Supporting info for

Metal-Metal Bond Umpolung in Heterometallic Extended Metal Atom Chains

Amelia M. Wheaton, Jill A. Chipman, Michael D. Roy, John. F. Berry*

Department of Chemistry, University of Wisconsin–Madison, 1101 University Ave., Madison, WI 53706

* To whom correspondence may be addressed: berry@chem.wisc.edu

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Experimental.

Materials and General Methods. All reactions were carried out under a dry N$_2$ atmosphere using Schlenk techniques and glovebox methods. Anhydrous hexanes, diethyl ether, and tetrahydrofuran were purchased from Sigma-Aldrich. Acetonitrile and dichloromethane were freshly distilled from CaH$_2$ under an N$_2$ atmosphere. Pentane was purified using a Vacuum Atmospheres solvent purification system. All solvents were stored over 3 Å molecular sieves under an N$_2$ atmosphere for at least 3 days before use. Naphthalene was purchased from Sigma-Aldrich and sublimed prior to use. The metal(II) chloride salts (M = Cr, Mn, Fe, Co, Ni) and TlOTf were purchased from Strem Chemicals and used as received. Eicosane was purchased from Sigma-Aldrich, melted and fused four times under vacuum, and stored under an atmosphere of N$_2$. The compounds Mo$_2$(dpa)$_4$, 5$^1$ and 7$^2$ were prepared as previously described in the literature. IR spectra were taken on a Bruker Tensor 27 FTIR spectrometer using an attenuated total reflectance (ATR) adapter under an atmosphere of Ar. Elemental analyses were carried out by Midwest Microlabs, LLC in Indianapolis, IN. $^{19}$F NMR spectra were obtained on a 400 MHz Bruker Advance III spectrometer. MALDI mass spectra were obtained on Bruker Impact™ II MALDI mass spectrometer.

Physical Measurements: EPR data for 4 at 10 K were acquired on a Bruker ELEXSYS E500 EPR spectrometer equipped with a Varian E102 microwave bridge. An Oxford Instruments ESR-900 continuous-flow helium cryostat and an Oxford Instruments 503S temperature controller were used to control the sample temperature. The measurement conditions were as follows: 9.38 GHz, 4 G modulation amplitude, 2500 G center field, 5000 G sweep width, 0.5024 mW microwave power, 52 dB gain, and 10.24 ms time constant and conversion time. Variable temperature magnetic susceptibility measurements of polycrystalline samples of 1, 3, and 4 suspended in eicosane in polycarbonate sample holders were performed at the University of Wisconsin-Madison on a SQUID magnetometer (MPMS 3 Quantum Design) in the temperature range 2–300 K with an applied field of 0.1 Tesla. Variable temperature/variable field measurements of the same samples of 1, 3, and 4 were also collected on the same magnetometer at 2, 4, 6, and 8 K with the field swept from 0.1 to 7 T. Experimental
susceptibility data were corrected for the underlying diamagnetism using Pascal’s constants.\textsuperscript{3} The data for \textbf{1} and \textbf{3} were modeled using the program PHI,\textsuperscript{4} while the data for \textbf{4} were modeled using the KaleidaGraph software (KaleidaGraph 4.0, Synergy Software, Reading, PA, USA). Data for \textbf{1} and \textbf{3} were parameterized using the following general formalism of the spin Hamiltonian:

$$\tilde{H} = \beta \tilde{S} \mathbf{g} \tilde{H} + \tilde{S} \mathbf{D} \tilde{S}$$

where $\beta$ is the Bohr magneton, $\tilde{H}$ is the applied external magnetic field, and $\tilde{S}$, $\mathbf{g}$, and $\mathbf{D}$ are the spin vector, electronic $\mathbf{g}$-tensor, and zero-field splitting (ZFS) tensors, respectively. Fits including rhombicity provided values of $E$ that were chemically unreasonable and therefore was excluded from models of the magnetic data for \textbf{1} and \textbf{3}. Simultaneous fits of the susceptibility and reduced magnetization data allowed for assignment of the sign of $D$ $< 0$ for both \textbf{1} and \textbf{3}. Temperature independent paramagnetism (TIP) contributions to the experimental susceptibility was included as a parameter in the susceptibility models for \textbf{1} and \textbf{3}.

Magnetic susceptibility data for \textbf{4} were modeled using a Roult’s law spin-equilibrium model\textsuperscript{5} that fits the susceptibility data with the following equation:

$$\chi T = (1 - p_{HS}) \frac{F_{HS} - F_{LS} \ast TIP \ast T}{1 + \exp \left( \frac{\Delta H}{R} \ast \left( \frac{1}{T} - \frac{1}{T_C} \right) \right)} + F_{LS} \ast TIP \ast T + p_{HS} F_{HS}$$

$$F_{HS} = \frac{g_{HS}^2 \ast C_{HS}}{4}; F_{LS} = \frac{g_{LS}^2 \ast C_{LS}}{4}$$

