

Tuning peripheral π -stacking motifs in $\{\text{Cr}(\text{tpy})_2\}^{3+}$ domains ($\text{tpy} = 2,2':6',2''\text{-terpyridine}$)

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Abstract

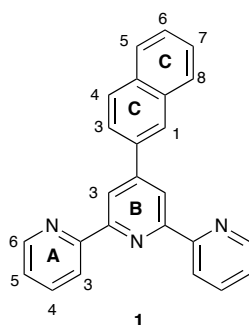
The homoleptic complexes $[\text{Cr}(\mathbf{1})_2][\text{PF}_6]_3$ and $[\text{Co}(\mathbf{1})_2][\text{PF}_6]_3$ ($\mathbf{1} = 4'\text{-(naphth-2-yl)-}2,2':6',2''\text{-terpyridine}$) have been prepared and structurally characterized. The packing interactions in both complexes are identical, consisting of a combination of naphthyl...naphthyl π -stacking interactions and double naphthyl...pyridine embraces generating chains of cations with alternating long and short M...M contacts.

Keywords: chromium; cobalt; terpyridine; naphthyl; crystal structure; π -embraces

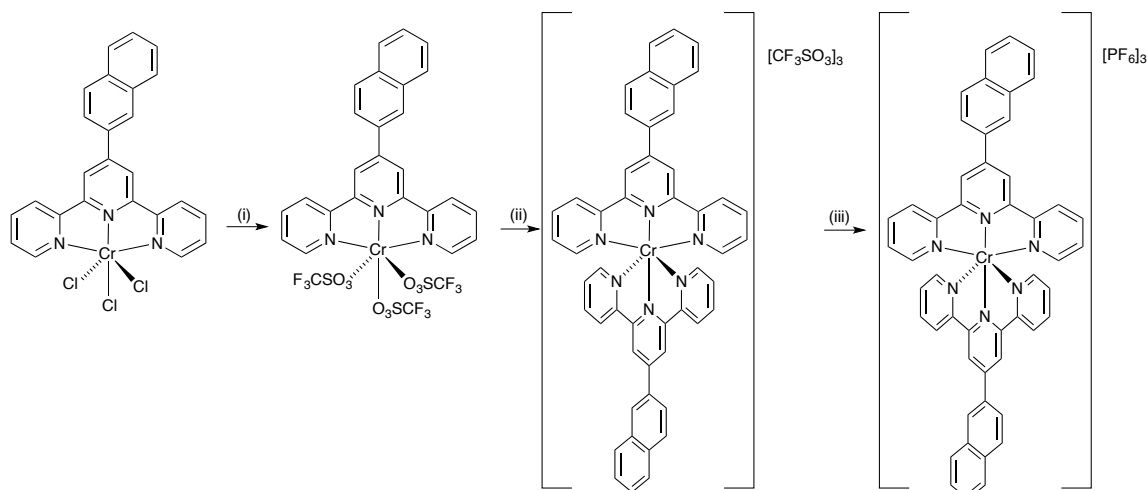
2,2':6',2''-Terpyridine (tpy) is a ubiquitous ligand and a vast range of complexes containing $\{\text{M}(\text{tpy})_2\}^{n+}$ domains has been reported. A search of the Cambridge Structural Database [1] (v. 5.35 with updates up to May 2014) using Conquest v. 1.16 [2] shows 636 hits for complexes containing a $\{\text{M}(\text{tpy})_2\}$ (M = any metal) unit. However, only seven have M = Cr [3,4,5,6] and the only chromium(III) examples are $2\{[\text{Cr}(\text{tpy})_2][\text{PF}_6]_3\} \cdot 5\text{MeCN}$ [6], $[\text{Cr}(\text{tpy})(4'\text{-(4-tolyl)tpy})][\text{PF}_6]_3 \cdot 3\text{MeCN}$ [6], $[\text{Cr}(\text{tpy})(5,5''\text{-Me}_2\text{tpy})][\text{PF}_6]_3 \cdot 3\text{MeCN}$ [6] and $[\text{Cr}(\text{tpy})_2][\text{ClO}_4]_3 \cdot \text{H}_2\text{O}$ [3,4]. We have recently focused on factors governing packing interactions in oligopyridine complexes of chromium(III) [7,8] showing the combined effect of a 1 : 3 cation : anion ratio and lattice solvent molecules on inter-cation embraces which dominate $[\text{M}(\text{bpy})_3]^{2+}$ [9] and $[\text{M}(\text{tpy})_2]^{2+}$ [10,11,12,13,14] lattices. We now report the consequences of introducing 4'-(naphth-2-yl) substituents and compare the structures of solvated $[\text{Cr}(\mathbf{1})_2][\text{PF}_6]_3$ and $[\text{Co}(\mathbf{1})_2][\text{PF}_6]_3$ where $\mathbf{1}$ is 4'-(naphth-2-yl)-2,2':6',2''-terpyridine (Scheme 1).

