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

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Abstract
The homoleptic complexes $[\text{Cr(1)}_2][\text{PF}_6]_3$ and $[\text{Co(1)}_2][\text{PF}_6]_3$ ($1 = 4'$-(naphth-2-yl)-2,2':6',2''-terpyridine) have been prepared and structurally characterized. The packing interactions in both complexes are identical, consisting of a combination of naphthyl...naphthyl $\pi$-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; $\pi$-embraces

2,2':6',2''-Terpyridine (tpy) is a ubiquitous ligand and a vast range of complexes containing $\{\text{M(tpy)}_2\}^{n+}$ 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 $\{\text{M(tpy)}_2\}$ (M = any metal) unit. However, only seven have M = Cr [3,4,5,6] and the only chromium(III) examples are $2\{[\text{Cr(tpy)}_2][\text{PF}_6]_3\}^+$;5MeCN [6], $[\text{Cr(tpy)}(4'-\text{(4-tolyl)tpy})][\text{PF}_6]_3$;3MeCN [6], $[\text{Cr(tpy)}(5,5''-\text{Me}_2\text{tpy})][\text{PF}_6]_3$;3MeCN [6] and $[\text{Cr(tpy)}_2][\text{ClO}_4]_3$;H$_2$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 $[\text{M(bpy)}_3]^{2+}$ [9] and $[\text{M(tpy)}_2]^{2+}$ [10,11,12,13,14] lattices. We now report the consequences of introducing 4'- (naphth-2-yl) substituents and compare the structures of solvated $[\text{Cr(1)}_2][\text{PF}_6]_3$ and $[\text{Co(1)}_2][\text{PF}_6]_3$ where 1 is 4'- (naphth-2-yl)-2,2':6',2''-terpyridine (Scheme 1).

Compound 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 $\{\text{Cr(4'-Xtpy)}_2\}^{3+}$ or heteroleptic $\{\text{Cr(4'-Xtpy)(4'-Ytpy)}\}^{3+}$ 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 [Cr(I)$_2$][CF$_3$SO$_3$]$_3$ with anion exchange in the last step yielding [Cr(I)$_2$][PF$_6$]$_3$ as an orange solid [18]. The synthesis of [Co(I)$_2$][PF$_6$]$_3$ as an orange solid in 84.3% yield was by Br$_2$ oxidation of [Co(I)$_2$][PF$_6$]$_2$ (prepared from Co(OAc)$_2$·4H$_2$O with two equivalents of I followed by anion exchange) and followed the reported general procedure [19]. $^1$H and $^{13}$C NMR spectra (assigned by 2D methods) for [Co(I)$_2$][PF$_6$]$_3$ [20] were consistent with a single ligand environment and the shift in the signal for H$_{A6}$ (see Scheme 1) from $\delta$ 8.75 ppm in 1 (CDCl$_3$) to $\delta$ 7.47 ppm in [Co(I)$_2$][PF$_6$]$_3$ (CD$_3$CN) is indicative of the formation of a {Co(tpy)$_2$}$_3^+$ domain with H$_{A6}$ of one ligand lying over the $\pi$-system of the second tpy.

![Scheme 1. Structure of ligand I with numbering for NMR spectroscopic assignments.](image1)

![Scheme 2. Synthetic route to [Cr(I)$_2$][PF$_6$]$_3$. Conditions: (i) CF$_3$SO$_3$H; (ii) ligand I; (iii) NH$_4$PF$_6$.](image2)

Both [Cr(I)$_2$][PF$_6$]$_3$·0.4MeCN and [Co(I)$_2$][PF$_6$]$_3$·0.7H$_2$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 [Cr(I)$_2$]$_3^{3+}$ 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 $[\text{Co}(1)_2]^{3+}$ cation in $[\text{Co}(1)_2][\text{PF}_6]_3\cdot 0.4\text{MeCN}$, 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 $\{\text{M(tpy)}_2\}$ units.

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 $[\text{Cr}(1)_2]^{3+}$ are 37.5 and 22.6°, respectively, and the corresponding angles in the $[\text{Co}(1)_2]^{3+}$ ion are 37.8 and 22.9°. 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° 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° 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 ($4^{'-}\text{Phtpy} = 4^{'-}\text{phenyl-2,2':6',2''-terpyridine}$) [11] and in $[\text{Cr}(4^{'-}(4\text{-tolyl})\text{tpy})_2][\text{CF}_3\text{SO}_3]_3\cdot 2\text{MeCN}$ ($4^{'-}(4\text{-tolyl})\text{tpy}-2,2':6',2''\text{-terpyridine}$) [8]. The presence of both naphthyl...naphthyl π-stacking interactions and dual naphthyl...pyridine embraces along chains of cations in $[\text{Cr}(1)_2][\text{PF}_6]_3\cdot 0.4\text{MeCN}$ and $[\text{Co}(1)_2][\text{PF}_6]_3\cdot 0.4\text{MeCN}$ 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 $[\text{Cr}(1)_2][\text{PF}_6]_3\cdot 0.4\text{MeCN}$, the Cr...Cr separations alternate 16.4427(8) and 11.9131(7) Å, compared to a constant separation of 10.9971(7) Å in $[\text{Cr}(4^{'-}(4\text{-tolyl})\text{tpy})_2][\text{CF}_3\text{SO}_3]_3\cdot 2\text{MeCN}$ [8].
[Co(1)2][PF6]3·0.4MeCN, 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 [Cr(1)2][PF6]3·0.4MeCN. (Colour online)