where $T_C$ is the critical temperature (the temperature where there are an equal number of high and low spin molecules), $p_{HS}$ is the portion of the complex that remains HS at all temperatures, $\Delta H$ is the enthalpy difference between the low and high spin states, and TIP is a correction for temperature independent paramagnetism (applied only to the low spin state). $F_{HS}/F_{LS}$ are functions that describe the temperature dependence of the low and high spin states; they depend on the $g$ factors for the high and low spin states and the expectation values for the Curie constants $C$ for an $S = 1/2$ (0.375 cm$^3$ K mol$^{-1}$) and 3/2 (1.875 cm$^3$ K mol$^{-1}$) system, respectively. In the model for \textbf{4}, the value of $g_{LS}$ was constrained to the $g_{avg}$ for \textbf{4} as determined from the EPR measurement. There was insufficient susceptibility data in the high temperature regime to model a chemically meaningful $g_{HS}$; this value was therefore fixed to the $g$ value obtained from EPR measurements of the $S = 3/2$ Co$^{2+}$ ion for the Mo$_2$Co(dpa)$_4$Cl$_2$ HEMAC.\textsuperscript{6}

Mössbauer spectroscopy measurements were performed with a 1024 channel See Co model W304 resonant gamma-ray spectrometer using $^{57}$Co on Rh foil as a gamma-ray source (initial strength = 25 mCi, obtained from Ritverc Isotope Products). The source velocity range used was $\pm 4$ mm s$^{-1}$ and measurements were conducted under vacuum. A Lakeshore model 336 temperature controller and a Janis model SHI-850 cryostat were used to reach cryogenic temperatures. Data were fitted with the WMOSS4F software package,\textsuperscript{7} using an adaptive nonlinear least-squares algorithm.\textsuperscript{8} Data were collected at 80 K for \textbf{2} and for Fe(OTf)$_2$. Refined parameters for each quadrupole doublet were the isomer shift ($\delta$), quadrupole splitting ($\Delta E_Q$), and a single linewidth ($\Gamma$) for both transitions was modeled by the full-width at half-maximum (FWHM). Isomer shifts are referenced to $\alpha$-Fe foil at 294 K. The quality of the chemical models used to fit \textbf{2} and the Fe(OTf)$_2$ precursor were assessed using the reduced $\chi^2$ of the overall fits.
Here, the reduced $\chi^2$ is defined as the $\chi^2/d$, where $d$ is the degrees of freedom (the number of data points – the number of fit parameters). The $\chi^2$ statistic is given by: $\chi^2 = \sum_1^n (\frac{\text{observed} - \text{expected}}{\sigma_x})^2$, where $n$ is the number of data points, $\chi_{\text{observed}}$ is the observed data, $\chi_{\text{expected}}$ is the expected data, and $\sigma_x$ is the standard deviation of the data.

For 2, a single quadrupole doublet was used to fit the Mössbauer spectrum to account for the single $\text{Fe}^{2+}S = 2$ environment present within the trimetallic complex (see Figure 3 in the main text). For fits of the $\text{Fe(OTf)}_2$ precursor, two different models were explored, as the structure of the compound in the solid state is not known. In the first, the Mössbauer spectrum was fitted to a single quadrupole doublet representing a single unique $\text{Fe}^{2+}S = 2$ site (Figure S4 for spectrum and fitting parameters). In the second, the single quadrupole doublet present in the spectrum was fitted as a combination of two sub-spectra, representing two different chemical environments for the $\text{Fe}^{2+}S = 2$ ions present within the powder sample (Figure S5 for spectrum and fitting parameters). These two sub spectra (rel. areas of sub-spectrum $1/2 = 39/61$) were fitted with identical isomer shifts ($\delta$ of sub-spectrum $1/2 = 1.45 / 1.45 \text{ mm/s}$) but with substantially different quadrupole splittings ($\Delta E_Q$ of sub-spectrum $1/2 = 2.23 / 1.96 \text{ mm/s}$). Given the similarity of the two sub-spectra $\delta$, as well as the corresponding $^{19}\text{F}$ NMR, IR, and EA results for samples of the $\text{Fe(OTf)}_2$ precursor, it is unlikely that the two sub-spectra correspond to $\text{Fe}^{2+}$ species with different chemical compositions. A potential explanation for two different $\text{Fe}^{2+}$ environments would be the presence of both monomeric and dimeric $\text{Fe(OTf)}_2$ sites within the powder sample which would have similar $\delta$, but different $\Delta E_Q$. This hypothesis is also consistent with commonly observed coordination modes for $\text{OTf}^-$ anions, which can act as both a tridentate ligand to a single metal center or a bidentate, bridging ligand between two metal centers.9-10

Importantly, the overall fits for both models are clearly consistent with samples of the $\text{Fe(OTf)}_2$ precursor containing only $\text{Fe}^{2+}S = 2$ ions, and possess $\delta$ that are consistent with the $\delta$ of the previously reported Mossbauer spectrum of the $\text{Fe(OTf)}_2$ at 80 K.11-12 Given the comparable quality of both model’s overall fits (reduced $\chi^2 = 15.3$ for single – site model and 4.36 for two – site model), we have chosen to report both herein.

