Heterobimetallic Triple-Stranded Helicates with Directional Benzene-o-dithiol/Catechol Ligands

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Syntheses of Complexes $2a$ and $2b$

All syntheses were carried out in Schlenk flasks. Solvents were dried and freshly distilled prior to use. Correct C, H, N analyses for all compounds. ESI mass spectra were recorded in the negative ion modus.

For the synthesis of $(PNP)_4[TiMo(\{1\}_3)]$ $2a$ 50.0 mg (0.12 mmol) of ligand H$_4$-1, 10.71 mg (0.04 mmol) [TiO(acac)$_2$] and 12.94 mg [MoCl$_4$(CH$_3$CN)$_2$] (0.04 mmol) were reacted with 3 mg (0.04 mmol) of Li$_2$CO$_3$ and 4.3 mg (0.04 mmol) of Na$_2$CO$_3$ in methanol at ambient temperature for 12 h. The reaction mixture was filtered after addition of 92 mg (4 eq, 0.16 mmol) of bis(triphenylphosphoranylidene) ammoniumchloride ((PNP)Cl). The dark green residue was dissolved in DMF. Slow diffusion of diethyl ether into this solution yielded 48 mg (0.013 mmol, 33 %) of dark green crystals of Li$_{0.5}$$(PNP)_{3.5}[TiMo(\{1\}_3)]·4.5$DMF·1.5EtOH·H$_2$O.

Compound Li$_{1.5}$Na$_{0.5}$(PNP)$_2[TiMo(\{1\})_3]$ $2b$ was prepared as described for $2a$. Only the number of PNP equivalents was varied. After addition of 46 mg (2 eq, 0.08 mmol) of (PNP)Cl and diffusion of diethyl ether into the methanolic solution 63 mg (0.024 mmol, 61 %) of black crystals of Li$_{1.5}$Na$_{0.5}$(PNP)$_2[TiMo(\{1\})_3]$·6H$_2$O were isolated. The $^1$H NMR and $^{13}$C NMR spectra of $2a$ and $2b$ are identical.

$^1$H NMR (400 MHz, [D$_7$]DMF, solvent-free compound, assignment of signals see Figure 1): $\delta = 11.94$ (s, 3 H, H$_a$), 11.90 (s, 3 H, H$_g$), 8.06 (m, 6 H, H$_f$), 7.98 (m, 6 H, H$_e$), 7.75-7.69 (m, 73 H, PNP-H), 7.68 (dd, $^3J = 7.6$ Hz, $^4J = 1.4$ Hz, 3 H, H$_j$), 7.63 (dd, $^3J = 7.6$ Hz, $^4J = 1.4$ Hz, 3 H, H$_h$), 7.59-7.55 (m, 47 H, PNP-H), 7.25 (dd, $^3J = 8.1$ Hz, $^4J = 1.6$ Hz, 3 H, H$_b$), 6.85 (t, $^3J = 7.6$ Hz, 3 H, H$_i$), 6.43 (t, $^3J = 8.1$ Hz, $^2J = 7.5$ Hz, 3 H, H$_h$), 6.31 (dd, $^3J = 7.5$ Hz, $^4J = 1.6$ Hz, 3 H, H$_d$); $^{13}$C NMR (100 MHz, [D$_7$]DMF, solvent-free compound): $\delta = 166.82$ (C=O), 166.06 (C=O), 161.65, 163.60, 158.75, 150.48, 136.54, 136.12 (C$_{Ar}$), 134.55, 133.12, 132.05, 130.40,
130.31, 128.13 (C\textsubscript{Ar}, PNP), 124.88, 121.39, 121.25, 120.34, 118.49, 116.68, 116.44, 113.5 (C\textsubscript{Ar}); ESI-MS: \textit{m/z} (%) : 456.9 (100) [TiMo(1)\textsubscript{3} + H\textsuperscript{+}]; 636.2 (16) [TiMo(1)\textsubscript{3} + (PNP)]\textsuperscript{3–}; 954.1 (5) [TiMo(1)\textsubscript{3} + H + (PNP)]\textsuperscript{2–}.

