

# Heteroleptic chromium(III) tris(diimine) $[\text{Cr}(\text{N}^{\wedge}\text{N})_2(\text{N}'^{\wedge}\text{N}')]^{3+}$ complexes

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## Abstract

A series of heteroleptic tris(diimine) complexes of chromium(III) is reported and the crystal structures of  $\{4[\text{Cr}(\text{bpy})_2(\text{phen})][\text{PF}_6]_3\} \cdot 11\text{MeCN}$  and  $4[\text{Cr}(4,4'\text{-Me}_2\text{bpy})_2(\text{bpy})][\text{PF}_6]_3 \cdot 12\text{MeCN} \cdot \text{H}_2\text{O}$  are described. The combined effects of a 1 : 3 cation : anion ratio and lattice solvent molecules are discussed, in particular in the context of the influence on intercation embraces. The presence of the methyl substituents in  $\{4[\text{Cr}(4,4'\text{-Me}_2\text{bpy})_2(\text{bpy})][\text{PF}_6]_3\} \cdot 12\text{MeCN} \cdot \text{H}_2\text{O}$  results in  $\text{Me} \dots \pi_{\text{bpy}}$  contacts becoming the dominant packing interactions and in the assembly of motifs distinct from those in  $\{4[\text{Cr}(\text{bpy})_2(\text{phen})][\text{PF}_6]_3\} \cdot 11\text{MeCN}$ .

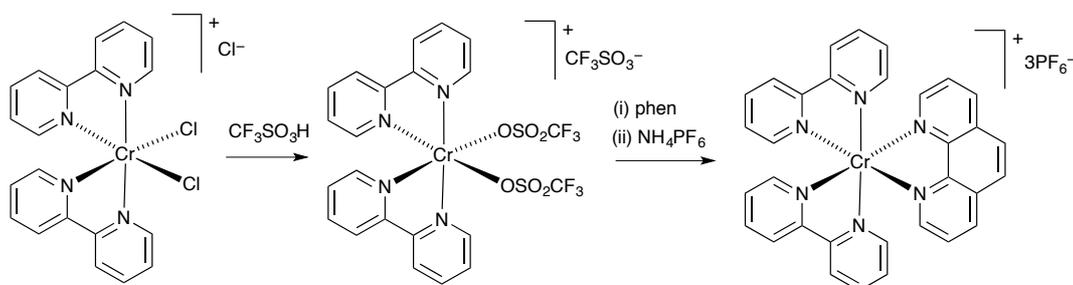
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*Keywords:* chromium; 2,2'-bipyridine; 1,1-phenanthroline; heteroleptic complexes; crystal structure; chelates

## 1. Introduction

Chromium(III) complexes containing diimine ligands are of potential interest as Earth abundant photo- and redox-active components for artificial photosynthesis and water-splitting systems, and their photophysical properties have therefore been studied in detail [1,2]. We have recently reported that, although chromium(III) complexes are classical 'kinetically inert  $d^3$  systems', those with 2,2':6',2''-terpyridine ligands can exhibit a

remarkable and unexpectedly high lability [3]. We also noted that the degree of lability is strongly dependent upon the nature of the ligands, the solvents and pH [3]. We have extended the study to heteroleptic tris(diimine)  $[\text{Cr}(\text{N}^{\wedge}\text{N})_2(\text{N}'^{\wedge}\text{N}')]^{3+}$  complexes and have embarked on a structural investigation of these complexes to probe the influence of the ligand set on the metal environment. Although the complexes  $[\text{Cr}(\text{bpy})_3]^{3+}$  (bpy = 2,2'-bipyridine) and  $[\text{Cr}(\text{phen})_3]^{3+}$  (phen = 1,10-phenanthroline) are well known [4], synthetic and structural studies of heteroleptic complexes remain sparse [5,6,7,8]. A convenient route to heteroleptic  $[\text{Cr}(\text{N}^{\wedge}\text{N})_2(\text{N}'^{\wedge}\text{N}')]^{3+}$  complexes ( $\text{N}^{\wedge}\text{N}$  and  $\text{N}'^{\wedge}\text{N}'$  are different bpy or phen-based ligands) involves the reaction of  $\text{CrCl}_3$  with  $\text{N}^{\wedge}\text{N}$  in the presence of powdered zinc in ethanol to give *cis*- $[\text{Cr}(\text{N}^{\wedge}\text{N})_2\text{Cl}_2]\text{Cl}$  [9], followed by reaction with triflic acid to give *cis*- $[\text{Cr}(\text{N}^{\wedge}\text{N})_2(\text{CF}_3\text{SO}_3)_2][\text{CF}_3\text{SO}_3]$  containing labile triflate ligands [10]. These are easily replaced by the second ligand  $\text{N}'^{\wedge}\text{N}'$  [11]. We have recently shown that an analogous approach can be applied for the preparation of heteroleptic  $[\text{Cr}(\text{tpy})(\text{tpy}') ]^{3+}$  complexes [3], which, like the heteroleptic diimine systems, are rather underexplored. The use of the triflate intermediate proves to be key to gaining heteroleptic chromium(III) complexes containing either tris(diimine) or bis(tpy) metal-binding domains, and in the former case, gives a route which is free of redistribution reactions involving the diimine ligands [11]. The method is preferred over routes involving perchlorates [6].



