcd} = 1.315$ Mg m^{-3}, $Z = 2$, $3.500 \le 2\theta \le 50.08°$; $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $F(000) = 592$, $T = 173(2)$ K; of a total of 8056 reflections collected on a Siemens SMART Platform CCD diffractometer, 4826 were independent ($R_{int} = 0.0348$), reflection/parameter ratio 4826/365, absorption correction: SADABS (Sheldrick, 1996), max./min. transmission factor 1.000/0.560; the structure was solved by direct methods (SHELXTL-V5.0); all urea and hydroxo hydrogen atoms were found in the Fourier difference map and refined positionally while holding the U_{eq} values at relative values; refinement by full-matrix least squares on F^2, $R1 = 0.0463$, $wR2 = 0.01055$ ($I > 2\sigma(I)$); GOF = 0.989, 0.500, −0.447 e Å^{-3}. For the disordered arm that is not involved in hydrogen bonding, all atoms beyond C3 were split into two fragments and refined with restraints. The refinement led to a 0.48:0.52 ratio in occupancy. In total, 52 SHELXTL SAME and FLAT restraints were applied to atoms of similar nature.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-111493 and CCDC-111494 (K_2-**2** · CH_3CN · DMA and K-**3**, respectively). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Self-Assembly of Predesigned Trimetallic Macrocycles Based on Benzimidazole as Nonlinear Bridging Motifs: Crystal Structure of a Luminescent Platinum(II) Cyclic Trimer**

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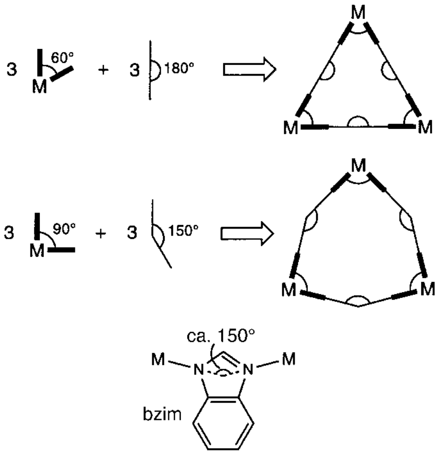
Self-assembly of mono- and polycyclic supermolecules is a challenging yet prolific area of research.[1] In the context of metallomacrocycles with internal cavities, efforts have focused on the design and construction of molecular squares,[2] while triangular arrays have remained relatively unexplored. In theory, if the building blocks are sufficiently rigid, the alternating combination of three subunits extending 60° bite angles with three linear linkers would constitute a equilateral triangle (Scheme 1). In practice, the former is difficult to attain at metal centers but is available in a number of bidentate ligands, and thus trimeric assemblies are formed in tandem with linear two-coordinate or *trans*-configured metallic bridges.[3] Triangular macrocycles bearing metal vertices and supported by 4,4′-bipyridine,[4] 2,2′-bipyrazine,[5] 1,3-bis(1-methylbenzimidazol-2-yl)benzene,[6] and various nucleobases[7] have been synthesized. However, only moderate selectivities are encountered in these reactions due to the presence of multiple chelating sites and other geometrical factors (ligand flexibility, angle strain at metal center), and mixtures of products are often afforded.



Scheme 1. Strategies for the syntheis of trimeric macrocycles with metal vertices.

We propose a *ligand-directed* strategy for the fabrication of trimetallic macrocycles by using bzim (bzim = N-anion of benzimidazole) as a rigid nonlinear bridging motif. Coupling of three edges exhibiting 150° angles with right-angled vertices (i.e. *cis* binding sites at metal centers residing in square-planar and octahedral environments) is anticipated to yield a cyclic trimer,[8] and based on this premise, the predefined geometry and unambiguous binding mode of the bidentate bzim ligand is ideal (Scheme 1). We report herein the highly efficient syntheses of luminescent platinum(II) trimeric assemblies directed by N-deprotonated benzimidazole.

Treatment of the luminescent cyclometalated Pt^{II} precursors $[Pt(thpy)(Hthpy)Cl]$[9a] (Hthpy = 2-(2′-thienyl)pyridine) and $[nBu_4N][Pt(bzqn)Cl_2]$[9b] (Hbzqn = 7,8-benzoquinoline) with sodium benzimidazolate afforded $[Pt(thpy)(bzim)]_3$ (**1**) and $[Pt(bzqn)(bzim)]_3$ (**2**) as orange and yellow crystalline solids, respectively, in high yields (80–90 %). In the FAB mass spectra, the anticipated molecular ion clusters for **1** and **2** are observed at *m/z* 1417 and 1471, respectively. The trimeric nature of **1** was confirmed by X-ray crystallography.[10]

The molecular structure of **1** (Figure 1) consists of alternating [(thpy)Pt] vertices and benzimidazolate edges. The slightly distorted square-planar geometry around each platinum center comprises the N and *ortho*-C atoms of thpy and

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