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4'-(*o*-Toluyl)-2,2':6',2"-terpyridine: synthesis, bromination, complexation, and X-ray crystallographic characterization

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The ligands 4'-(*o*-toluyl)-2,2': 6',2"-terpyridine and 4'-[2-(bromomethyl)phenyl]-2,2': 6',2"-terpyridine were synthesized. X-ray crystallographic studies have been performed on complexes that were prepared using these ligands. In one case, a halogen exchange reaction occurs, resulting in a dinuclear copper complex in which the bromine in the terpyridine derivative is replaced by chlorine and is ultimately found as a disordered bridging bromide.

Keywords: Terpyridine; Crystallography; Halogen exchange; Cobalt; Copper

1. Introduction

Morgan and Burstall [1] were the first to isolate terpyridine (tpy) in the 1930s. Since this discovery, terpyridines have been widely studied. The extent of this study can be attributed to the wide, varied, and practical applications [2] of terpyridines. Some of these applications include photovoltaic cells [3], electronic memory storage [4], light emitting diodes [5], and plastic solar cells [6]. Many of these applications depend on the ability to tune the electronic and spectroscopic properties of tpy complexes, and this can be achieved by preparing molecules that differ in the position(s) and electron donating/ withdrawing characteristics of the substituents [7].

There are many positions where the tpy ligand can be substituted, and these substituents are usually introduced as part of tpy precursors [8]. By far, the most common site of substitution is the 4' position of the central pyridine ring, principally because of the ease of synthesis of the substituted terpyridine from the related aldehyde. In these terpyridine molecules, the substituent is directed away from the meridional coordination site of the ligand, and in the particular case of the *p*-toluylterpyridine (ttp) ligand, even the methyl group is remote from the metal binding site. Numerous complexes of ttp have been synthesized [9].

In this article, we investigate the synthesis and characterization of terpyridine ligands that are a step towards enabling a 4' substituent to interact with the coordinated

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metal ion. Thus we describe the preparation and X-ray crystallographic characterization of 4'-(o-toluyl)-2,2':6',2"-terpyridine (ottp), and bromination to give its α -bromo derivative, 4'-[2-(bromomethyl)phenyl]-2,2':6',2"-terpyridine. We also report the results of several crystallographic studies of complexes that resulted from attempts to coordinate these ligands to copper(II) and cobalt(II).

2. Experimental

All reagents and solvents were of reagent grade or better and were used as received unless otherwise stated. Carbon tetrachloride (CCl₄) (\sim 500 mL) was stored over phosphorus pentoxide (P₂O₅) for initial drying for at least 4 days and refluxed under N₂ for 4h before distillation. All deuterated NMR solvents were supplied by Cambridge Isotope Laboratories.

¹H, COSY, NOESY, and HSQC experiments were recorded on a Varian INOVA 500 spectrometer at 23°C, operating at 500 MHz. The INOVA was equipped with a variable temperature, inverse-detection 5 mm probe or a triple-resonance indirect detection PFG probe. The ¹³C-NMR spectra were recorded on either a Varian UNITY 300 NMR spectrometer equipped with a variable temperature direct broadband 5 mm probe, at 23°C, operating at 75 MHz or on a Varian INOVA 500 spectrometer at 23°C, operating at 125 MHz, using a 5 mm variable temperature switchable PFG probe. Chemical shifts are expressed in parts per million (ppm) on the δ scale and were referenced to the appropriate solvent peaks: CDCl₃ referenced to CHCl₃ at $\delta_{\rm H}$ 7.25 (¹H) and CHCl₃ at $\delta_{\rm C}$ 49.3 (¹³C); and DMSO-*d*₆ referenced to CD₃(CHD₂)SO at $\delta_{\rm H}$ 2.50 (¹H) and (CD₃)₂SO at $\delta_{\rm C}$ 39.6 (¹³C). The peaks are described as singlets (s), doublets (d), triplets (t), or multiplets (m).

