A metallopolymer case-history: polymer, ring or ligand reaction?†

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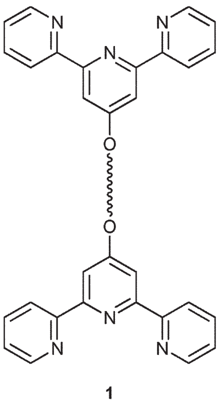
Multinuclear cobalt(II) complexes of ditopic ligands with α,ω-dioxy spacers linking two tpy metal-binding domains react with alcohols to generate monouclear 4′-alkoxy-species.

Metallopolymers are materials with considerable potential, incorporating redox- and photo-active centres within the polymeric structure.[1,2] Although many coordination and organometallic motifs have been investigated, an important class of metallopolymers is derived from ditopic ligands of generic structure **1** incorporating two 2,2′:6′,2″-terpyridine (tpy) metal-binding domains linked by α,ω-dioxy chains.[1,3–5] The reaction of ligands of type **1** with labile metal ions leads to metallopolymers,[3–5] although these are predominantly kinetic products and we have shown that the thermodynamic products (under entropic control) are metallocycles.[6–10] The average molecular weights of solution species are reported to be time- and concentration-dependent,[11,12] consistent with equilibration leading eventually to cyclic systems. In this paper we show that 4′-alkoxy-2,2′:6′,2″-terpyridines undergo an unprecedented metal-promoted reaction which provides an additional explanation for the time-dependent changes in molecular weight and which raises significant doubts about the long-term stability of metallopolymers of this type in aqueous or alcoholic conditions.



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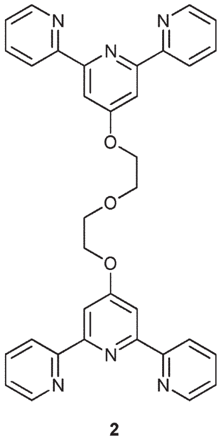

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Ligand **2** is a typical example of a ditopic bis(tpy) ligand with a relatively short flexible spacer and we report here studies using this as a convenient model for analogues with longer poly(ethyleneoxy) spacers. The interaction of cobalt(II) with **2** is particularly informative as we have previously demonstrated the use of paramagnetically shifted ^{1}H NMR spectra of cobalt(II) complexes in investigating the solution behaviour and speciation with oligopyridine ligands.[13,14] Solutions of cobalt(II) complexes in various solvents or mixed solvents were prepared by adding the desired solvent (or solvent mixture) to a 1 : 1 mixture of **2** and $Co(OAc)_2 \cdot 4H_2O$ to give a final concentration of Co^{2+} of 5.9 mM. The coordination of diimine ligands to high-spin $[Co(ROH)_6]^{2+}$ cations (R = H or alkyl) is fast,[15] although ligand exchange of tpy ligands between complexes may be significantly slower.[16] After a given period of time, the solutions were treated with methanolic ammonium hexafluorophosphate, the precipitates collected and ^{1}H NMR spectra recorded in CD_3CN solution. The ^{1}H NMR spectra of compounds isolated from MeOH–$CHCl_3$ mixtures initially indicated the expected library of compounds but we noticed that solutions containing methanol slowly developed a new species, a pure sample of which exhibited peaks at δ 112.6, 75.7, 71.0, 34.8, 14.5, 6.4 ppm in an integrated ratio of 1 : 1 : 1 : 1 : 1.5 : 1. This species was the only cobalt(II) complex observed after heating the reaction mixture to reflux in MeOH for 17 h or heating to 125 °C for 15 min under microwave conditions (Fig. 1). As noted above, the spectra were recorded on material obtained after precipitation with $[NH_4][PF_6]$ and we noted that the spectra of material containing only the new species exhibited no peaks that could be assigned to the ethyleneoxy spacer. We originally thought that the simple spectrum obtained represented quantitative conversion to a single metallocyclic product but the lack of ethyleneoxy signals precluded this explanation. Mass spectrometric studies of the final reaction

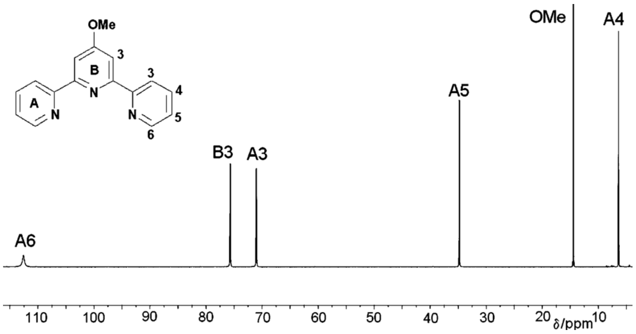

Fig. 1 ^{1}H NMR spectrum (500 MHz, CD_3CN) of $[Co(\mathbf{3})_2][PF_6]_2$ obtained from heating $\{Co(\mathbf{2})\}_n(OAc)_{2n}$ in methanol. Assignments made from the ^{1}H–^{1}H COSY spectrum.