Computational Methods. The initial coordinates for the calculations were obtained from the crystallographic data for all compounds with solvent molecules of crystallization removed and the dominant orientation for any disorder utilized. All calculations were performed with ORCA version 4.2.1.13-14 The BP86 functional15-16 with the RI approximation was used for all calculations except for that of the Mossbauer parameters of 3, described below. The ZORA approximation was applied to account for relativistic effects17 and Grimme’s dispersion correction (DFT-D3)18 was used for all calculations. The SARC-TZVP basis set used with the SARC/J auxiliary basis set for Mo.19 The def2-TZVP basis set and def2/J auxiliary basis set was used for the heterometal ($M = \text{Cr, Mn, Fe, Co, and Ni}$) atoms.20-21 The def2-SVP basis set and def2/J auxiliary basis set were used for all other atoms.22-23 Tight optimization and very tight self-consistent field convergence criteria were employed along with the grid4 keyword; the integration grid was increased to grid5 for the final integration for all calculations. Frequency calculations were performed following geometry optimizations to ensure the structures were at local minima. Zero-field splitting calculations24-25 were performed with BP86 with grid 5 and final grid6 for all non-metal atoms, and intacc 9 for Mo and heterometal ions. The conductor-like polarizable continuum model (CPCM) was also implemented to model the solvent effects of dichloromethane in time-dependent calculations.26 Löwdin population analysis was used to determine spin densities and orbital contributions.27-28 Visualizations were carried out with the
UCSF Chimera package. Symmetry labels presented in the molecular orbital diagram were assigned by inspection to conform with the idealized \( C_4 \) point group.

For Mössbauer parameter calculations, the TPSS\(^{30-31} \) functional was used. The basis set on the Fe atom was replaced with the core properties basis set (CP(PPP))\(^{32-33} \), the basis set on the Mo atom was changed to def2-TZVPP and the basis set on the N atoms was replaced with a def2-TZVP. The radial integration grid was increased for the Mo, Fe, and N atoms (IntAcc = 8 radial shells). Isomer shifts were obtained from the calculated densities at the Fe nuclei according to the equation

\[
\delta_{\text{calc}} = \alpha (\rho - \beta) + C
\]

where \( \delta_{\text{calc}} \) is the calculated isomer shift and \( \rho \) is the calculated electron density at a given Fe nucleus. The constants \( \alpha, C, \) and \( \beta \) were obtained from linear regressions on training sets of compounds with known isomer shifts calibrated to specific density functional/basis set combinations.\(^{34-35} \)

**Synthetic Methods.**

All M(OTf)\(_2\) compounds were prepared using a similar general procedure, which is described only for the Cr(OTf)\(_2\) salt.

Cr(OTf)\(_2\): Solid CrCl\(_2\) (0.801 g, 6.52 mmol) was added to 20 mL of MeCN, forming a sea-foam green suspension. In a separate flask, TlOTf (4.613 g, 13.03 mmol) was dissolved in 40 mL of MeCN, forming a colorless solution. The TlOTf solution was then slowly added to the CrCl\(_2\) suspension, resulting in a bright blue solution with a white precipitate. The mixture was allowed to stir for 12 h, after which time the mixture was filtered over Celite and the resulting blue solution was reduced to dryness under vacuum. This afforded a light blue powder, which was dried under vacuum (ca. 0.1 torr) for an additional 24 hr at 80 °C; the resulting blue-white powder was isolated by decantation. Yield: 1.85 g, 81 %. IR (ATR, cm\(^{-1}\)) 1267 m, 1215 s, 1042 m, 635 m. Anal. Calcd for Cr(OTf)\(_2\): C, 6.86; H, 0.00. Found: C, 6.87; H, 0.00. \(^{19}\)F NMR (400 MHz, CD\(_3\)CN): \( \delta \) (ppm) 66.3 (s), 184 (s).

Mn(OTf)\(_2\): Yield: 1.95 g, 93 % white solid. IR (ATR, cm\(^{-1}\)) 1300 s, 1195 m, 1039 m, 628 m. Anal. Calcd for Mn(OTf)\(_2\): C, 6.80; H, 0.00. Found: C, 6.88; H, 0.00. \(^{19}\)F NMR (400 MHz, CD\(_3\)CN): \( \delta \) (ppm) 40.2 (s), 182 (s).

Fe(OTf)\(_2\): Yield: 2.22 g, 89 % white solid. IR (ATR, cm\(^{-1}\)) 1229 s, 1194 m, 1037 m, 629 m. Anal. Calcd for Fe(OTf)\(_2\): C, 6.79; H, 0.00. Found: C, 7.32; H, 0.00. \(^{19}\)F NMR (400 MHz, CD\(_3\)CN): \( \delta \) (ppm) 57.2 (s), 184 (s).

Co(OTf)\(_2\): Yield: 1.10 g, 55 % pale violet solid. IR (ATR, cm\(^{-1}\)) 1228 s, 1194 m, 1039 m, 632 m. Anal. Calcd for Co(OTf)\(_2\): 1/6 CH\(_3\)CN: C, 7.70; H, 0.14. Found: C, 7.70; H, 0.15. \(^{19}\)F NMR (400 MHz, CD\(_3\)CN): \( \delta \) (ppm) 70.0 (s), 184 (s).
Ni(OTf)$_2$: Yield: 1.81 g, 90 % pale yellow solid. IR (ATR, cm$^{-1}$) 1226 s, 1173 m, 1019 m, 763 w, 627 m. Anal. Calcd for Ni(OTf)$_2$: C, 6.73; H, 0.00. Found: C, 6.39; H, 0.00. $^{19}$F NMR (400 MHz, CD$_3$CN): $\delta$ (ppm) 79.6 (s), 181 (s).