2.1. Ligand synthesis

2.1.1. 4'-(*o*-Toluyl)-2,2':6',2''-terpyridine (ottp) (1). *o*-Tolualdehyde (2.4 g, 20 mmol) was added to stirred propane-2-ol (100 mL). To this solution, 2-acetylpyridine (4.84 g, 40 mmol), KOH pellets (3.08 g, 40 mmol), and concentrated ammonia solution (58 mL, 50 mmol) were added. The solution was then heated at reflux for 4 h during which a white precipitate was formed. The solution was cooled to room temperature and filtered under vacuum. The ppt was washed with 50% ethanol and then recrystallized from ethanol.

Yield = 3.54 g (51.2%). M.p. (170–173°C). ¹H-NMR (500 MHz CDCl₃): δ = 8.72 (d, 2H, H_{6,6}"), 8.71 (d, 2H, H_{3,3}"), 8.49 (s, 2H, H₃',5'), 7.90 (t, 2H, H_{4,4"}) 7.30–7.36 (m, 6H, H_{5,5",toluyl}), and 2.38 (s, 3H, CH₃). ¹³C-NMR (75 MHz, CDCl₃) 156.5, 155.6, 152.2, 149.4, 139.9, 137.1, 135.4, 130.7, 129.7, 128.5, 126.2, 124.1, 121.9, 121.6, 20.7 (CH₃). MS(ES) *m*/*z*: 324.1383 ([M + H⁺], 100%).

2.1.2. 4'-[2-(Bromomethyl)phenyl]-2,2':6',2"-terpyridine (2). CCl_4 (50 mL) was transferred from the bulk sample using a dry syringe under N₂. It was added to a dry three-necked round bottom flask that had been flushed with N₂. While stirring

under N₂, 4'-(o-toluyl)-2,2' : 6',2"-terpyridine (0.84 g, 2.6 mmol), purified N-bromosuccinimide (NBS) [10] (0.46 g, 2.6 mmol), and a catalytic amount of purified dibenzoyl peroxide [10] were added. The solution was irradiated with a tungsten lamp while being heated at reflux, under N₂, for 4 h. The solution was cooled to room temperature and filtered. The filtrate contained the crude 4'-[2-(bromomethyl)phenyl]-2,2' : 6',2"-terpyridine. Remaining CCl₄ was removed under vacuum. The crude product could be recrystallized from a 2:1 mixture of EtOH and acetone, but remained contaminated with starting material. Further attempts to purify the brominated material resulted in lower yields due to decomposition of the product. The pale yellow ppt was filtered and dried under vacuum. The ppt was stored in the dark, in an airtight container.

Yield = 2.60 g (64%); m.p. (138–140°C); ¹H-NMR (500 MHz CDCl₃): δ = 8.72 (d, 2H), 8.71 (d, 2H), 8.58 (s, 2H), 7.91 (t, 2H), 7.58 (d, 1H), 7.35–7.44 (m, 5H), and 4.45 (s, 2H, CH₂Br). ¹³C-NMR (75 MHz CDCl₃) 156.2, 155.8, 150.5, 149.5, 140.1, 137.3, 135.3, 131.2, 130.4, 129.2, 129.0, 124.2, 121.8, 121.7, 31.8 (CH₂Br). MS(ES) *m*/*z*: 402.0603, 403.0625 ([M + H⁺]).

2.2. Crystalline samples of metal complexes

2.2.1. $[Co(ottp)_2]Cl_2 \cdot 2.25CH_3OH$ (3). Cobalt(II) chloride $(30.7 \text{ mg}, 1.29 \times 10^{-4} \text{ mol})$ was dissolved in methanol (5 mL) and added to a solution of 4'-(o-toluyl)-2,2':6',2''-terpyridine (83.4 mg, $2.58 \times 10^{-4} \text{ mol})$ in CHCl₃ (2 mL). The resulting solution turned red/brown. The solution was exposed to diethyl ether vapor and the resulting ethanol/CHCl₃ solution formed a small number of red/brown cubic crystals after 2 days.

2.2.2. Cu(ottp)Cl₂·CH₃OH (4). Copper(II) chloride (11.3 mg, 6.648×10^{-4} mol) was dissolved in methanol (5 mL) and added to a solution of 4'-(o-toluyl)-2,2':6',2"-terpyridine (21.5 mg, 6.648×10^{-4} mol) in CHCl₃ (2 mL). The resulting solution turned blue. Vapor diffusion of diethyl ether into the ethanol/CHCl₃ solution through a small hole resulted in the formation of a small number of blue cubic crystals after a week.

