Full Paper

Hybrid Pyrazolyl-1,2,3-Triazolyl Tripodal Tetraamine Ligands: Click Synthesis and Cobalt(III) Complexes

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A family of tripodal tetraamine ligands incorporating two pyrazolyl and one 1,2,3-triazolyl donor arm have been synthesized in modest-to-excellent yields (42–90 %) using the copper(I)-catalyzed azide–alkyne cycloaddition (CuAAC) reaction. Mono-, bis-, and tris-tripodal ligand scaffolds were readily generated using this method. The coordination chemistry of the ligands with cobalt(III) ions has been studied, and cobalt(III) carbonato complexes of the ligands have been isolated and characterized spectroscopically and crystallographically. X-ray crystallography and NMR spectroscopy of the mono-metallic complexes showed that racemic mixtures of the *cis*-isomer are formed selectively. The di- and tri-metallic systems could not be crystallized, but NMR spectroscopy indicates that these compounds were isolated as mixtures of stereoisomers.

Introduction

In 2002, the copper-catalyzed azide–alkyne cycloaddition (CuAAC, Fig. 1) reaction was shown[1] to be an efficient, selective, and functional group tolerant method for the creation of 1,4-disubstituted 1,2,3-triazoles from an azide and an alkyne. With these functionalized 1,2,3-triazole units now readily accessible, there has been an explosion of interest in their coordination chemistry.[2] The 1,2,3-triazole unit can coordinate to metal ions in a variety of modes and a wide range of polydentate ligand scaffolds have been created. Most commonly, these polydentate donor systems coordinate to metal ions through the more electron rich N3 nitrogen atom of the 1,2,3-triazole and these types of systems have been termed 'regular' click ligands. However, systems that coordinate through the N2 nitrogen atom of the triazole are also known, and these are called 'inverse' chelators.

Several symmetric tris-1,2,3-triazole- containing tripodal tetraamine ligands (**A** and **B**, Fig. 1)[3] have been created using CuAAC chemistry and lower symmetry tripodal ligands that incorporate pyridyl and/or quinolyl and 1,2,3-triazolyl donor arms are known (**C**–**F**, Fig. 1).[4] These ligands have been used to generate a variety of metal complexes and some have been shown to display spin crossover behaviour.[5] Additionally, metal complexes of these 'click' tripodal ligands have been exploited in catalysis,[6] sensing,[7] and medical imaging.[8]

Given our experience with both tripodal tetraamine[9] and functionalized 'click' ligands,[10] we were interested in exploring the coordination chemistry of mixed pyrazole-1,2,3-triazole tripodal systems. Herein, we report the synthesis and characterization of a family of novel tripodal, tetraamine ligands bearing two pyrazolyl donors and one 1,2,3-triazolyl donor. The use of the mild CuAAC reaction to generate these systems allowed a variety of functional groups to be appended to the tripodal ligands, and three mono-tripodal ligands with identical metal binding sites, but with different peripheral functionalities were synthesized. More importantly the CuAAC methodology was exploited to generate di- and tri-tripodal ligand scaffolds in an efficient manner.[7c,11] The coordination chemistry of these hybrid tripodal ligands with cobalt(III) ions has been studied, and mono-, di- and tri- cobalt(III) carbonato complexes of the ligands have been isolated and characterized spectroscopically and, where possible, crystallographically.

