Homoleptic and heteroleptic complexes of chromium(III) containing 4'-diphenylamino-2,2':6',2''-terpyridine ligands

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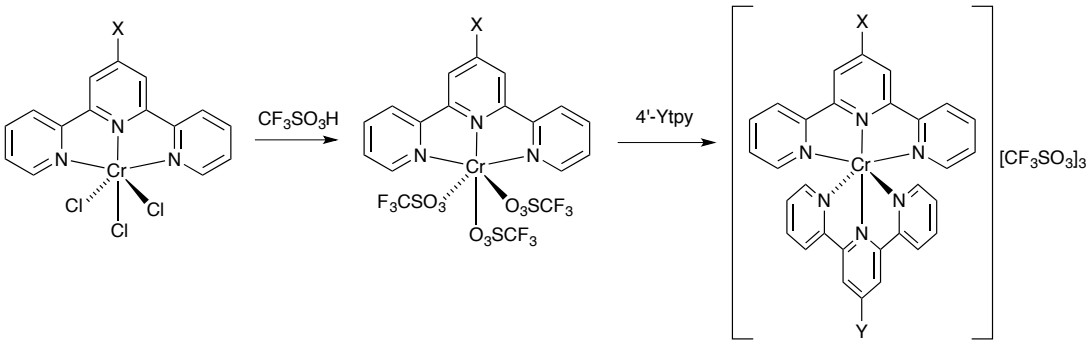
Abstract

Two heteroleptic bis(2,2':6',2''-terpyridine)chromium(III) complexes [Cr(**1**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$ and [Cr(**2**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$ in which **1** and **2** contain 4'-(4-(*N,N*-diphenylamino)phenyl) or 4'-(4-(*N,N*-di(4-methoxyphenyl)amino)phenyl) domains, respectively, have been prepared and their spectroscopic and electrochemical properties compared with those of [Cr(4'-(4-tolyl)tpy)$_2$][CF_3SO_3]$_3$ and [Cr(**1**)$_2$][CF_3SO_3]$_3$. The single crystal structure of [Cr(4'-(4-tolyl)tpy)$_2$][CF_3SO_3]$_3$·2MeCN is presented, and the effects of accommodating three triflate anions and two MeCN molecules per cation are discussed in terms of related structures. The coordination of **1** or **2** to chromium(III) red-shifts the ILCT band and this band exhibits a negative solvatochromic effect in some solvents. However, in H_2O, MeOH, DMSO and DMF, the tpy ligands are labile; spectroscopic data for a study of [Cr(**2**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$ are consistent with the formation of [Cr(4'-Xtpy)(Solv)$_3$]$^{3+}$ (Solv = solvent) rather than complete ligand displacement or a ligand redistribution.

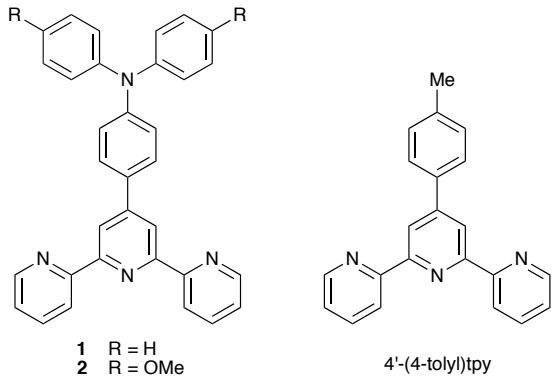
Keywords: Chromium(III); 2,2':6',2''-terpyridine; solvatochromic; absorption spectra; heteroleptic complex

1. Introduction

Although large numbers of metal complexes containing 2,2':6',2''-terpyridine (tpy) metal-binding domains have been reported in the past 80 years, those with chromium(III) remain underexplored since the homoleptic $[Cr(tpy)_2]^n$ (n = +3, +2, +1, 0, –1) complexes were described in the 1960s [1,2,3,4,5,6]. In 2012, Sproules, Wieghardt and coworkers proposed that in the series $[Cr(tpy)_2][PF_6]_n$ with n = 3, 2 1, 0, all one-electron redox processes are ligand-based with the chromium centre remaining in the +3 oxidation state [7]. This and other photophysical and electrochemical investigations of complexes having $\{Cr(tpy)_2\}^{3+}$ cores have dealt with homoleptic complexes [8,9,10,11,12,13,14,15,16]. The complexes excited some interest as potential catalysts for photoelectrochemical water-splitting with the observation that in the solid state water molecules were located close to the metal centre in pockets created by the two orthogonal tpy ligands [17,18]. We recently showed that heteroleptic $[Cr(4'\text{-}Xtpy)(4'\text{-}Ytpy)]^{3+}$ complexes can be conveniently accessed using the general method shown in Scheme 1, and demonstrated that these complexes do not behave as typical kinetically inert d^3 species [19]. We now describe the preparation and properties of chromium(III) complexes incorporating ligands **1** and **2** (Scheme 2). The extended π-systems and peripheral diphenylamine domains in **1** and **2** provide a facile means of tuning the photophysical properties of the $\{Cr(tpy)_2\}^{3+}$ complex.



Scheme 1. General route to heteroleptic $[Cr(4'\text{-}Xtpy)(4'\text{-}Ytpy)][CF_3SO_3]_3$ complexes.



Scheme 2. Structures of ligands.

2. Experimental

2.1 General

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III-500 spectrometer with chemical shifts referenced to residual solvent peaks (∂(TMS) = 0 ppm). Absorption spectra were recorded on a Cary 5000 spectrophotometer on an Agilent Technologies UV-Visble 8453 spectrophotometer. Electrochemical measurements were made on a CH Instruments 900B potentiostat using glassy carbon, platinum wire and a silver wire as the working, counter, and pseudo reference electrodes, respectively. Samples were dissolved in HPLC grade MeCN (10^{-4} to 10^{-5} mol dm^{-3}) containing 0.1 mol dm^{-3} [$^{n}Bu_4N$][PF_6] as supporting electrolyte; all solutions were degassed with argon. Cp_2Fe was used as internal reference added at the end of experiments.

The compounds 4'-(4-tolyl)-tpy [20], **1** [21] and **2** [21] were prepared as reported.