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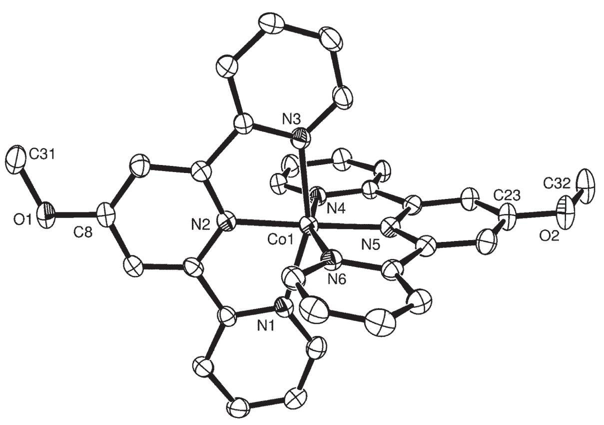
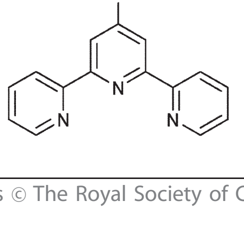


Fig. 2 Molecular structure of the $[Co(\mathbf{3})_2]^{2+}$ cation in $[Co(\mathbf{3})_2][PF_6]_2\cdot MeCN$ with ellipsoids plotted at the 40% probability level. Selected bond distances and angles: Co1–N1 = 2.108(2), Co1–N2 = 1.913(2), Co1–N3 = 2.118(2), Co1–N4 = 2.068(2), Co1–N5 = 1.903(2), Co1–N6 = 2.056(2), C8–O1 = 1.348(3), C31–O1 = 1.440(4), C23–O2 = 1.352(3), C32–O2 = 1.443(4) Å; N1–Co1–N2 = 79.07(8), N2–Co1–N3 = 79.66(8), N4–Co1–N5 = 79.93(8), N5–Co1–N6 = 79.98(8), C31–O1–C8 = 116.8(2), C32–O2–C23 = 117.2(2)°.

mixtures exhibiting the simple ^1H NMR spectra exhibited a peak at *m*/*z* 730.0 assigned to the species $\{CoL_2(PF_6)\}^+$ with the ligand 4′-methoxy-2,2′:6′,2″-terpyridine **3**. An authentic sample of $[Co(\mathbf{3})_2][PF_6]_2$ prepared from **3**[17,18] and cobalt acetate exhibited identical mass and ^1H NMR spectra.

Confirmation of the formation of $[Co(\mathbf{3})_2][PF_6]_2$ came from the determination of the solid-state structure of $[Co(\mathbf{3})_2][PF_6]_2\cdot MeCN$‡ which confirmed the proposed formation of ligand **3**. The structure of the $[Co(\mathbf{3})_2]^{2+}$ cation is shown in Fig. 2 and selected bond parameters are listed in the caption. The coordination environment about the cobalt(II) centre is unexceptional, with Co–N bond distances ranging from 1.903(2) to 2.118(2) Å. The non-hydrogen atoms of each OMe substituent lie in the plane of the pyridine ring to which it is attached; the angles between the least squares planes of the C8O1C31 unit and the ring containing N2 = 8.9(6)°, and of the C23O2C32 unit and the ring containing N5 = 3.1(3)°. This, coupled with the difference in the C_{py}–O and C_{Me}–O bond distances (see caption to Fig. 2), is consistent with conjugation of the π-system across the C_{py}–O bond. The C–O–C bond angles are consistent with sp^2 hybridization. In the lattice, $[Co(\mathbf{3})_2]^{2+}$ cations engage in face-to-face and edge-to-face interactions between $\{Co(tpy)_2\}$ units.

The formation of **3** from **2** was completely unexpected and reactions of this type are, to the best of our knowledge, unprecedented. In order to further investigate the origin of the product **3** we have performed a series of experiments. Replacing the methanol by ethanol resulted in the formation of $[Co(\mathbf{4})_2][PF_6]_2$ containing 4′-ethoxy-2,2′:6′,2″-terpyridine[18] **4**.