Results and Discussion

Ligand Synthesis

The synthesis of the hybrid pyrazolyl-1,2,3-triazolyl ligands is outlined in Scheme 1. The alkyne **1** was synthesized in excellent yield (93 %) by heating an acetonitrile (CH₃CN) solution of bis(pyrazolylethyl)amine,[9a] propargyl bromide, and potassium carbonate at reflux for 20 h. The 'click' ligands **2a**, **2b**, **2d**,
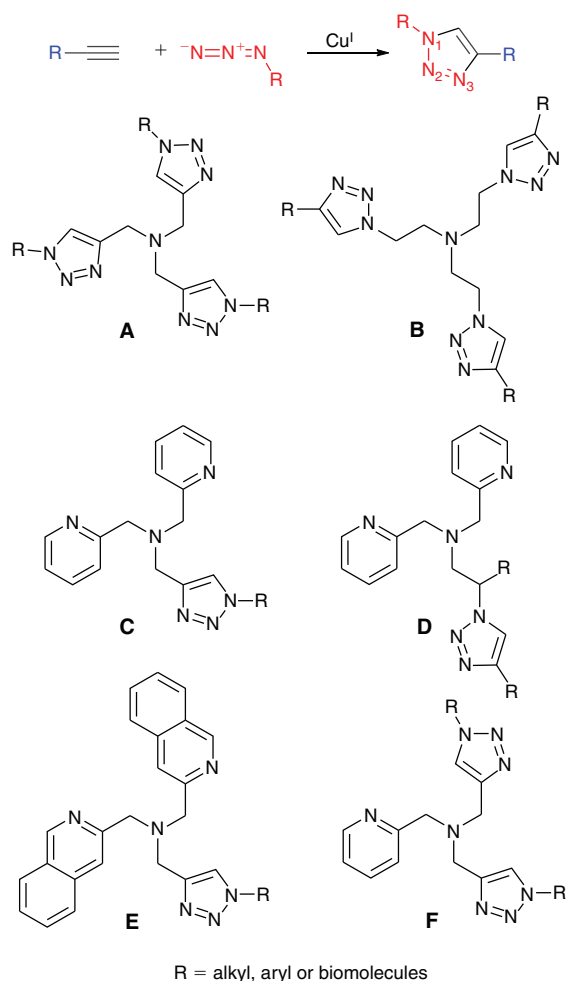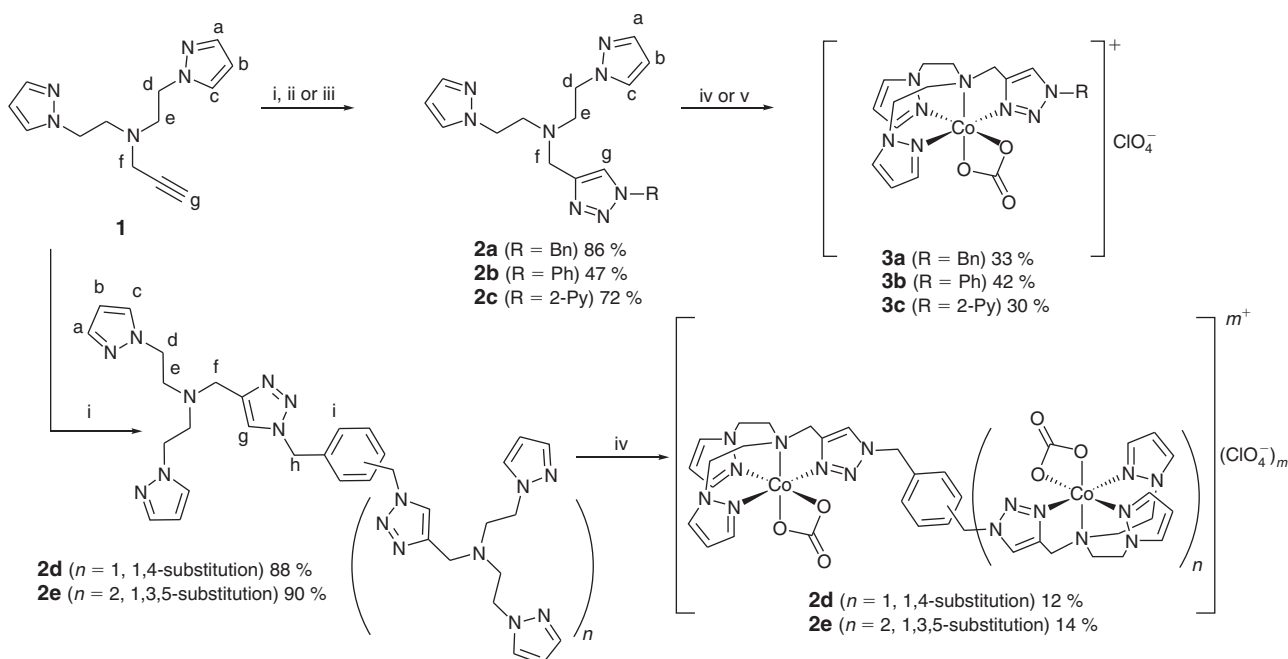
R = alkyl, aryl or biomolecules

Fig. 1. The CuAAC reaction and generic representations of known tripodal ligands containing 1,4-disubstituted 1,2,3-triazole units (**A**–**F**).

and **2e** were safely generated, without the need to isolate the potentially explosive azide intermediates, in good-to-excellent yields (47–90 %) from the alkyne **1** and the corresponding aryl or benzyl bromides by exploiting previous reported in situ azide formation 'click' conditions.[10j,10n,10o]