Scheme 1. General route to heteroleptic complexes illustrated by the formation of  $[\text{Cr}(\text{bpy})_2(\text{phen})][\text{PF}_6]_3$ .

We first prepared  $[\text{Cr}(\text{bpy})_2(\text{phen})][\text{PF}_6]_3$  as a representative heteroleptic complex using the literature procedure (Scheme 1) [11]. The same strategy was then used to prepare  $[\text{Cr}(\text{bpy})_2(4,4'\text{-Me}_2\text{bpy})][\text{PF}_6]_3$ ,  $[\text{Cr}(\text{bpy})_2(5,5'\text{-Me}_2\text{bpy})][\text{PF}_6]_3$  and  $[\text{Cr}(4,4'\text{-Me}_2\text{bpy})_2(\text{bpy})][\text{PF}_6]_3$  [12].  $[\text{Cr}(\text{bpy})_2(\text{phen})][\text{PF}_6]_3$  has previously been characterized by elemental analysis and electronic absorption spectroscopy, and we were able to confirm the structure of the complex by single crystal X-ray diffraction [13]. In  $\{4[\text{Cr}(\text{bpy})_2(\text{phen})][\text{PF}_6]_3\} \cdot 11\text{MeCN}$ , the octahedral tris(chelate) crystallizes as a racemate and Figure 1a shows the structure of the  $\Lambda$ - $[\text{Cr}(\text{bpy})_2(\text{phen})]^{3+}$  cation. Bond

distances and angles are as expected (caption to Figure 1). Dance *et al.* [14] demonstrated that  $\Lambda$ - and  $\Delta$ -cations in  $[\text{Cr}(\text{bpy})_3][\text{PF}_6]_3$  (CSD [15] refcode FERYEG01) engage in aryl embraces and pack into columns running along 3-fold axes in the lattice. This packing motif is retained in  $[\text{Cr}(\text{phen})_3][\text{PF}_6]_2 \cdot 2.5\text{MeCN}$  [16] (CSD refcode QEJQAZ), i.e. the lower oxidation state for chromium and consequent reduction in the number of anions is compensated for by incorporation of solvent molecules. The limit to which the packing can tolerate the needs of anions and solvent is tested in  $\{4[\text{Cr}(\text{bpy})_2(\text{phen})][\text{PF}_6]_3\} \cdot 11\text{MeCN}$ , where we observe that the accommodation of three  $[\text{PF}_6]^-$  anions per cation in addition to lattice MeCN molecules switches off the columnar packing motif. Hexafluoridophosphate anions are sandwiched between  $[\text{Cr}(\text{bpy})_2(\text{phen})]^{3+}$  cations of the same handedness (Figure 1b), dominant interactions being CH...F contacts involving the bpy H3 and H3' protons ( $\text{C4H4A...F12} = 2.49 \text{ \AA}$ ,  $\text{C7H7A...F12} = 2.64 \text{ \AA}$ ), and  $\pi_{\text{bpy}} \dots \text{F}$  and  $\pi_{\text{phen}} \dots \text{F}$  contacts. The chains of cations (Figures 1b and 1c) follow the crystallographic  $a$ -axis with Cr...Cr separations of  $10.286(1) \text{ \AA}$ . Although the phen domains in adjacent chains approach closely (Figure 1c), there is no ring overlap and, therefore, there are no  $\pi$ - $\pi$  interactions.

