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Preparation and structures of dinuclear complexes containing M^{II} –OH centers†

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The synthesis of M^{II}_2 complexes (M^{II} = Co, Mn) with terminal hydroxo ligands has been achieved utilizing a dinucleating ligand containing a bridging pyrazolate unit and appended (neopentyl)-aminopyridyl groups. Structural studies on the complexes revealed that the M^{II} –OH units are positioned in a *syn*-configuration, placing the hydroxo ligands in close proximity (*ca.* 3 Å apart), which may be a prerequisite for water oxidation.

Multinuclear metal complexes with terminal hydroxo or oxo ligand(s) have been proposed to participate in a variety of different biochemical processes, including the catalytic cycle of water oxidation in photosystem II (PSII).¹ Exploring the chemistry of related synthetic systems has provided information into the structural and mechanistic requirements necessary for catalysis, yet most artificial systems still lack the catalytic efficiency found in metalloproteins. One synthetic approach is to develop complexes that initially place two M –OH_{*n*} (*n* = 1, 2) units in close proximity.^{2,3} This approach is often hampered because of the tendency for hydroxo and aquo ligands to bridge between metal ions. Nonetheless, there are structurally characterized examples of dinuclear complexes containing discrete M –OH_{*n*} units.⁴ Meyer reported that the [(bpy)₂Ru–OH₂]₂(μ–O) complex contains a diruthenium core with two terminal aquo ligands⁵ and Ménage showed that the [(trpy)₂Fe–OH]₂(μ–O) has two Fe^{III}–OH units;⁶ however, in these complexes the M –OH_{*n*} units have an *anti*-configuration in the solid state with the two OH_{*n*} groups separated by over 5 Å. Success in preparing dinuclear complexes with M –OH_{*n*} units in the *syn*-configuration has been achieved using dinucleating ligands.⁷ For instance, Llobet and Meyer have reported complexes containing Ru₂–(H₃O₂),^{7a} Zn₂–(H₃O₂)^{7b,c} and Ni–(H₃O₂)^{7d} units respectively, utilizing a pyrazolate bridging group that prevents the formation hydroxo or oxo bridges. In this report we describe the preparation of a new dinucleating ligand that supports the formation of [Co^{II}–OH]₂ and [Mn^{II}–OH]₂ complexes. The M^{II} –OH units in these complexes adopt *syn*-configurations, which are stabilized by intramolecular hydrogen bonding (H-bonding) networks.

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We have been preparing dinucleating ligands that also utilize a bridging pyrazolate group to separate the metal centers. Using the structural concepts developed by Meyer,⁸ we reasoned that ligands containing a (3,5-diaminomethylene)-pyrazolate unit would provide sufficient spacing between the metal ions (*ca.* 3.5–4.5 Å) to allow the binding of two terminal hydroxo ligands. In addition, our ligands include H-bond donors within the secondary coordination sphere to form intramolecular H-bonding networks with the M –OH units;^{7d,9} these types of noncovalent interactions have previously been exploited in the isolation of mononuclear M –OH analogues.¹⁰ Two earlier versions of this design contained urea ([H₄P^Rbuam]^{5–})¹¹ and carboxyamido-pyridyl ([H₃bppap]^{2–})¹² groups (Fig. 1) but we were unable to prepare dinuclear M –OH complexes. For instance, the Co^{II}₂ complex of [H₃bppap]^{2–} had only one terminal Co^{II}–OH center: the binding of a second hydroxo ligand appeared to be hindered by the coordination of the oxygen atoms of the appended carboxyamido groups.¹³ These results suggested that reduction of carboxyamido groups to neopentylamino moieties would produce 3,5-bis[bis(*N*-6-neopentylamino-2-pyridylmethyl)aminomethyl]-1*H*-pyrazole (H₅bnppap), a compound containing H-bond donors that cannot readily coordinate to the metal ions.^{10c,d,14}

H₅bnppap was synthesized from H₃bppap in nearly quantitative yield by reduction using LiAlH₄ in THF (Scheme 1). The dinuclear Co^{II} and Mn^{II} complexes of [H₄bnppap][–] were prepared according to the route outlined in Scheme 2. H₅bnppap in MeOH was treated with 3 equiv of NaH under an argon atmosphere. After stirring for 30 min, the M^{II} precursors (either Co^{II}(NO₃)₂·6H₂O or Mn^{II}(OTf)₂·2MeCN) were added in one portion and stirred for an additional 30 min. The reaction mixtures were then treated with 2 equiv of H₂O, followed by the addition of NaBPh₄, which resulted in the immediate formation of precipitates. The solids were isolated *via* filtration and purified by recrystallization from THF/pentane.