*2.2 [Cr(**1**)Cl_3]*

Anhydrous $CrCl_3$ (188 mg, 1.18 mmol) and 1 (731 mg, 1.53 mmol) were suspended in EtOH (15 mL). Granulated zinc (16.9 mg, 0.259 mmol) was added, and then the reaction

mixture was heated at reflux for 6 h, after which it was filtered, leaving excess zinc in the reaction flask. The precipitated [Cr(**1**)Cl_3] was collected on the filter-frit, washed with EtOH and used in the next step without further purification. IR: (solid, ν /cm^{-1}) 501 (s), 519 (m), 612 (w), 650 (w), 661 (s), 690 (s), 695 (s), 719 (w), 728 (s), 751 (s), 790 (s), 827 (w), 834 (s), 890 (m), 899 (w), 1017 (w), 1026 (s), 1034 (w), 1066 (w), 1078 (w), 1099 (w), 1186 (w), 1205 (m), 1244 (s), 1262 (w), 1271 (w), 1289 (w), 1338 (m), 1367 (w), 1411 (m), 1436 (w), 1446 (w), 1467 (m), 1489 (m), 1520 (m), 1547 (w), 1568 (m), 1576 (s), 1582 (s), 1603 (m), 3059 (w), 3061 (w), 3998 (w). Found C 62.57, H 4.07, N 9.07; $C_{33}H_{24}Cl_3CrN_4$ requires C 62.43, H 3.81, N 8.82.

*2.3 [Cr(**1**)$(O_3SCF_3)_3$]*

[Cr(**1**)Cl_3] (75.0 mg, 0.118 mmol) was dissolved in CF_3SO_3H (0.4 mL, 4.4 mmol) and the dark red solution was stirred overnight at room temperature. The mixture was then cooled to 0 ^oC and Et_2O (20 mL) was added, yielding a dark red precipitate. The solid was separated by filtration, washed with Et_2O and dried in air. [Cr(**1**)$(O_3SCF_3)_3$] was isolated as a dark red solid (72.8 mg, 0.0746 mmol, 67.8 %). Found C 43.96, H 2.71, N 6.03; $C_{36}H_{24}CrF_9N_4O_9S_3$ requires C 44.31, H 2.48, N 5.74.

*2.4 [Cr(**1**)$_2$][CF_3SO_3]$_3$*

A mixture of [Cr(**1**)$(CF_3SO_3)_3$] (50.0 mg, 51.2 μmol) and **1** (26.9 mg, 56.4 μmol) in MeCN (2 mL) was heated at reflux for 7 h. The crude product was recrystallized from EtOH and [Cr(**1**)$_2$][CF_3SO_3]$_3$ was isolated as a dark red solid (18.2 mg, 12.5 μmol, 24.4 %). IR: (solid, ν/cm^{-1}) 503 (s), 570 (m), 635 (s), 661 (m), 691 (m), 717 (m), 749 (m), 786 (m), 829 (m), 1026 (s), 1068 (m), 1094 (m), 1120 (m), 1142 (s), 1198 (s), 1222 (s), 1240 (s), 1332

(m), 1366 (m), 1418 (m), 1439 (m), 1476 (s), 1520 (m), 1568 (s), 1575 (s), 1605 (m), 3075 (w), 3497 (w). Found C 56.24, H 3.64, N 7.83; $C_{69}H_{48}CrF_9N_8O_9S_3 \cdot H_2O$ requires C 56.36, H 3.43, N 7.62.

2.5 [Cr(4'-(4-tolyl)tpy)Cl$_3$]

The compound was prepared by the same procedure as [Cr(**1**)Cl_3], starting with anhydrous $CrCl_3$ (761 mg, 4.76 mmol) and 4'-(4-tolyl)tpy (2.00 g, 6.18 mmol) suspended in EtOH (60 mL). Granulated zinc (68.2 mg, 1.05 mmol) was added and the mixture was heated at reflux for 4.25 h. [Cr(4'-(4-tolyl)tpy)Cl_3] precipitated and was collected on a filter-frit, washed with EtOH and used in the next step without further purification. IR: (solid, ν/cm^{-1}) 501 (s), 519 (m), 612 (w), 650 (w), 661 (s), 690 (s), 695 (s), 719 (w), 728 (s), 751 (s), 790 (s), 827 (w), 834 (s), 890 (m), 899 (w), 1017 (w), 1026 (s), 1034 (w), 1066 (w), 1078 (w), 1099 (w), 1186 (w), 1205 (m), 1244 (s), 1262 (w), 1271 (w), 1289 (w), 1338 (m), 1367 (w), 1411 (m), 1436 (w), 1446 (w), 1467 (m), 1489 (m), 1520 (m), 1547 (w), 1568 (m), 1576 (s), 1582 (s), 1603 (m), 3059 (w), 3061 (w), 3998 (w). Found C 54.96, H 3.86, N 8.58; $C_{22}H_{17}Cl_3CrN_3$ requires C 54.85, H 3.56, N 8.72.

2.6 *[Cr(**1**)(4'-(4-tolyl)tpy)][CF$_3$SO$_3$]$_3$*

[Cr(4'-(4-tolyl)tpy)Cl_3] (91.9 mg, 0.191 mmol) was dissolved in CF_3SO_3H (1.7 ml, 7.6 mmol) and the dark red solution was stirred at room temperature overnight. The mixture was then cooled to 0 ^oC and Et_2O (20 mL) was added to precipitate [Cr(4'-(4-tolyl)tpy)$(O_3SCF_3)_3$]. The product was separated by filtration, washed with Et_2O and dried under a flow of N_2, before being dissolved in MeCN (10 mL). This solution was added to a flask containing **1** (100 mg, 0.210 mmol). The reaction mixture was heated at reflux for

5.5 h, after which time solvent was removed. The product was purified by recrystallization from EtOH and was washed with Et_2O. [Cr(**1**)(4'-(4-tolyl)tpy)][O_3SCF_3]$_3$ was isolated as a dark red solid (236 mg, 0.182 mmol, 95.2 %). IR: (solid, ν/cm^{-1}) 573 (m), 635 (s), 662 (m), 693 (m), 725 (w), 755 (m), 786 (m), 823 (w), 846 (w), 885 (w), 1026 (s), 1068 (w), 1096 (m), 1147 (s), 1198 (m), 1222 (s), 1244 (s), 1336 (w), 1367 (w), 1423 (m), 1464 (m), 1475 (m), 1478 (m), 1520 (w), 1538 (m), 1564 (m), 1569 (m), 1579 (m), 1602 (m), 3071 (w), 3498 (w). Found C 51.99, H 3.36, N 7.42; $C_{58}H_{41}CrF_9N_7O_9S_3 \cdot 2H_2O$ requires C 52.17, H 3.40, N 7.34.

