

**Pyrazolate-Bridging Dinucleating Ligands Containing Hydrogen Bond Donors:
Synthesis and Structure of Their Cobalt Analogs**

Supporting Information

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General Methods

All reagents were purchased from commercial sources and used as received, unless otherwise noted. Solvents were purified according to standard procedures. Anhydrous solvents were purchased from Aldrich. Anhydrous DMA and CH₂Cl₂ were eluted through a column of alternating bands of silica gel and neutral alumina and stored over molecular sieves before use. Potassium hydride (KH) as a 30% dispersion in mineral oil was filtered with a medium porosity glass frit and washed five times each with pentane and Et₂O. The solid KH was dried under vacuum and stored under an inert atmosphere. The syntheses of metal complexes were conducted in a Vacuum Atmospheres, Co. drybox under an argon atmosphere. Elemental analyses were accomplished at Desert Analytics, Tucson, AZ.

Preparative Methods

Ligand Synthesis

3,5-Bis{bis[(*N'*-*tert*-butylureayl)-*N*-ethyl]aminomethyl}-1-(tetrahydropyran-2-yl)-1*H*-pyrazole. A mixture of 3,5-bis(chloromethyl)-(tetrahydropyran-2-yl)-1*H*-pyrazole¹ (**3**) (1.33 g, 5.17 mmol), bis[(*N'*-*tert*-butylureayl)-*N*-ethyl]amine² (**4**) (3.19 g, 10.6 mmol), oven dried sodium carbonate (5.48 g, 51.7 mmol), and anhydrous acetonitrile (66 mL) was refluxed under nitrogen for 25 h. TLC indicated that 3,5-bis(chloromethyl)-(tetrahydropyran-2-yl)-1*H*-pyrazole was not present in the reaction mixture (*R*_f = 0.80; silica plate with acetone) after 24 h. The boiling reaction mixture was filtered and the white solid was washed with boiling acetonitrile. As the combined filtrate began to cool to room temperature, a white precipitate formed. The suspension was placed in a freezer (~ -10 °C) overnight and the resulting white solid was filtered. The white solid was washed with diethyl ether and dried by vacuum, 3.65 g (91%). Foam: 132 °C. Mp: 180-184 °C. LRMS (FAB+; *m/z*): 779.7 [*M*⁺]. IR (KBr; cm⁻¹): ν(NH) 3373, ν(CO) 1641, ν(NH) 1560. ¹H-NMR (DMSO-*d*₆): δ 6.23 (s, 1H, Pz-*H*⁴), 5.75 (m, 8H, C(O)NH), 5.49 (dd, ³*J* = 1.7, 9.8 Hz, 1H, *H*²-thp), 3.86 (m, 1H, *H*⁶-thp), 3.72 (d, *J* = 14.1 Hz, 1H, Pz-C⁵-CH₂N), 3.55 (m, 1H, *H*⁶-thp), 3.52 (m, 2H, Pz-C³-CH₂N), 3.45 (d, *J* = 14.1 Hz, 1H, Pz-C⁵-CH₂N), 3.00 (m, 8H, CH₂CH₂NH), 2.50-2.33 (m, 8H, NCH₂CH₂), 2.24 (m, 1H, *H*³-thp), 1.93 (m, 1H, *H*⁴-thp), 1.80 (m, 1H, *H*³-thp), 1.68 (m, 1H, *H*⁴-thp), 1.49 (m, 2H, *H*⁵-thp), 1.21 (d, *J* = 4.7 Hz, 36H, C(CH₃)₃). ¹³C-NMR (DMSO-*d*₆): δ 157.50 (C(O)), 147.84 (Pz-C³), 140.63 (Pz-C⁵), 107.38 (Pz-C⁴), 83.24 (C²-thp), 66.36 (C⁶-thp), 54.13 (NCH₂CH₂), 53.70 (NCH₂CH₂), 51.38 (Pz-C³-CH₂N), 48.93 (NH-C(CH₃)₃), 48.74 (Pz-C⁵-CH₂N), 37.04 (CH₂CH₂NH), 36.98 (CH₂CH₂NH), 29.32 (C(CH₃)₃), 28.74 (C³-thp), 24.77 (C⁵-thp), 22.23 (C⁴-thp).