Figure 3. (a) Inter-cation double pyridine...naphthyl embrace in [Cr(1)2][PF6]3 and [Co(1)2][PF6]3, compared to (b) a double pyridine...phenyl embrace in [M(4'-Phtpy)2]2+ complexes.

In conclusion, we demonstrate that the introduction of the naphth-2-yl domain in [Cr(1)2][PF6]3 and [Co(1)2][PF6]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 [Cr(1)2][PF6]3 and [Co(1)2][PF6]3.

Appendix 1 Supplementary data
Crystallographic data for [Cr(1)2][PF6]3·0.4MeCN and [Co(1)2][PF6]3·0.7H2O 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 and may be obtained free of charge on quoting deposition numbers CCDC 1036545 and 1036546.
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References

[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 NH$_3$ (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%).
[18] [Cr(O)$_2$][PF$_6$]: CrCl$_3$ (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)(O2SCF3)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)3][PF6]3 as an orange solid (302 mg, 0.263 mmol, 77.0%).

[19] E. C. Constable, K. Harris, C. E. Housecroft, M. Neuburger, J. A. Zampese,

[20] [Co(1)3][PF6]3: 1H NMR (500 MHz, CD2CN) δ / ppm 9.43 (s, 4H, Hβ3), 8.97 (d, J = 2.0
Hz, 2H, Hα1), 8.78 (d, J = 8.0 Hz, 4H, Hα2), 8.41 (dd, J = 8.6, 2.0 Hz, 2H, Hα1), 8.36 (d,
J = 8.7 Hz, 2H, Hα2), 8.34-8.23 (m, 6H, Hα4+α8), 8.16 (m, 2H, Hα5+α6), 7.84-7.74 (m, 4H,
Hα6+α6-C7), 7.47 (m, 8H, Hα5+α6). 13C NMR (126 MHz, CDCl3) δ / ppm 158.6 (Cβ3),
157.3 (Cα2+β2), 153.4 (Cα6), 144.0 (Cα4), 135.7 (Cα4+α8), 134.4 (Cα4+α8), 133.0 (Cα2),
131.8 (Cα5), 130.9 (Cα4), 130.4 (Cα1), 130.1 (Cα8), 129.4 (Cα5+α6−C7), 128.9 (Cα5+α8),
128.1 (Cα1), 126.1 (Cβ5), 125.4 (Cα3). Found C 48.52, H 2.83, N 6.93;
C50H34CoF18N6P32H2O requires C 48.80, H 2.95, N 6.83.

[21] [Cr(1)3][PF6]3: 0.4MeCN: C50H38O35.20CrF18N6.40P3, M = 1222.16, orange block, triclinic,
space group P–1, a = 11.4677(5), b = 14.9613(6), c = 15.2475(6) Å, α = 100.0920(10),
β = 108.6350(10), γ = 92.1140(10)°, U = 2428.41(17) Å3, Z = 2, Dc = 1.671 Mg m−3,
μ(Cu-Kα) = 3.920 mm−1, T = 123 K. Total 25679 reflections, 8765 unique, Rint = 0.023.
Refinement of 8274 reflections (861 parameters) with I > 2σ(I) converged at final R1 =
0.0580 (R1 all data = 0.0596), wR2 = 0.0683 (wR2 all data = 0.0689), gof = 1.0213.

[22] [Co(1)2][PF6]3: 0.7H2O: C50H34CoF18N6O8P3, M = 1223.88, orange needle, triclinic,
space group P–1, a = 11.3654(7), b = 14.8737(9), c = 15.2586(9) Å, α = 100.8843(3), β =
108.520(2), γ = 92.448(3)°, U = 2387.17(14) Å3, Z = 2, Dc = 1.703 Mg m−3, μ(Cu-Kα) =
4.840 mm−1, T = 123 K. Total 31021 reflections, 8364 unique, Rint = 0.028.
Refinement of 8126 reflections (788 parameters) with I > 2σ(I) converged at final R1 =
0.0472 (R1 all data = 0.0482), wR2 = 0.1192 (wR2 all data = 0.1195), gof = 0.9783.