A New Family of Low-Spin Co^{III} Bis(amidate) Complexes with Two *cis* or *trans* Cyanides

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Four low-spin dicyanodicarboxamidocobalt(III) complexes have been prepared from N, N'-bis(8-quinolyl)malonamide derivatives, the malonyl fragment of which was either unsubstituted (Et₄N)[Co(BQM)(CN)₂] (**3a**), monosubstituted by a benzyl group (Et₄N)[Co(mono-BenzBQM)(CN)₂] (**3b**), or disubstituted by two benzyl or two phenylethyl groups, (Et₄N)[Co(di-BenzBQM)(CN)₂] (**3c**) and (Et₄N)[Co(di-PhEtBQM)(CN)₂] (**3d**), respectively. The X-ray crystal structures of **3a** and **3c** reveal that the tetradentate ligand adopts a helical or a planar configuration around the cobalt centre of **3a** and **3c**, respectively. Complexes **3a–3d** were charac-

Introduction

Prompted by the work of Collins' group showing the capacity of deprotonated amides to be strong metal donors and to stabilize high oxidation states,^[1] this area of chemistry has received increased attention with the recent findings that amides from a peptide backbone could also be nitrogen donors to the metal centre of metalloproteins, such as the nitrogenase P-cluster^[2] or the nitrile hydratase family.^[3] Our group^[4] and others^[5,6] have synthesised iron and cobalt mimics of the nitrile hydratase active site. Our choice of N₂S₂ tetradentate ligands has illustrated the new properties of this series of complexes.^[4] We are now aiming to develop nitrogen-containing ligands to prepare new mononuclear complexes that could be used as catalysts for oxidation reactions.

It is well-known that introducing one or more carboxamido nitrogens in the metal environment increases the stability of Fe^{III} or Co^{III} complexes^[1,7] and provides catalysts with significant catalytic activity for the oxidation of olefins

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terised in solution by ¹H NMR spectroscopy by 1D and 2D COSY H-H techniques. The solid-state structures of **3a** and **3c** are retained in solution, and complexes **3b** and **3d** adopt structures similar to **3a** and **3c**, respectively, showing that the level of the malonic substitution determines the configuration of the tetradentate ligand around the cobalt centre and forces the cyanide ligands to adopt either *cis* or *trans* orientations.

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or hydrocarbons with *t*BuOOH or H_2O_2 .^[7,8] Tetradentate ligands containing two amides usually derive from picolinic acid and afford six-coordinate complexes with four nitrogens that occupy the equatorial plane and two exogenous ligands in the axial positions.^[9] We report here the synthesis and characterisation of a new family of dicyano Co^{III} complexes of *N*,*N'*-bis(8-quinolyl)malonamide derivatives. We show that different substitutions of the malonic fragment control the coordination geometry of the four nitrogen donors to the metal centre. The tetradentate chelate adopts a planar or a helical configuration around the metal cation, providing two types of complexes with two *cis* or *trans* cyanides.

Results and Discussion

Synthesis of Co^{III} Complexes

We have prepared a series of N,N'-bis(8-quinolyl)malonamide (BQM) derivatives, shown in Scheme 1, containing a malonyl fragment that is either unsubstituted (1a), monosubstituted by a benzyl group (1b), or disubstituted by two benzyl (1c), or two 2-phenylethyl (1d) groups. These ligands were easily synthesised by condensing 8-aminoquinoline with malonyl dichloride derivatives, as previously reported for the disubstituted malonamide compounds.^[10] Cobalt(II) was reacted with the ligands as CoCl₂ in the presence of triethylamine as a soft base. Depending on the ligand sub-

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stitution, two different procedures were applied, as outlined in Scheme 1. For the unsubstituted or monosubstituted compounds 1a and 1b, the Co^{II} insertion was carried out in a mixture of CH₂Cl₂ and MeOH and led to the precipitation of the Co^{II} complex 2a and 2b, respectively. Complex 2a precipitated readily from the solution, and 2b precipitated after concentration in vacuo. Once isolated, the Co^{II} complexes are sparingly soluble in any solvent and were oxidized suspended in aerated CH₂Cl₂ after addition of two equivalents of tetraethylammonium cyanide to stabilize the Co^{III} complexes (Scheme 1, route A). Orange precipitates of the Co^{III} complexes 3a and 3b were obtained after partial removal of the solvent and addition of diethyl ether. The Co^{II} complexes of the disubstituted compounds 1c and 1d are highly soluble in CH₂Cl₂/MeOH and, consequently, more difficult to isolate. The one-pot synthesis of the dicyano Co^{III} complexes in DMF was therefore preferred. After preparing the Co^{II} complexes in solution, the cyanide ligands were added as Et_4NCN at -30 °C and the oxidation was performed with the one-electron oxidizing agent 4-fluorobenzenediazonium hexafluorophosphate^[10] (Scheme 1, route B). After removing the solvent, the crude products were redissolved in CH₂Cl₂ and complexes 3c and 3d were precipitated by addition of diethyl ether and isolated as orange powders in good yields.