Compound $\mathbf{1}$ was prepared by a one-pot method [15] from 2-naphthaldehyde and two equivalents of 2-acetylpyridine under basic conditions in the presence of NH_3 [16]; spectroscopic data were consistent with those reported [17]. A convenient route to homoleptic $\{\text{Cr}(4'\text{-Xtpy})_2\}^{3+}$ or heteroleptic $\{\text{Cr}(4'\text{-Xtpy})(4'\text{-Ytpy})\}^{3+}$ complexes uses a stepwise approach starting with the reaction of one equivalent of a tpy ligand with

anhydrous CrCl_3 . Subsequent exchange of the chlorido ligands by the more labile triflate, followed by reaction with a second equivalent of tpy yields the triflate salt of the desired complex [7,8]. Scheme 2 summarizes the approach for the preparation of $[\text{Cr}(\mathbf{1})_2][\text{CF}_3\text{SO}_3]_3$ with anion exchange in the last step yielding $[\text{Cr}(\mathbf{1})_2][\text{PF}_6]_3$ as an orange solid [18]. The synthesis of $[\text{Co}(\mathbf{1})_2][\text{PF}_6]_3$ as an orange solid in 84.3% yield was by Br_2 oxidation of $[\text{Co}(\mathbf{1})_2][\text{PF}_6]_2$ (prepared from $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ with two equivalents of $\mathbf{1}$ followed by anion exchange) and followed the reported general procedure [19]. ^1H and ^{13}C NMR spectra (assigned by 2D methods) for $[\text{Co}(\mathbf{1})_2][\text{PF}_6]_3$ [20] were consistent with a single ligand environment and the shift in the signal for H^{A6} (see Scheme 1) from δ 8.75 ppm in $\mathbf{1}$ (CDCl_3) to δ 7.47 ppm in $[\text{Co}(\mathbf{1})_2][\text{PF}_6]_3$ (CD_3CN) is indicative of the formation of a $\{\text{Co}(\text{tpy})_2\}^{3+}$ domain with H^{A6} of one ligand lying over the π -system of the second tpy.



Scheme 1. Structure of ligand $\mathbf{1}$ with numbering for NMR spectroscopic assignments.



Scheme 2. Synthetic route to $[\text{Cr}(\mathbf{1})_2][\text{PF}_6]_3$. Conditions: (i) $\text{CF}_3\text{SO}_3\text{H}$; (ii) ligand $\mathbf{1}$; (iii) NH_4PF_6 .

Both $[\text{Cr}(\mathbf{1})_2][\text{PF}_6]_3 \cdot 0.4\text{MeCN}$ and $[\text{Co}(\mathbf{1})_2][\text{PF}_6]_3 \cdot 0.7\text{H}_2\text{O}$ crystallize in the triclinic $P\bar{1}$ space group [21,22] and are isostructural if one ignores the solvent molecules. (The partial occupancy solvent molecules occupy the same cavities in the two lattices.) Figure 1 shows the structure of the $[\text{Cr}(\mathbf{1})_2]^{3+}$ cation. Atom Cr1 is octahedrally coordinated by two bis(chelating) tpy units, and bond parameters within the

coordination sphere (Figure 1 caption) are unexceptional. For the $[\text{Co}(\mathbf{1})_2]^{3+}$ cation in $[\text{Co}(\mathbf{1})_2][\text{PF}_6]_3 \cdot 0.4\text{MeCN}$, the Co–N bond distances for the outer pyridine rings lie in the range 1.941(2)–1.952(2) Å, but are shorter (1.855(2) and 1.858(2) Å) for the central pyridine, typical of $\{\text{M}(\text{tpy})_2\}$ units.

