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Binding of Co^{3+} and $CoCl_4^{2-}$ within a Pyridine-cored Molecular Cleft

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When the novel pyridine-2,6-dicarboxylic acid bis[(quinolin-8-ylmethyl)amide] (PDQA) is treated with $CoCl_2$ a 1:1 complex $[(PDQAH_2)][Co^{II}Cl_4]$ (2), is formed. Treatment of 2 with $NaNO_2$ results in oxidation of the $CoCl_4^{2-}$ to Co^{III} affording $[(PDQA\text{-}H)Co^{III}(NO_2)_2]$ (3) whereas under basic conditions a 2:1 (ligand:Co^{III}) paddle-like structure $[Co^{III}(PDPA\text{-}2H)_2K(H_2O)_2(CH_3OH)_1]\cdot(H_2O)_2$ (1) is obtained.

Keywords: Tetrachlorocobaltate complexation; Anion binding; Cobalt complexes; Pyridine-cored ligands; Supramolecular assemblies

INTRODUCTION

Interest in anion and cation binding receptors has greatly increased in recent years reflecting potential applications in areas such as recognition, catalysis, and material design [1–4]. Whilst a number of reports of the ligand properties of pyridine-2,6-dicarboxamide-based systems have appeared in the literature [5–8], little attention has as yet been paid to the chemistry of *N*,*N*′-*bis*(arylmethyl) derivatives such as PDQA and its analogues (Fig. 1). Mascharak [5–11] and others [12–16] have shown that analogues of PDPA readily form complexes with iron(III), cobalt (III), and copper(II). We report here the complexation behaviour of the ligands shown in Fig. 1 with $CoCl_2$.

RESULTS AND DISCUSSION

The collection of novel (PDNA, PDQA) and known (PDBA [17], PDPA [9–11]) pincer-like ligands shown in Fig. 1 was easily prepared by reaction of the appropriate amine with pyridine-2,6-dicarbonyl dichloride. Reaction of these ligands with $CoCl_2$ afforded three different types of complex: (i) an anionic paddle-like structure involving the coordination of PDPA $[Co^{III}(PDPA\text{-}2H)_2\text{-}K(H_2O)_2(CH_3OH)_1]\cdot(H_2O)_2$ (**1**) as shown in Fig. 2; (ii) a complex involving a doubly protonated PDQA ligand coordinated to a tetrachlorocobaltate anion $[(PDQAH_2)][Co^{II}Cl_4]$ (**2**) (Fig. 3) and (iii) a singly deprotonated PDQA ligand coordinated to an octahedral Co^{III} metal centre with two nitrite ligands attatched $[(PDQA\text{-}H)Co^{III}(NO_2)_2]$ (**3**) (Fig. 4).

Complex (**1**) was prepared by mixing PDPA with $CoCl_2$ then KOH in MeOH followed by stirring at room temperature for 30 min (the colour changing from pale pink to dark brown on addition of the base). Crystals of X-ray diffraction quality were obtained by slow diffusion of diethyl ether into the methanol solution to give the structure shown in Fig. 2.

Similar complexes were also prepared with each of the other ligands (PDNA, PDBA, and PDQA). Evidence for this comes from colour change (pale pink to dark brown), mass spectroscopic and infra-red data. This result is not suprising as the core of the ligand is the only part of the structure involved in binding to the metal centre. Therefore any non-sterically-hindering side-arms should be an acceptable appendage for the formation of a similar complex [12–16].

Complex **2** was formed when PDQA was reacted with $CoCl_2$ in MeCN at room temperature for 3 hours (the colour changing from blue to green). Crystals of this material were isolated by the slow diffusion of diethyl ether into the reaction solution to give the structure shown in Fig. 3.