Scheme 1. Reaction pathways for the synthesis of the $\mathrm{Co}^{\mathrm{III}}$ dicyano complexes

Characterisation of [Co^{II}(BQM)] (2a)

Co^{II} complexes were formed as intermediates during the synthesis of Co^{III} derivatives and, with the exception of **2a**, are not very stable under aerobic conditions, even as solids. Consequently, we characterised only **2a** to obtain some insight into the cobalt coordination. Its elemental analysis is in agreement with the formulation [Co^{II}(BQM)]. The IR spectrum of the ligand **1a** shows $v_{(N-H)}$ and $v_{(C=O)}$ vibrations at 3279 and 1646 cm⁻¹, respectively. The absence of the $v_{(N-H)}$ band and the shift of the $v_{(C=O)}$ band to a lower energy of 1605 cm⁻¹ in the metal complex confirm that the amide nitrogens are coordinated to the Co in their deprotonated form. The X-band powder EPR spectrum at 4 K shows a single resonance at g = 1.99 characteristic of a low-spin Co^{II} state. This complex is four-coordinate and is probably square planar, as previously proposed for the

Co^{II} complex of *N*,*N'*-bis(pyridin-2-ylmethylene)benzene-1,2-diamine, Co(bpb).^[11] Co^{III} complexes with carboxamido nitrogen donors are typically six coordinate.^[9] Thus, the oxidation was performed in the presence of cyanides to introduce two strong exogenous ligands to complete the cobalt coordination sphere and to stabilize the Co^{III} state.

X-ray Crystal Structure of $(Et_4N)[Co(BQM)(CN)_2]$ (3a) and $(Et_4N)[Co(di-BenzBQM)(CN)_2]$ (3c)

Crystals suitable for X-ray analysis were grown from CH₂Cl₂/hexane for 3a and from acetonitrile/diethyl ether for 3c. Views of the anions of 3a and 3c are presented in Figure 1 and 2. Selected bond angles and distances are listed in Table 1. In both structures the cobalt is six-coordinate in an octahedral environment to two deprotonated amide and two pyridyl nitrogens of the ligand and two exogenous cyanides. However, while the four nitrogen donors N1-N4 in 3c (Figure 2) lie in the equatorial plane, with the two cyanides situated axially trans to each other, in 3a (Figure 1) only three nitrogens (N1, N2 and N3) lie in the equatorial plane, with the fourth (N4) in an apical position and with the two cyanides occupying cis sites, one equatorial (C22-N5) and the other axial (C23-N6). Whereas in the trans configuration C11 deviates from the mean plane defined by N1N2C10C12N3N4 by 0.3 Å, the distortions are more important in the *cis* configuration. The angle between the planes N1N2N3 and N2C10C12N3 is 22° and the angle between C10C11C12 and N2C10C12N3 is 44°. Consequently the CH₂ fragment is in close proximity to the axial cyanide (C23N6). The distance between C11 of the CH_2 and C23 of the CN is 3.02 Å. This explains why a disubstituted derivative cannot adopt a *cis* configuration.



Figure 1. Thermal ellipsoid plot (50% probability level) of the anion of 3a; H atoms are omitted for clarity

An unexpected aspect of the structure of 3a, which crystallises with two water molecules per metal complex, is that the water molecules form an extended hydrogen-bonded network that links three chelates through the N5 nitrogens of the cyano group to the oxygens O1 and O2 of two additional ligands, as shown in Figure 3. The distance between the oxygen of a water and the cyano group (N5–O:



Figure 2. Thermal ellipsoid plot (50% probability level) of the anion of 3c; H atoms are omitted for clarity

Table 1. Selected bond angles (°) and distances (Å) for complexes $[Co(BQM)(CN)_2]Et_4N$ (3a) and $[Co(di-BenzBQM)(CN)_2]Et_4N$ (3c)

	3a	3c
Co-N1	1.934(3)	1.957(4)
Co-N2	1.945(3)	1.933(4)
Co-N3	1.930(3)	1.931(4)
Co-N4	1.995(3)	1.959(4)
Co-C22	1.889(4)	1.932(6)
Co-C23	1.875(4)	1.922(6)
C22-N5	1.156(6)	1.132(7)
C23-N6	1.148(5)	1.151(7)
N2-Co-N4	98.06(12)	174.27(18)
N1-Co-N4	91.33(14)	99.22(16)
C23-Co-C22	83.7(2)	177.01(18)
C22-Co-N2	174.18(14)	92.4(2)
C23-Co-N4	170.6(2)	86.24(19)

2.89 Å) is clearly indicative of hydrogen bonding, as are the O2–O4 water molecule and O1–O3 water molecule distances of 2.73 and 2.82 Å, respectively. The water (O3)–water (O4) distance is 2.78 Å.