Compounds 1, 3, and 4 were prepared from analogous procedures; details are provided only for 1.

Mo$_2$Cr(dpa)$_4$(OTf)$_2$ (1): Solid brick-red Mo$_2$(dpa)$_4$ (0.249 g, 0.285 mmol) and Cr(OTf)$_2$ (0.172 g, 0.491 mmol) were combined with naphthalene (4 g) in a Schlenk flask. The flask was placed in a sand bath that had been preheated to 190 °C. The reaction mixture was stirred for 90 min, during which time the reaction mixture became dark green in color. After cooling to room temperature, the solidified reaction mixture was washed with hot hexanes (3 × 75 mL) and extracted into dichloromethane (40 mL). The dark green solution was then layered with diethyl ether (100 mL). Dark green colored X-ray quality blocks were obtained after 3 days. Yield: 223 mg, 63 %. IR (ATR, cm$^{-1}$) 1605 m, 1596 m, 1546 w, 1477 m, 1462 s, 1421 s, 1354 m, 1312 m, 1286 w, 1258 s, 1232 s, 1214 m, 1155 m, 1111 w, 1025 m, 1017 m, 884 w, 858 w, 768 m, 751 w, 636 s. MALDI-MS m/z 872 [M-Cr(OTf)$_2$]$^+$. Anal. Calcd for Mo$_2$Cr(dpa)$_4$(OTf)$_2$: C, 40.34; H, 2.63; N, 13.28. Found: C, 39.61; H, 2.50; N, 13.47.

Mo$_2$Fe(dpa)$_4$(OTf)$_2$ (3): Yield: 264 mg, 63 % dark green crystals. IR (ATR, cm$^{-1}$) 1603 m, 1594 m, 1460 s, 1421 s, 1349 m, 1310 m, 1286 w, 1258 w, 1232 m, 1213 s, 1171 m, 1154 m, 1018 m, 885 w, 858 w, 769 s, 750 w, 742 w, 635 s. MALDI-MS m/z 872 [M-Fe(OTf)$_2$]$^+$. Anal. Calcd for Mo$_2$Fe(dpa)$_4$(OTf)$_2$: C, 41.02; H, 2.62; N, 13.67. Found: C, 40.47; H, 2.55; N, 13.86.

Mo$_2$Co(dpa)$_4$(OTf)$_2$ (4): Yield: 216 mg, 58 % dark green crystals. IR (ATR, cm$^{-1}$) 1606 m, 1597 m, 1547 w, 1462 m, 1423 s, 1360 m, 1316 m, 1298 m, 1287 m, 1258 w, 1232 s, 1207 m, 1155 m, 1018 m, 964 w, 883 w, 858 w, 765 m, 741 m, 728 m, 701 w, 635 s. MALDI-MS m/z 1080 [M-(OTf)$_2$]$^+$. Anal. Calcd for Mo$_2$Co(dpa)$_4$(OTf)$_2$: C, 41.28; H, 2.41; N, 13.67. Found: C, 40.37; H, 2.55; N, 13.86.

Mo$_2$Mn(dpa)$_4$(OTf)$_2$ (2): Mo$_2$Mn(dpa)$_4$Cl$_2$ (0.205 g, 0.205 mmol) was dissolved in dichloromethane (40 mL), forming a dark brown solution. Solid TiOTf (0.656 g, 1.86 mmol) was added to the brown solution and the resulting mixture was allowed to stir for two weeks. Over this time, the color slowly turned from brown into a dark green color and a pale tan precipitate formed. The mixture was then filtered over a fine porosity frit with 5 mm Celite, and the solution volume was reduced under vacuum to 25 mL, and then layered with pentane (75 mL). Trace dark green crystals were obtained after two weeks. Poor yields prevented further characterization.
Figure S1: IR spectra of initial M(OTf)$_2$·xCH$_3$CN salts prepared in this work after drying under vacuum (ca. 0.1 torr) to a free-flowing powder state but before drying at 80 °C. Inset: picture of the M(OTf)$_2$ samples used for the IR spectra; from left to right: Cr(OTf)$_2$, Mn(OTf)$_2$, Co(OTf)$_2$, Fe(OTf)$_2$, and Ni(OTf)$_2$.