Slight elongation of the Co1—Cl4 bond in comparison to the other Co—Cl bonds may suggest an H-bonding interaction between Cl4 and the amide

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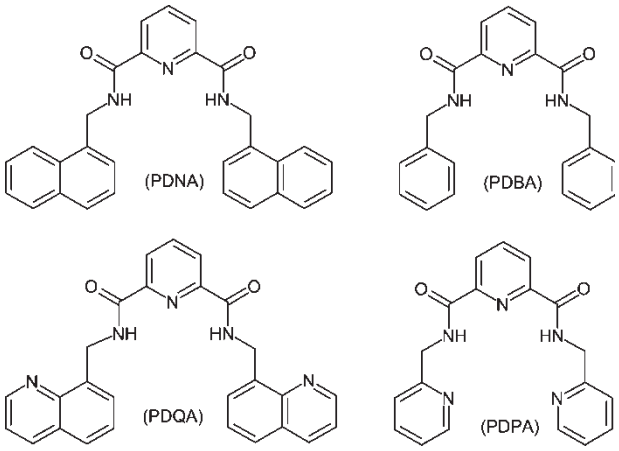

FIGURE 1 Pyridine-2,6-dicarboxylic acid bis[(naphthalen-1-ylmethyl)amide] (PDNA). Pyridine-2,6-dicarboxylic acid bis-benzylamide (PDBA). Pyridine-2,6-dicarboxylicacid bis[(quinolin-8-ylmethyl)amide] (PDQA). Pyridine-2,6-dicarboxylic acid bis[(pyridin-2-ylmethyl)amide] (PDPA).

N—H groups [18–20]. Complexation behaviour of PDPA with Co^{II} paralleled that seen for PDQA with the analytical data consistent with the formation of $[(PDPAH_2)][Co^{II}Cl_4]$. This is almost certainly because the terminal pyridyl groups provide a basic site (similar to that in PDQA) which, when protonated, provide an electrostatic attraction encouraging the association of $CoCl_4^{2-}$, producing a neutral complex.

Each of the protons attached to N4 and N5 (Fig. 3), which were located during the X-ray structure solution, are involved in a conformational locking hydrogen bonding interaction to the amide carbonyl groups. This interaction seems to widen the cleft increasing the bite angle of the pincer, thereby improving the coordination potential of the amide N—H groups.

When an excess of $NaNO_2$ is added to complex **2** in MeCN complex **3** is formed (the solution turning from green to brown). Single crystal X-ray diffraction quality crystals of **3** were prepared by slow diffusion of diethyl ether into the acetonitrile solution to give the structure shown in Fig. 4.

Complex **3** shows a structure in which only one of the two amide N—H protons has been lost. The non-deprotonated side-arm rotates so that the carbonyl oxygen atom (O1) coordinates to the metal centre. This reaction has resulted in the oxidation of $CoCl_4^{2-}$ to Co^{III} which then binds directly into the cavity of PDQA, with the Cl^- ligands being displaced by NO_2^-. Spectroscopic studies suggest that the PDPA complex behaves similarly forming $[(PDPA\text{-}H)Co^{III}(NO_2)_2]$.

When both complexes **2** and **3** are reacted in MeOH with KOH it appears from the colour changes and mass spectrometry data that a paddle-type complex, similar to (**1**), is formed. The addition of the KOH seems to be an important factor as this does not occur by simply adding extra equivalents of the pincer ligand. When complex **2** is dissolved in