*2.7 [Cr(**2**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$*

The method was as for [Cr(**1**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$, starting with [Cr(4'-(4-tolyl)tpy)Cl_3] (34.8 mg, 72.2 μmol) and CF_3SO_3H (0.5 ml, 5.6 mmol) in the first step, and then **2** (42.6 mg, 79.4 μmol) and a reaction time of 6 h in the second step. [Cr(**2**)(4'-(4-tolyl)tpy)][O_3SCF_3]$_3$ was isolated as a dark red solid (85.7 mg, 63.1 μmol, 43.7%). Found C 52.77, H 3.85, N 6.99; $C_{60}H_{45}CrF_9N_7O_{11}S_3$ requires C 53.02, H 3.34, N 7.21.

2.8 [Cr(4'-(4-tolyl)tpy)$_2$][CF_3SO_3]$_3$

The method was as for [Cr(**1**)(4'-(4-tolyl)tpy)][O_3SCF_3]$_3$, starting with [Cr(4'-(4-tolyl)tpy)Cl_3] (164 mg, 0.341 mmol) and CF_3SO_3H (1.2 mL, 14 mmol) in the first step, and then 4'-(4-tolyl)tpy (121 mg, 0.375 mmol) and a reaction time of 6.5 h in the second step. The product precipitated during the reaction and was separated by filtration and recrystallized from hot MeCN. [Cr(4'-(4-tolyl)tpy)$_2$][CF_3SO_3]$_3$ was isolated as an orange solid (302 mg, 0.263 mmol, 77.0%). IR: (solid, n/cm–1) 500 (s), 505 (s), 517 (s),

529 (m), 572 (m), 613 (m), 625 (s), 634 (s), 662(w), 693 (w), 727 (w), 778 (m), 788 (m), 823 (m), 949 (w), 996 (m), 1027 (s), 1097 (w), 1116 (m), 1138 (m), 1158 (s), 1210 (m), 1222 (m), 1249 (s), 1363 (w), 1406 (w), 1435 (w), 1478 (w), 1533 (w), 1539 (w), 1601 (s), 1618 (w), 3066 (w). Found C 49.34, H 3.40, N 8.70; $C_{47}H_{34}CrF_9N_6O_9S_3 \cdot MeCN$ requires C 49.58, H 3.14, N 8.26.

2.9 Crystallography

Single crystal data were collected on a Bruker APEX-II diffractometer with data reduction, solution and refinement using the programs APEX [22] and SHELX-13 [23]. The structural diagrams and structure analysis were carried out using Mercury v. 3.0.1 or 3.3 [24,25].

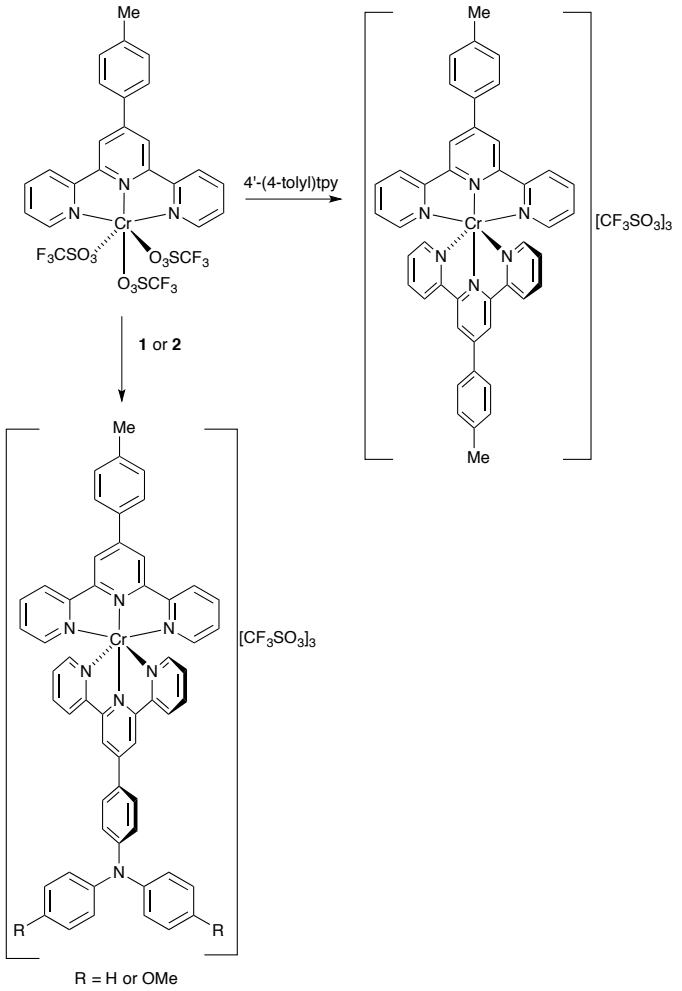
$[Cr(4'\text{-}(4\text{-tolyl})tpy)_2][CF_3SO_3]_3 \cdot 2MeCN$: $C_{51}H_{40}CrF_9N_8O_9S_3$, M = 1228.12, yellow needle, monoclinic, space group $C2/c$, a = 14.5535(8), b = 17.1633(11), c = 21.9247(14) Å, β = 108.308(4)°, U = 5199.3(6) Å^3, Z = 4, D_c = 1.569 Mg m^{-3}, μ(Cu-Kα) = 3.802 mm^{-1}, T = 123 K. Total 17034 reflections, 4644 unique, R_{int} = 0.0512. Refinement of 3700 reflections (404 parameters) with $I > 2\sigma(I)$ converged at final $R1$ = 0.0383 ($R1$ all data = 0.0539), $wR2$ = 0.0906 ($wR2$ all data = 0.0984), gof = 1.019.

3 Results and discussion

3.1 Synthesis of the chromium(III) complexes

The ligands 4'-(4-tolyl)tpy, **1** and **2** were prepared as previously reported [20,21]. The synthesis of related pairs of homoleptic and heteroleptic coplexes containing a $\{Cr(tpy)_2\}^{3+}$ core was achieved using the general method shown in Scheme 1. $[Cr(4'\text{-}(4\text{-tolyl})tpy)Cl_3]$ and $[Cr(\mathbf{1})Cl_3]$ were prepared by treating $CrCl_3$ with the appropriate ligand in the presence of zinc in ethanol [19], and subsequent reaction with triflic acid gave [Cr(4'-(4-

tolyl)tpy)$(O_3SCF_3)_3$] and [Cr(**1**)$(O_3SCF_3)_3$], respectively. Although these complexes may be isolated, it is more convenient to prepare them as required and use them in situ for reaction with a second equivalent of tpy ligand. Scheme 3 summarizes the formation of [Cr(4'-(4-tolyl)tpy)$_2$][CF_3SO_3]$_3$, [Cr(**1**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$ and [Cr(**2**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$. The homoleptic complex [Cr(**1**)$_2$][O_3SCF_3]$_3$ was prepared in an analogous manner by treatment of [Cr(**1**)$(O_3SCF_3)_3$] with ligand **1**. Elemental analyses for the homoleptic and heteroleptic triflate salts were satisfactory. Attempts to record their MALDI-TOF or electrospray mass spectra did not yield interpretable data, a problem encountered with other bis(tpy) chromium(III) complexes [19].