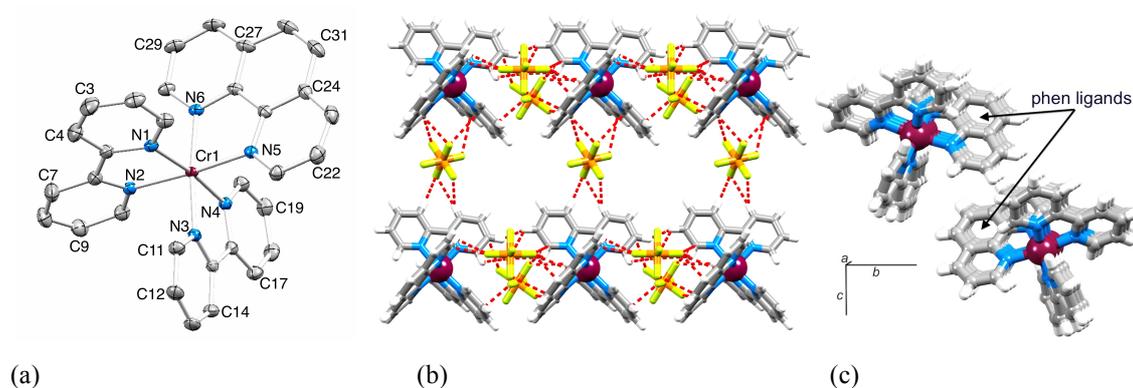


Fig. 1. (a) Structure of the  $\Lambda$ - $[\text{Cr}(\text{bpy})_2(\text{phen})]^{3+}$  cation in  $\{4[\text{Cr}(\text{bpy})_2(\text{phen})][\text{PF}_6]_3\} \cdot 11\text{MeCN}$ ; H atoms are omitted and ellipsoids are plotted at 40% probability level. Selected bond metrics: Cr1–N3 = 2.0361(18), Cr1–N4 = 2.0373(19), Cr1–N6 = 2.0468(18), Cr1–N5 = 2.0494(19), Cr1–N1 = 2.0506(19), Cr1–N2 = 2.0527(19)  $\text{\AA}$ ; N1–Cr1–N2 = 79.53(8), N3–Cr1–N4 = 79.81(8), N6–Cr1–N5 = 80.75(8) $^\circ$ . (b) Cation...anion F...H and F... $\pi$  contacts. (c) Packing of chains of cations along the  $a$ -axis. (Colour online)

Crystals of  $\{4[\text{Cr}(4,4'\text{-Me}_2\text{bpy})_2(\text{bpy})][\text{PF}_6]_3\} \cdot 12\text{MeCN} \cdot \text{H}_2\text{O}$  [17] were grown from MeCN solution by overlaying with Et<sub>2</sub>O. The chromium(III) centre is octahedrally coordinated (Figure 2a) and both enantiomers of the tris(chelate) are present in the unit cell. Bond parameters within the coordination sphere of atom Cr1 are given in the caption to Figure 2a. One  $[\text{PF}_6]^-$  ion is disordered and was modelled over two sites with 0.57 and 0.43 occupancies; residual electron density was modelled as a partial

occupancy H<sub>2</sub>O molecule. The cation : anion ratio in {4[Cr(4,4'-Me<sub>2</sub>bpy)<sub>2</sub>(bpy)][PF<sub>6</sub>]<sub>3</sub>}·12MeCN·H<sub>2</sub>O and {4[Cr(bpy)<sub>2</sub>(phen)][PF<sub>6</sub>]<sub>3</sub>}·11MeCN is the same, and the solvent content is comparable. It is therefore noteworthy that the cations in {4[Cr(4,4'-Me<sub>2</sub>bpy)<sub>2</sub>(bpy)][PF<sub>6</sub>]<sub>3</sub>}·12MeCN·H<sub>2</sub>O approach more closely than in {4[Cr(bpy)<sub>2</sub>(phen)][PF<sub>6</sub>]<sub>3</sub>}·11MeCN, and associate through Me... $\pi$  interactions (Figure 2b, C<sub>Me</sub>...centroid = 3.53 Å). Only the 4,4'-Me<sub>2</sub>bpy ligands containing N1 and N2 engage in these interactions, which build up chains running parallel to the *b*-axis (Figure 2c). Solvent molecules and anions occupy the cavities between the chains.