2.2.3. [(Cl-ottp)Cu(μ -Cl)(μ -Br)Cu(Cl-ottp)][PF₆]₂ (5). Copper(II) chloride (15.6 mg, 9.15 × 10⁻⁵ mol) was dissolved in water (5 mL) and added to a solution of 4'-[2-(bromomethyl)phenyl]-2,2':6',2"-terpyridine (36.8 mg, 9.15 × 10⁻⁵ mol) dissolved in ethanol (5 mL). The resulting solution turned blue/green. Two drops of a saturated methanolic ammonium hexafluorophosphate solution were added, resulting in a pale blue/green precipitate. The solution was filtered and the precipitate washed with water and CH₂Cl₂. The precipitate was dissolved in CH₃CN (1 mL) and vapor diffusion of petroleum ether into the CH₃CN solution resulted in formation of a few blue/green needle-like crystals over 1 week.

2.3. X-ray structure analysis

Crystals were mounted on a glass fiber using perfluorinated oil. Data were collected at low temperature using an APEX II CCD area detector. The crystals were mounted 37.5 mm from the detector and irradiated with graphite monochromated Mo-K α

 $(\gamma = 0.71073 \text{ Å})$ radiation. The data reduction was performed using SAINTPLUS [11]. Intensities were corrected for Lorentzian polarization effects and for absorption effects using multi-scan methods [12]. Space groups were determined from systematic absences and checked for higher symmetry (table 1). Structures were solved by direct methods using SHELXS-97 [13] and refined with full-matrix least squares on F^2 using SHELXL-97 [13] or with SHELXTL [14]. All non-hydrogen atoms were refined anisotropically, unless specified otherwise. Hydrogen atoms were placed at ideal positions and refined with a riding model (Supplementary material).

3. Results and discussion

3.1. Ligand synthesis and structural study

The preparation of 4'-(o-toluyl)-2,2':'6',2"-terpyridine (1) was straightforward using the method described. Complete assignments of ¹H and ¹³C-NMR spectra were made and were consistent with values given in the literature [15]. The melting point range measured for the compound was somewhat higher than that reported (170–173°C, cf 158°C), but has proven reproducible over numerous preparations. The ottp ligand (1) crystallizes in the monoclinic space group C2/c. The molecule (figure 1) has a very slight, 0.051 Å, deviation from planarity, with the planar toluyl group twisted 78.4° with respect to this plane. This is slightly larger than reported in the Pt complex of the same ligand [15]. The methyl group is slightly, 0.4 Å, out of the plane of the toluyl ring.

The radical bromination to form 4'-[2-(bromomethyl)phenyl]-2,2':6',2"-terpyridine was performed in carbon tetrachloride. The crude product of this reaction was used without purification in complexation reactions because of its tendency to decompose. The yields from this reaction were sometimes lower (in 30–40% range, by NMR), but that mixture can be resubmitted to the reaction conditions in order to achieve better outcomes. The crude 4'-[2-(bromomethyl)phenyl]-2,2':6',2"-terpyridine was characterized using ¹H-NMR, COSY, HSQC, and ¹³C-NMR spectroscopy. The ¹H-NMR spectrum clearly shows a new peak, in comparison to the ¹H-NMR spectrum for 4'-(o-toluyl)-2,2':6',2"-terpyridine, at 4.45 ppm that can be assigned to the brominated methylene group. There is also a small peak at 2.30 ppm in the spectrum which can be assigned to the o-toluyl-methyl group of unreacted 4'-(o-toluyl)-2,2':6',2"-terpyridine. The mass spectrum of **2** (figure 2) shows significant m/z peaks at 402.0603 and at 404.0605, which are in good agreement with the theoretical isotope distribution. This two peak set, two units apart, is typical of mass spectra for molecules containing a single bromine atom.

3.2. Structural studies of complexes

Crystals of the complexes have been prepared as described and then structurally characterized. The small amounts isolated precluded full characterization of the solid material, so that the following results are of necessity limited to the single crystal that was examined in each case. However, with the exception of the halogen exchange reaction observed for **5**, the fact that such complexes are formed is unsurprising.