Scheme 3. Synthetic routes to [Cr(4'-(4-tolyl)tpy)$_2$][CF_3SO_3]$_3$, [Cr(**1**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$ and [Cr(**2**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$.

3.2 Crystal structure of [Cr(4'-(4-tolyl)tpy)$_2$][CF$_3$SO$_3$]$_3$·2MeCN

Structural data for complexes containing {Cr(tpy)$_2$} domains are surprisingly few. The Cambridge Structural Database [26] (searched using Conquest v. 1.16 [24], CSD v. 5.35 with updates up to May 2014) contains only seven examples, four of which contain chromium(III) [17,18,19]. The structure of the [Cr(4'-(4-tolyl)tpy)$_2$]$^{3+}$ cation (Figure 1) was confirmed by a single crystal determination of [Cr(4'-(4-tolyl)tpy)$_2$][CF$_3$SO$_3$]$_3$·2MeCN. The crystals were grown serendipitously from a MeOH solution of the crude product of a trial reaction of [Cr(4'-(4-tolyl)tpy)(CF$_3$SO$_3$)$_3$] with 5,5"-dimethyl-2,2':6',2"-terpyridine (5,5"-Me$_2$tpy) in MeCN under microwave conditions (150 ^{o}C, 11 bar); crystals grew after slow evaporation of solvent over a period of several weeks. The isolation of the homoleptic complex rather than the target [Cr(4'-(4-tolyl)tpy)(5,5"-Me$_2$tpy)][CF$_3$SO$_3$]$_3$ can be understood in terms of lability of the ligands in [Cr(tpy)$_2$]$^{3+}$ complexes [19]. [Cr(4'-(4-tolyl)tpy)$_2$][CF$_3$SO$_3$]$_3$·2MeCN crystallizes in the monoclinic space group *C*2/*c*, and the asymmetric unit contains half of the cation, the other half being generated by rotation about a 2-fold axis. The asymmetric unit also contains one ordered [CF$_3$SO$_3$]$^-$ ion, one half-occupancy, disordered anion which lies on a 2-fold axis, and one ordered MeCN molecule. The bond distances and angles in the coordination sphere of atom Cr1 (caption to Figure 1) are comparable with those in [Cr(tpy)(4'-(4-tolyl)tpy)][PF$_6$]$_3$·3MeCN [19]. The phenyl ring is twisted through 18.5^o with respect to the plane of the pyridine ring containing C8, and this compares to 24.4^o in [Cr(tpy)(4'-(4-tolyl)tpy)]$^{3+}$ [19], and with 29.2^o and 16.0^o or 28.7^o and 27.8^o for the two independent molecules in each of the two polymorphs of the free 4'-(4-tolyl)tpy ligand [27,28].

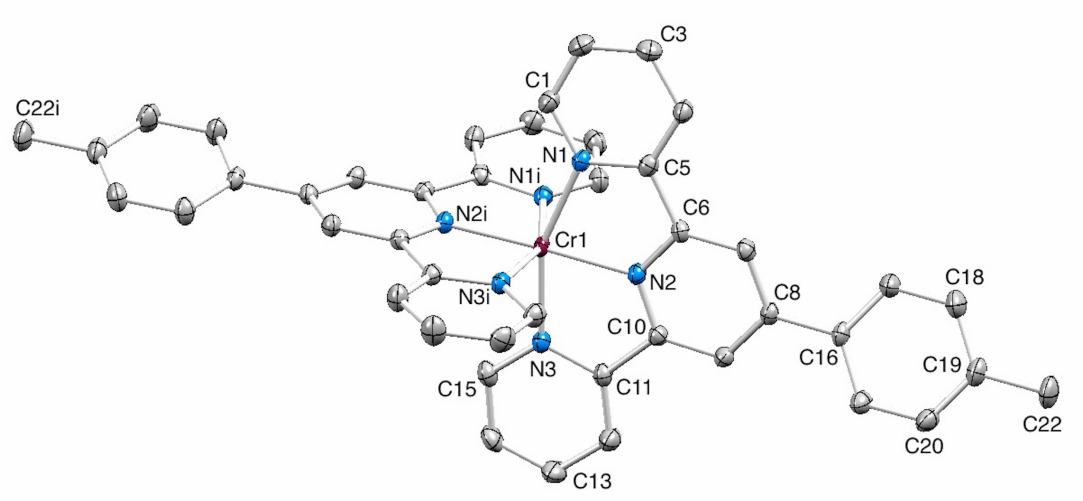
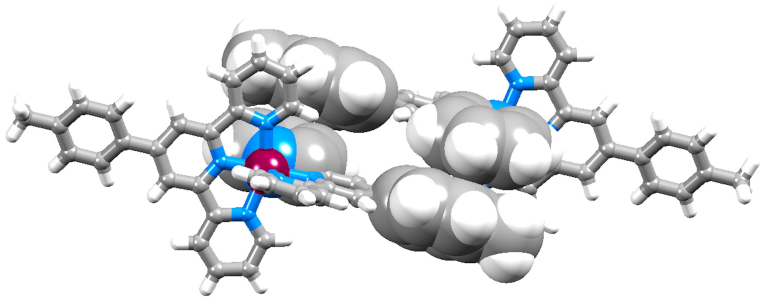
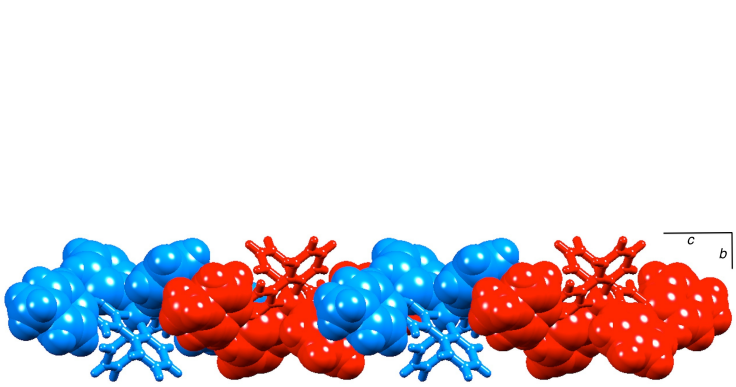


Fig. 1. Structure of the $[Cr(4'\text{-}(4\text{-tolyl})tpy)_2]^{3+}$ cation in $[Cr(4'\text{-}(4\text{-tolyl})tpy)_2][CF_3SO_3]_3 \cdot 2MeCN$ (ellipsoids plotted at 50% probability level and H atoms omitted for clarity). Important bond distances and angles: Cr1–N1 = 2.061(2), Cr1–N2 = 1.9717(18), Cr1–N3 = 2.055(2) Å; N2–Cr1–N1 = 78.79(8), N2–Cr1–N3 = 78.59(8), N2–Cr1–$N2^i$ = 177.92(11)^o (symmetry code i = 1–*x*, *y*, $^1/_2$–*z*).