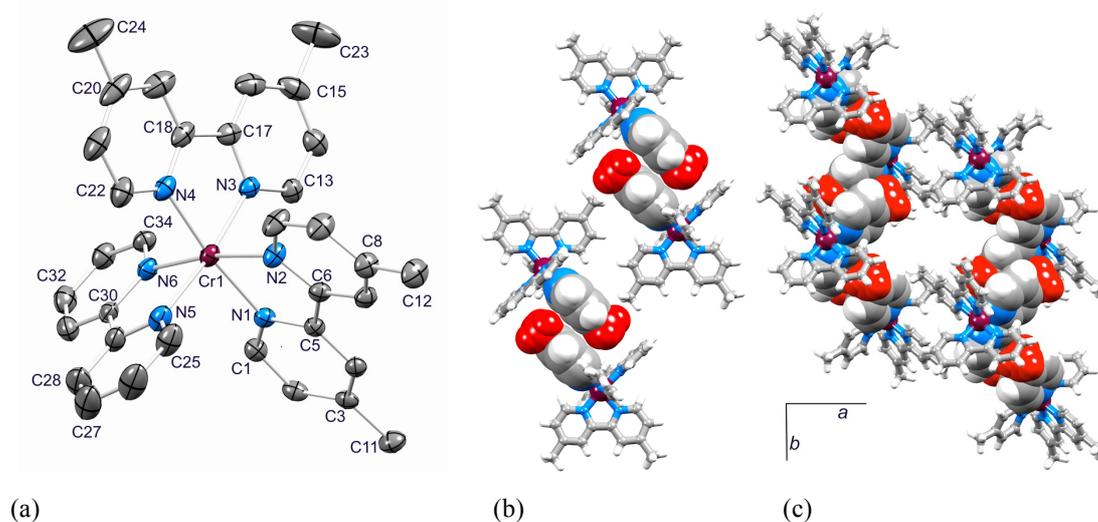


Fig. 2. (a) Structure of the  $\Delta$ -[Cr(4,4'-Me<sub>2</sub>bpy)<sub>2</sub>(bpy)]<sup>3+</sup> cation in {4[Cr(4,4'-Me<sub>2</sub>bpy)<sub>2</sub>(bpy)][PF<sub>6</sub>]<sub>3</sub>}·12MeCN·H<sub>2</sub>O; H atoms omitted and ellipsoids plotted at 40% probability level. Important bond lengths and angles: Cr1–N4 = 2.031(3), Cr1–N6 = 2.032(3), Cr1–N3 = 2.038(3), Cr1–N5 = 2.041(3), Cr1–N2 = 2.044(3), Cr1–N1 = 2.044(3) Å; N1–Cr1–N2 = 79.56(12), N3–Cr1–N4 = 80.15(13), N5–Cr1–N6 = 79.34(13)°. (b) Centrosymmetric pairs of cations associate through Me... $\pi$  contacts (Me groups shown in red). (c) Chains of cations follow the *b*-axis. (Colour online)

In conclusion, we have prepared a series of heteroleptic tris(diimine)chromium(III) complexes and presented the structures of two representative examples. The 1 : 3 cation : anion ratio coupled with accommodation of solvent forces the packing away from the aryl embraces described by Dance [<sup>14</sup>] for related structures. The presence of methyl substituents in {4[Cr(4,4'-Me<sub>2</sub>bpy)<sub>2</sub>(bpy)][PF<sub>6</sub>]<sub>3</sub>}·12MeCN·H<sub>2</sub>O leads to Me... $\pi$ <sub>bpy</sub> contacts being dominant packing interactions, and the assembly of motifs which contrast sharply with those in {4[Cr(bpy)<sub>2</sub>(phen)][PF<sub>6</sub>]<sub>3</sub>}·11MeCN.

#### Appendix 1 Supplementary data

Crystallographic data for [Cr(bpy)<sub>2</sub>(phen)][PF<sub>6</sub>]<sub>3</sub>·11MeCN and {4[Cr(4,4'-Me<sub>2</sub>bpy)<sub>2</sub>(bpy)][PF<sub>6</sub>]<sub>3</sub>}·12MeCN·H<sub>2</sub>O have been deposited with the CCDC (Cambridge

Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336 033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or www: <http://www.ccdc.cam.ac.uk>) and may be obtained free of charge on quoting the deposition numbers CCDC 1029169 and 1029170.

#### *Acknowledgements*

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- [12]  $[Cr(bpy)_2(4,4'-Me_2bpy)][PF_6]_3$ :  $[Cr(bpy)_2(O_3SCF_3)_2][CF_3SO_3]$  (169 mg, 0.208 mmol) and 4,4'-Me<sub>2</sub>bpy (40.4 mg, 0.219 mmol) were dissolved in MeCN (12 mL) and the mixture was heated at reflux ( $\approx$ 6 h) to give a yellow solution. Solvent was removed and the product dissolved in water (3 mL) with the aid of sonication. After filtration, the filtrate was poured into aqueous NH<sub>4</sub>PF<sub>6</sub> (excess) and the yellow precipitate that formed was separated by filtration and