Figure 3. Hydrogen-bond network between water and 3a molecules

Solution Structure of $(Et_4N)[Co(BQM)(CN)_2]$ (3a) and $(Et_4N)[Co(di-BenzBQM)(CN)_2]$ (3c)

With the strong cyanide ligands, these complexes exist in a low-spin Co^{III} state. Their structures can be readily analysed by ¹H NMR spectroscopy. NMR assignments were based on 1D and 2D COSY H-H experiments. The spectrum of 3c, shown in Figure 4, indicates a solution structure with a C_2 symmetry, as in the solid state (Figure 2). Both quinolyl rings are equivalent and the pyridyl proton spin system (H^1, H^2, H^3) appears as a set of three well-resolved resonances between $\delta = 7.7$ and 9.0 ppm. The proton labelling is indicated in Scheme 1. The same NMR spectrum was obtained when compound 3c was prepared according to the procedure following route A (Scheme 1), or when the NMR sample was heated up to 360 K. In contrast, the spectrum of **3a**, shown in Figure 4, exhibits a more complicated pattern indicative of the lack of any symmetry, as in the crystal structure (Figure 1). The quinolyl resonances are split into two spin systems H¹, H², H³, H⁴, H⁵, H⁶ and H^{1'}, H^{2'}, H3', H4', H5', H6'. Correlations were made by a 2D COSY experiment. For the assignments, the protons of the quinolyl ring in the equatorial plane were assumed to appear at chemical shifts very close to those found in the trans complex 3c. The two pyridyl systems are very different. The ortho and meta pyridyl protons in the axial position are shifted upfield relative to those in the equatorial plane ($H^{1'}$: $\delta = 6.17$ ppm; H¹: $\delta = 9.07$ ppm; H²': $\delta = 7.28$ ppm; H²: $\delta = 7.87$ ppm). Finally, the two malonyl protons are inequivalent; their signals appeared at two chemical shifts $(\delta = 2.97 \text{ and } 5.02 \text{ ppm})$ located apart from the value of the unique CH_2 resonance ($\delta = 3.87$ ppm) found for the free ligand. These results show that the unexpected solidstate structure of 3a is retained in solution.

Solution Structure of (Et₄N)[Co(mono-BenzBQM)(CN)₂] (3b) and (Et₄N)[Co(di-PhEtBQM)(CN)₂] (3d)

Since NMR spectroscopy proved suitable for the analysis of the two structurally related complexes **3a** and **3c**, we also used this technique to determine whether the cyanides in complexes 3b and 3d were orientated in a cis or a trans fashion. The aim was to determine the influence of the malonyl substitution level on the coordination geometry and, for the disubstituted derivatives, the effect of lengthening the chain by one C-C bond. The NMR spectra of 3d (Figure 4) and 3c are very similar, supporting a planar configuration of the tetradentate chelate and a trans coordination of the cyanides to the cobalt cation. In contrast, the NMR spectrum of the monobenzylated derivative 3b (Figure 4) displays, as for 3a, two quinolyl proton spin-systems. The H^{1'} and H¹ resonances are located in the upfield and downfield regions at $\delta = 6.11$ ppm and 9.06 ppm, respectively. The H^{α} malonyl proton signal appears at $\delta = 5.55$ ppm, a value similar to that of the low-field resonance found for one of the two malonyl protons H^{α} and $H^{\alpha'}$ in **3a**. The benzylic resonance appears at $\delta = 3.18$ ppm, showing that the benzylic protons in **3b** are slightly shielded relative to those in the trans complex 3c. Thus, the monobenzylated



Figure 4. ¹H NMR spectra of the *cis*-3a and -3b and the *trans*-3c and -3d complexes at 250 MHz in $[D_6]DMSO$

and the unsubstituted complex, **3b** and **3a**, adopt the same helical arrangement of the N4 ligand and the same *cis* configuration of the cyanides.