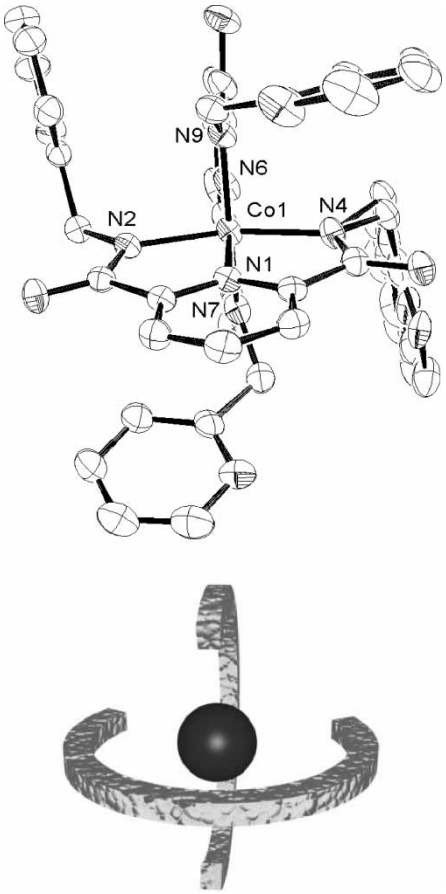

FIGURE 2 Crystal structure and schematic representation of the complex $[Co^{III}(PDPA\text{-}2H)_2K(H_2O)_2(CH_3OH)_1]\cdot(H_2O)_2$ (**1**). Selected bond lengths and interatomic distances (Å): Co1—N1 1.857(3), Co1—N2 1.951(4), Co1—N4 1.969(4), Co1—N6 1.859(3), Co1—N7 1.957(4), Co1—N9 1.946(4). Hydrogen atoms, potassium atom, water molecules, and methanol molecule have been removed for clarity.

MeOH a colour change is observed (the green solid forming a yellow/brown solution) before the base is added. This is possibly due to association of MeOH around the metal centre. Investigation into the specific details of all these reactions is still underway.

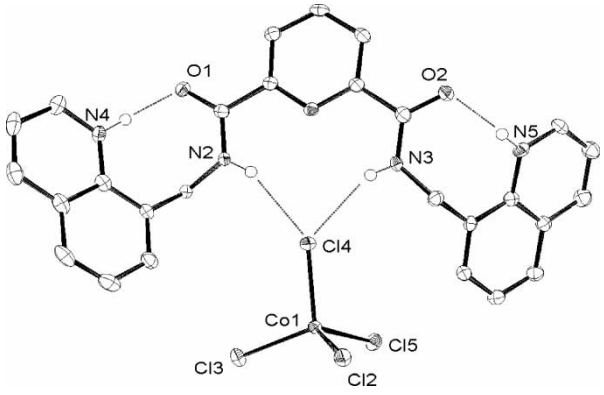

FIGURE 3 Crystal structure of $(PDQA)2H^+CoCl_4^{2-}$ (**2**). Selected bond lengths and interatomic distances (Å): Co1—Cl2 2.2793(8), Co1—Cl3 2.2713(8), Co1—Cl4 2.3051(8), Co1—Cl5 2.2708(7) N2—H···Cl4 2.456, N3—H···Cl4 2.558, N4—H···O1 1.806, N5—H···O2 1.910. C—H hydrogen atoms have been removed for clarity.

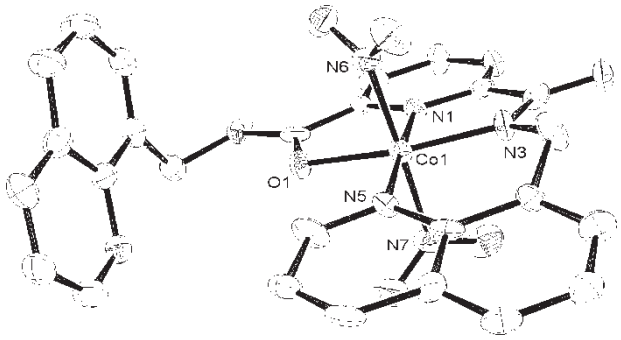

FIGURE 4 Crystal structure of $\{(PDQA)\text{-}H^+\}^-Co(III)[(2NO_2)^{2-}]$ (**3**). Selected bond lengths and interatomic distances (Å): Co1—N1 1.854(6), Co1—N3 1.880(6), Co1—N5 1.933(5), Co1—N6 1.935(6), Co1—N7 1.964(6), Co1—O1 1.979(4). C—H hydrogen atoms have been removed for clarity.

TABLE I Complexation summary of all ligands with $CoCl_2$

	Complex type		
Ligand type8	**1**	**2**	**3**
PDNA	√	X	X
PDBA	√	X	X
PDQA	√	√	√
PDPA	√	√	√

CONCLUSION

In summary we have prepared four pincer-style ligands, two of which are novel (PDQA and PDNA) and we have shown that they form similar complexes when reacted with $CoCl_2$. A summary of the complexation behaviour for each individual ligand with $CoCl_2$ is shown in Table I.

The versatility of these pincer ligands for binding metal cations and anions in a variety of motifs suggests that they still have much potential for forming more complex supramolecular assemblies [1–4].

EXPERIMENTAL

Reagents

All reagents were purchased from the Aldrich Chemical Company and were used as received.