Crystallographic Details

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\text{Li}_{0.5}(\text{PNP})_3\text{[TiMo[\text{I}])_3]\cdot4.5\text{DMF}\cdot1.5\text{EtOH}\cdot\text{H}_2\text{O} \quad 2a-4.5\text{DMF}\cdot1.5\text{EtOH}\cdot\text{H}_2\text{O}: \\
C_{202.5}H_{183.5}N_{14}Li_{0.5}O_{19}P_7S_6\text{MoTi}, \quad M = 3673.74, \text{dark green crystal, } 0.40 \times 0.11 \times 0.07 \text{ mm}^3, \quad a = 24.1839(6), \quad b = 24.1839(6), \quad c = 112.362(4) \text{ Å}, \quad \alpha = 90, \quad \beta = 90, \quad \gamma = 120^\circ, \quad V = 56912(3) \text{ Å}^3, \quad \rho_{\text{calc}} = 1.285 \text{ g cm}^{-3}, \quad \mu = 2.615 \text{ mm}^{-1}, \quad \text{semiempirical absorption correction } (0.4211 \leq T \leq 0.8381), \quad \omega- \text{ und } \phi-\text{scans, Cu-K}\alpha \text{ radiation } \theta = 1.54178 \text{ Å}, \quad 107689 \text{ measured intensities, } (5.3^\circ \leq 2\theta \leq 140.2^\circ), \quad 11678 \text{ independent } (R_{\text{int}} = 0.0916) \text{ and } 6552 \text{ observed } (I \geq 2\sigma(I)) \text{ intensities, } T = 153(2) \text{ K}, \quad Z = 12, \quad R-3c, \quad R(\text{all}) = 0.0569, \quad wR^2(\text{all}) = 0.1492 \text{ (refinement against } |F^2|) \text{ with H atoms on calculated positions.}
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\text{Li}_{1.5}\text{Na}_{0.5}(\text{PNP})_2\text{[TiMo[\text{I}])_3]\cdot6\text{H}_2\text{O} \quad 2b-6\text{H}_2\text{O}: \quad C_{132}H_{96}N_8\text{Li}_{1.5}\text{Na}_{0.5}O_{12}P_4S_6\text{MoTi}, \quad M = 2576.25, \quad \text{black crystal, } 0.60 \times 0.15 \times 0.10 \text{ mm}^3, \quad a = 40.679(1), \quad b = 25.385(1), \quad c = 15.644(1) \text{ Å}, \quad \alpha = 90, \quad \beta = 94.28(1), \quad \gamma = 90^\circ, \quad V = 16109.5(13) \text{ Å}^3, \quad \rho_{\text{calc}} = 1.062 \text{ g cm}^{-3}, \quad \mu = 2.612 \text{ mm}^{-1}, \quad \text{semiempirical absorption correction } (0.303 \leq T \leq 0.780), \quad \omega- \text{ und } \phi-\text{scans, Cu-K}\alpha \text{ radiation } \theta = 1.54178 \text{ Å}, \quad 73424 \text{ measured intensities } (7.4^\circ \leq 2\theta \leq 136.4^\circ), \quad 25473 \text{ independent } (R_{\text{int}} = 0.055) \text{ and } 20810 \text{ observed } (I \geq 2\sigma(I)) \text{ intensities, } T = 223 \text{ K}, \quad Z = 4, \quad C2, \quad R(\text{all}) = 0.1180, \quad wR^2(\text{all}) = 0.2820. \quad \\
\text{CCDC 679616 (2a) and CCDC 679617 (2b) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.}
Figure S1. Packing diagram for $\text{Li}_{1.5}\text{Na}_{0.5}\text{(PNP)}_2\text{[TiMo(1)}_3\text{]}\cdot6\text{H}_2\text{O}$. The PNP cations and the water molecules in the crystal lattice are not depicted.