It is noteworthy that while the NMR spectra of the two types of complexes are very different, their IR spectra do not reveal significant differences. They show a unique v_{CN} stretching band at 2120 cm⁻¹ suggesting that the two cyanides have the same surroundings. A similar observation has been reported for other *cis*-dicyano complexes such as *cis*-dicyanobis(1,10-phenanthroline)iron(II)^[12] or bis(2,2'-bi-pyridine)-*cis*-dicyanoiron(III) perchlorate.^[13]

Conclusion

In conclusion, we have prepared four new six-coordinate low-spin Co^{III} dicyano complexes that contain an N,N'-bis(8-quinolyl)malonamide ligand. Interestingly, the substitution level of the malonyl fragment determines whether the

two cyanides are oriented *cis* or *trans* to the cobalt centre. The crystal structures of two representative complexes of this series have been solved. When unsubstituted or monosubstituted, the stable configuration is twisted with three nitrogens and one cyanide in the equatorial plane, and the fourth nitrogen and the second cyanide in apical positions. When disubstituted by two benzyl or two phenylethyl groups, the steric interaction of the malonyl substituent with the axial cyanide ligand destabilizes the cis configuration and forces the ligand to adopt a planar arrangement with two trans cyanides. Consequently, without changing the nature of the nitrogen donors, a disubstitution at the periphery of the ligand framework modulates the *cis* or trans coordination of the two exogenous ligands. Cyanides were introduced to facilitate the characterisation of the dicyano CoIII complexes, and therefore we next intend to introduce more labile exogenous ligands to compare the chemical reactivity of these complexes with the same nitrogen donor set and two cis or trans labile sites.

Experimental Section

Chemicals: All solvents and chemicals were purchased in analytical grade from SDS, Fluka or Aldrich. Sephadex LH-20 resin was purchased from Amersham Biosciences. Solvents were dried by standard procedures.

Spectroscopic Measurements: UV/Visible spectra were recorded at room temperature on a Safas UV mc^2 spectrophotometer. X-band EPR spectra were recorded on a Bruker ESP300 spectrometer operating at a 9.5 GHz microwave frequency, with a 100 kHz modulation frequency and a 1 G modulation amplitude. ¹H NMR spectra were recorded at 300 K on a Bruker ARX-250 spectrometer. Chemical shifts are reported in ppm downfield from TMS. Infrared spectra were obtained with a Perkin–Elmer Spectrum One FT-IR spectrometer equipped either with a sample holder for KBr pellets or with a MIRacleTM single reflection horizontal ATR unit which allowed spectra of solid compounds to be recorded directly (marked as "neat"). Mass spectrometry (ESI⁻ and ESI⁺) was performed on a Thermo Finnigan LCD Advantage spectrometer. Elemental analyses were carried out by the microanalysis service of Paris VI University.

N,N'-Bis(8-quinolyl)malonamide (BQMH₂) (1a): Malonic acid chloride (972 μ L, 9.5 mmol) was added under argon to a CH₂Cl₂ solution (100 mL) of 8-aminoquinoline (3.17 g, 22 mmol) and triethylamine (Et₃N, 3.0 mL, 20 mmoL). Then the mixture was stirred for 12 h at room temperature. After dissolution of all the precipitated condensation product by further addition of CH₂Cl₂ the solution was washed three times with water, then with saturated aqueous NaHCO₃ (30 mL each) and dried over MgSO₄. Removal of the solvent and recrystallisation of the product from CH₂Cl₂ afforded ligand 1a as a white solid (1.32 g, 39%). C₂₁H₁₆N₄O₂ (356.13): calcd. C 70.78, H 4.49, N 15.73; found C 70.60, H 4.66, N 15.68. UV/Vis (CH_2Cl_2) $\lambda_{max}~(\epsilon)$ = 243 (80000 $\mbox{m}^{-1}\mbox{\cdot} cm^{-1}\mbox{)},$ 319 (13000) nm. IR (neat): $\tilde{v} = 3279$ w (v_{NH}) and 1646 s (v_{CO}) cm⁻¹. ¹H NMR $(250 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 10.78$ (s, 2 H, NH), 8.89 (dd, ${}^{3}J = 4.4$, ${}^{4}J = 1.6 \text{ Hz}, 2 \text{ H}, \text{H}^{1}$), 8.83 (dd, ${}^{3}J = 3.6, {}^{3}J = 5.6 \text{ Hz}, 2 \text{ H}, \text{H}^{5}$), 8.16 (dd, ${}^{3}J = 8.4$, ${}^{4}J = 1.6$ Hz, 2 H, H³), 7.54 (d, ${}^{3}J = 3.6$, 2 H, H^4 or H^6), 7.55 (d, ${}^{3}J = 5.6$ Hz, 2 H, H^4 or H^6), 7.46 (dd, ${}^{3}J =$ 4.4, ${}^{3}J = 8.4$ Hz, 2 H, H²), 3.87 (s, 2 H, CH₂) ppm.