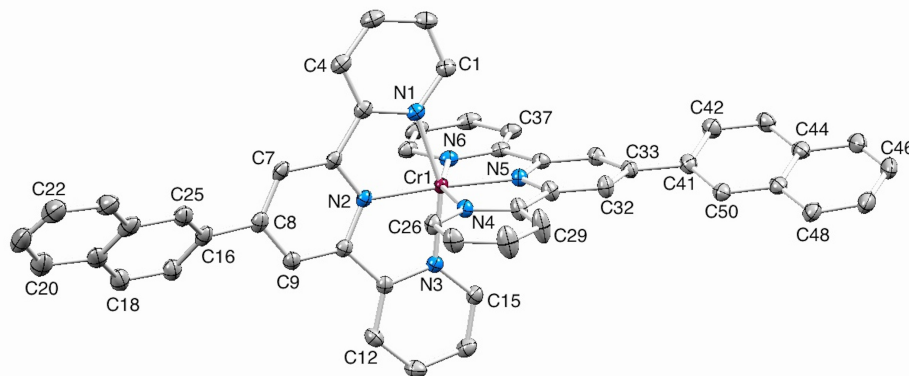


Figure 1. Structure of the $[\text{Cr}(\mathbf{1})_2]^{3+}$ cation in $[\text{Cr}(\mathbf{1})_2][\text{PF}_6]_3 \cdot 0.4\text{MeCN}$ (H atoms omitted; ellipsoids plotted at 40% probability level). Selected bond lengths and angles: Cr1–N1 = 2.058(2), Cr1–N2 = 1.967(2), Cr1–N3 = 2.061(2), Cr1–N4 = 2.055(2), Cr1–N5 = 1.971(2), Cr1–N6 = 2.047(2) Å; N1–Cr1–N2 = 78.68(8), N2–Cr1–N3 = 78.95(8), N4–Cr1–N5 = 79.07(8), N5–Cr1–N6 = 78.46(8) $^\circ$. (Colour online)

Each naphthyl unit is twisted out of the plane of the pyridine ring to which it is bonded, minimizing inter-ring H...H repulsions. The angles between the planes of rings containing N2/C16 and N5/C41 in $[\text{Cr}(\mathbf{1})_2]^{3+}$ are 37.5 and 22.6 $^\circ$, respectively, and the corresponding angles in the $[\text{Co}(\mathbf{1})_2]^{3+}$ ion are 37.8 and 22.9 $^\circ$. The different naphthyl orientations result from inter-cation packing interactions involving alternating naphthyl...naphthyl and naphthyl...pyridine interactions along chains of cations (Figure 2). The 37.8 $^\circ$ twist angle is associated with the centrosymmetric naphthyl...naphthyl π -stacking interaction (interplane separation = 3.53 Å, intercentroid separation = 3.78 Å). The naphthyl unit twisted at 22.9 $^\circ$ interacts with an outer pyridine ring of an adjacent cation, and symmetry related pairs of these interactions result in a double embrace (Figure 3a) that resembles one of the packing motifs (Fig. 3b) seen in $[\text{M}(4'\text{-Phtpy})_2]^{2+}$ complexes (4'-Phtpy = 4'-phenyl-2,2':6',2''-terpyridine) [11] and in $[\text{Cr}(4'\text{-(4-tolyl)tpy})_2][\text{CF}_3\text{SO}_3]_3 \cdot 2\text{MeCN}$ (4'-(4-tolyl)tpy-2,2':6',2''-terpyridine) [8]. The presence of both naphthyl...naphthyl π -stacking interactions and dual naphthyl...pyridine embraces along chains of cations in $[\text{Cr}(\mathbf{1})_2][\text{PF}_6]_3 \cdot 0.4\text{MeCN}$ and $[\text{Co}(\mathbf{1})_2][\text{PF}_6]_3 \cdot 0.4\text{MeCN}$ suggests a small energy difference between the two packing motifs. As a result of the different embraces along the chains of cations (Fig. 2) in $[\text{Cr}(\mathbf{1})_2][\text{PF}_6]_3 \cdot 0.4\text{MeCN}$, the Cr...Cr separations alternate 16.4427(8) and 11.9131(7) Å, compared to a constant separation of 10.9971(7) Å in $[\text{Cr}(4'\text{-(4-tolyl)tpy})_2][\text{CF}_3\text{SO}_3]_3 \cdot 2\text{MeCN}$ [8]. In

$[\text{Co}(\mathbf{1})_2][\text{PF}_6]_3 \cdot 0.4\text{MeCN}$, the Co...Co separations along a chain are 16.248(1) and 12.0354(9) Å.

