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

Gary K.-Y. Ng, **Joseph W. Ziller**, and **A. S. Borovik**
Department of Chemistry, University of California-Irvine, 1102 Natural Science II, Irvine, CA 92697, USA

A. S. Borovik: aborovik@uci.edu

Abstract

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. Structurally 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 $[(bpy)_2Ru\text{-}OH_2]_2(\mu\text{-}O)$ complex contains a diruthenium core with two terminal aquo ligands[5] and Ménage showed that the $[(trpy)_2Fe\text{-}OH]_2(\mu\text{-}O)$ 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 unit in the *syn*-configuration has been achieved using dinucleating ligands.[7] For instance, Llobet and Meyer have reported complexes containing $Ru_2\text{-}(H_3O_2)$,[7a] $Zn_2\text{-}(H_3O_2)$[7b,c] and $Ni\text{-}(H_3O_2)$[7d] unit 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 $[Co^{II}\text{–}OH]_2$ and $[Mn^{II}\text{–}OH]_2$ complexes. The M^{II}–OH units in these complexes adopt *syn*-configurations, which are stabilized by intramolecular hydrogen bonding (H-bonding) networks.

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

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[†] Electronic Supplementary Information (ESI) available: Crystallographic data, FT-IR spectra, absorption spectra, ESI-MS spectra. For ESI and crystallographic data in CIF see DOI: 10.1039/b000000x/

Correspondence to: A. S. Borovik, `aborovik@uci.edu`.

sphere to form intramolecular H-bonding networks with the M–OH units;[9,7d] 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 ($[H_4P^Rbuam]^{5-}$) [11] and carboxyamidopyridyl ($[H_3bppap]^{2-}$)[12] groups (Fig. 1) but we were unable to prepare dinuclear M–OH complexes. For instance, the Co^{II}_2 complex of $[H_3bppap]^{2-}$ 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 (H_5bnppap), a compound containing H-bond donors that cannot readily coordinate to the metal ions.[14,10c,d]

H_5bnppap was synthesized from H_5bppap in nearly quantitative yield by reduction using $LiAlH_4$ in THF (Scheme 1). The dinuclear Co^{II} and Mn^{II} complexes of $[H_4bnppap]^-$ were prepared according to the route outlined in Scheme 2. H_5bnppap in MeOH was treated with 3 equiv of NaH under an argon atmosphere. After stirring for 30 min, the M^{II} precursors (either $Co^{II}(NO_3)_2 \cdot 6H_2O$ or $Mn^{II}(OTf)_2 \cdot 2MeCN$) were added in one portion and stirred for an additional 30 min. The reaction mixtures were then treated with 2 equiv of H_2O, followed by the addition of $NaBPh_4$, which resulted in the immediate formation of precipitates. The solids were isolated via filtration and purified by recrystallization from THF/pentane.

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 $[Co_2^{II}H_4bnppap(OH)_2]^+$ 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 ($[Mn_2^{II}H_4bnppap(OH)_2]^+$ 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 $[Co^{II}_2H_4P^Rbuam(\mu\text{-}OH)]^{2-}$ (greater than 2.1 Å) (Figure 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···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)°

[¶] ESI-MS data: $[Co_2\,^{II}H_4bnppap(^{18}OH)_2]^+$: *m/z* = 985.8 (calcd, 985.5); ($[Mn_2\,^{II}H_4bnppap(^{18}OH)_2]^+$: *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.

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 promixity 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 $[H_4bnppap]^-$. 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 $[Co^{II}_2H_4bnppap(OH)_2]^+$ with broad signals from the amino NH groups appearing at 3235 cm^{-1}. We were unable to observed FTIR signals from the hydroxo ligand, presumably because they are significantly broadened because of the H-bonds.