3,5-Bis{bis[(*N'*-*tert*-butylureayl)-*N*-ethyl]aminomethyl}-1*H*-pyrazole (H₉P^{bu}buam). To a solution of 3,5-Bis{bis[(*N'*-*tert*-butylureayl)-*N*-ethyl]aminomethyl}-1-(tetrahydropyran-2-yl)-1*H*-pyrazole (3.65 g, 4.69 mmol) in absolute ethanol (44 mL), 21 mL of freshly prepared ethanolic HCl was added, and the reaction mixture was stirred at room temperature for 17 h. The solvent was removed under reduced pressure to obtain an off-white solid. The solid was then dissolved in water (35 mL) and 35 mL of saturated sodium carbonate solution was added, resulting in a white precipitate. The pH of the aqueous solution was found to be ≥ 8. Next, the product was extracted with three 70 mL portions of dichloromethane and the combined organic layers were dried with sodium

sulfate. The mixture was filtered and the filtrate was concentrated under reduced pressure to yield an off-white solid, 3.13 g (96%). Mp: 133-137 °C. HRMS (ESI; m/z): 695.5392 [M^+]. Exact mass calcd for $C_{33}H_{67}N_{12}O_4$ [$M + H$], 695.5408. IR (KBr; cm^{-1}): $\nu(NH)$ 3365, 3314, $\nu(CO)$ 1641, $\nu(NH)$ 1561. 1H -NMR (DMSO- d_6): δ 6.08 (s, 1H, Pz- H^4), 5.71 (s, 4H, C(O)NHC(CH₃)₃), 5.67 (t, $J = 5.4$ Hz, 4H, CH₂NHC(O)), 3.63 (s, 2H, Pz-CH₂N), 3.55 (s, 2H, Pz-CH₂N), 3.02 (m, 8H, CH₂CH₂NH), 2.38 (m, 8H, NCH₂CH₂), 1.21 (s, 36H, C(CH₃)₃). ^{13}C -NMR (DMSO- d_6): δ 157.49 (C(O)), 157.46 (C(O)), 148.60 (Pz-C^{3,5}), 139.55 (Pz-C^{3,5}), 104.63 (Pz-C⁴), 53.39 (NCH₂CH₂), 51.01 (Pz-C^{3,5}-CH₂), 48.95 (C(CH₃)₃), 48.92 (C(CH₃)₃), 47.96 (Pz-C^{3,5}-CH₂), 36.96 (CH₂CH₂NH), 36.80 (CH₂CH₂NH), 29.32 (C(CH₃)₃).

3,5-Bis{bis[(*N'*-isopropylureayl)-*N*-ethyl]aminomethyl}-1-(tetrahydropyran-2-yl)-1*H*-pyrazole. A mixture of 3,5-bis(chloromethyl)-(tetrahydropyran-2-yl)-1*H*-pyrazole¹ (**3**) (1.00 g, 3.89 mmol), bis[(*N'*-isopropylureayl)-*N*-ethyl]amine² (**5**) (2.18 g, 7.97 mmol), oven dried sodium carbonate (4.12 g, 38.9 mmol), and anhydrous acetonitrile (50 mL) was refluxed under nitrogen for 24 h. TLC indicated that 3,5-bis(chloromethyl)-(tetrahydropyran-2-yl)-1*H*-pyrazole was not present in the reaction mixture ($R_f = 0.80$; silica plate with acetone) after 24 h. The reaction mixture was cooled to room temperature and filtered. The white solid obtained was washed with acetonitrile and dried under reduced pressure. Next, the dry solid was thoroughly washed with water, then with copious amounts of diethyl ether, and placed under vacuum to obtain a dry white powder, 2.27 g (81%). Mp: 183-185 °C. LRMS (ESI; m/z): 723.53 [M^+]. IR (KBr; cm^{-1}): $\nu(NH)$ 3335, $\nu(CO)$ 1628, $\nu(NH)$ 1574. 1H -NMR (DMSO- d_6): δ 6.17 (s, 1H, Pz- H^4), 5.95 (t, $J = 5.1$ Hz, 2H, CH₂NH-C(O)), 5.85 (d, $J = 3.7$, 2H, C(O)NH-CH), 5.83 (d, $J = 3.9$, 2H, C(O)NH-CH), 5.76 (t, $J = 5.4$, 2H, CH₂NH-C(O)), 5.50 (dd, $^3J = 1.9$, 9.9 Hz, 1H, H^2 -thp), 3.85 (m, 1H, H^6 -thp), 3.73 (d, $J = 13.8$ Hz, 1H, Pz-C⁵-CH₂N), 3.64 (o, $J = 6.7$ Hz, 4H, CH(CH₃)₂), 3.53 (m, 1H, H^6 -thp), 3.50 (s, 2H, Pz-C³-CH₂N), 3.37 (m, 1H, Pz-C⁵-CH₂N), 3.02 (m, 8H, CH₂CH₂NH), 2.50-2.30 (m, 8H, NCH₂CH₂), 2.22 (m, 1H, H^3 -thp), 1.90 (m, 1H, H^4 -thp), 1.77 (m, 1H, H^3 -thp), 1.65 (m, 1H, H^4 -thp), 1.46 (m, 2H, H^5 -thp), 1.01 (d, $J = 6.5$ Hz, 24H, (CH(CH₃)₂)). ^{13}C -NMR (DMSO- d_6): δ 158.03 (C(O)), 157.99 (C(O)), 148.59 (Pz-C³), 141.14 (Pz-C⁵), 107.89 (Pz-C⁴), 83.59 (C²-thp), 66.71 (C⁶-thp), 54.55 (NCH₂CH₂), 54.06 (NCH₂CH₂), 51.92 (Pz-C³-CH₂N), 49.24 (Pz-C⁵-CH₂N), 41.23 (CH(CH₃)₂), 41.19 (CH(CH₃)₂), 37.49 (CH₂CH₂NH), 37.44 (CH₂CH₂NH), 29.02 (C³-thp), 25.20 (C⁵-thp), 23.65 (CH(CH₃)₂), 23.50 (CH(CH₃)₂), 22.66 (C⁴-thp).