Apparatus

H NMR and C NMR were recorded on a Bruker AC 300 spectrometer. Chemical shifts (δ) are quoted relative to trimethylsilane at 0 ppm or to residual solvent peaks. Electrospray Mass spectra were recorded on a Micromass Platform, recorded with a quadrupole mass analyser. Infra-red spectra were obtained using a Golden Gate sampling attachment on a Mattson Satellite 3000FTIR instrument. Melting points were measured on an Electrothermal melting point apparatus and are uncorrected. Elemental Analyses were performed by MEDAC Ltd.[1] Single Crystal X-ray Diffraction experiments were carried out on a Nonius Kappa CCD diffractometer at 120(2) K with graphite-monochromated Mo-Kα 0.71073 Å radiation and corrected for Lorentz and polarization effects, and for absorption. Structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods anisotropically for non-hydrogen atoms.[2] Data were solved using WinGX [21] or Crystals [22] software and refined by SHELX-97 [23]. The programs Cameron [24], Rasmol [25], Ortep-3 [26], and Mercury [27] were used to investigate crystal architecture and produce the figures found in this publication.

Method

General Procedure for the Preparation of the Pincer Ligands

Pyridine-2,6-dicarbonyl chloride (0.61 g; 3.0 mmol) was stirred in dichloromethane (50 ml) in a 100 ml round bottomed flask. Primary amine (6.0 mmol) was then added, followed by triethylamine (0.83 ml; 6.0 mmol) [*n.b* for PDQA two equivalents of triethylamine were used]. On completion the reaction mixture was washed with water (3 × 50 ml) and the dichloromethane layer was separated, dried over magnesium sulphate, and was removed via rotary evaporation. The product was then recrystallized from hot dichloromethane and pentane, and dried to constant weight under high vacuum.

PDNA

White solid, yield 88%, mp 146–148°C. IR (Golden Gate): ν (cm^{-1}) 3267 (NH), 1655 (C═O), 1510 (C═C); ^{1}H NMR ($CDCl_3$): δ 8.25 (2H, d, $J = 7.7$ Hz), 8.10 (2H, t,$J = 5.9$ Hz), 7.93 (2H, d.d, $J = 8.1$, 1.5 Hz), 7.85 (1H, t, $J = 7.7$ Hz), 7.78 (2H, d.d, $J = 7.7$, 1.5 Hz), 7.68 (2H, d, $J = 7.7$ Hz), 7.45–7.21 (8H, multiplet), 4.87 (4H, d, $J = 5.9$ Hz); ^{13}C NMR ($CDCl_3$): δ 163.2 [C═O], 148.4, 138.7, 133.7, 133.1, 131.2, 128.8, 128.5, 126.6, 126.3, 126.0, 125.3, 125.2, 123.2 [aromatic], 41.4 [CH_2]; m/z (Electrospray positive, MeCN): 891.1 $[2M + H]^+$; Anal. Calcd for $C_{29}H_{23}O_2N_3$: C, 78.18; H, 5.20; N, 9.43; Found: C, 77.81; H, 5.16; N, 9.34.

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[2]EPSRC National Crystallographic Service, School of Chemistry, University of Southampton, Southampton, Hampshire, UK, SO17 1BJ.

PDBA **[17]**

White solid, yield 73%, mp 178–180°C (lit. 180°C [17]). IR (Golden Gate): ν (cm^{-1}) 3343 (NH), 1673 (C═O), 1654 (C═O), 1529 (C═C); ^1H NMR ($CDCl_3$): δ 8.49 (2H, t, broad), 8.35 (2H, d, $J = 7.4$ Hz), 7.99 (1H, t, $J = 7.4$ Hz), 7.20 (10H, multiplet), 4.55 (4H, d, $J = 6.6$ Hz); ^{13}C NMR ($CDCl_3$): δ 163.9 [C═O], 148.8, 139.1, 138.2, 128.8, 127.8, 127.6, 125.4 [aromatic], 43.5 [CH_2]; m/z (high resolution electrospray positive, MeCN): 368.1368 $[M + Na]^+$.