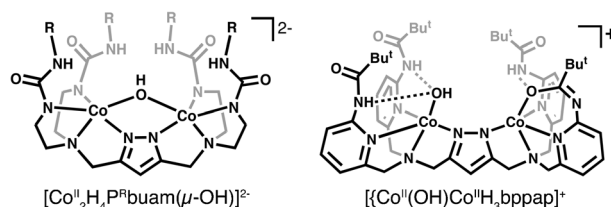
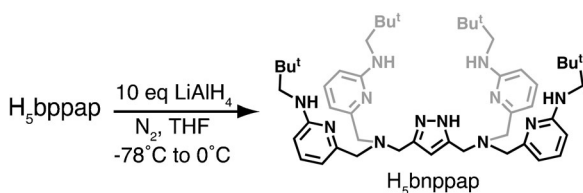
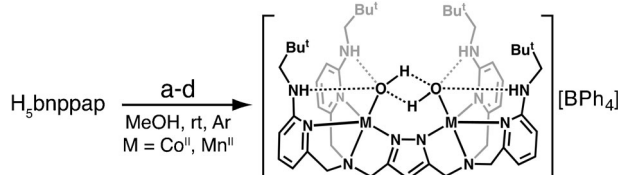


Fig. 1 Co^{II}–OH complexes of [H₄P^Rbuam]^{5–} and [H₃bppap]^{2–}.



Scheme 1 Preparative route of $H_5bnppap$ from H_5bppap .



Scheme 2 Synthetic route to $[M^{II}_2H_4bnppap(OH)_2]^+$ ($M = Co^{II}, Mn^{II}$). Conditions: (a) 3 equiv NaH , (b) 2 equiv $Co(NO_3)_2 \cdot 6H_2O$ or $Mn(OTf)_2 \cdot 2MeCN$ (c) 2 equiv of H_2O (d) 1 equiv $NaBPh_4$.

Analytical and spectroscopic investigations indicated that the salts contained the dinuclear metal complexes, $[M^{II}_2H_4bnppap(OH)_2]^+$ ($M^{II} = Co, Mn$). The electrospray ionization mass spectrum (ESI-MS) of $[Co^{II}_2H_4bnppap(OH)_2]^+$ contained a large ion peak at a charge-to-mass ratio (m/z) of 981.4, which matches the expected mass and isotopic distribution of a $(Co^{II}-OH)_2$ complex (calcd, 981.5). Similarly the ESI-MS spectrum for $[Mn^{II}_2H_4bnppap(OH)_2]^+$ exhibited a peak at a m/z of 973.5 (calcd, 973.5). Each peak shifted by 4 mass-units when $H_2^{18}O$ was used in the synthesis, indicating that the source of the hydroxo ligands is water.[‡] Effective magnetic moments (μ_{eff}) at 298 K of 8.01 and 5.23 μ_{BM} were obtained for $[Co^{II}_2H_4bnppap(OH)_2]^+$ and $[Mn^{II}_2H_4bnppap(OH)_2]^+$ respectively,[§] values that are close to the spin-only values for two individual high-spin Mn^{II} and Co^{II} centers.¹⁵ These preliminary findings suggest weak magnetic coupling, which is inconsistent with the presence of single atom bridge(s) between the metal centers.

The solid-state structures of the complexes were investigated using X-ray diffraction methods to reveal dinuclear species in which each metal center has a coordinated hydroxo ligand. In $[Co^{II}_2H_4bnppap(OH)_2]^+$ (Fig. 2A) both Co^{II} centers have trigonal bipyramidal coordination geometries as judged by index of trigonality parameter (τ) of 0.99 measured for both metal ions.¹⁶ An N_4O primary coordination sphere exists about each Co^{II} ion, consisting of pyrazolate and pyridyl nitrogen atoms defining the trigonal plane, and the tertiary amino nitrogen and hydroxo oxygen atoms in the axial positions. The $Co1-O1$ and $Co2-O2$ bond distances of 1.9379(2) Å and 1.9444(2) Å are similar to the $Co-O(H)$ bond length of 1.931(2) Å observed in $[Co^{II}(OH)Co^{II}H_3bppap]^+$, but are significantly shorter than those in $[Co^{II}_2H_4P^Rbuam(\mu-OH)]^{2-}$ (greater than 2.1 Å) (Fig. 1).^{10b} The pyrazolate unit bridges between the Co^{II} centers with $Co1-N4$ and $Co2-N10$ bond distances of 2.034(2) and 2.046(2) Å, and a $Co1 \cdots Co2$ separation of 4.286 Å. The remaining $Co-N$ bond distances and angles are unexceptional with avg. $Co-N_{trig}$ and $Co-N_{axial}$ bond lengths of 2.108(2) Å and 2.194(2) Å, and avg. $N_{trig}-Co-N_{trig}$ angle and $O-Co-N_{axial}$ angles of 115.11(8)° and 176.66(8)°.