3,5-Bis{bis[(*N'*-isopropylureayl)-*N*-ethyl]aminomethyl}-1*H*-pyrazole (H₉P^{iPr}buam). To a suspension of 3,5-Bis{bis[(*N'*-isopropylureayl)-*N*-ethyl]aminomethyl}-1-(tetrahydropyran-2-yl)-1*H*-pyrazole (2.23 g, 3.09 mmol) in absolute ethanol (29 mL), 14 mL of freshly prepared ethanolic HCl was added, and the reaction mixture was stirred at room temperature for 17 h. The solvent was removed under reduced pressure to obtain an off-white solid. The solid was then dissolved in water (45 mL) and 45 mL of saturated sodium carbonate solution was added. The pH of the aqueous solution was found to be ≥ 8 . The resulting murky solution was placed in a separatory funnel and 90 mL of CH₂Cl₂ was poured in. A white gel-like solid was formed when the mixture was mixed for a few minutes. Filtered mixture and washed gel-like solid with water and then with copious amounts of diethyl ether. The resulting solid was placed under vacuum for a few hours to

obtain a dry, white powder, 1.73 g (88%). Mp: 224 °C (decomp.). HRMS (ESI; m/z): 639.4762 [M^+]. Exact mass calcd for $C_{29}H_{59}N_{12}O_4$ [$M + H$], 639.4782. IR (KBr; cm^{-1}): $\nu(NH)$ 3350, 3337, $\nu(CO)$ 1630, $\nu(NH)$ 1562. 1H -NMR (DMSO- d_6): δ 6.09 (s, 1H, Pz- H^4), 5.84 (d, $J = 7.7$ Hz, 4H, C(O)NH-CH), 5.78 (t, $J = 5.4$ Hz, 4H, $CH_2NH-C(O)$), 3.65 (o, $J = 6.7$ Hz, 4H, $CH(CH_3)_2$), 3.57 (s, 4H, Pz- $C^{3,5}$ - CH_2), 3.04 (dt, $J = 5.7, 5.9$, 8H, CH_2CH_2NH), 2.39 (t, $J = 6.2$ Hz, 8H, NCH_2CH_2), 1.02 (d, $J = 6.5$, 24H, $CH(CH_3)_2$). ^{13}C -NMR (DMSO- d_6): δ 157.54 (C(O)), 128.16 (Pz- $C^{3,5}$), 126.96 (Pz- $C^{3,5}$), 104.57 (Pz- C^4), 53.39 (NCH_2CH_2), 49.45 (Pz- $C^{3,5}$ - CH_2N), 40.82 ($CH(CH_3)_2$), 37.20 (CH_2CH_2NH), 23.23 ($CH(CH_3)_2$).

Complex Synthesis

Tetrapropylammonium μ -chloro- μ -{3,5-bis{bis[(N' -*tert*-butylureaylato)- N -ethyl]aminatomethyl}-1*H*-pyrazolato}dicobaltate(II) [nPr_4N] $_2$ [Co II $_2$ H $_4$ P tBu buam(μ -Cl)]. A solution of 3,5-bis{bis[(N' -*tert*-butylureayl)- N -ethyl]aminomethyl}-1*H*-pyrazole (H_9P^{tBu} buam) (0.100 g, 0.144 mmol) in anhydrous N,N -dimethylacetamide (DMA, 5 mL) was treated with solid KH (0.029 g, 0.72 mmol) under an Ar atmosphere. After gas evolution ceased, solid $CoCl_2$ (0.037 g, 0.29 mmol) was added. The resulting blue-purple solution was stirred for 30 min. Next, tetrapropylammonium chloride (0.064 g, 0.29 mmol) was added and stirred for 1 h. The solvent was removed under reduced pressure at room temperature and the resulting solid residue was washed with diethyl ether and dried under vacuum to afford a light blue-purple powder. The powder was then dissolved in anhydrous CH_2Cl_2 and the insoluble impurities and KCl were filtered. The solvent was then evaporated from the filtrate under reduced pressure to afford a blue-purple solid, 0.108 g (62%). X-ray quality crystals were obtained by vapor diffusion of diethyl ether in a DMA solution of the isolated metal salt. Anal. Calcd (found) for [nPr_4N] $_2$ [Co II $_2$ H $_4$ P tBu buam(μ -Cl)] \cdot 0.6 CH_2Cl_2 , $C_{57.6}H_{118.2}Cl_{2.2}Co_2N_{14}O_4$: C, 54.61 (55.15); H 9.40 (9.12); N 15.48 (14.96). IR (Nujol; cm^{-1}): $\nu(NH)$ 3359, 3284, $\nu(CO)$ 1640, $\nu(CO)$ 1587. UV/vis (DMA): $\lambda_{max}(\epsilon) = 312$ (4390), 562 (195), 592 (sh), 652 (sh), 791 (25).