Identification code	ottp (1)	Co(ottp) (3)	Cu(ottp) (4)	Cu(Brottp) (5)
Empirical formula	$C_{22}H_{17}N_3$	$C_{46,25}H_{42}CI_{2}CO_{10}N_{6}O_{22}O$	C ₂₃ H ₂₁ Cl ₂ CuN ₃ O	C22H16Br043Cl1 57CuFN3P
Formula weight	323.39	847.69	489.87	621.0
Temperature (K)	293(2)	114(2)	110(2)	122(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	C2/c	$P2_{I}/n$	$P\bar{1}$	P2/n
Unit cell dimensions (A, ⁻)				
a	16./40(6)	(8)6600	8.0345(11)	16.6918(10)
<i>p</i>	11.254(4)	41.426(6)	9.0879(14)	7.0247(4)
c	11.074(4)	11.7307(16)	15.404(2)	19.6665(12)
α	90	90	74.437(4)	60
β	127.337(5)	107.140(3)	76.838(4)	100.442(3)
Υ.	90	90	82.023(4)	06
Volume (Å ³), Z	1658.7(10), 4	4205.3(9), 4	1051.4(3), 2	2267.8(2), 4
Density calculated (Mg m^{-3})	1.295	1.339	1.547	1.819
Absorption coefficient (mm ⁻¹)	0.078	0.582	1.313	2.047
F(0 0 0)	680	1762	502	1184
Crystal size (mm ³)	$0.68 \times 0.37 \times 0.30$	$0.34 \times 0.11 \times 0.08$	$0.42 \times 0.36 \times 0.20$	$0.76 \times 0.20 \times 0.14$
θ range for data collection	2.37° to 26.44°	$0.98^{\circ} \text{ to } 25.05^{\circ}$	2.33° to 25.05°	2.48° to 27.70°
Index ranges	$-19 \le h \le 20;$	$-10 \le h \le 10;$	$-9 \le h \le 5;$	$-21 \le h \le 21;$
	$-13 \le k \le 13;$	$-49 \le k \le 49;$	$-10 \le k \le 10;$	$-9 \le k \le 8;$
	$-13 \le l \le 11$	$-13 \le l \le 13$	$-18 \le l \le 18$	$-25 \le l \le 25$
Reflections collected	4774	78,312	6994	49,115
Independent reflections	1694 [R(int) = 0.0279]	7427 [$R(int) = 0.1427$]	3664 [R(int) = 0.0432]	5290 [R(int) = 0.0528]
Completeness to $\theta = 27.70 ~(\%)$	99.3	6.66	98.0	99.4
Absorption correction	Semi-empirical from	Semi-empirical from	Semi-empirical from	Semi-empirical from
	equivalents	equivalents	equivalents	equivalents
Max. and min. transmission	0.980 and 0.797	1 and 0.810678	0.769 and 0.367	0.7456 and 0.5504
Refinement method	Full-matrix least-squares	Full-matrix least-squares	Full-matrix least-squares	Full-matrix least- squares
	on F^{2}	on F^{2}	on F^{2}	on F^{2}
Data/restraints/parameters	1694/0/135	7427/0/525	3664/0/274	5290/0/321
Goodness-of-fit on F^{2}	1.049	1.073	1.122	1.011
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0403,$	$R_1 = 0.0706,$	$R_1 = 0.0401,$	$R_1 = 0.0475,$
	$wR_2 = 0.1121$	$wR_2 = 0.1852$	$wR_2 = 0.1164$	$wR_2 = 0.1330$
R indices (all data)	$R_1 = 0.0530,$	$R_1 = 0.1050,$	$R_1 = 0.0429$,	$R_1 = 0.0685$,
T 1 1 1 1 1 1 2 1 2 1 2 1 2 1 2 1 2 2 1 2	$wR_2 = 0.1222$	$wR_2 = 0.2052$	$wR_2 = 0.1188$	$wR_2 = 0.1522$
Largest difference peak and hole (e.A. ⁻)	0.1/6 and -0.210	1.220 and -0.493	0.442 and -0.801	1.041 and -0.564

Table 1. Crystallographic and structure refinement data for 1, 3, 4, and 5.