The packing of cations in $[Cr(4'\text{-}(4\text{-tolyl})tpy)_2][CF_3SO_3]_3 \cdot 2MeCN$ involves multiple embraces [29]. Figure 2a depicts the principal packing motif, comprising a head-to-tail π-stacking interaction between centrosymmetric pairs of cations. The pyridine ring containing N3 stacks over the arene ring of the tolyl substituent containing atom $C19^{ii}$ (symmetry code ii = 1–*x*, –*y*, 1–*z*). The inter-centroid distance is 3.71 Å, and the angle between the ring planes is 17.4^o. Propagaton of this motif results in the assembly of chains that follow the crystallographic *c*-axis (Figure 2b), although there are no close π-contacts between chains. This is seen in Figure 2c which views four adjacent chains, the cavities between which are occupied by the triflate anions and MeCN molecules.



(a)



(b) (c)

Figure 2. (a) Centrosymmetric head-to-tail embrace of $[Cr(4'\text{-}(4\text{-tolyl})tpy)_2]^{3+}$ cations. Assembly of chains along the *c*-axis; adjacent molecules are coloured red and blue. (c) Four adjacent chains viewed down the *c*-axis. (Colour online)

The interactions between cations in $[Cr(4'\text{-}(4\text{-tolyl})tpy)_2][CF_3SO_3]_3\cdot 2MeCN$ contrasts dramatically with the motifs observed in $[Fe(4'\text{-}(4\text{-tolyl})tpy)_2][PF_6]_2\cdot 2.2MeCN$ and $[Ru(4'\text{-}(4\text{-tolyl})tpy)_2][PF_6]_2\cdot 1.75MeCN$ in which the cations pack into rows with face-to-face π-interactions between pairs of outer pyridine rings [28]. In order to ascertain whether this change in structural paradigm is associated with the change in oxidation state of the metal, we have considered other structurally determined $[M(4'\text{-}(4\text{-tolyl})tpy)_2]^{3+}$ complexes.

The space group and cell dimensions for $[Cr(4'\text{-}(4\text{-tolyl})tpy)_2][CF_3SO_3]_3 \cdot 2MeCN$ (*C*2/*c*, *a* = 14.5535(8), *b* = 17.1633(11), *c* = 21.9247(14) Å, β = 108.308(4)^o) are very similar to those for $[Mn(4'\text{-}(4\text{-tolyl})tpy)_2][PF_6]_3 \cdot 2MeCN$ (CSD refcode QOQJOW, *C*2/*c*, *a* = 14.788(2), *b* = 16.140(2), *c* = 21.467(3) Å, β = 105.93(1)^o [30] and $[Ir(4'\text{-}(4\text{-tolyl})tpy)_2][PF_6]_3 \cdot 2MeCN$ (refcode YIDAU01, *C*2/*c*, *a* = 14.7995(5), *b* = 16.4658(5), *c* = 21.5521(7) Å, β = 105.5450(8)^o [31], and YIDAU02, *C*2/*c*, *a* = 14.6977(14), *b* = 16.3737(16), *c* = 21.420(2) Å, β = 105.639(2)^o [32]). An additional determination for $[Ir(4'\text{-}(4\text{-tolyl})tpy)_2][PF_6]_3 \cdot 2MeCN$ (refcode YIDAU) reports that the complex crystallizes in the *Cc* space group with *a* = 14.7995(5), *b* = 16.4658(5), *c* = 21.5521(7) Å, β = 105.5450(8)^o [33]. Each of these metal(III) complexes assembles with the same π-stacked motif shown in Figure 2a, although the change from triflate to hexafluoridophosphate anions causes a shift in the chains from following the *c*-axis to running obiquely through the *ac*-plane. The common assembly motif seen in these metal(III) salts is not present in any of the salts of $[M(4'\text{-}(4\text{-tolyl})tpy)_2]^{2+}$ complexes deposited in the CSD (refcodes DIKYIG [30,34], KAYHIC [35], KEMWEG [36], KUWKOD [37] and QOLYUM [38]). These observations suggest that the accommodation of three anions ($[PF_6]^-$ or $[CF_3SO_3]^-$) and two MeCN molecules per $[M(4'\text{-}(4\text{-tolyl})tpy)_2]^{3+}$ (M = Mn, Cr or Ir) leads to a common packing motif.

3.3 Absorption spectroscopic properties

Compared to tpy or 4'-(4-tolyl)tpy, the introduction of 4'-(4-(*N,N*-diphenylamino)phenyl) or 4'-(4-(*N,N*-di(4-methoxyphenyl)amino)phenyl) substituents results in the solution electronic absorption spectra of the free ligands extending into the visible region [21]. The ligands exhibit a characteristic intra-ligand charge transfer (ILCT) band with the tertiary

amine acting as an electron donor [39]. This charge separation is stabilized by coordination, causing a red-shift in the ILCT band [39,40], as reported for complexes of ruthenium, osmium, iridium, zinc and cadmium containing **1** or **2** [21,41,42,43,44,45,46]. In MeCN solution, the ILCT maxima for [Cr(**1**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$ and [Cr(**2**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$ are 507 nm (ε = 22 200 dm^3 mol^{-1} cm^{-1}) and 523 nm (ε = 21 100 dm^3 mol^{-1} cm^{-1}), respectively, and the solutions are dark red. Figure 3 compares the absorption spectra of MeCN solutions of [Cr(4'-(4-tolyl)tpy)$_2$][CF_3SO_3]$_3$, [Cr(**1**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$ and [Cr(**2**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$. Each of the heteroleptic complexes exhibits a broad, low intensity band (665 nm for [Cr(**1**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$ and 708 nm for [Cr(**2**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$).