PDQA

White solid, yield 41%, mp 153–155°C. IR (Golden Gate): ν (cm^{-1}) 3383 broad (NH), 3289 broad (NH), 3060 (CH), 1667 (C═O), 1546 (C═C); ^1H NMR ($CDCl_3$): δ 9.47 (2H, t, $J = 6.6$ Hz), 8.96 (2H, d.d, $J = 4.4,\ 2.2$ Hz), 8.27 (2H, d, $J = 8.1$ Hz), 8.17 (2H, d.d, $J = 8.1,\ 1.5$ Hz), 7.92 (1H, t, $J = 8.1$ Hz), 7.83 (2H, d, $J = 6.6$ Hz), 7.76 (2H, d.d, $J = 8.1,\ 1.5$), 7.50 (2H, d.d, $J = 8.1,\ 6.6$ Hz), 7.32 (2H, d.d, $J = 8.1,\ 4.4$ Hz), 5.19 (4H, d, $J = 6.6$ Hz); ^{13}C NMR ($CDCl_3$): δ 163.5 [C═O], 149.6, 148.8, 146.7, 138.7, 136.7, 135.9, 129.6, 128.6, 127.7, 126.6, 124.6, 121.2 [aromatic], 40.9 [CH_2]; m/z (electrospray positive, MeCN): 448 $[M + H]^+$, 470 $[M + Na]^+$; Anal. Calcd for $C_{27}H_{21}O_2N_5 \cdot (H_2O)$: C, 69.66; H, 4.98; N, 15.04; Found: C, 68.63; H, 4.96; N, 14.76.

PDPA **[9–11]**

White solid, yield 94%, mp 150–153°C. IR (Golden Gate): ν (cm^{-1}) 3286 (NH), 1683 (C═O) 1662 (C═O), 1539 (C═C); ^1H NMR ($CDCl_3$): δ 9.28 (2H, t, $J = 5.9$ Hz), 8.5 (2H, d, $J = 4.4$ Hz), 8.32 (2H, d, $J = 7.7$ Hz), 8.0 (1H, t, $J = 7.7$ Hz), 7.65 (2H, d.t, $J = 7.7,\ 1.8$ Hz), 7.38 (2H, d, $J = 7.7$ Hz), 7.20 (2H, d.d, $J = 6.6,\ 5.1$ Hz), 4.78 (4H, d, $J = 5.9$ Hz); ^{13}C NMR ($CDCl_3$): δ 163.6 [C═O], 156.9, 149.2, 148.7, 138.9, 137.1, 124.8, 122.5, 122.5 [aromatic], 44.6 [CH_2]; m/z (electrospray positive, MeCN): 348.2 $[M + H]^+$; 695.5 $[2M + H]^+$; Anal. Calcd for $C_{19}H_{17}O_2N_5$: C, 65.69; H, 4.93; N, 20.16; Found: C, 65.48; H, 4.77; N, 20.05.

Preparation of 8-aminomethyl Quinoline Hydrochloride

8-Bromomethyl Quinoline **[28]**

N-Bromo-succinimide (2.56 g; 14.4 mmol) and 8-methyquinoline (1.64 ml; 12.0 mmol) were stirred under reflux in carbon tetrachloride (150 ml). Benzoyl peroxide (1/2 spatula) was added and the reaction was left for 3 h. On completion the reaction mixture was filtered, washed with sodium bicarbonate solution (3 × 100 ml), dried over magnesium sulphate, and the solvent was removed under reduced pressure to yield a red/brown solid. This was recrystallised from hot ethanol and water to furnish a white crystalline solid, which was dried to constant weight under high vacuum.

Yield 90%, mp 82–84°C. IR (Golden Gate): ν (cm^{-1}) 3040–2960 (CH); ^1H NMR ($CDCl_3$): δ 9.02 (1H, dd, $J = 4.41,\ 1.47$ Hz), 8.18 (1H, dd, $J = 8.07,\ 1.23$ Hz), 7.83 (2H, multiplet), 7.58–7.41 (2H, multiplet), 5.28 (2H, s); ^{13}C NMR ($CDCl_3$): δ 150.3, 146.0, 136.5, 136.3, 130.8, 129.0, 128.7, 126.5, 121.7 [aromatic], 29.8 [CH_2]; m/z (electrospray positive, MeCN): 221.8 $[M + H]^+$.