3 R = Me
4 R = Et
5 R = ^nPr

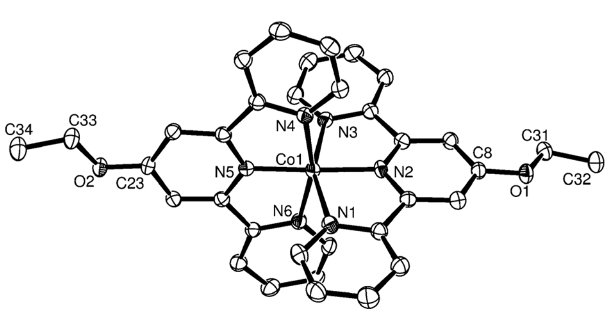


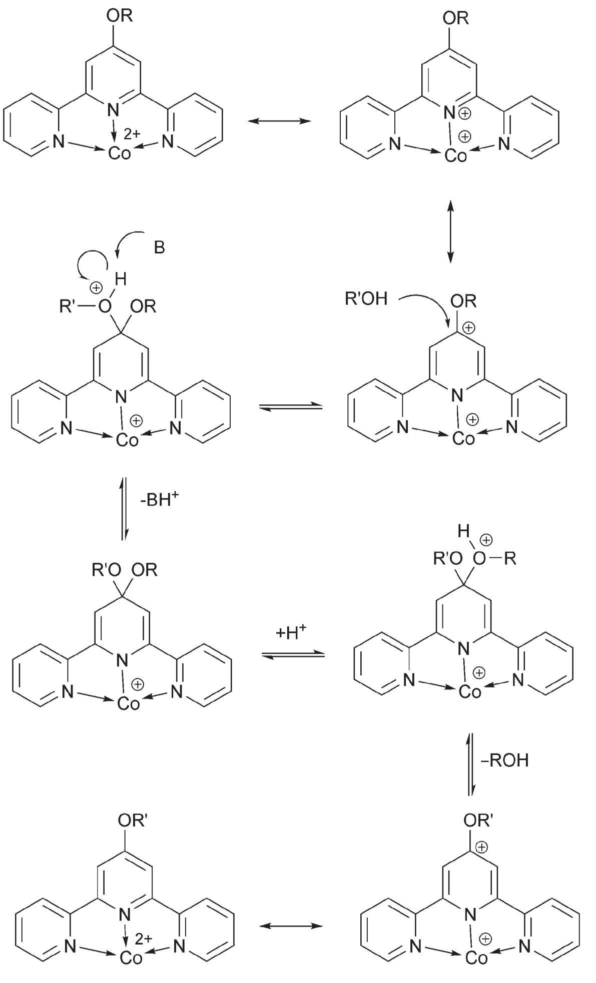
Fig. 3 Molecular structure of the $[Co(\mathbf{4})_2]^{2+}$ cation in $[Co(\mathbf{4})_2][PF_6]_2\cdot 2MeCN$ with ellipsoids plotted at the 30% probability level. Selected bond distances and angles: Co1–N1 = 2.156(3), Co1–N2 = 1.919(3), Co1–N3 = 2.161(3), Co1–N4 = 2.007(3), Co1–N5 = 1.874(3), Co1–N6 = 2.009(3), C8–O1 = 1.348(4), C31–O1 = 1.453(4), C23–O2 = 1.347(4), C33–O2 = 1.452(4) Å; N1–Co1–N2 = 79.3(1), N2–Co1–N3 = 78.4(1), N4–Co1–N5 = 81.5(1), N5–Co1–N6 = 80.6(1), C31–O1–C8 = 116.3(3), C33–O2–C23 = 116.3(3)°.

The formation of ligand **4** was also confirmed by the solid-state structural characterisation of $[Co(\mathbf{4})_2][PF_6]_2\cdot 2MeCN$,§ and the structural features observed for $[Co(\mathbf{3})_2]^{2+}$ are also exhibited by $[Co(\mathbf{4})_2]^{2+}$ (Fig. 3). Similarly, heating solutions of the acetate salt of $\{Co(\mathbf{2})\}_n^{2n+}$ in n-propanol yielded, after addition of $[NH_4][PF_6]$, $[Co(\mathbf{5})_2][PF_6]_2$ (**5** = 4′-(1-propoxy)-2,2′:6′,2″-terpyridine)[19,20] establishing the generality of the reaction.