Tetrapropylammonium μ -chloro- μ -{3,5-bis{bis[(N' -isopropylureaylato)- N -ethyl]aminatomethyl}-1*H*-pyrazolato}dicobaltate(II) [nPr_4N] $_2$ [Co II $_2$ H $_4$ P iPr buam(μ -Cl)]. A solution of 3,5-bis{bis[(N' -isopropylureayl)- N -ethyl]aminomethyl}-1*H*-pyrazole (H_9P^{iPr} buam) (0.100 g, 0.157 mmol) in anhydrous N,N -dimethylacetamide (DMA, 5 mL) was treated with solid KH (0.031 g, 0.79 mmol) under an Ar atmosphere. After gas evolution ceased, solid $CoCl_2$ (0.041 g, 0.31 mmol) was added. The resulting blue-purple solution was stirred for 30 min. Next, tetrapropylammonium chloride (0.070 g, 0.31 mmol) was added and stirred for 1 h. The solvent was removed under reduced pressure at room temperature and the resulting solid residue was washed with diethyl ether and dried under vacuum to afford a light blue-purple powder. The powder was then dissolved in anhydrous CH_2Cl_2 and the insoluble KCl was filtered. The solvent was then evaporated from the filtrate under reduced pressure to afford a blue-purple solid, 0.182 g (100%). X-ray quality crystals were obtained by vapor diffusion of diethyl ether in a DMA solution of the isolated metal salt. Anal. Calcd (found) for [nPr_4N] $_2$ [Co II $_2$ H $_4$ P iPr buam(μ -Cl)] \cdot 0.1 CH_2Cl_2 , $C_{53.1}H_{109.2}Cl_{1.2}Co_2N_{14}O_4$: C, 54.59 (54.71); H, 9.42 (9.07); N, 16.78 (16.24). IR (Nujol; cm^{-1}): $\nu(NH)$ 3350, $\nu(CO)$ 1638, $\nu(CO)$

1577. UV/vis (DMA): $\lambda_{\text{max}}(\epsilon) = 312 (6130), 470 (\text{sh}), 494 (81), 568 (158), 594 (\text{sh}), 620 (\text{sh}), 774 (27)$.

Physical Methods

NMR spectra were recorded on Bruker Avance 400 or 500 MHz spectrometers equipped with a Silicon Graphics workstation. Chemical shifts are reported in ppm relative to residual solvent. Most assignments are based on a series of 2D experiments. Fast atom bombardment mass spectra (FAB-MS) were recorded on a Hewlett-Pachard 5989A spectrometer with HPLC (HP 1050) HP particle-beam interface mass system and a phasor FAB gun. FAB experiments were carried out in a thioglycerol/glycerol (TG/G) matrix and a xenon fast atom beam was used. Electrospray ionization mass spectra (ESI) were recorded on a Micromass LCT Premier spectrometer operating in W mode (high and low resolution modes). Melting points were obtained with a Laboratory Devices MEL-TEMP apparatus and are uncorrected. Fourier transform infrared spectra were collected on a Mattson Genesis series FTIR instrument with values reported in wavenumbers. Electronic spectra were collected on a Cary 50 spectrophotometer using 1.00 mm or 1.00 cm quartz cuvetts. Perpendicular-mode X-band EPR spectra were collected using a Bruker EMX spectrometer equipped with an ER041XG microwave bridge and an Oxford Instrument liquid He quartz cryostat. Parallel-mode X-band EPR spectra were recorded on a Bruker ESP300 spectrometer equipped with an Oxford ESR910 cryostat and a bimodal cavity (Bruker ER4116DM).