The molecular structure of $[Mn^{II}_2H_4bnppap(OH)_2]^+$ 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 $\tau_{Mn1} = 0.99$ and $\tau_{Mn2} = 0.95$ 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, $[H_4bnppap]^-$ 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 futher investigations into the interactions between M–O(H) groups, including exploring their reactivities.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Notes and references

1. (a) Umena Y, Kawakami K, Shen J-R, Kamiya N. Nature. 2011; 473:55–61. [PubMed: 21499260] (b) Surendranath Y, Kanan MW, Nocera DG. J Am Chem Soc. 2010; 132:16501–16509. [PubMed: 20977209] (c) Romero I, Rodrígues M, Sens C, Mola J, Kolllpara MR, Francàs L, Mas-Marza E, Esrlche L, Llobet A. Inorg Chem. 2008; 47:1824–1834. [PubMed: 18330973] (d) Betley TA, Wu Q, Voorhis TV, Nocera DG. Inorg Chem. 2008; 47:1849–1861. [PubMed: 18330975]
2. Mononuclear systems Alliger GE, Müller P, Cummins CC, Nocera DG. Inorg Chem. 2010; 49:3697–3699. [PubMed: 20337489] . Que L Jr, Tolman WB. Angew Chem Int Ed. 2002; 41:1114.
3. For examples of mononuclear systems that form O–O bonds see: Mirica LM, Ottenwaelder X, Stack TDP. Chem Rev. 2004; 104:1013–1046. [PubMed: 14871148] . Lewis EA, Tolman WB. Chem Rev. 2004; 104:1047–1076. [PubMed: 14871149]

[¶] For $[Co_2{}^{II}H_4bnppap(OH)_2]^+$ 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 crystal that gave a better structure of $[Mn_2{}^{II}H_4bnppap(OH)_2](BPh_4)$ were unsuccessful. The freely rotating neopentyl groups impose high intrinsic disorder to the cationic complex, which likely explains the poor diffraction of the crystals.

4. For examples of M–OH$_n$ in main group clusters see Roesky HW, Singh S, Jancik V, Chandrasekhar V. Acc Chem Res. 2004:969–981. [PubMed: 15609989] . Leeland JW, White FJ, Love JB. J Am Chem Soc. 2011; 133:7320–7323. [PubMed: 21517021]

5. Gilbert JA, Eggleston DS, Murphy WR Jr, Geselowitz DA, Gersten SW, Hodgson DJ, Meyer TJ. J Am Chem Soc. 1985; 107:3855–3864.

6. Duboc-Toia C, Ménage S, Vincet J-M, Thérèse A-P, Fontecave M. Inorg Chem. 1997; 36:6148–6149.

7. (a) Bozoglian F, Romain S, Ertem MZ, Todorova TK, Sens C, Mola J, Rodrígues M, Romero L, Benet-Buchholz J, Fontrodona X, Cramer CJ, Gagliardi L, Llobet A. J Am Chem Soc. 2009; 131:15176–15187. [PubMed: 19791789] (b) Meyer F, Rutsch R. Chem Commun. 1998:1037–1038. (c) Baner-Siebenlist B, Meyer F, Farkas E, Vidovic D, Dechert S. Chem–Eur J. 2005; 11:4349–4360. [PubMed: 15880544] (d) Graef T, Galezowska J, Dechert S, Meyer F. Eur J Inorg Chem. 2011; 2011:4161–4167.(e) Strautmann JBH, Walleck S, Strammler A, Glaser T. Chem Commun. 2010; 47:695–697.

8. (a) Roder JC, Meyer F, Pritzkow H. Organometallics. 2001; 20:811–817.(b) Klingele J, Dechert S, Meyer F. Coord Chem Rev. 2009; 253:2698–2741.

9. (a) Arii H, Funahashi Y, Jitsukawa K, Masuda H. Dalton Trans. 2003:2115–2116.(b) Feng G, Natale D, Prabaharan R, Mareque-Rivas JC, Williams NH. Angew Chem Int Ed. 2006; 118:7214–7217.

10. Shook RL, Borovik AS. Inorg Chem. 2011; 49:3646–3660. [PubMed: 20380466] and references therin. Borovik AS. Acc Chem Res. 2005; 38:54–61. [PubMed: 15654737] and references therein. Ogo S, Wada S, Watanabe Y, Iwase M, Wada A, Harata M, Jitsukawa K, Masuda H, Einaga H. Amgew Chem Int Ed. 1998; 37:2102–2104.. Marqes-Rivas JC, Prabaharan R, Parsons S. Dalton Trans. 2004:1648–1655. [PubMed: 15252616]

11. (a) Zinn PJ, Powell DR, Day VW, Hendrich MP, Sorrell TN, Borovik AS. Inorg Chem. 2006; 45:3484–3486. [PubMed: 16634575] (b) Zinn PJ, Sorrell TN, Powell DR, Day VW, Borovik AS. Inorg Chem. 2007; 46:10120–10132. [PubMed: 17973474]