Heating methanolic solutions of **2** under normal thermal or microwave conditions did not result in the formation of **3**. We considered that the cobalt(II) might be acting as a general Lewis acid, activating the ligand to nucleophilic attack analogous to the known activation of coordinated 4-halopyridines.[21–23] Heating **2** in methanol containing hydrochloric acid also resulted in no formation of **3**, indicating a specific role of the metal ion. Somewhat to our surprise, methanolic solutions of $\{Fe(\mathbf{2})\}_n^{2n+}$ (prepared from $FeCl_2\cdot 4H_2O$ in the presence or absence of sodium acetate, *vide infra*) were not cleanly converted to $[Fe(\mathbf{3})_2]^{2+}$. We suggest that the difference lies in the open- and closed-shell configurations of cobalt(II) and iron(II), respectively, and the degree of polarisation although we have no quantitative justification of this statement.

These observations suggested that the reaction might be more general than we initially thought. Firstly, we treated a methanolic solution of 4′-ethoxy ligand **4** with 0.05 equivalents of $Co(OAc)_2\cdot 4H_2O$ and heated the mixture in a microwave to 125 °C for 15 min. After this period, an additional 0.45 equivalents of cobalt(II) acetate were added and the hexafluorophosphate salts immediately precipitated. The ^1H NMR spectrum of the resultant cobalt(II) complex indicated complete conversion of **4** to **3**. The reaction is not limited to ditopic ligands, and we have demonstrated that complexes $[CoL_2]^{2+}$ (L = **3**–**5**) are freely interconverted simply by microwave heating for 15 min in the appropriate alcohol.

In purely organic terms, the reaction may be seen as a transesterification of vinylogous azaester proceeding along the route indicated in Scheme 1. The key steps involve (i) addition of the nucleophilic alcohol to the activated complex to give a 1,4-dihydropyridine and subsequent deprotonation of the adduct by a general base B. When the reaction was performed using cobalt(II) chloride rather than cobalt(II) acetate, none of



Scheme 1 Proposed mechanism for alkoxy exchange.

the exchange product was observed. On this basis, we propose that the base B is the acetate ion.

We have shown that in alcohol-containing solvents, cobalt(II) complexes of ditopic 2,2′:6′,2″-terpyridine ligands are unstable with respect to an alkoxy-group exchange reaction. In the case of the ditopic ligands, this results in the conversion of the originally formed metallopolymer to low molecular weight mononuclear complexes. This observation imposes severe limitations on the application of metallopolymers of this type in alcoholic solution and suggests that the observed reduction in average molecular weight of such metallopolymers with time is due both to the formation of metallomacrocycles and the degradation of the ligand. We note that similar reactions might be anticipated with long-term exposure to water, although we have not observed the hydrolysis reaction to date.

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Notes and references

‡ Crystallographic data were collected on a Bruker-Nonius Kappa CCD instrument; data reduction, solution and refinement used the programs COLLECT,[24] SIR92,[25] DENZO/SCALEPACK[26] and CRYSTALS.[27] X-Ray data for $[\mathrm{Co}(\mathbf{3})_2][\mathrm{PF}_6]_2\cdot\mathrm{MeCN}$: $\mathrm{C_{34}H_{29}CoF_{12}N_7O_2P_2}$, M = 916.51, dark red plate, orthorhombic, space group $Pccn$, $Z = 8$, $a = 30.2955(4)$, $b = 12.4698(1)$, $c = 19.6441(2)$ Å, $V = 7421.1(1)$ Å^3, $D_c = 1.641$ Mg m^{-3}, μ(Mo-Kα) = 0.653 mm^{-1}, T = 173 K, 8864 reflections collected. Refinement with 5265 reflections (524 parameters) with $I > 1.4\sigma(I)$ converged at final $R_1 = 0.0373$ (R_1 all data = 0.0696), $wR_2 = 0.0432$ (wR_2 all data = 0.0740), $R_{\mathrm{int}} = 0.046$, gof = 1.0935. CCDC 693546.

§ X-Ray data for $[\mathrm{Co}(\mathbf{4})_2][\mathrm{PF}_6]_2\cdot2\mathrm{MeCN}$: $\mathrm{C_{38}H_{36}CoF_{12}N_8O_2P_2}$, M = 985.61, dark red plate, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 9.8293(1)$, $b = 21.7694(3)$, $c = 19.6786(2)$ Å, $\beta = 103.1996(7)°$, $V = 4099.54(8)$ Å^3, $D_c = 1.597$ Mg m^{-3}, μ(Mo-Kα) = 0.598 mm^{-1}, T = 173 K, 9749 reflections collected. Refinement with 9705 reflections (568 parameters) with $I > 2\sigma(I)$ converged at final R_1 = 0.0445 (R_1 all data = 0.0988), $wR_2 = 0.0917$ (wR_2 all data = 0.1515), $R_{\mathrm{int}} = 0.075$, gof = 0.9868. CCDC 693545.

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