Crystallographic Methods

$[\text{nPr}_4\text{N}]_2[\text{Co}^{\text{II}}_2\text{H}_4\text{P}^{\text{tBu}}\text{buam}(\mu\text{-Cl})]\cdot\text{DMA}$

Purple rectangular parallelepiped-shaped crystals of $[\text{Co}_2(\text{Cl})\text{-(N}_{12}\text{O}_4\text{C}_{33}\text{H}_{61})][\text{N}(\text{C}_3\text{H}_7)_4]_2 \cdot \text{CH}_3\text{CON}(\text{CH}_3)_2$ are, at 100(2) K, monoclinic, space group $\text{P2}_1(\text{C}_2^2 - \text{No. } 4)^3$ with $a = 15.293(3) \text{ \AA}$, $b = 22.333(4) \text{ \AA}$, $c = 21.971(4) \text{ \AA}$, $\beta = 99.132(5)^\circ$, $V = 7409(2) \text{ \AA}^3$ and $Z = 4$ formula weights $\{\rho_{\text{calcd}} = 1.168 \text{ g/cm}^3; \mu_{\text{a}}(\text{MoK}\alpha) = 0.536 \text{ mm}^{-1}\}$. A full hemisphere of diffracted intensities (1850 10-second frames with an ω scan width of 0.30°) was measured for a single-domain specimen using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker SMART APEX CCD Single Crystal Diffraction System.⁴ X-rays were provided by a fine-focus sealed x-ray tube operated at 50kV and 30mA. Lattice constants were determined with the Bruker SAINT software package using peak centers for 7738 reflections. A total of 88982 integrated reflection intensities having $2\theta(\text{MoK}\alpha) < 60.06^\circ$ were produced using the Bruker program SAINT;⁵ 42956 of these were unique and gave $R_{\text{int}} = 0.091$ with a coverage which was 99.4% complete. The intensity data were corrected empirically for variable absorption effects using 2243 equivalent reflections; the relative transmission factors ranged from 0.938 to 1.000. The Bruker software package SHELXTL Version 6.10⁶ was used to solve the structure using “direct methods” techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL software package. A total of 1573 parameters were refined using 25 restraints, 42956 data and weights of $w = 1/[\sigma^2(F_o^2) + (0.0322 P)^2]$, where $P = [F_o^2 + 2F_c^2]/3$. Final agreement factors at convergence are: $R_1(\text{unweighted, based on } F) = 0.062$ for 18819 independent absorption-corrected reflections having $2\theta(\text{MoK}\alpha) < 60.06^\circ$ and $I > 2\sigma(I)$; $R_1(\text{unweighted, based on}$

$R = 0.135$ and wR_2 (weighted, based on F^2) = 0.122 for all 42956 independent absorption-corrected reflections having $2\theta(\text{MoK}\alpha) < 60.06^\circ$. The largest shift/s.u. was 0.001 in the final refinement cycle. The final difference map had maxima and minima of 0.74 and $-0.72 \text{ e}^-/\text{\AA}^3$, respectively. The absolute configuration was reliably established experimentally; the "Flack" absolute structure parameter refined to a final value of $-0.01(1)$.

The final structural model incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. The eight urea hydrogen atoms were located from a difference Fourier and included in the structural model as independent isotropic atoms whose positional parameters were allowed to vary in least-squares refinement cycles; the isotropic thermal parameters for the urea protons of the first crystallographically-independent molecule were also allowed to vary. The 30 methyl groups in the two crystallographically-independent anions and the two crystallographically-independent dimethylacetamide $\text{CH}_3\text{CON}(\text{CH}_3)_2$ solvent molecules of crystallization were included in the structural model as rigid groups (using idealized sp^3 -hybridized geometry and a C-H bond length of 0.98 Å) which were allowed to rotate about their C-N or C-C bonds in least-squares refinement cycles. The 16 methyl groups in the four crystallographically-independent cations were included in the structural model as rigid groups (using idealized sp^3 -hybridized geometry and a C-H bond length of 0.98 Å) with a "staggered" orientation. The remaining hydrogen atoms were included in the structural model as idealized atoms (assuming sp^2 - or sp^3 -hybridization of the carbon atoms and C-H bond lengths of 0.95 - 0.99 Å). The isotropic thermal parameters of all idealized hydrogen atoms and the four urea protons of the second crystallographically-independent anion were fixed at values 1.2 (nonmethyl) or 1.5 (methyl) times the equivalent isotropic thermal parameter of the nitrogen or carbon atom to which they are covalently bonded.

One of the $[\text{N}(\text{C}_3\text{H}_7)_4]^+$ cations and one of the dimethylacetamide molecules of crystallization appear to be somewhat disordered in the crystal. Reasonable metrical parameters could only be obtained for these moieties when restraints were imposed on some of their bond lengths and angles.

Several of the N-C and C-C bond lengths for the fourth $[\text{N}(\text{C}_3\text{H}_7)_4]^+$ cation were restrained to have values that were within 0.005 Å of being 1.000 and 1.013 times, respectively, the value of a free variable that refined to a final value of 1.493(2) Å. Several $\text{N4C}\cdots\text{C4x2}$, $\text{C4x1}\cdots\text{C4y1}$ and $\text{C4x1}\cdots\text{C4x3}$ (where x and y = 1, 2 or 3 but $x \neq y$) separations were restrained to values which were 1.633 times the value of this same free variable.