2-Benzyl(ethyl malonate): NaH (0.96 g, 40 mmol) and then benzyl bromide (4.7 mL, 40 mmol) were slowly added to a dried THF solution (80 mL) of diethyl malonate (6 mL, 40 mmol). The reaction mixture was refluxed for 24 h. Then, diethyl ether was added (120 mL) and the solution was washed three times with water (3 × 80 mL) and dried over MgSO₄. After evaporation of the solvent, the slightly yellow residue was distilled off as a clear oil (bp, 133–135 °C, P 0.6 Torr, 6.3 g, 63%). ¹H NMR (250 MHz, CDCl₃): $\delta = 7.30-7.15$ (m, 5 H, H-Ph), 4.14 (q, ³J = 7.1 Hz, 4 H, CH₂(OEt)), 3.63 (t, ³J = 7.8 Hz, 1 H, CH), 3.20 (d, ³J = 7.8 Hz, 2 H, CH₂), 1.19 [t, ³J = 7.1 Hz, 6 H, CH₃(OEt)] ppm.

2-Benzylmalonic Acid: 2-Benzyl(ethyl malonate) (5.2 g, 21 mmol) was poured onto pulverized KOH (4.7 g, 94 mmol) in an ice/water bath. The mixture rapidly became highly viscous and ethanol (2 mL) and water (1.3 mL) were added to allow stirring. After 6 h of stirring at 90 °C, the suspension was dissolved in H₂O (30 mL) and twice washed with CH₂Cl₂ (3 × 10 mL) before concentrated HCl was added to reach pH 1. The reaction product was collected by washing with CH₂Cl₂ (5 × 20 mL). The solution was dried over MgSO₄, and evaporation of the solvent afforded 2-benzylmalonic acid (1.7 g, 41%). ¹H NMR (250 MHz, [D₄]MeOH): δ = 7.30–7.10 (m, 5 H, H-Ph), 3.62 (t, ³J = 7.7 Hz, 1 H, CH), 3.15 (d, ³J = 7.7 Hz, 2 H, CH₂) ppm.

2-Benzyl-*N*,*N*'-bis(8-quinolyl)malonamide (mono-BenzBQMH₂) (1b): Under argon, 2-benzylmalonic acid (0.25 g, 1.3 mmol) was dissolved in 4 mL of SOCl₂ and the mixture was stirred for 4 h at 60 °C. After removal of the excess thionyl chloride in vacuo, 2benzyldiethylmalonic acid chloride was obtained as a yellow oil, which was directly converted into 1b. Two equiv. of 8-aminoquinoline (0.37 g, 2.6 mmol) were added to the acid chloride dissolved in dry toluene (5 mL). The orange suspension was stirred for 1 h at room temperature, then Et₃N (0.33 mL, 2.5 mmol) was added and the mixture stirred overnight at 60 °C. Then, CH₂Cl₂ (20 mL) was added, the solution was washed with H_2O (4 \times 10 mL) and the organic layer was dried over MgSO₄. After recrystallization from CH₂Cl₂ 1b was obtained as a white solid (0.37 g, 63%). UV/Vis $(CH_2Cl_2) \lambda_{max} (\epsilon) = 248 (18800 \text{ M}^{-1} \cdot \text{cm}^{-1}), 307 (11700) \text{ nm. IR}$ (neat): $\tilde{v} = 3271$ w (v_{NH}) and 1666 s (v_{CO}) cm⁻¹. ¹H NMR $(250 \text{ MHz}, \text{ CDCl}_3): \delta = 10.60 \text{ (s, 2 H, NH)}, 8.85-7.76 \text{ (m, 4 H, })$ $H^1 + H^5$), 8.12 (d, ${}^{3}J = 8.2 Hz$, 2 H, H³), 7.55–7.48 (m, 4 H, H⁴ + H⁶), 7.43 (dd, ${}^{3}J = 8.2$, ${}^{3}J = 4.2$ Hz, 2 H, H²), 7.38-7.05 (m, H-Ph, 5 H), 3.91 (t, ${}^{3}J = 7.6$ Hz, 1 H, CH), 3.59 (d, ${}^{3}J = 7.6$ Hz, 2 H, CH₂) ppm. MS: m/z (%) = 447 (100) [M + H]⁺).