- washed with Et<sub>2</sub>O. [Cr(bpy)<sub>2</sub>(4,4'-Me<sub>2</sub>bpy)][PF<sub>6</sub>]<sub>3</sub> was isolated as a yellow powder (139 mg, 0.141 mmol, 67.8%). Found C 37.86, H 2.90, N 8.48; C<sub>32</sub>H<sub>28</sub>CrF<sub>18</sub>N<sub>6</sub>P<sub>3</sub>·1.5H<sub>2</sub>O requires C 38.03, H 3.09, N 8.32%. [Cr(bpy)<sub>2</sub>(5,5'-Me<sub>2</sub>bpy)][PF<sub>6</sub>]<sub>3</sub>: The method was as above starting with [Cr(bpy)<sub>2</sub>(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>][CF<sub>3</sub>SO<sub>3</sub>] (200.0 mg, 0.246 mmol) and 5,5'-Me<sub>2</sub>bpy (47.8 mg, 0.259 mmol), and [Cr(bpy)<sub>2</sub>(5,5'-Me<sub>2</sub>bpy)][PF<sub>6</sub>]<sub>3</sub> was isolated as a yellow powder (191 mg, 0.194 mmol, 78.9%). Found C 38.83, H 2.90, N 8.50; C<sub>32</sub>H<sub>28</sub>CrF<sub>18</sub>N<sub>6</sub>P<sub>3</sub> requires C 39.08, H 2.87, N 8.55%. [Cr(4,4'-bpy)<sub>2</sub>(bpy)][PF<sub>6</sub>]<sub>3</sub>: The method was as above starting with [Cr(4,4'-bpy)<sub>2</sub>(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>][CF<sub>3</sub>SO<sub>3</sub>] (46.4 mg, 0.0535 mmol) and bpy (10.4 mg, 0.0667 mmol). [Cr(4,4'-Me<sub>2</sub>bpy)<sub>2</sub>(bpy)][PF<sub>6</sub>]<sub>3</sub> was isolated as a yellow-orange powder (10.7 mg, 0.0106 mmol, 19.8%). Found C 39.72, H 3.30, N 8.25; C<sub>34</sub>H<sub>32</sub>CrF<sub>18</sub>N<sub>6</sub>P<sub>3</sub>·0.5H<sub>2</sub>O requires C 40.01, H 3.26, N 8.23%.
- [13] {4[Cr(bpy)<sub>2</sub>(phen)][PF<sub>6</sub>]<sub>3</sub>}·11MeCN: C<sub>150</sub>H<sub>129</sub>Cr<sub>4</sub>F<sub>72</sub>N<sub>35</sub>P<sub>12</sub>, M = 4369.52, yellow block, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 10.2863(9), *b* = 34.025(4), *c* = 13.0344(12) Å, β = 94.356(7)°, *U* = 4548.8(8) Å<sup>3</sup>, *Z* = 1, *D*<sub>c</sub> = 1.595 Mg m<sup>-3</sup>, μ(Mo-Kα) = 0.471 mm<sup>-1</sup>, *T* = 173 K. Total 43616 reflections, 9061 unique, *R*<sub>int</sub> = 0.0353. Refinement of 8430 reflections (681 parameters) with *I* > 2σ(*I*) converged at final *R*1 = 0.0487 (*R*1 all data = 0.0521), *wR*2 = 0.1287 (*wR*2 all data = 0.1312), *gof* = 1.039.
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- [17] {4[Cr(4,4'-Me<sub>2</sub>bpy)<sub>2</sub>(bpy)][PF<sub>6</sub>]<sub>3</sub>}·12MeCN·H<sub>2</sub>O: C<sub>160</sub>H<sub>166</sub>Cr<sub>4</sub>F<sub>72</sub>N<sub>36</sub>OP<sub>12</sub>, M = 4556.93, yellow block, monoclinic, space group *C*2/*c*, *a* = 24.4712(17), *b* = 12.9795(8), *c* = 31.013(2) Å, β = 95.608(6)°, *U* = 9803.4(12) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.543 Mg m<sup>-3</sup>, μ(Mo-Kα) = 0.441 mm<sup>-1</sup>, *T* = 173 K. Total 46492 reflections, 8641 unique, *R*<sub>int</sub> = 0.0442. Refinement of 7928 reflections (720 parameters) with *I* > 2σ(*I*) converged at final *R*1 = 0.0684 (*R*1 all data = 0.0730), *wR*2 = 0.1607 (*wR*2 all data = 0.1632), *gof* = 1.131.