Figure S2: The M(OTf)$_2$ salts after drying at 80 °C for 24 hr under vacuum (ca. 0.1 torr). Inset: picture of the M(OTf)$_2$ samples used for the IR spectra; from left to right: Cr(OTf)$_2$, Mn(OTf)$_2$, Fe(OTf)$_2$, Co(OTf)$_2$, and Ni(OTf)$_2$. 
Figure S3: $^{19}$FNMR (400 MHz) spectra in CD$_3$CN for the M(OTf)$_2$ (M = Cr, Mn, Fe, Co, Ni) salts prepared in this work. Inset: $^{19}$F peak for the Ni–O$_3$SC$^{19}$F$_3$ coordinated triflate ion with signal intensities magnified.
Figure 4. Mossbauer spectrum of Fe(OTf)$_2$ at 80 K with a single species fit with a reduced $\chi^2 = 15.3$. The black circles correspond to experimental data and the red trace corresponds to the overall fit ($\delta = 1.45$ mm/s, $\Delta E_Q = 2.03$ mm/s, $\Gamma = 0.33$ mm/s).

Figure 5. Mossbauer spectrum of Fe(OTf)$_2$ at 80 K with a two species fit and a reduced $\chi^2 = 4.38$. The black circles correspond to data, the red trace to the overall fit, the green trace to the first sub-spectrum ($\delta = 1.45$ mm/s, $\Delta E_Q = 2.23$ mm/s, $\Gamma = 0.38$ mm/s, rel. area = 39 %), and the blue trace to the second sub-spectrum ($\delta = 1.45$ mm/s, $\Delta E_Q = 1.96$ mm/s, $\Gamma = 0.25$ mm/s, rel. area = 61 %).
Figure S6: Electronic absorption spectrum of the green-brown powder obtained from attempted preparations of 2 using a molten naphthalene synthetic route.

Figure S7: Infrared spectrum of the green-brown powder obtained from attempted preparations of 2 using a molten naphthalene synthetic route.
|                | 1·1.5 CH₂Cl₂ | 2          | 3          | 4·1.5 CH₂Cl₂ |
|----------------|-------------|-----------|-----------|-------------|
| **Empirical formula** | Mo₂Cr(C₁₀H₈N₃)₄(O₃SCF₃)₂·1.5CH₂Cl₂ | Mo₂Mn(C₁₀H₈N₃)₄(O₃SCF₃)₂ | Mo₂Fe(C₁₀H₈N₃)₄(O₃SCF₃)₂ | Mo₂Co(C₁₀H₈N₃)₄(O₃SCF₃)₂·1.5CH₂Cl₂ |
| **Crystal system** | monoclinic | monoclinic | monoclinic | monoclinic |
| **Space group** | P₂₁/c | P₂₁/c | P₂₁/c | P₂₁/c |
| **a/Å** | 18.7140(5) | 15.847(5) | 15.770(5) | 18.565(5) |
| **b/Å** | 35.7287(9) | 17.198(5) | 17.164(5) | 35.619(10) |
| **c/Å** | 16.4046(4) | 17.841(7) | 17.819(5) | 16.242(6) |
| **α°** | 90 | 90 | 90 | 90 |
| **β°** | 112.446(2) | 107.526(11) | 107.51(2) | 111.867(8) |
| **γ°** | 90 | 90 | 90 | 90 |
| **Volume/Å³** | 10137.6(5) | 4637(3) | 4600(2) | 9967(6) |
| **Z** | 8 | 4 | 4 | 8 |
| **ρcalc g/cm³** | 1.769 | 1.756 | 1.771 | 1.809 |
| **R₁, wR₂ [I≥2σ(I)]** | 0.0426; 0.0995 | 0.0323, 0.0713 | 0.0390, 0.1183 | 0.0308, 0.0700 |
| **R₁, wR₂ [all data]** | 0.0624; 0.1074 | 0.0385, 0.0733 | 0.0437, 0.1210 | 0.0413, 0.0746 |


\[ R₁ = \frac{\sum|F_o| - |F_c|}{\sum|F_o|} \]


\[ wR₂ = \left( \frac{\sum[w(F_o^2 - F_c^2)]}{\sum[w(F_o^2)]} \right)^{1/2}, \quad w = 1/σ^2(F_o^2) + (aP)^2 + bP, \text{ where } P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3 \]
Table S2: Selected crystallographic and calculated bond distances for 1 - 5. Mo_o = outer Mo; Mo_i = inner Mo atom; M = heterometal atom, L_{ax} = O.

|      | Mo–Mo (Å) | Mo–M (Å) | M–N (Å) | Mo_i–N (Å) | Mo_o–N (Å) | Mo–L_{ax} (Å) | M–L_{ax} (Å) | Ref.     |
|------|-----------|----------|---------|------------|------------|---------------|---------------|----------|
| 1·1.5 CH_2Cl_2 | 2.092[3]  | 2.6237[13] | 2.120[6] | 2.130[4]   | 2.202[18]  | 2.46[3]       | 2.251[4]     | This work |
| 1 DFT | 2.115     | 2.600    | 2.094   | 2.130       | 2.197      | 2.409         | 2.118        |          |
| 2    | 2.090(3)  | 2.746(3) | 2.240[2] | 2.132[2]   | 2.199[4]   | 2.5086(14)    | 2.0140(17)   | This work |
| 2 DFT| 2.113     | 2.702    | 2.213   | 2.139       | 2.197      | 2.411         | 2.017        |          |
| 3    | 2.095(4)  | 2.628(4) | 2.200[3] | 2.123[7]   | 2.182[4]   | 2.4576(18)    | 2.045(2)     | This work |
| 3 DFT| 2.114     | 2.645    | 2.157   | 2.132       | 2.206      | 2.389         | 1.972        |          |
| 4·1.5 CH_2Cl_2 | 2.085[4]  | 2.4485[15]| 1.978[6]| 2.112[4]   | 2.204[18]  | 2.38[3]       | 2.408[12]    | This work |
| 4 (S = 1/2) DFT | 2.112    | 2.424    | 1.977   | 2.122       | 2.212      | 2.368         | 2.360        |          |
| 4 (S = 3/2) DFT | 2.120    | 2.505    | 2.109   | 2.130       | 2.208      | 2.388         | 2.050        |          |
| 5    | 2.110(8)  | 2.485(8) | 2.157[1] | 2.114[2]   | 2.157[5]   | 2.364(4)      | 2.086(5)     | 1         |
| 5 DFT| 2.116     | 2.463    | 2.077   | 2.117       | 2.184      | 2.218         | 2.067        |          |