8-Azidomethyl Quinoline **[29,30]**

8-Bromomethyl quinoline (2.0 g; 9.0 mmol) and NaN_3 (2.3 g; 36.0 mmol) were stirred in dry DMF (100 ml) and heated to 100°C for 4 h. On completion the reaction was left to cool and poured into water (200 ml) and the organic material was extracted into diethyl ether (3 × 50 ml), dried over magnesium sulphate, and the solvent was removed under reduced pressure to yield a yellow oil, which was dried to constant weight under high vacuum, and was then used without further purification.

Yield 95%, IR (Golden Gate): ν (cm^{-1}) 3040–2920 (CH), 2100 (N═N); ^1H NMR ($CDCl_3$): δ 9.02 (1H, dd, $J = 4.4,\ 2.2$ Hz), 8.18 (1H, d.d, $J = 8.1,\ 2.2$ Hz), 7.82 (1H, d.d, $J = 8.1,\ 1.5$ Hz), 7.77 (1H, d, $J = 6.6$ Hz), 7.5 (1H, d.d, $J = 8.1,\ 7.4$ Hz), 7.48 (1H, d.d, $J = 8.1,\ 4.4$ Hz), 5.1 (2H, s); ^{13}C NMR ($CDCl_3$): δ 150.2, 146.0, 136.5, 134.2, 129.3, 128.5, 128.5, 126.4, 121.6 [aromatic], 51.1 [CH_2]; m/z (electrospray positive, MeCN): 184.9 $[M + H]^+$.

8-Aminomethyl Quinoline Hydrochloride **[29,31]**

8-Azidomethyl quinoline (1.5 g; 8.2 mmol) was dissolved in dry tetrahydrofuran (100 ml). Triphenylphosphine (2.1 g; 8.2 mmol) was added and the reaction was left to stir for 48 h. Water (0.22 ml; 12.3 mmol) was added and reaction was left for a further 24 h. The solvent was removed under reduced pressure to yield an orange gum, which was dissolved in benzene (100 ml) and through which HCl gas was bubbled to liberate the desired white crystalline hydrochloride salt, which was then dried to constant weight under high vacuum.

Yield 84%, mp 273–275°C. IR (Golden Gate): ν (cm^{-1}) 3030–2950 (CH). ^1H NMR ($CDCl_3$): δ 9.05 (1H, d.d, $J = 5.2,\ 1.5$ Hz), 9.02 (1H, d.d, $J = 8.1,\ 1.5$ Hz), 8.25 (1H, d.d, $J = 8.1,\ 1.5$ Hz), 8.10 (1H, d, $J = 7.34$ Hz), 7.97 (1H, d.d, $J = 8.1,\ 5.2$ Hz), 7.86 (1H, d.d, $J = 8.1,\ 7.4$ Hz), 4.75 (2H, s); ^{13}C NMR ($CDCl_3$): δ 149.9, 148.5, 138.7, 136.1, 133.7, 123.12, 132.0, 127.1, 124.8 [aromatic], 41.0 [CH_2]; m/z (electrospray positive, MeCN): 159.0 $[M - Cl]^+$.

General Procedure for the Preparation of Complex 1

Cobalt (II) chloride (0.065 g; 0.5 mmol) and pincer ligand (1.0 mmol) were dissolved in methanol (5 ml) and stirred at room temperature. Potassium hydroxide (0.11 g; 2.0 mmol) was added instantly turning the solution from pale pink to dark brown. The solvent was removed under reduced pressure to yield a brown micro-crystalline solid. This was mixed with acetone (10 ml) and then filtered to furnish a brown solid which was dried to constant weight under high vacuum.

Complex 1—(PDPA)

Brown solid, yield 79%, mp > 360°C. IR (Golden Gate): ν (cm^{-1}) 3065 (CH), 1661 (C═O), 1568 (C═O); m/z (high resolution electrospray negative, MeOH): 749.6413 $[M - K]^-$.