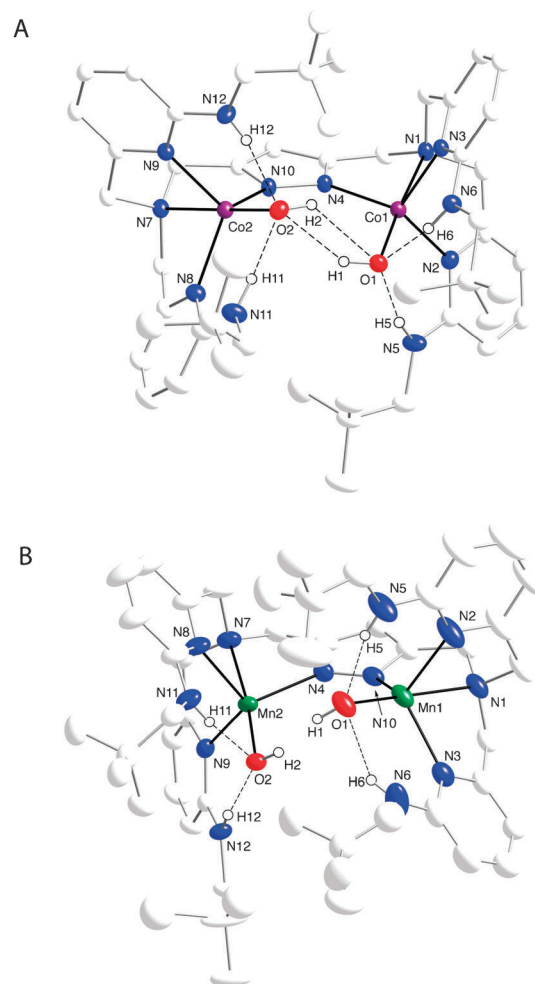


Fig. 2 Thermal ellipsoid plots of $[Co^{II}_2H_4bnppap(OH)_2]^+$ (A) and $[Mn^{II}_2H_4bnppap(OH)_2]^+$ (B). Thermal ellipsoids are drawn at the 50% probability level. Only hydroxo and amino hydrogen atoms are shown for clarity. Selected bond lengths (Å) and angles (°) for $[Co^{II}_2H_4bnppap(OH)_2]^+$ and $[Mn^{II}_2H_4bnppap(OH)_2]^+$: $Co1-O1$, 1.938(2); $Co1-N4$, 2.034(2); $Co1-N3$, 2.102(2); $Co1-N2$, 2.107(2); $Co1-N1$, 2.192(2); $Co2-O2$, 1.944(2); $Co2-N10$, 2.046(2); $Co2-N9$, 2.119(2); $Co2-N8$, 2.104(2); $Co2-N7$, 2.195(2); $O1-Co1-N4$, 106.28(8); $O1-Co1-N3$, 101.94(8); $N4-Co1-N3$, 114.64(8); $O1-Co1-N2$, 100.48(2); $N4-Co1-N2$, 116.10(8); $N3-Co1-N2$, 114.73(8); $O1-Co1-N1$, 176.51(8); $N4-Co1-N1$, 76.99(8); $N3-Co1-N1$, 77.50(8); $N2-Co1-N1$, 76.78(8); $O2-Co2-N10$, 106.61(8); $O2-Co2-N8$, 102.23(8); $N10-Co2-N8$, 115.00(8); $O2-Co2-N9$, 100.11(8); $N10-Co2-N9$, 117.25(8); $N8-Co2-N9$, 112.95(8); $O2-Co2-N7$, 176.81(8); $N10-Co2-N7$, 76.25(8); $N8-Co2-N7$, 77.51(8); $N9-Co2-N7$, 77.17(8). $Mn1-O1$, 2.003(3); $Mn1-N4$, 2.128(4); $Mn1-N3$, 2.204(4); $Mn1-N2$, 2.234(4); $Mn1-N1$, 2.330(4); $Mn2-O2$, 2.006(4); $Mn2-N10$, 2.137(4); $Mn2-N9$, 2.230(5); $Mn2-N8$, 2.207(5); $Mn2-N7$, 2.285(5); $O1-Mn1-N4$, 111.20(2); $O1-Mn1-N3$, 101.67(2); $N4-Mn1-N3$, 112.52(2); $O1-Mn1-N2$, 100.60(1); $N4-Mn1-N2$, 114.75(2); $N3-Mn1-N2$, 114.56(2); $O1-Mn1-N1$, 174.00(2); $N4-Mn1-N1$, 74.57(2); $N3-Mn1-N1$, 76.94(2); $N2-Mn1-N1$, 74.98(2); $O2-Mn2-N10$, 113.07(2); $O2-Mn2-N8$, 102.03(2); $N10-Mn2-N8$, 114.23(2); $O2-Mn2-N9$, 99.19(2); $N10-Mn2-N9$, 115.2(2); $N8-Mn2-N9$, 111.3(2); $O2-Mn2-N7$, 172.13(2); $N10-Mn2-N7$, 74.46(2); $N8-Mn2-N7$, 75.94(2); $N9-Mn2-N7$, 74.84(2).