*in instances of metal–atom chain disorder, the majority position was used for geometric parameters.

Table S3: Selected crystallographic bond distances for 6 - 10. Mo_o = outer Mo; Mo_i = inner Mo atom; M = heterometal atom, L_{ax} = O.

|      | Mo–Mo (Å) | Mo–M (Å) | M–N (Å) | Mo_i–N (Å) | Mo_o–N (Å) | Mo–L_{ax} (Å) | M–L_{ax} (Å) | Ref.     |
|------|-----------|----------|---------|------------|------------|---------------|---------------|----------|
| 6·2 CH_2Cl_2 | 2.0984(4) | 2.6885(6) | 2.127[2] | 2.127[2]   | 2.217[2]   | 2.7891(8)     | 2.535(1)      | 36       |
| 7    | 2.094(3)  | 2.793(4) | 2.249[2] | 2.136[3]   | 2.210[9]   | 2.7684(13)    | 2.327(3)      | 2         |
| 8·2 CH_2Cl_2 | 2.104(1)  | 2.762(1) | 2.186[2] | 2.129[2]   | 2.214[2]   | 2.747(1)      | 2.337(1)      | 37       |
| 9·1.5 CH_2Cl_2 | 2.1072(5) | 2.6170(7) | 2.1025[11]| 2.1205[4]  | 2.2155[9]  | 2.7200(9)     | 2.430(1)      | 6         |
| 10·C_4H_8O | 2.107(2)  | 2.525(4) | 2.146[3] | 2.115[3]   | 2.174[3]   | 2.627(2)      | 2.394(3)      | 38       |

*in instances of metal–atom chain disorder, the majority position was used for geometric parameters.
Crystallographic methods and refinement details for 1 - 4:

Crystallographic data were measured at the Molecular Structure Laboratory in the Department of Chemistry at the University of Wisconsin–Madison. Crystals were selected under oil under an atmosphere of Ar and attached to the tip of a MiTeGen MicroMount. Each crystal was mounted under a stream of cold nitrogen at 100(1) K and centered in the X-ray beam using a video camera. The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo Kα (λ = 0.71073 Å) radiation with a detector to crystal distance of 5.0 cm. The data were collected using a routine to survey the entire sphere of reciprocal space and were indexed by the SMART program.24 The structures were solved using direct methods and refined by least squares refinement on F^2 followed by difference Fourier synthesis.25 All hydrogen atoms were included in the final structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The Mo_2M(dpa)_4(OTf)_2 HEMAC complexes crystallize in one of two isomorphs (Table S1). The first includes 2, 3, and 5, which crystallize in the space group P2_1/c with one molecule of HEMAC complex in the symmetry independent unit. They also display positional disorder of the metal-atom chain and the central amide N atoms of the dpa ligand. The major components of the metal-atom chain disorder are 61.2(2) %, 54.7(3) %, and 55.8(4) % for 2, 3, and 5, respectively. The second isomorphic category includes 1 and 4. These complexes crystallize in the space group P2_1/c with two HEMAC complexes (Z' = 2) and three molecules of solvent CH_2Cl_2 in the symmetry independent unit. There is no metal-atom chain disorder in this isomorph. Both crystallographically independent molecules in each structure display similar geometries.

Table S2 contains selected structural data for the Mo_2M(dpa)_4(OTf)_2 HEMAC complexes. The Mo–Mo distances for the Mo_2M(dpa)_4(OTf)_2 series range from 2.09-2.11 Å, within the expected range for a Mo_2 quadruple bond.39-40 Compound 4 is a special case, having the shortest Mo≡Mo and Mo–M distances, at 2.085[4] and 2.4485[15] Å, respectively. The reason for this change, as described in the main text, is that only 4 exists in a low-spin electron configuration, as evidenced by significantly shorter Co–N bond distances than those seen for the other metals.