2,2'-Dibenzyl-*N*,*N*'-bis(8-quinolyl)malonamide (di-BenzBQMH₂; 1c) and 2,2'-Bis(2-phenylethyl)-*N*,*N*'-bis(8-quinolyl)malonamide (di-PhEtBQMH₂; 1d): The disubstituted ligands 1c and 1d were synthesised according to Hirose et al,^[14] but the saponification of the malonic esters was carried out as reported by Maslak et al.^[15]

[Co(BQM)] (2a): Et₃N (0.56 mL, 4.2 mmol) was added under argon to a solution of the BQMH₂ ligand (**1a**; 0.3 g, 0.84 mmol) in a CH₂Cl₂/MeOH mixture (30 mL/20 mL). Upon addition of a methanolic solution (10 mL) of CoCl₂ (0.12 g, 0.92 mmol) the mixture turned orange and within five minutes [Co^{II}(BQM)] precipitated as a completely insoluble orange solid that was washed with CH₂Cl₂, MeOH and diethyl ether (20 mL each) (0.3 g, 73%). C₂₁H₁₆CoN₄O₂·1.5H₂O (440.06): calcd. C 55.89, H 3.65, N 12.40; found C 57.28, H 3.89, N 12.72. IR (KBr): $\tilde{\nu} = 1605$ s (v_{CO}) cm⁻¹. EPR (powder, 4 K) g = 1.99.

 $(Et_4N)[Co(BQM)(CN)_2]$ (3a): Complex 2a (0.1 g, 0.24 mmol) was suspended in CH₂Cl₂ (2 mL). Addition of a CH₂Cl₂ solution (5 mL) of tetraethylammonium cyanide (Et₄NCN, 75 mg,

0.48 mmol) resulted in the dissolution of the complex. Exposure of the solution to air caused oxidation of the cobalt. Stirring was continued for 2 h, then half of the solvent was evaporated and the product was precipitated by addition of diethyl ether. Purification over LH-20 (30 g) with CH2Cl2/MeOH (8:2) as eluent, and precipitation from CH₂Cl₂/pentane afforded (Et₄N)[Co(BQM)(CN)₂] as an orange powder (70 mg, 50%). C₃₁H₃₄CoN₇O₂·H₂O·CH₂Cl₂ (697.17): calcd. C 55.02, H 5.48, N 14.04; found C 54.89, H 5.46, N 13.99. UV/Vis (MeOH) λ (ϵ) = 257 (29900 m⁻¹cm⁻¹), 380 (6040) nm. IR (KBr): $\tilde{v} = 2126 \text{ w} (v_{CN})$ and 1601s (v_{CO}) cm⁻¹. ¹H NMR (250 MHz, $[D_6]DMSO$): $\delta = 9.07$ (d, ${}^{3}J = 5.0$ Hz, 1 H, H¹), 8.81 (d, ${}^{3}J = 7.1$ Hz, 1 H, H⁴ or H⁶), 8.71 (d, ${}^{3}J = 8.2$ Hz, 1 H, H³), 8.41 (d, ${}^{3}J = 8.1$ Hz, 1 H, H ${}^{3'}$), 8.15 (d, ${}^{3}J = 7.2$ Hz, 1 H, H ${}^{4'}$ or $H^{6'}$), 7.87 (dd, ${}^{3}J = 8.2$, ${}^{3}J = 5.0$ Hz, 1 H, H²), 7.75-7.40 (m, 4 H, H⁵ + H^{5'}, H⁴ or H^{4'} and H⁶ or H^{6'}), 7.28 (dd, ${}^{3}J = 8.1, {}^{3}J =$ 4.9 Hz, 1 H, H^{2'}), 6.17 (d, ${}^{3}J = 4.9$ Hz, 1 H, H^{1'}), 5.02 (d, ${}^{2}J =$ 15.1 Hz, 1 H, H^{α} or H^{α'}), 2.97 (d, ²J = 15.1 Hz, 1 H, H^{α} or H^{α'}) ppm. MS: m/z (%) = 465 (100) [Co(BQM)(CN)₂]⁻.