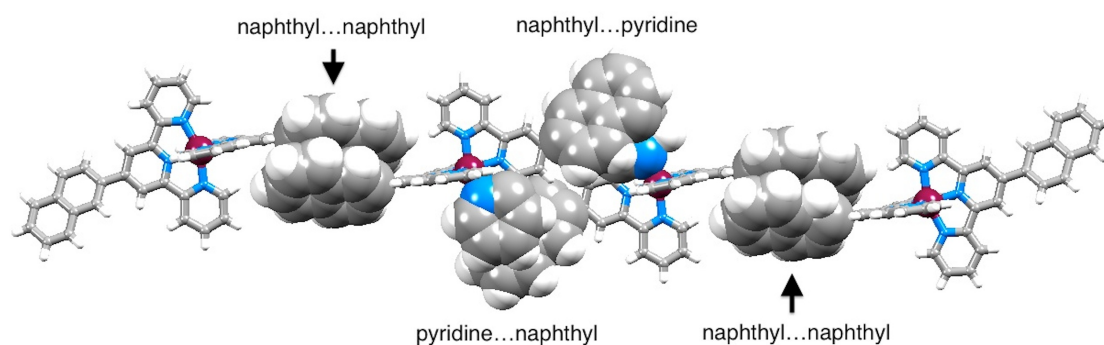


Figure 2. Part of one chain formed by face-to-face π -interactions between cations in $[\text{Cr}(\mathbf{1})_2][\text{PF}_6]_3 \cdot 0.4\text{MeCN}$. (Colour online)

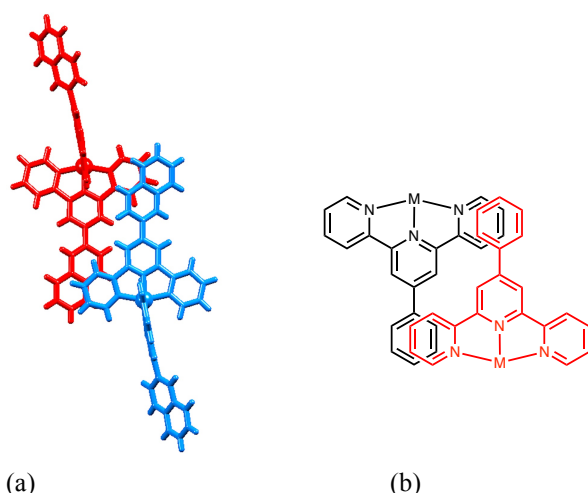


Figure 3. (a) Inter-cation double pyridine...naphthyl embrace in $[\text{Cr}(\mathbf{1})_2][\text{PF}_6]_3$ and $[\text{Co}(\mathbf{1})_2][\text{PF}_6]_3$ compared to (b) a double pyridine...phenyl embrace in $[\text{M}(4'\text{-Phtpy})_2]^{2+}$ complexes.

In conclusion, we demonstrate that the introduction of the naphth-2-yl domain in $[\text{Cr}(\mathbf{1})_2][\text{PF}_6]_3$ and $[\text{Co}(\mathbf{1})_2][\text{PF}_6]_3$ leads to packing in the solid state involving a combination of face-to-face naphthyl...naphthyl π -interactions and double naphthyl...pyridine embraces. The latter resemble phenyl...pyridine embraces in related complexes, but the favourable π -stacking of pairs of naphthyl units has a dominant effect on the overall packing in both $[\text{Cr}(\mathbf{1})_2][\text{PF}_6]_3$ and $[\text{Co}(\mathbf{1})_2][\text{PF}_6]_3$.

Appendix 1 Supplementary data

Crystallographic data for $[\text{Cr}(\mathbf{1})_2][\text{PF}_6]_3 \cdot 0.4\text{MeCN}$ and $[\text{Co}(\mathbf{1})_2][\text{PF}_6]_3 \cdot 0.7\text{H}_2\text{O}$ have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk) and may be obtained free of charge on quoting deposition numbers CCDC 1036545 and 1036546.

Acknowledgements

We thank the Swiss National Science Foundation (grant 200020_144500), the European Research Council (Advanced Grant 267816 LiLo) and the University of Basel for support.

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- [16] Ligand **1**: 2-Acetylpyridine (2.24 ml, 20.0 mmol) and 2-naphthaldehyde (1.36 ml, 10.0 mmol) were dissolved in EtOH (50 ml). Solid KOH (1.12 g, 20.0 mmol) was added and, after stirring to dissolve the KOH, aqueous NH₃ (1 ml, conc. 32%) was added. The mixture was stirred overnight at room temperature, and the precipitate was collected by filtration, washed with cold EtOH and recrystallized from EtOH. **1** was isolated as a white needles (1.22 g, 3.38 mmol, 33.8%).
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- [18] [Cr(**1**)₂][PF₆]₃: CrCl₃ (188 mg, 1.18 mmol) and **1** (550 mg, 1.53 mmol) were suspended in EtOH (15 ml) and granulated Zn (16.9 mg, 0.259 mmol) was added; after heating at