The O1s-C1s and N1s-C1s bond lengths for the disordered DMA molecule of crystallization were restrained to have values that were within 0.01 Å of being 1.000 and 1.104 times, respectively, the value of a second free variable that refined to a final value of 1.232(6) Å. The O1s \cdots N1s, N1s \cdots C2s and C1s \cdots C3s separations were restrained to values which were 1.732 times the value of this same (second) free variable.

$[\text{nPr}_4\text{N}]_2[\text{Co}^{\text{II}}_2\text{H}_4\text{P}^{\text{iPr}}\text{buam}(\mu\text{-Cl})]\cdot 0.5\text{DMA}$

Red rectangular parallelepiped shaped crystals of $[\text{Co}_2(\text{Cl})-(\text{N}_{12}\text{O}_4\text{C}_{29}\text{H}_{53})][\text{N}(\text{C}_3\text{H}_7)_4]_2 \cdot 0.5 \text{CH}_3\text{CON}(\text{CH}_3)_2$ are, at 100(2) K, triclinic, space group $\bar{C}2_1$ – No. 2³ with $a = 13.6311(6)$ Å, $b = 15.3318(7)$ Å, $c = 17.3877(8)$ Å, $\alpha = 109.945(1)^\circ$, β

= 98.922(1)°, γ = 94.224(1)°, V = 3343.1(3) Å³ and Z = 2 formula weights { d_{calcd} = 1.195 g/cm³; $\mu_a(\text{MoK}\alpha)$ = 0.588 mm⁻¹}. A full hemisphere of diffracted intensities (1850 10-second frames with an ω scan width of 0.30°) was measured for a single-domain specimen using graphite-monochromated MoK α radiation (λ = 0.71073 Å) on a Bruker SMART APEX CCD Single Crystal Diffraction System.⁴ X-rays were provided by a fine-focus sealed x-ray tube operated at 50kV and 30mA. Lattice constants were determined with the Bruker SAINT software package using peak centers for 8747 reflections. A total of 39968 integrated reflection intensities having $2\theta(\text{MoK}\alpha)$ < 60.06° were produced using the Bruker program SAINT;⁵ 19262 of these were unique and gave R_{int} = 0.029 with a coverage which was 98.5% complete. The intensity data were corrected empirically for variable absorption effects using 8431 equivalent reflections; the relative transmission factors ranged from 0.933 to 1.000. The Bruker software package SHELXTL Version 6.10 was used to solve the structure using “direct methods” techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL software package.⁶ A total of 755 parameters were refined using 49 restraints, 19262 data and weights of $w = 1/[\sigma^2(F^2) + (0.0663 P)^2]$, where $P = [F_o^2 + 2F_c^2] / 3$. Final agreement factors at convergence are: R_1 (unweighted, based on F) = 0.038 for 15074 independent absorption-corrected reflections having $2\theta(\text{MoK}\alpha)$ < 60.06° and $I > 2\sigma(I)$; R_1 (unweighted, based on F) = 0.049 and wR_2 (weighted, based on F^2) = 0.106 for all 19262 independent absorption-corrected reflections having $2\theta(\text{MoK}\alpha)$ < 60.06°. The largest shift/s.u. was 0.001 in the final refinement cycle. The final difference map had maxima and minima of 0.82 and -0.52 e⁻/Å³, respectively.

The final structural model incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. The four urea hydrogen atoms were located from a difference Fourier and included in the structural model as independent isotropic atoms whose parameters were allowed to vary in least-squares refinement cycles. The 18 methyl groups were refined as rigid rotors (using idealized sp³-hybridized geometry and a C-H bond length of 0.98 Å) which were allowed to rotate about their N-C or C-C bonds in least-squares refinement cycles. The remaining hydrogen atoms were included in the structural model as idealized atoms (assuming sp²- or sp³-hybridization of the carbon atoms and C-H bond lengths of 0.95 – 1.00 Å). The isotropic thermal parameters of all idealized hydrogen atoms were fixed at values 1.2 (nonhydrogen) or 1.5 (methyl) times the equivalent isotropic thermal parameter of the carbon atom to which they are covalently bonded. The dimethylacetamide molecule of crystallization is disordered with two possible orientations about the crystallographic inversion center at the origin of the unit cell. The inversion center lies at the midpoint of the amide C-N bond and therefore causes the two ends of the molecule to be essentially superimposed for the two different orientations. All six nonhydrogen atoms and six of the nine methyl hydrogens that corresponded to one of these orientations were therefore included in the structural model with occupancy factors of 0.50; restraints were also imposed on the positional and thermal parameters for these six disordered nonhydrogen atoms.