(Et₄N)[Co(mono-BenzBQM)(CN)₂] (3b): Under argon, the monosubstituted ligand mono-BenzBQMH₂ (1b) (0.1 g, 0.22 mmol) was dissolved in CH₂Cl₂ (30 mL) and Et₃N (0.15 mL, 1.1 mmol) was added, followed by a solution of CoCl₂ (32 mg, 0.24 mmol) in MeOH (5 mL). After removal of three quarters of the solvent [CoII-(mono-BenzBQM)] (2b) precipitated as a yellow powder and was collected by filtration, then washed with CH2Cl2, MeOH and diethyl ether (50 mg, 45%). Like 2a, it is insoluble. The oxidation procedure described for 2a was applied to 2b (20 mg, 0.04 mmol) Et₄NCN with (12.5 mg, 0.08 mmol). (Et₄N)[Co(mono-BenzBQM)(CN)₂] (3b) was obtained as an orange powder (18 mg, 65%). C₃₈H₄₀CoN₇O₂ (685.26): calcd. C 66.56, H 5.88, N 14.30; found C 66.06, H 5.85, N 14.20. UV/Vis (MeOH): λ_{max} (ϵ) = 259 $(31300 \text{ M}^{-1}\text{cm}^{-1})$ and 387 (6230) nm. IR (KBr): $\tilde{v} = 2125 \text{ w} (v_{CN})$ and 1618 s (v_{CO}) cm⁻¹. ¹H NMR (250 MHz, [D₆]DMSO): $\delta = 9.06$ (d, ${}^{3}J = 5.2$ Hz, H¹, 1 H), 8.90 (dd, ${}^{3}J = 7.3$, ${}^{4}J = 1.2$ Hz, 1 H, H⁴ or H⁶), 8.69 (d, ${}^{3}J = 8.1$ Hz, 1 H, H³), 8.40 (d, ${}^{3}J = 8.0$ Hz, 1 H, $H^{3'}$), 8.00 (d, ${}^{3}J = 7.1 \text{ Hz}$, 1 H, $H^{4'}$ or $H^{6'}$), 7.86 (dd, ${}^{3}J = 8.1$, ${}^{3}J = 5.2$ Hz, 1 H, H²), 7.75–7.45 (m, 4 H, H⁵ +H^{5'}, H⁴ or H^{4'} and H⁶ or H^{6'}), 7.45–7.00 (m, 6 H, H^{2'} and H-Ph,), 6.11 (d, ${}^{3}J =$ 4.6 Hz, 1 H, H^{1'}), 5.55 (t, ${}^{3}J = 6.5$ Hz, 1 H, CH), 3.18 (d, ${}^{3}J =$ 6.5 Hz, 2 H, CH₂) ppm. MS: m/z (%) = 555 (100) [Co(mono- $BenzBQM)(CN)_2]^-$.

(Et₄N)[Co(di-BenzBQM)(CN)₂] (3c) and (Et₄N)[Co(di-PhEtBQM)-(CN)₂] (3d): A mixture of CoCl₂ (27 mg, 0.21 mmol) and the ligand di-BenzBQMH₂ (1c; 0.11 g, 0.21 mmol) or di-PhEtBQMH₂ (1d; 0.12 g, 0.21 mmol), respectively, was dissolved in dry DMF (10 mL) under argon. After addition of Et₃N (0.11 mL, 0.84 mmol) the solution turned orange. Stirring at room temperature was continued for 30 min before the solution was cooled to -30 °C. Et₄NCN (0.2 g, 1.3 mmol) in DMF (5 mL) was then added, and the solution was stirred for a further 30 min at this temperature. Oxidation to CoIII was performed by addition of the oxidizing agent C₆H₄FN₂PF₆^[10] (1.5 equiv.), dissolved in DMF (2 mL). The reaction mixture was allowed to warm to room temperature and DMF was removed in vacuo. The brown/orange solid was dissolved in acetonitrile (20 mL), the remaining white residue — unconverted ligand — was filtered off. An orange product was obtained after evaporation of the solvent. The product was further purified over LH-20 (30 g) with MeOH and finally precipitated with diethyl ether as an orange powder (3c: 0.13 g, 79%; 3d: 59 mg, 35%).

3c: $C_{45}H_{46}CoN_7O_2 \cdot 3H_2O \cdot 3MeOH \cdot 1.5MeCN$ (945.93): calcd. C 62.18, H 6.98, N, 11.10; found C 61.94, H 6.96, N 11.07. UV/Vis (MeOH): λ_{max} (ϵ) = 268 (26500 m⁻¹·cm⁻¹) and 400 (6090) nm. IR