Additional molecular drawings and details about the crystallographic models for 1-4 are described below:

1·1.5CH_2Cl_2: The structure consists of two symmetry-independent heterometallic extended metal atom chain (HEMAC) complexes and three molecules of solvent dichloromethane, giving the symmetry-independent unit formula as follows: 2 [Mo_2Cr(C_10H_8N_3)_4(O_3SCF_3)_2] · 3 CH_2Cl_2. Each of the three molecules of solvent dichloromethane displayed positional disorder, which is described below:

The central C atom and one of the Cl atoms of the C85 molecule of dichloromethane were disordered over two positions with a major component occupancy of 62.3 %. The occupancies of the major and minor component were fixed. The central C atoms of both disorder
The C86 molecule of dichloromethane is disordered over two positions with a major component occupancy of 83.4(3)%. The central C atoms were refined isotropically, and the central C atoms as well as the Cl atoms in the minor disorder component were refined with atomic displacement parameter constraints. Both the major and minor disorder components were refined with idealized geometries.\textsuperscript{41}

The C87 molecule of dichloromethane is disordered over two positions with a major component occupancy of 90.8(4)%. The central C atoms were refined isotropically, and the central C atoms as well as the Cl atoms in the minor disorder component were refined with atomic displacement parameter constraints. The minor disorder component was refined with an idealized geometry.\textsuperscript{41}

*Figure S8.* A molecular drawing of 1•1.5CH\textsubscript{2}Cl\textsubscript{2} shown with 50% probability ellipsoids and atom labels for solvent molecules and metal atoms. All H atoms are omitted.
Figure S9. A molecular drawing of the first symmetry-independent HEMAC complex in 1·1.5(CH₂Cl₂) shown with 50% probability ellipsoids. All H atoms are omitted.

Figure S10. A molecular drawing of the second symmetry independent HEMAC complex in 1·1.5(CH₂Cl₂) shown with 50% probability ellipsoids. All H atoms are omitted.
2: The HEMAC complex metal atoms (atoms Mo1, Mo2, and Mn1) and the central amide N atoms of the dipyridylamine ligands (atoms N2, N5, N8, and N11) are disordered over two positions with a major component occupancy of 61.22(16)%. The N atoms in the minor disorder component were refined isotropically. Atom pairs N2/N2A and N11/N11A were restrained to have similar N–Mo1/Mo1A distances. Atoms N8/N8A and N11/N11A were restrained to have similar bond distances with atom C25 and C36, respectively.

**Figure S11.** A molecular drawing of 2 shown with 50% probability ellipsoids. All H atoms and minor disorder components are omitted.
Figure S12: A molecular drawing showing both the major and minor components of the metal-atom chain and amide N atom disorder in 2 with selected atom labels. All atoms are shown at with 50% probability ellipsoids; all H atoms are omitted for clarity.
The HEMAC complex metal atoms (atoms Mo1, Mo2, and Fe1) and the central amide N atoms of the dipyridylamine ligands (atoms N2, N5, N8, and N11) are disordered over two positions with a major component occupancy of 54.7(3)%. The N2–C5 and N2A–C5 distances were refined with similarity restraints.

**Figure S13.** A molecular drawing of 3 shown with 50% probability ellipsoids. All H atoms and minor disorder components are omitted.
**Figure S14:** A molecular drawing showing both the major and minor components of the metal-atom chain and amide N atom disorder in 3 with selected atom labels. All atoms are shown at with 50% probability ellipsoids; all H atoms are omitted for clarity.
4·1.5CH₂Cl₂: The structure consists of two HEMAC complexes and three molecules of solvent dichloromethane, giving the symmetry-independent unit formula as follows:

\[ \text{[Mo}_2\text{Co(C}_{10}\text{H}_{8}\text{N}_3)_{4}(\text{O}_3\text{SCF}_3)_{2}]_2 \cdot 3\text{CH}_2\text{Cl}_2. \]

One of the molecules of dichloromethane was disordered over two positions with a major disorder component occupancy of 85.3(2) %. The C atoms in the disordered dichloromethane molecule were refined isotropically, and the disordered C and Cl atoms were constrained to have equivalent atomic displacement parameters.

**Figure S15.** A molecular drawing of 4·1.5CH₂Cl₂ shown with 50% probability ellipsoids and atom labels for solvent molecules and metal atoms. All H atoms are omitted.
Figure S16. A molecular drawing of the first symmetry-independent HEMAC complex in 4·1.5CH₂Cl₂ shown with 50% probability ellipsoids. All H atoms are omitted.

Figure S17. A molecular drawing of the second symmetry-independent HEMAC complex in 4·1.5CH₂Cl₂ shown with 50% probability ellipsoids. All H atoms are omitted.
Table S4: Electronic absorption spectra maxima and molar absorptivities for 1, 3, 4, and 5.

|       | A (δ → dpa π*) | B (δ → dpa π*) | C (δ → δ*)   |
|-------|---------------|---------------|--------------|
| 1     | 401 nm        | 475 nm        | 638 nm       |
|       | (9800 L mol⁻¹ cm⁻¹) | (4400 L mol⁻¹ cm⁻¹) | (2100 L mol⁻¹ cm⁻¹) |
| 3     | 414 nm        | 474 nm        | 682 nm<sup>a</sup> |
|       | (11700 L mol⁻¹ cm⁻¹) | (9000 L mol⁻¹ cm⁻¹) | (1840 L mol⁻¹ cm⁻¹) |
| 4     | 407 nm        | 470 nm        | 623 nm       |
|       | (9300 L mol⁻¹ cm⁻¹) | (7900 L mol⁻¹ cm⁻¹) | (2200 L mol⁻¹ cm⁻¹) |
| 5     | 413 nm        | 476 nm        | 650 nm       |
|       | (17900 L mol⁻¹ cm⁻¹) | (9200 L mol⁻¹ cm⁻¹) | (2300 L mol⁻¹ cm⁻¹) |