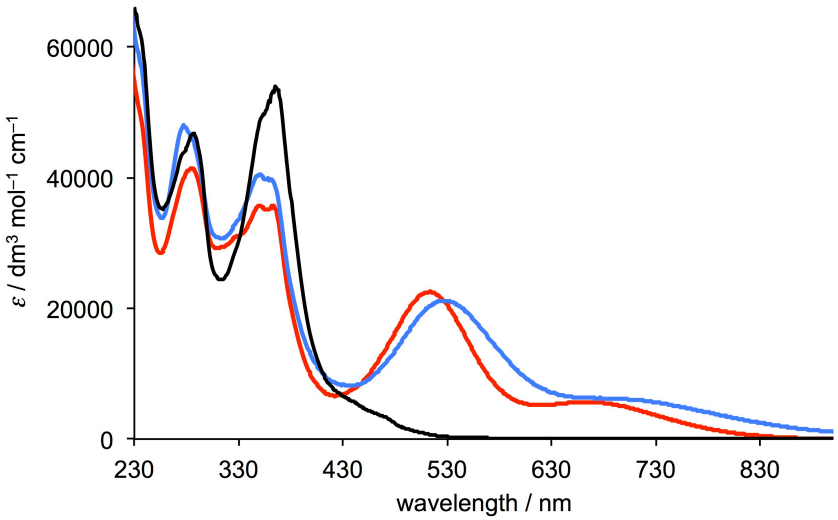


Figure 3. Absorption spectra of solutions of [Cr(4'-(4-tolyl)tpy)$_2$][CF_3SO_3]$_3$ (black line), [Cr(**1**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$ (red line) and [Cr(**2**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$ (blue line) in MeCN (5×10^{-5} mol dm^{-3}).

The ILCT absorption band in the solution spectra of [Cr(**1**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$ and [Cr(**2**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$ shifts to higher energies in solvents of increasing polarity, and we investgated this negative solvatochromism [47] in more detail for [Cr(**2**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$. Figure 4 illustrates the shift in λ_{max} from 574 nm in

$CHCl_3$ to 526 nm in MeCN, and the data correlate well with trends in solvent dipole moments and dielectric constants (Table 1).

Table 1 Relationship between λ_{max} for the ILCT band in [Cr(**2**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$ and dipole moment and dielectric constant of the solvent.

Solvent	λ_{max}/ nm	Dipole moment / D	Dielectric constant
$CHCl_3$	574	1.15	4.81
CH_2Cl_2	563	1.14	8.93
EtOH	550	1.69	24.3
Acetone	526	2.69	20.7
MeCN	528	3.44	37.5

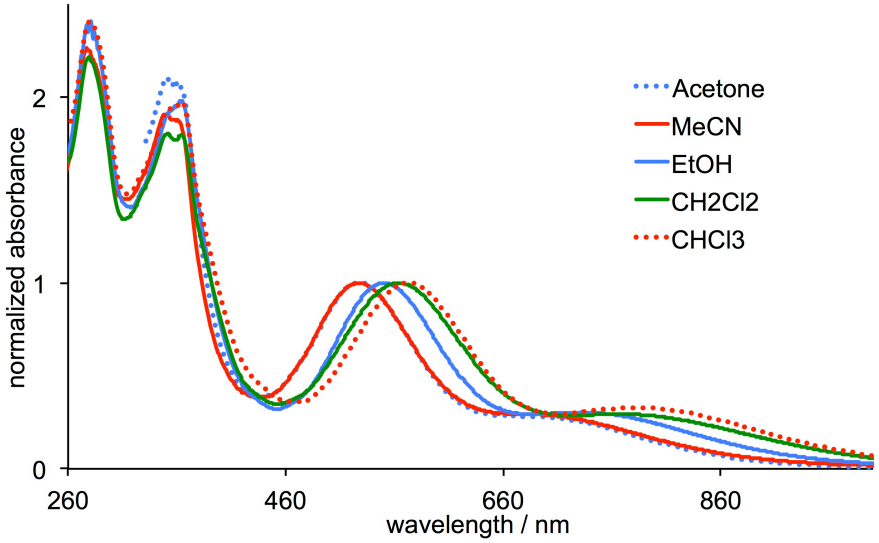
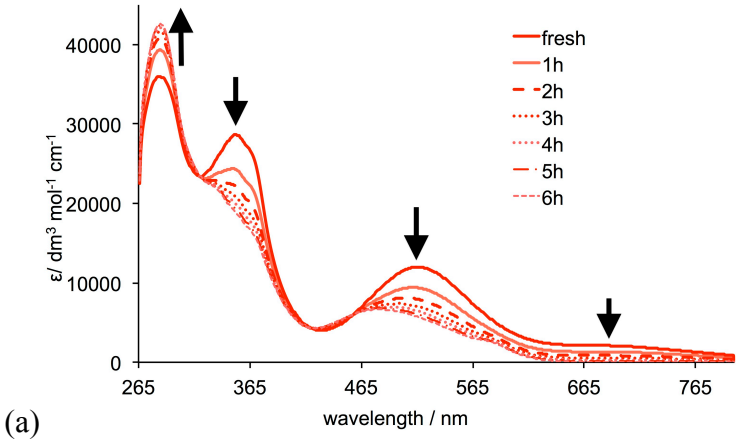


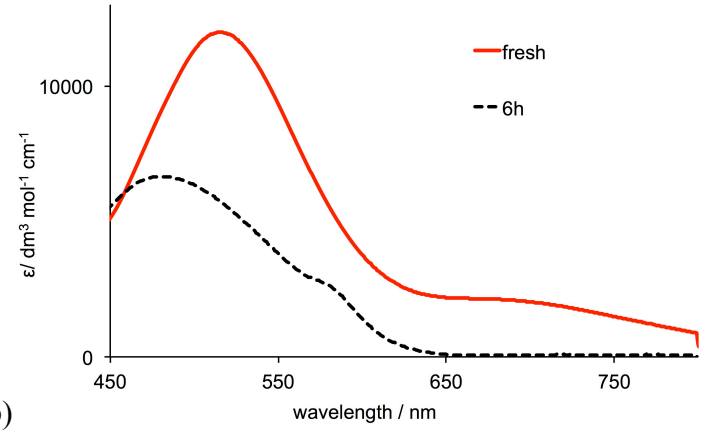
Figure 4. Solution absorption spectra of [Cr(**2**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$ in different solvents (concentration = 5×10^{-5} mol dm^{-3}), normalized with respect to the band ca. 500 nm. (Colour on line.)