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Formula	$C_{31}H_{34}C_0N_7O_2\cdot 2H_2O$	$C_{37}H_{26}C_0N_6O_2\cdot C_8H_{20}N\cdot C_2H_3N$
Crystallized from	dichloromethane/hexane	acetonitrile/diethyl ether
Mol. mass	631.61	816.87
Space group	C2/c	$Pbc2_1$
Z	8	4
<i>T</i> (K)	150	293
a (Å)	33.789 (4)	11.170 (2)
$b(\mathbf{A})$	13.707 (2)	19.199 (3)
c (Å)	14.358 (2)	19.375 (3)
α (°)	90	90
β (°)	92.43(1)	90
$V(Å^3)$	6643 (9)	4155.0 (1)
Crystal colour	orange	orange
Crystal shape	irregular wedge	parallelepiped
Density calcd.	1.263	1.306
Dimensions (mm)	0.14 imes 0.12 imes 0.10	0.5 imes 0.3 imes 0.2
$\mu (mm^{-1})$	0.561	0.462
λ (Å)	0.9037	0.71069
2θ range (°)	2.04 - 30.48	3.50-24.71
Absorption correction	none	MULABS ^[21]
reflections total/independent	43991/4614	20155/5343
Reflections with $I > 2\sigma(I)$	4306	4406
No of parameters refined	390	528
R1; $wR2 [I > 2\sigma(I)]$	$0.072; 0.196^{[19]}$	0.0514; 0.1138
R1; wR2 (all data)	0.079; 0.209	0.0631; 0.1214
GOF	1.129	1.057

(KBr): $\tilde{v} = 2120 \text{ w} (v_{CN})$ and 1601 s (v_{CO}) cm⁻¹. ¹H NMR (250 MHz, [D₆]DMSO): $\delta = 9.03$ (dd, ³J = 7.3, ⁴J = 1.9 Hz, 2 H, H⁴ or H⁶), 8.95 (d, ³J = 5.3 Hz, 2 H, H¹), 8.60 (d, ³J = 8.1 Hz, 2 H, H³), 7.84 (dd, ³J = 8.1, ³J = 5.3 Hz, 2 H, H²), 7.60–7.45 (m, 4 H, H⁵ and H⁴ or H⁶), 7.35–7.00 (m, 10 H, H-Ph), 3.6–3.5 (m, 4 H, CH₂) ppm. MS: m/z (%) = 645 (100) [Co(di-BenzBQM)(CN)₂]⁻.

3d: $C_{47}H_{50}CoN_7O_2\cdot 2/3DMF\cdot 1/3H_2O$ (858.04): calcd. C 68.54, H 6.50, N 12.51; found C 68.02, H 6.48, N 12.55. UV/Vis (MeOH): λ_{max} (ε) = 266 (28900 M⁻¹·cm⁻¹) and 394 (7180) nm. IR (KBr): \tilde{v} = 2117 w (v_{CN}) and 1603 s (v_{CO}) cm⁻¹. ¹H NMR (250 MHz, [D₄]MeOH): δ = 9.31 (d, ³J = 7.8 Hz, 2 H, H⁴ or H⁶), 8.94 (d, ³J = 5.3 Hz, 2 H, H¹), 8.52 (d, ³J = 8.1 Hz, 2 H, H³), 7.76 (dd, ³J = 8.1, ³J = 5.3 Hz, 2 H, H²), 7.69 (t, ³J = 7.8 Hz, 2 H, H⁵), 7.57 (d, ³J = 7.8 Hz, 2 H, H⁴ or H⁶), 7.3-7.0 (m, 10 H, H-Ph), 2.95-2.80 (m, 4 H, CH₂), 2.6-2.4 (m, 4 H, CH₂) ppm. MS: *m*/*z* (%) = 673 (100) [Co(di-PhEtBQM)(CN)₂]⁻.

X-ray Crystallography: Crystal data for 3a and 3c are presented in Table 2. Data for **3a** were collected at beamline X7B ($\lambda = 0.9376$ Å) at the Brookhaven National Synchrotron Light Source with a MAR 345 image-plate detector and data for 3c with an Excalibur system equipped with a CCD area detector. The structures were solved by use of isomorphous replacement for 3a^[16] and SHELXS $97^{[17]}$ for **3c**. Refinement, based on F^2 , was carried out by fullmatrix least-squares with SHELXL-93^[18] (3a) and SHELXL-97^[19] (3c). Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned geometrically and refined riding on their carrier atom with isotropic thermal displacement parameters fixed at 1.2-times those of their parent atoms. The lattice of 3a contains an extremely disordered molecule of solvation, which was unmodelable. The program SOUEEZE in the PLATON^[20] suite of programs was used to treat this problem. The structure-factor calculation including SQUEEZE contribution for the final FCF file gave the following results: R1 = 0.078 for 4366 reflections with I >

 $2\sigma(I)$ and wR2 = 0.216 for 4614 reflections. ORTEP^[21] diagrams of **3a** and **3c** are given in Figures 1 and 2.

CCDC-214648 (**3a**) and -211026 (**3c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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