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Figure 1. Molecular structure of 4'-(o-toluyl)-2,2':6',2"-terpyridine (1) with thermal ellipsoids at 30% probability.



Figure 2. 4'-[2-(Bromomethyl)phenyl]-2,2': 6',2"-terpyridine mass spectrum (bottom) and calculated isotope pattern (top).

3.2.1. [Co(ottp)₂]Cl₂·2.25CH₃OH. Two 4'-(*o*-toluyl)-2,2': 6',2"-terpyridine ligands are bound by cobalt, forming the distorted octahedral complex shown in figure 3. The crystal system is monoclinic and the space group $P2_1/n$. As a consequence of geometrical constraints enforced by the ligand structure, the two central pyridine



Figure 3. The molecular diagram of the bis[4'-(o-toluyl)-2,2':6',2''-terpyridine] cobalt complex (3) with thermal ellipsoids at 30% probability.

nitrogen–cobalt bond lengths of 1.865(5)Å (N2–Co1) and 1.946(5)Å (N5–Co1) are significantly shorter than the four outer pyridine nitrogen–cobalt bond lengths, 1.999(5)–2.175(5)Å. One of the terpyridine units sits further from the cobalt, approximately 0.15Å, than the other terpyridine unit. One methanol site containing O101 is present at ¹/₄ occupancy.

The presence of two chloride ions in the X-ray structure implies that it is a cobalt(II) complex. Yu *et al.* [16] describe two *bis*(terpyridine) cobalt complexes in which the cobalt is in either the 2+ or 3+ oxidation state, red and orange, respectively. Table 2 lists the Co–N bond lengths and the observed crystal colors for some cobalt terpyridine complexes with cobalt in a variety of oxidation and spin states and includes data from the complex [Co(ottp)₂]Cl₂·2.25CH₃OH. The color and bond length comparisons are consistent with a cobalt(II) oxidation state which agrees with the charge balance from the X-ray structure.

The complex is chiral, due to the relative positioning of the methyl substituents on the terpyridine ligands. The substituent on each ligand removes the mirror plane that would otherwise be coincident with the plane of the other terpyridine group and relates the two halves of the terpyridine ligand containing the substituent. Both enantiomers are present in the crystal, and the packing diagram (figure 4) shows these isomers in the

N atom	Co(II) LS [17]	Co(II) HS [17]	Co(III) [18]	$[Co(ottp)_2 \cdot Cl_2] \cdot 2.25CH_3OH$
1	1.950	2.083	1.930	2.003
2	1.856	1.904	1.863	1.869
3	1.955	2.089	1.926	2.001
4	1.944	2.093	1.937	2.182
5	1.862	1.906	1.853	1.939
6	1.948	2.096	1.921	2.162
Crystal color	Green	Brown	Pale yellow	Red/brown

Table 2. Bond lengths (Å) and colors of cobalt terpyridine complexes with cobalt in different oxidation and spin states.

LS, low spin and HS, high spin.



Figure 4. The hydrogen bonding and short contacts between the chlorides, methanol, and the bis[4'-(o-toluyl)-2,2':6',2''-terpyridine] cobalt complex (3) are shown. Only hydrogens involved in these interactions have been included and portions of the cations have also been excluded for clarity.

structure, and the intermolecular interactions that link them. Chloride ions 1 and 2 are hydrogen bonded to methanol (Cl1–O100 2.322 Å and Cl2–O200 2.831 Å) and to *o*-toluyl methyl hydrogens (Cl1–H44 Å 2.776 Å and Cl2–H43C 2.902 Å). There are a number of other short contacts to aromatic hydrogen atoms as shown in the diagram.

3.2.2. [Cu(ottp)Cl₂]·CH₃OH. The X-ray crystal structure (figure 5) shows copper bound to one 4'-(o-toluyl)-2,2':6',2"-terpyridine ligand and two chlorides. The geometry around copper is distorted square pyramidal. The crystal system is triclinic



Figure 5. The molecular structure of the 4'-(o-toluyl)-2,2': 6',2"-terpyridine copper complex (4) with thermal ellipsoids at 30% probability. H atoms have been omitted for clarity.

and the space group $P\overline{1}$. Although not shown in this diagram, there is hydrogen bonding between the chloride (Cl1) and the methanol at a distance of 2.381 Å.