12. Ng GK-Y, Ziller JW, Borovik AS. Inorg Chem. 2011; 50:7922–7924. [PubMed: 21793511]

13. (a) Shook RL, Peterson SM, Greaves J, Moore C, Rheingold AL, Borovik AS. J Am Chem Soc. 2011; 133:5810–5817. [PubMed: 21425844] (b) Ingle GK, Makowska-Grzyka MM, Szajna-Fuller E, Sen I, Price JC, Arif AM, Berreau LM. Inorg Chem. 2007; 46:1471–1480. [PubMed: 17249660] (c) Rudzka K, Arif AM, Berreau LM. J Am Chem Soc. 2006; 128:17018–17023. [PubMed: 17177453] (d) Szajna E, Makowska-Grzyka MM, Wasden CC, Arif AM, Berreau LM. Inorg Chem. 2005; 44:7595–7605. [PubMed: 16212386] (e) Marques-Rivas JC, Salvagni E, Parsons S. Dalton Trans. 2004:4185–4192. [PubMed: 15573171] (g) Marques-Rivas JC, de Rosoles RTM, Parsons S. Dalton Trans. 2003:2156–2163.

14. Grubel L, Fuller AL, Chambers BM, Arif AM, Berreau LM. Inorg Chem. 2010; 49:1071–1081. [PubMed: 20039645]

15. Drago, RS. Physical Methods for Chemists. 2. Vol. Chapter 11. Surfside; Gainesville, FL: 1992.

16. Addison AW, Rao TN, Reedijk J, Van Rijin J, Verschoor GC. J C S Dalton Trans. 1984:1349–1356.

17. Parthasarathi, R.; Subramanian, V. Hydrogen Bonding—New Insights. Grabowski, SJ., editor. Vol. chapter 1. Springer; Dordrecht: 2006. p. 1-50.

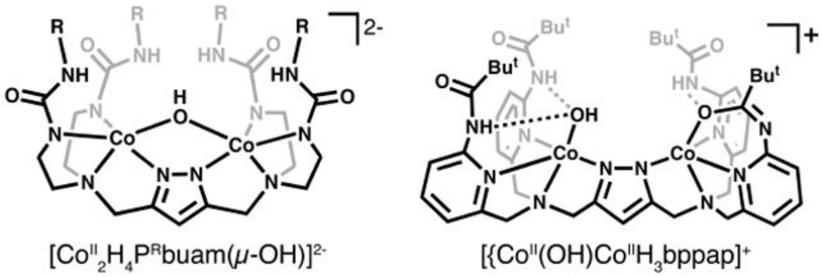


Fig. 1.

Co^{II}–OH complexes of [H$_4$P^{R}buam]$^{5-}$ and [H$_3$bppap]$^{2-}$.