A striking feature of the molecular structure of $[Co^{II}_2H_4bnppap(OH)_2]^+$ is the *syn*-configuration of the two $Co-OH$ units. Their close proximity is reflected in the

relatively short O1...O2 separation of 2.971(2) Å, a distance that is indicative of H-bonds being present between the two ligands.^{17¶} In addition, the hydroxo ligands formed intramolecular H-bonds with the neopentylamino groups of [H₄bnppap][−]. All the N–H vectors are positioned toward the hydroxo ligands with N–H...O angles of greater than 164°. This alignment produced O...N distances that are less than 2.8 Å, which, taken together, are consistent with the formation of strong H-bonds. FTIR measurements are also consistent with intramolecular H-bonds being present in [Co^{II}₂H₄bnppap(OH)₂]⁺ with broad signals from the amino NH groups appearing at 3235 cm^{−1}. We were unable to observe FTIR signals from the hydroxo ligand, presumably because they are significantly broadened because of the H-bonds.

The molecular structure of [Mn^{II}₂H₄bnppap(OH)₂]⁺ was also determined and contains nearly the same structural features as the cobalt analogue (Fig. 2B). Disorder in the neopentyl groups limited the quality of the structure; nevertheless, it is clear at the present resolution that each Mn^{II} center has trigonal bipyramidal coordination geometry with $\tau_{\text{Mn1}} = 0.99$ and $\tau_{\text{Mn2}} = 0.95$ and a Mn1...Mn2 separation of 4.303 Å. Note that this type of coordination also promotes the Mn1–O1 and Mn2–O2 vectors to assume a *syn*-configuration (O1...O2, 3.235 Å) that is supported by an extensive intramolecular H-bonding network.

In summary, a new dinucleating ligand, [H₄bnppap][−] has been developed that contains four appended amino groups connected *via* a pyrazolate bridge. The ligand allows for the preparation of new dinuclear complexes of cobalt and manganese, each of which has two M–OH units. The intramolecular H-bonding network and the rigidity of ligand framework successfully reinforces terminal hydroxide coordination and the orientation of the hydroxo groups. These attributes result in rare examples of discrete molecular species with terminal metal hydroxides arranged in a *syn*-fashion that are in close proximity (less than 3.2 Å). Systems of this type allow for further investigations into the interactions between M–O(H) groups, including exploring their reactivities.

Notes and references

‡ ESI-MS data: [Co^{II}₂H₄bnppap(¹⁸OH)₂]⁺: *m/z* = 985.8 (calcd, 985.5); [Mn^{II}₂H₄bnppap(¹⁸OH)₂]⁺: *m/z* = 977.5 (calcd, 977.5).

§ Magnetic moments were determined in DMSO using the Evans' method. The calculations were done relative to the shift in the solvent peak.

¶ For [Co^{II}₂H₄bnppap(OH)₂]⁺ hydrogen atoms on the amino groups were located from a difference-Fourier map and refined (*x*, *y*, *z*, and *U*_{iso}), while those of the hydroxo ligands were included using a riding model.

|| Various attempts using different solvents, experimental conditions, and counter anions to obtain crystals that gave a better structure of [Mn^{II}₂H₄bnppap(OH)₂](BPh₄) were unsuccessful. The freely rotating neo-pentyl groups impose high intrinsic disorder to the cationic complex, which likely explains the poor diffraction of the crystals.

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