Figure 6 shows interactions between complexes in the crystal. The chloride at the base of the square pyramid of each complex interacts over a longer distance with the copper of a second complex, and *vice versa*, forming a kind of dimer. The copper–copper distance in this dimer is 4.029 Å, the copper–basal-chloride bond length is 2.509 Å, and the copper–chloride interaction to an adjacent complex is 3.772 Å. There are also hydrogen bonds holding pairs of complexes to other pairs of complexes. This involves hydrogen bonding between, for example, the 3,3″ or 5,5″ hydrogen atoms and the chloride ions, Cl2A and Cl2F, respectively.

3.2.3. [(Cl-ottp)Cu(μ -Cl)(μ -Cl)(μ -Br)Cu(Cl-ottp)][PF₆]₂. The asymmetric unit is shown in figure 7. Figure 8 views the structure along the plane of the pyridine rings showing the structural relationships in the bridging halide–dicopper unit, and the packing diagram is shown in figure 9. The coordination geometry around each copper center is approximately square pyramidal. The dimer is bridged by one chloride and one bromide. Each bridging halide position has an occupancy of 50% Br and 50% Cl, while the bromine in the original ligand has been displaced by a chlorine.

The only source of bridging bromide is from 4'-[2-(bromomethyl)phenyl]-2,2' : 6',2"terpyridine starting material. On the basis of the X-ray crystallographic results, the bromine atom in the starting material has exchanged with chloride from the copper salt. This appears to be a facile process [17]. The preparation of heavier halides from lighter



Figure 6. The X-ray crystal structure packing diagram for **4** with chloride/copper interactions and the chloride/hydrogen interactions.



Figure 7. The asymmetric unit of 5 with a view of the Br/Cl \sim 50% occupancy. Thermal ellipsoids are shown at 30% probability.

halides by first row transition metals was first reported in 1925 by Biltz and Keunecke [18]. The enthalpy of a carbon–bromine bond is $276 \text{ kJ} \text{ mol}^{-1}$ and for a copper–bromide bond it is $331 \text{ kJ} \text{ mol}^{-1}$ [19]. The enthalpy of a copper–chloride bond is $383 \text{ kJ} \text{ mol}^{-1}$ and for a carbon–chlorine bond it is $397 \text{ kJ} \text{ mol}^{-1}$ [20]. It is therefore enthalpically favorable for the bromide to be bonded to copper and the chlorine to be bonded to carbon, rather than the other way around.

In principle, this result could represent a single complex containing one bridging bromide and one bridging chloride, or from the mixture within the crystal of complexes containing two bridging bromides, two bridging chlorides, or one of each halide. The single complex is the best description as, if the refinement outcome were due to a mixture of the three complexes being present, there would be a number of different Cu–Cu distances (due to the different combinations of bridging ligands) present in the same crystal. This would result in significantly larger thermal parameters along the Cu–Cu vector for the coppers. There is no evidence of this (figure 8), hence our conclusion that there is only one complex present with one bridging bromide and one bridging chloride in the crystal analyzed. Searching the CCDC for a similar Cu–Cl/Br–Cu motif revealed only one other structure with this unit [21]. In that report the occupancy of the Cl and Br sites was varied by changing the initial stoichiometry of the halides, with the preferential formation of mixed Cl/Br complexes. The pendant chloromethyl group has some residual electron density nearby. This is due to some disorder which was not considered significant enough to model.

The dinuclear structural element of this complex bears some similarity to that of $[Cu(ottp)Cl_2]$ described above. In both structures, the tpy-based ligand and a halide form an approximate square plane, and the halide in this plane is also associated with



Figure 8. The [(Cl-ottp)Cu(μ -Cl)(μ -Br)Cu(Cl-ottp)] complex (5) viewed along the plane of the pyridine rings.



Figure 9. The packing diagram of 5 showing the PF₆ counter ions.

the second copper. The difference appears to be that the presence of the additional chloride in the mononuclear complex leads to a weakening of the axial bridging interaction.