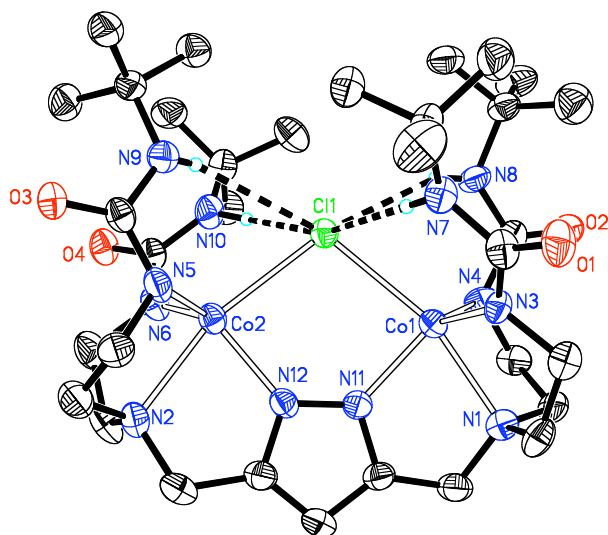


Figure S1. Thermal ellipsoid diagram of $[\text{Co}^{\text{II}}_2\text{H}_4\text{P}^{\text{rBu}}\text{buam}(\mu\text{-Cl})]^{2-}$ (one of the two crystallographically independent anions). The ellipsoids are drawn at the 50% probability level and only the urea hydrogen atoms are shown for clarity. Selected bond lengths (Å) and angles (°): Co1-Cl1 2.561(1), Co1-N1 2.230(3), Co1-N3 1.996(3), Co1-N4 1.994(4), Co-N11 2.008(3), Co2-Cl1 2.548(1), Co2-N2 2.271(3), Co2-N5 2.009(4), Co2-N6 1.982(4), Co2-N12 1.982(3), Co1...Co2 3.985(1), N7...Cl1 3.271(4), N8...Cl1 3.382(4), N9...Cl1 3.434(4), N10...Cl1 3.269(4), N3-Co1-N4 115.01(13), N3-Co1-N11 116.33(14), N4-Co1-N11 120.91(14), N3-Co1-Cl1 107.56(10), N4-Co1-Cl1 103.97(10), N11-Co1-Cl1 86.65(9), N3-Co1-N1 83.36(13), N4-Co1-N1 81.34(13), N11-Co1-N1 77.47(12), N1-Co1-Cl1 163.64(9), N5-Co2-N6 114.01(13), N5-Co2-N12 118.23(14), N6-Co2-N12 119.76(14), N5-Co2-Cl1 105.30(10), N6-Co2-Cl1 105.87(10), N12-Co2-Cl1 87.54(9), N5-Co2-N2 80.63(13), N6-Co2-N2 83.82(13), N12-Co2-N2 77.26(13), N2-Co2-Cl1 164.66(9), Co1-Cl1-Co2 102.50(4).

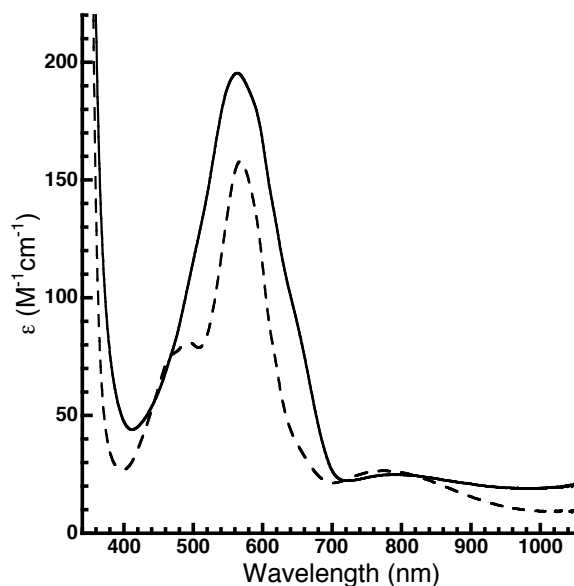


Figure S2. Visible absorbance spectra for $[\text{nPr}_4\text{N}]_2[\text{Co}^{\text{II}}_2\text{H}_4\text{P}^{\text{rBu}}\text{buam}(\mu\text{-Cl})]$ in DMA (—) and $[\text{nPr}_4\text{N}]_2[\text{Co}^{\text{II}}_2\text{H}_4\text{P}^{\text{iPr}}\text{buam}(\mu\text{-Cl})]$ in DMA (---).