(Crystals of X-ray quality were isolated via the slow diffusion of diethyl ether into a methanol soution)

Crystal data for **1**—(PDPA): $C_{39}H_{42}N_{10}O_9Co_1K_1$, $M = 892.86$, triclinic, space group P-1, $a = 10.981(2)$, $b = 10.942(2)$, $c = 17.992(4)$ Å, $\alpha = 101.26(3)$, $\beta = 90.84(3)$, $\gamma = 109.83(3)°$, $V = 1975.4(7)$ Å^3. $Dc = 1.501\,g\,cm^{-3}$, $Z = 2$, $T = 120$ K. Of the 8348 unique reflections collected ($3 \leq \theta \geq 27$) with Mo-Kα ($l = 0.71073$ Å) 6449 with $F_0^2 > 2.0\,s\,(F_0^2)$ were used in the final least-squares refinement to yield $R = 0.0764$ and $Rw = 0.2099$.

(Note: The pyridyl ring containing C16–C20 shows disorder and the split occupancy of water molecule O4W and O5W).

General Procedure for the Preparation of Complex 2

Cobalt (II) chloride (0.13 g; 1.0 mmol) and pincer ligand (1.0 mmol) were dissolved in acetonitrile (5 ml) and the solution was then stirred at room temperature for 3 h (the colour changing from blue to green). The solvent was removed under reduced pressure to yield a green micro-crystalline solid, that was dried to constant weight under high vacuum.

Complex 2—(PDQA)

Green solid, yield 86%, mp 175–180°C. IR (Golden Gate): ν (cm^{-1}) 3280 (NH), 3075 (CH), 1631 (C═O), 1532 (C═O), 788, 755.

(Crystals of X-ray quality were isolated via the slow diffusion of diethyl ether into an acetonitrile soution)

Crystal data **2**—(PDQA): $C_{29}H_{26}N_6O_2Co_1Cl_4$, $M = 691.31$, triclinic, space group P-1, $a = 9.6796(2)$, $b = 11.9956(3)$, $c = 15.0680(4)$ Å, $\alpha = 93.7800(10)$, $\beta = 107.9540(10)$, $\gamma = 112.635(2)°$, $V = 1501.87(6)$ Å^3. $Dc = 1.283\,g\,cm^{-3}$, $Z = 2$, $T = 120$ K. Of the 5295 unique reflections collected ($3 \leq \theta \geq 25$) with Mo-Kα ($l = 0.71073$ Å) 4349 with $F_0^2 > 2.0\,s\,(F_0^2)$ were used in the final least-squares refinement to yield $R = 0.0388$ and $Rw = 0.0901$.

General Procedure for the Preparation of Complex 3

Complex **2** (1.0 mmol) was dissolved in acetonitrile (5 ml). Sodium nitrite (4.0 mmol) was added and the reaction mixture was stirred at room temperature for 3 h (the colour changing from green to brown). The solvent was removed under reduced pressure to yield a brown micro-crystalline solid, which was dried to constant weight under high vacuum.

Complex 3—(PDQA)

Brown solid, yield 88%, mp 195–200°C. IR (Golden Gate): ν (cm^{-1}) 3065 (CH), 1658 (C═O), 1530 (N═O), 1401 (N═O), 1312 (N═O); m/z (high resolution electrospray positive, MeCN): 504.0853 $[M - 2(NO_2) - H^+]^+$.

(Crystals of X-ray quality were isolated via the slow diffusion of diethyl ether into an acetonitrile soution)

Crystal data for **3**—(PDQA): $C_{27}H_{20}N_7O_6Co_1$, $M = 597.43$, monoclinic, space group $P121/n1$, $a = 8.4091(4)$, $b = 16.1659(8)$, $c = 18.5666(12)$ Å, $\alpha = 90$, $\beta = 100.4456(19)$, $\gamma = 90°$, $V = 2482.1(2)$ Å^3. $Dc = 1.599\,g\,cm^{-3}$, $Z = 3$, $T = 120$ K. Of the 5152 unique reflections collected ($3 \leq \theta \geq 27$) with Mo-Kα ($l = 0.71073$ Å) 4583 with $F_0^2 > 3.0\,s\,(F_0^2)$ were used in the final least-squares refinement to yield $R = 0.0490$ and $Rw = 0.0548$.

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