4. Conclusion

4'-(o-Toluyl)-2,2': 6',2"-terpyridine has been prepared and derivatized. This ligand and its brominated derivative can be used to form metal complexes, although in the latter case a halogen exchange reaction occurred. 4'-[2-(Bromomethyl)phenyl]-2,2': 6',2"terpyridine promises to be a useful synthon to allow additional donors to be added to the terpyridine unit. We plan to introduce groups that can interact with the metal ion bound to the terpyridine, or that are capable of binding a second metal ion.

Supplementary material

CCDC 788100 (1), CCDC 788101 (4), CCDC 788102 (5), and CCDC 788103 (3) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/ci.

References

- [1] S.G. Morgan, F.H. Burstall. J. Chem. Soc., 20 (1932).
- [2] C. Bazzicalupi, A. Bencini, A. Bianchi, A. Danesi, E. Faggi, C. Giorgi, S. Santarelli, B. Valtancoli. *Coord. Chem. Rev.*, 252, 1052 (2008), and references 30–86 therein.
- [3] K.W. Cheng, C.S.C. Mak, W.K. Chan, A.M.C. Ng, A.B. Djurišić. J. Polymer Sci., Part A: Polymer Chem., 46, 1305 (2008).
- [4] C. Li, W. Fan, D.A. Straus, B. Lei, S. Asano, D. Zhang, J. Han, M. Meyyappan, C. Zhou. J. Am. Chem. Soc., 126, 7750 (2004).
- [5] R.H. Friend. Pure Appl. Chem., 73, 425 (2001).
- [6] C.J. Brabec, N.S. Sariciftci, J.C. Hummelen. Adv. Funct. Mater., 1, 11 (2001).
- [7] U.S. Schubert, H. Hofmeier, G.R. Newkome. *Modern Terpyrdine Chemistry*, Wiley-VCH, Germany (2006).
- [8] E.C. Constable, J.M. Holmes, R.C.S. McQueen. J. Chem. Soc., Dalton Trans., 5 (1987).
- [9] (a) L. Xiang-Hong, L.Z. Qiang, L. Fu-You, D. Xin-Fang, H. Chun-Hui. *Chin. J. Chem.*, 25, 186 (2007);
 (b) M.H. Chisholm, C.M. Hada, K. Heinze, K. Hempel, N. Singh, S. Vyas. *J. Cluster Sci.*, 19, 209 (2008);
 (c) Z.-Q. Liang, C.-X. Wang, J.-X. Yang, H.-W. Gao, Y.-P. Tian, X.-T. Tao, M.-H. Jiang. *New J. Chem.*, 31, 906 (2007).
- [10] D.D. Perrin, W.L.F. Armarego. Purification of Laboratory Chemicals, 3rd Edn, Pergamon Press, Oxford (1988).
- [11] SAINT-Plus. Bruker AXS Inc., Madison, Wisconsin, USA (2009).
- [12] G.M. Sheldrick. SADABS. Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen, Germany (2008).
- [13] G.M. Sheldrick. SHELXS-97, Bruker, University of Göttingen, Göttingen, Germany (1997).
- [14] G.M. Sheldrick. SHELXTL, Bruker, University of Göttingen, Göttingen, Germany (1997).
- [15] J.S. Field, R.J. Haines, D.R. McMillan, G.C. Summerton. J. Chem. Soc., Dalton Trans., 1369 (2002).
- [16] Z. Yu, A. Nabei, T. Izumi, T. Okubo, T. Kuroda-Sowa. Acta Cryst., Sect. C, 64, m209 (2008).
- [17] D.B. Dell'Amico, F. Calderazzo, G. Pampaloni. Inorg. Chim. Acta, 361, 2997 (2008).
- [18] W. Biltz, E. Keunecke. Z. Anorg. Allg. Chem., 147, 171 (1925).

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- [19] P. Atkins, J. de Paula. *Elements of Physical Chemistry*, 4th Edn, p. 71, Oxford University Press, Oxford (2005).
- [20] M. Winter. Copper: bond enthalpies in gaseous diatomic species (2003–2009, 5 March 2009–last update). Available online at: http://www.webelements.com/copper/bond_enthalpies.html.
- [21] R.D. Willett, R. Butcher, C.P. Landee, B. Twamley. Polyhedron, 24, 2222 (2005).

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