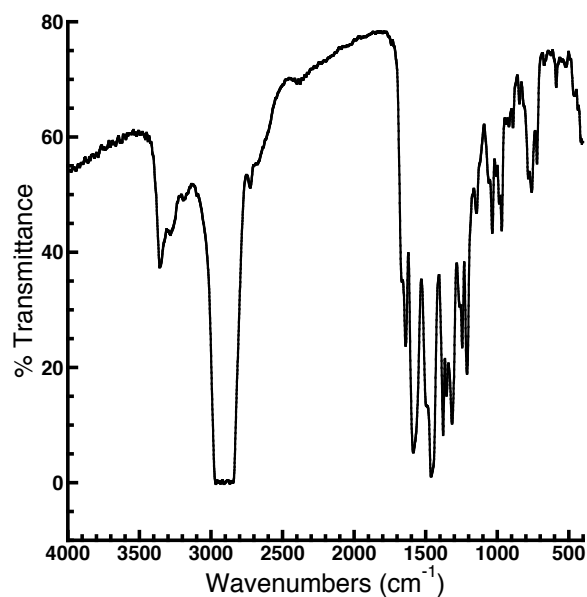


Figure S3. Infrared Spectrum for $[\text{nPr}_4\text{N}]_2[\text{Co}^{\text{II}}_2\text{H}_4\text{P}^{\text{Bu}}\text{buam}(\mu\text{-Cl})]$ as a mull.

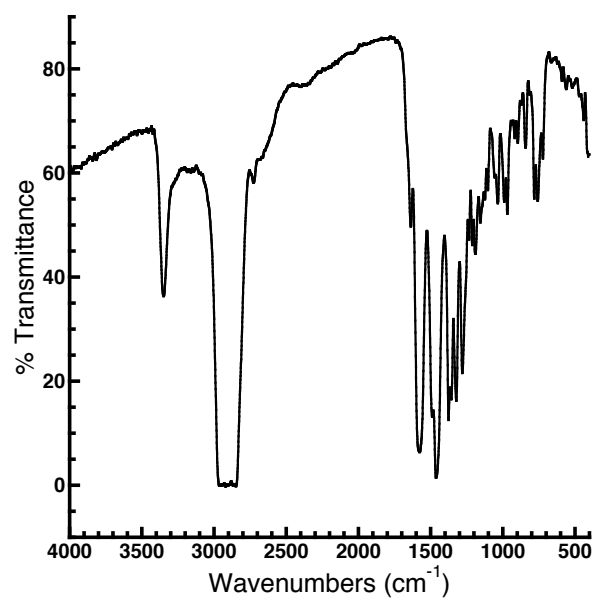


Figure S4. Infrared Spectrum for $[\text{nPr}_4\text{N}]_2[\text{Co}^{\text{II}}_2\text{H}_4\text{P}^{\text{iPr}}\text{buam}(\mu\text{-Cl})]$ as a mull.

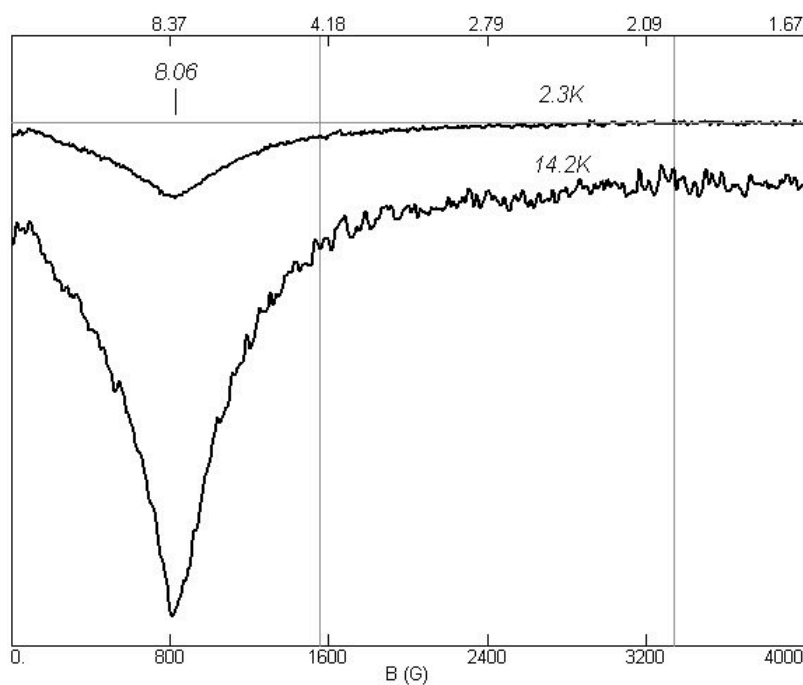


Figure S5. Parallel-mode X-band EPR spectra for $[\text{nPr}_4\text{N}]_2[\text{Co}^{\text{II}}_2\text{H}_4\text{P}^{\text{iPr}}\text{buam}(\mu\text{-Cl})]$ as a solid recorded at $T = 2.3\text{ K}$ and 14.2 K .

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