reflux for 6 h, the mixture was cooled, decanted from excess Zn, then filtered. Solid [Cr(1)Cl₃] was collected and used without purification. A solution of [Cr(1)Cl₃] (100 mg, 0.195 mmol) in CF₃SO₃H (0.70 ml, 7.8 mmol) was stirred overnight at room temperature. After cooling to 0 °C, Et₂O (20 ml) was added, giving dark red [Cr(1)(O₃SCF₃)₃] which was collected on a frit. MeCN (10 ml) was poured through the frit and the red filtrate transferred under N₂ to a flask containing **1** (77.3 mg, 0.215 mmol); the mixture was heated at reflux for 7 h, then cooled. Solvent was removed, the residue dissolved in MeOH (2 ml), and the mixture filtered into a MeOH solution of excess NH₄PF₆ giving an orange precipitate that was collected by filtration, washed with hexane and Et₂O to give [Cr(1)₂][PF₆]₃ as an orange solid (302 mg, 0.263 mmol, 77.0%).

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- [20] [Co(1)₂][PF₆]₃: ¹H NMR (500 MHz, CD₃CN) δ / ppm 9.43 (s, 4H, H^{B3}), 8.97 (d, J = 2.0 Hz, 2H, H^{C1}), 8.78 (d, J = 8.0 Hz, 4H, H^{A3}), 8.41 (dd, J = 8.6, 2.0 Hz, 2H, H^{C3}), 8.36 (d, J = 8.7 Hz, 2H, H^{C4}), 8.34-8.23 (m, 6H, H^{A4+C8}), 8.16 (m, 2H, H^{C5/C6}), 7.84-7.74 (m, 4H, H^{C5/C6+C7}), 7.47 (m, 8H, H^{A5+A6}). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ / ppm 158.6 (C^{B4}), 157.3 (C^{A2+B2}), 153.4 (C^{A6}), 144.0 (C^{A4}), 135.7 (C^{C4a/C8a}), 134.4 (C^{C4a/C8a}), 133.0 (C^{C2}), 131.8 (C^{A5}), 130.9 (C^{C4}), 130.4 (C^{C1}), 130.1 (C^{C8}), 129.4 (C^{C5/C6+C7}), 128.9 (C^{C5/C6}), 128.1 (C^{A3}), 126.1 (C^{B3}), 125.4 (C^{C3}). Found C 48.52, H 2.83, N 6.93; C₅₀H₃₄CoF₁₈N₆P₃·H₂O requires C 48.80, H 2.95, N 6.83.
- [21] [Cr(1)₂][PF₆]₃·0.4MeCN: C_{50.80}H_{35.20}CrF₁₈N_{6.40}P₃, $M = 1222.16$, orange block, triclinic, space group $P\bar{1}$, $a = 11.4677(5)$, $b = 14.9613(6)$, $c = 15.2475(6)$ Å, $\alpha = 100.0920(10)$, $\beta = 108.6350(10)$, $\gamma = 92.1140(10)^\circ$, $U = 2428.41(17)$ Å³, $Z = 2$, $D_c = 1.671$ Mg m⁻³, $\mu(\text{Cu-K}\alpha) = 3.920$ mm⁻¹, $T = 123$ K. Total 25679 reflections, 8765 unique, $R_{\text{int}} = 0.023$. Refinement of 8274 reflections (861 parameters) with $I > 2\sigma(I)$ converged at final $R1 = 0.0580$ ($R1$ all data = 0.0596), $wR2 = 0.0683$ ($wR2$ all data = 0.0689), $\text{gof} = 1.0213$.
- [22] [Co(1)₂][PF₆]₃·0.7H₂O: C₅₀H₃₄CoF₁₈N₆O_{0.70}P₃, $M = 1223.88$, orange needle, triclinic, space group $P\bar{1}$, $a = 11.3654(7)$, $b = 14.8737(9)$, $c = 15.2586(9)$ Å, $\alpha = 100.884(3)$, $\beta = 108.520(2)$, $\gamma = 92.448(3)^\circ$, $U = 2387.17(14)$ Å³, $Z = 2$, $D_c = 1.703$ Mg m⁻³, $\mu(\text{Cu-K}\alpha) = 4.840$ mm⁻¹, $T = 123$ K. Total 31021 reflections, 8364 unique, $R_{\text{int}} = 0.028$. Refinement of 8126 reflections (788 parameters) with $I > 2\sigma(I)$ converged at final $R1 = 0.0472$ ($R1$ all data = 0.0482), $wR2 = 0.1192$ ($wR2$ all data = 0.1195), $\text{gof} = 0.9783$.