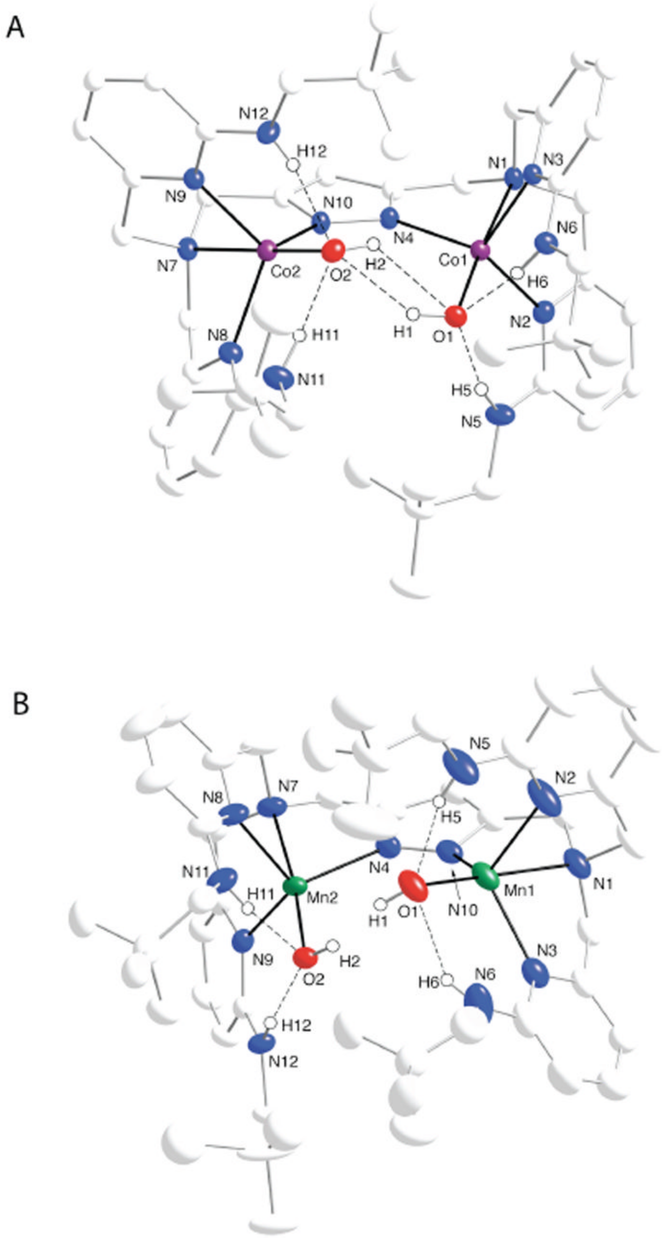
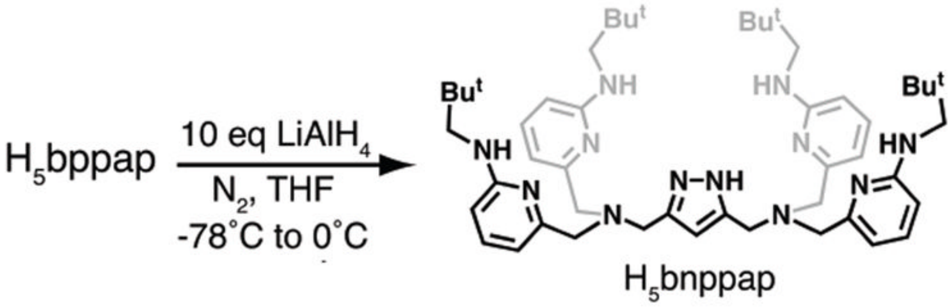


Fig. 2.

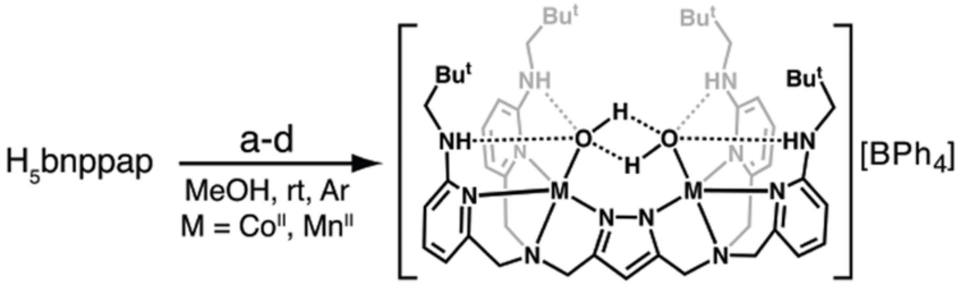
Thermal ellipsoid plots of $[\mathrm{Co^{II}}_2\mathrm{H_4bnppap(OH)_2}]^+$ (**A**) and $[\mathrm{Mn^{II}}_2\mathrm{H_4bnppap(OH)_2}]^+$ (**B**). Thermal ellipsoids are drawn at the 50% probability level. Only hydroxo and amino hydrogen atoms are shown for clarity. Selected bond lengths (Å) and angles (°) for $[\mathrm{Co^{II}}_2\mathrm{H_4bnppap(OH)_2}]^+$ and $[\mathrm{Mn^{II}}_2\mathrm{H_4bnppap(OH)_2}]^+$: 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–N9, 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–N9, 172.13(2); N10–Mn2–N7, 74.46(2); N8–Mn2–N7, 75.94(2); N9–Mn2–N7, 74.84(2).



Scheme I.

Preparative route of H_5bnppap from H_5bppap.



Scheme II.

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 $NaBPh_4$.