<sup>a</sup> Transition C for 3 is best described as a MMCT transfer transition rather than δ-δ*.
Figure S18: Calculated (TDDFT) electronic absorption spectra of 1 – 5 with the CPCM: CH₂Cl₂ solvation model; the inset shows an expansion of the calculated low-energy features. The ca. 300 nm redshift of the calculated spectral features from their experimental counterparts is well within the typical error of transition energies calculated by TDDFT methods.⁴²⁻⁴³
**Figure S19:** Typical TDDFT donor and acceptor orbitals for transition C of 1 (1), 2 (2), 3 (3), and 4 (4) and electron density difference maps (EDDMs). Blue represents a loss of electron density; red represents a gain.
Figure S20: Orbital contributions of the outer Mo atom (Mo_o), inner Mo atom (Mo_i) and heterometal ion to the σ and σ_{nb} orbitals of the Mo_2 M(dpa)_4(OTf)_2 HEMACs. From left to right: 1, 2, 3, 4, 5.
Figure S21: Orbital contributions of the outer Mo atom (Mo_o), inner Mo atom (Mo_i) and heterometal ion to the σ and σ_{nb} orbitals of the Mo_2M(dpa)_4Cl_2 HEMACs. From left to right: M = Cr (6), Mn (7), Fe (8), Co (9), and Ni (10). Calculated orbital populations were taken from ref. 44.
Table S5. Calculated Mayer bond orders (MBOs) for 1-5; calculated Löwdin spin densities for 1-5

|     | Mo-Mo MBO | Mo-M' MBO | \(^a\)Mo\(_o\) spin density | \(^a\)M' spin density | \(^a, b\)Total Mo\(_o\) spin density | \(^a, b\) Total M' spin density | \(^a\)Total Mo\(_o\) / total M' spin density ratio |
|-----|------------|------------|-----------------------------|-----------------------|-------------------------------------|-------------------------------|----------------------------------|
| 1 DFT | 2.734      | 0.156      | 0.405                       | 3.510                 | 0.410                               | 3.400                         | 0.093                            |
| 2 DFT | 2.735      | 0.220      | 0.246                       | 4.504                 | 0.268                               | 4.642                         | 0.046                            |
| 3 DFT | 2.623      | 0.351      | 0.242                       | 3.527                 | 0.253                               | 3.788                         | 0.055                            |
| 4 DFT, S = 1/2 | 2.481      | 0.604      | 0.288                       | 0.691                 | 0.302                               | 0.693                         | 0.462                            |
| 4 DFT, S = 3/2 | 2.554      | 0.485      | 0.393                       | 2.351                 | 0.388                               | 2.604                         | 0.113                            |
| 5 DFT | 2.441      | 0.572      | 0.235                       | 1.307                 | 0.254                               | 1.627                         | 0.206                            |

\(^a\)Mo\(_o\) = outer Mo atom; M' = heterometal ion \(^b\)Total spin density refers to the summation of the spin populations of the atoms in the first coordination sphere of the respective metal atom. For M', this summation includes the spin populations of the four N atoms of the dipyridylamine ligand and the O atom of the OTf\(^-\) at the M' axial site. For Mo\(_o\), this summation is the same as for M’, with the exception that the inner Mo atom of 1-5 was included in the total Mo\(_o\) spin density.
Figure S22: MO diagram of 1. Orbitals localized on the Mo≡Mo unit are given with blue labels, green labels represent Cr based orbitals, and the red labels indicate orbitals that are delocalized across the Mo≡Mo···Cr chain.
Figure S23: MO diagram of 2. Orbitals localized on the Mo≡Mo unit are given with blue labels, green labels represent Mn based orbitals, and the red labels indicate orbitals that are delocalized across the Mo≡Mo⋯Mn chain.
Figure S24: MO diagram of 3. Orbitals localized on the Mo≡Mo unit are given with blue labels, green labels represent Fe based orbitals, and the red labels indicate orbitals that are delocalized across the Mo≡Mo···Fe chain.
Figure S25: MO diagram of 4, $S = 1/2$. Orbitals localized on the Mo≡Mo unit are given with blue labels, green labels represent Co based orbitals, and the red labels indicate orbitals that are delocalized across the Mo≡Mo···Co chain.
Figure S26: MO diagram of $4$, $S = 3/2$. Orbitals localized on the Mo≡Mo unit are given with blue labels, green labels represent Co based orbitals, and the red labels indicate orbitals that are delocalized across the Mo≡Mo⋯Co chain.
Figure S27: MO diagram of 5. Orbitals localized on the Mo≡Mo unit are given with blue labels, green labels represent Ni based orbitals, and the red labels indicate orbitals that are delocalized across the Mo≡Mo···Ni chain.
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