The absorption spectra of solutions of [Cr(**2**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$ in the solvents shown in Figure 4 did not change when monitored over a period of a week. However, in H_2O, MeOH, DMSO and DMF, significant changes were observed, indicating that the complexes are not stable in these solvents. Figure 5a illustrates the absorption spectrum of a DMF solution of [Cr(**2**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$ monitored over 6 hours; no further change was observed after this period. The ILCT band initially with λ_{max} = 520 nm (ε = 11950 dm^3 mol^{-1} cm^{-1}) decays to a band with λ_{max} = 483 nm (ε = 6600 dm^3 mol^{-}

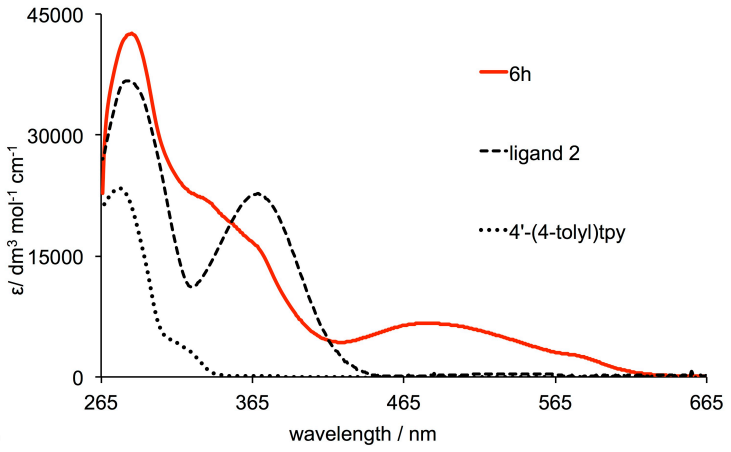
^{1} cm^{-1}), and the weaker absorption (initially at 695 nm) evolves into a shoulder at 580 nm (Figure 5b). Several reaction pathways (Scheme 4) can be considered: (i) complete ligand displacement by DMF to give $[Cr(DMF)_6]^{3+}$, (ii) partial ligand displacement, or (iii) ligand redistribution to give a mixture of $[Cr(\mathbf{2})(4'\text{-}(4\text{-tolyl})tpy)]^{3+}$, $[Cr(\mathbf{2})_2]^{3+}$ and $[Cr(4'\text{-}(4\text{-tolyl})tpy)_2]^{3+}$. Absorptions >450 nm can only arise from chromium(III)-containing species. $[Cr(DMF)_6]^{3+}$ exhibits an absorption at 592 nm (assigned to the $^4T_{2g} \leftarrow {}^4A_{2g}$ transition and with ε = 54 dm^3 mol^{-1} cm^{-1}) [48,49,50], but the ≈1000-fold difference in extinction coefficients allows us to eliminate $[Cr(DMF)_6]^{3+}$ as the origin of the absorption. The lowest energy absorption in the spectrum of a DMF solution of **2** appears at 367 nm (ε = 22700 dm^3 mol^{-1} cm^{-1}). Hence, we assign the absorption at 483 nm to chromium(III)-bound **2**, rather than free ligand (Figure 5c). The intense absorption at 344 nm in Figure 5a which loses intensity over time is characteristic of a $\{Cr^{III}(4'\text{-}(4\text{-tolyl})tpy)\}$ chromophore (Figure 3) [19]. These data, coupled with the increase in intensity of the high energy absorption at 288 nm, are consistent with the lability of both **2** and 4'-(4-tolyl)tpy in DMF. Similar spectral changes are also seen over time for H_2O, DMSO or MeOH solutions of $[Cr(\mathbf{2})(4'\text{-}(4\text{-tolyl})tpy)][CF_3SO_3]_3$. In each case, the final spectrum is not consistent with complete ligand loss (Figure 5c), but rather suggests the presence of a mixture of the solvento complexes $[Cr(\mathbf{2})(Solv)_3]^{3+}$ and $[Cr(4'\text{-}(4\text{-tolyl})tpy)(Solv)_3]^{3+}$ where Solv = solvent. The results are consistent with our previous observations that both ligands in $[Cr(tpy)(4'\text{-}(4\text{-tolyl})tpy)][PF_6]_3$ and $[Cr(tpy)(5,5''\text{-}Me_2tpy)][PF_6]_3$ are labile in the presence of fluoride ion; in this case we were able to show that the absorption maximum of the final solution corresponded to that reported for $[Cr(tpy)F_3]$ [19,51].



(a)

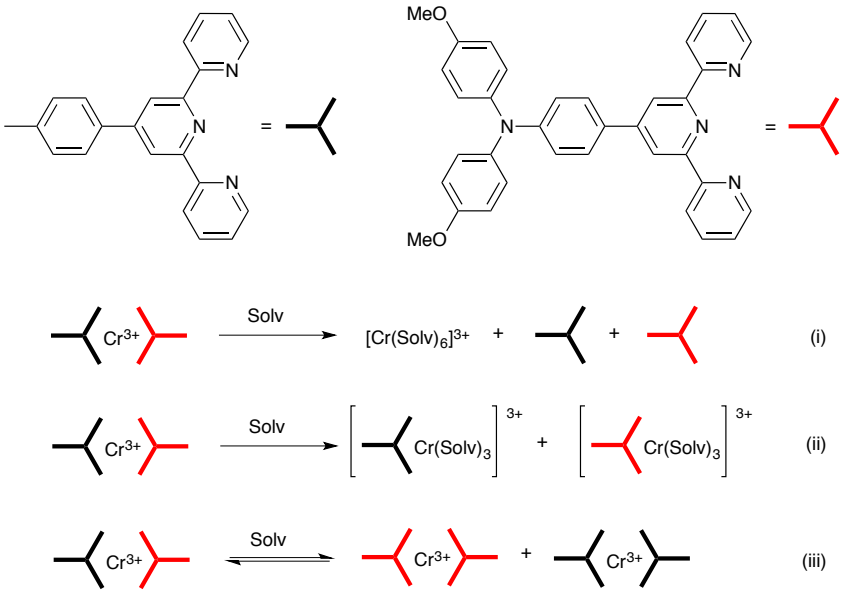


(b)



(c)

Figure 5. (a) Solution absorption spectra of [Cr(**2**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$ in DMF (concentration = 5×10^{-5} mol dm^{-3}) over a period of 6 hours, and (b) an expansion of the ILCT bands for the initial and final spectra. (c) Comparison of the DMF solution spectra of free ligands **2** and 4'-(4-tolyl)tpy and the aged solution of [Cr(**2**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$.



Scheme 4. Possible pathways for the reaction of [Cr(**2**)(4'-(4-tolyl)tpy)]$^{3+}$ in DMF, DMSO, H_2O and MeOH. Experimental data for DMF solutions support pathway (ii).

3.4 Electrochemistry

The electrochemical behaviour of homoleptic and heteroleptic complexes containing **1** and 4'-(4-tolyl)tpy was investigated by cyclic voltammetry, and the results are given in Table 2. Wieghardt and coworkers have proposed [7] that the three reversible reduction processes observed for [Cr(tpy)$_2$]$^{3+}$ are all ligand based, with stepwise reduction occurring sequentially on one, then the other, ligand. Each of [Cr(4'-(4-tolyl)tpy)$_2$][CF_3SO_3]$_3$, [Cr(**1**)(4'-(4-tolyl)tpy)][CF_3SO_3]$_3$ and [Cr(**1**)$_2$][CF_3SO_3]$_3$ also exhibits three reversible reductions, and in addition, the complexes containing **1** exhibit a reversible oxidation (Table 2). The latter is presumably centred on the diphenylamine unit. The first reduction step occurs at increasingly more negative potential on going from [Cr(tpy)$_2$]$^{3+}$ to [Cr(4'-(4-tolyl)tpy)$_2$]$^{3+}$ and [Cr(**1**)(4'-(4-tolyl)tpy)]$^{3+}$ to [Cr(**1**)$_2$]$^{3+}$, and the similarity of the first reduction potentials for [Cr(4'-(4-tolyl)tpy)$_2$]$^{3+}$ and [Cr(**1**)(4'-(4-tolyl)tpy)]$^{3+}$ suggests that the 4'-(4-tolyl)tpy ligand is the first to be reduced in the heteroleptic complex.

Table 2 Cyclic voltammetric data with respect to Fc/Fc^+; MeCN solutions with $[^nBu_4N][PF_6]$ supporting electrolyte, and scan rate of 0.1 V s^{-1}.

Compound	$E^{ox}_{1/2}{}^{4+/3+}$ / V	$E^{red}_{1/2}{}^{3+/2+}$ / V	$E^{red}_{1/2}{}^{2+/1+}$ / V	$E^{red}_{1/2}{}^{1+/0}$ / V
$[Cr(tpy)_2][PF_6]_3$ [a]		–0.533	–0.953	–1.469
$[Cr(4'\text{-}(4\text{-tolyl})tpy)_2][CF_3SO_3]_3$		–0.581	–0.949	–1.278
$[Cr(\mathbf{1})(4'\text{-}(4\text{-tolyl})tpy)][CF_3SO_3]_3$	+0.660	–0.587	–0.955	–1.276
$[Cr(\mathbf{1})_2][CF_3SO_3]_3$	+0.683	–0.601	–0.955	–1.431

a Data from reference [19].

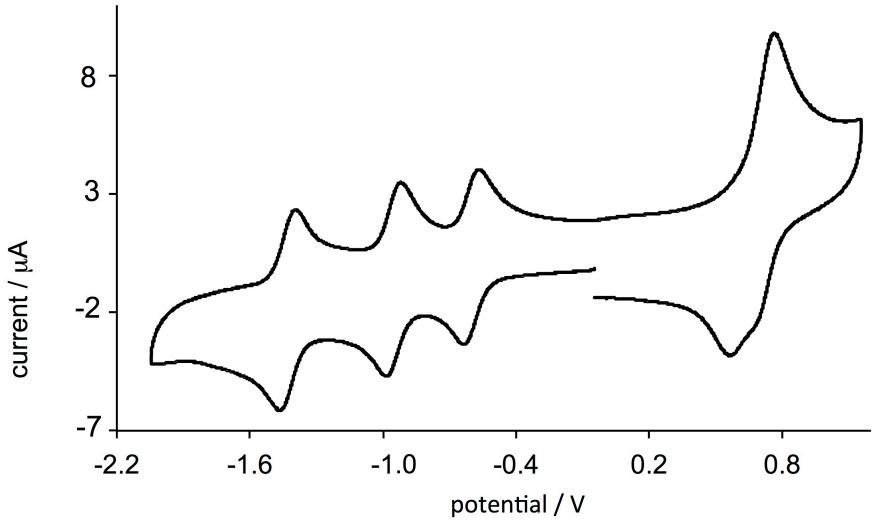


Figure 6. Cyclic voltammogram of $[Cr(\mathbf{1})_2][CF_3SO_3]_3$, measured in MeCN (with respect to Fc/Fc^+, with $[^nBu_4N][PF_6]$ as supporting electrolyte at a scan rate of 0.1 V s^{-1}).

4 Conclusions

We have prepared and characterized $[Cr(\mathbf{1})(4'\text{-}(4\text{-tolyl})tpy)][CF_3SO_3]_3$ and $[Cr(\mathbf{2})(4'\text{-}(4\text{-tolyl})tpy)][CF_3SO_3]_3$ and the spectroscopic and electrochemical behaviours compared to those of $[Cr(4'\text{-}(4\text{-tolyl})tpy)_2][CF_3SO_3]_3$ and $[Cr(\mathbf{1})_2][CF_3SO_3]_3$. The single crystal structure of $[Cr(4'\text{-}(4\text{-tolyl})tpy)_2][CF_3SO_3]_3 \cdot 2MeCN$ reveals packing features which result from the need to accommodate three anions and two solvent molecules per cation; embraces

between cations differ from those observed with salts of $[M(4'\text{-}(4\text{-tolyl})tpy)_2]^{2+}$. The characteristic ILCT absorption of **1** or **2** is red-shifted upon coordination to Cr^{3+} ions, and exhibits a negative solvatochromic effect. In $CHCl_3$, CH_2Cl_2, MeCN, acetone or EtOH, $[Cr(\mathbf{1})(4'\text{-}(4\text{-tolyl})tpy)][CF_3SO_3]_3$ and $[Cr(\mathbf{2})(4'\text{-}(4\text{-tolyl})tpy)][CF_3SO_3]_3$ appear to be stable, but in H_2O, MeOH, DMSO and DMF, the tpy ligands are labile. Changes in the absorption spectra of $[Cr(\mathbf{2})(4'\text{-}(4\text{-tolyl})tpy)][CF_3SO_3]_3$ in DMF over time are consistent with the formation of $[Cr(4'\text{-}Xtpy)(DMF)_3]^{3+}$ rather than complete ligand displacement or a ligand redistribution.

Acknowledgements

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Appendix

Crystallographic data 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 or www: http://www.ccdc.cam.ac.uk) and may be obtained free of charge on quoting the deposition numbers CCDC 1030355.

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