The ligand **2c** was generated from pyridotetrazole[12] and compound **1** using a slight modification of a recently reported procedure.[13] Copper(I) iodide was used to catalyze the CuAAC reaction and provided **2c** in 72 % yield.[14]

The 'click' ligands **2a**–**e** were characterized using high-resolution electrospray ionization mass spectrometry (HRMS ESI), infrared (IR), ^{1}H and ^{13}C NMR spectroscopy techniques (Supplementary Material). The IR spectra of the ligands displayed no peaks corresponding to the azide ($\sim$2100 cm^{-1}) or alkyne ($\sim$2150 cm^{-1}) functional groups, and the [1]H NMR spectra of the compounds contained a diagnostic singlet corresponding to the triazole unit (found between 8.4 and 6.7 ppm). The mass spectra (Supplementary Material) of the ligands displayed prominent signals corresponding to the [**2a**–**e**(Na)]$^+$ or [**2a**–**e**(H)]$^+$ ions.

Metal Complex Synthesis

Cobalt(III) carbonato complexes of ligands **2a**–**e** were prepared by dissolution of the ligands in a solution of aqueous HCl and subsequent addition of excess Na$_3$[Co(CO$_3$)$_3$]·3H$_2$O. Crude products were filtered through Celite and further purified by chromatography on a Sephadex cation exchange column eluted with 0.1 M NaClO$_4$. Cooling the solutions to 4°C resulted in precipitation of the desired complexes **3a**–**e** as red solids or crystals in poor-to-modest yields (12–42 %).[15]

The complexes were characterized using elemental analysis, HRMS ESI, IR, UV-visible, and ^{1}H and ^{13}C NMR spectroscopy techniques, and in the case of the mono-metallic complexes **3a**–**c** by X-ray crystallography. Elemental analyses were consistent with the expected 1 : 1 (**3a**–**c**), 2 : 1 (**3d**), and 3 : 1 (**3e**) metal-to-ligand

Scheme 1. Synthesis of ligands and complexes: (i) NaN$_3$, benzyl bromide, CuSO$_4$·5H$_2$O, sodium ascorbate, DMF/H$_2$O (4 : 1); (ii) NaN$_3$, iodobenzene, CuSO$_4$·5H$_2$O, sodium ascorbate, TMEDA, DMSO/H$_2$O (9 : 1), 60°C then room temperature (RT); (iii) pyridotetrazole, CuI, toluene, 100°C; (iv) Na$_3$[Co(CO$_3$)$_3$]·3H$_2$O, HCl then NaClO$_4$; and (v) Co(ClO$_4$)$_2$·6H$_2$O, H$_2$O$_2$ (30 %), NaHCO$_3$, CH$_3$CN then NaClO$_4$, H$_2$O.

ratios. Infrared spectra displayed the expected skeletal C–H vibrations between 3100– 2900 cm^{-1} and 1600–1450 cm^{-1} corresponding to the heterocyclic ligand framework. Additionally, peaks at ~1660 cm^{-1} and ~1040 cm^{-1} confirmed the presence of the bidentate carbonato ligand,[16] and the perchlorate counteranions in the isolated solids.

Mono-Metallic Complexes

The ^{1}H NMR spectra (CD$_3$CN, 298 K) of the complexes **3a–c** are indicative of coordination of the cobalt(III) carbonato moiety to the tripodal ligands (Fig. 2 and Supplementary Material). Large downfield shifts, relative to the free ligands **2a–c**, of up to 1 ppm were observed for the peaks due to pyrazolyl (H$_{a–c}$) and triazolyl (H$_g$) units, consistent with metal complexation in the tripodal pocket. Furthermore, the ethyl (H$_{d \text{ and } e}$) and methylene (H$_f$) protons of the tripods are all diastereotopically split in the complexes, consistent with the expected reduction in symmetry upon metal coordination. Conversely, the proton resonances associated with the 1,2,3 triazole substituents of the complexes **3a–c** move very little relative to the free ligands. Combined,

these observations are completely consistent with metal ion coordination in the tripodal binding pocket of the ligand scaffolds **2a–c**.[17]

The inequivalence of the donor arms of tripodal ligands **2a–c** results in the possibility of different stereoisomers for these complexes, with the isomeric possibilities of the cobalt centres of these complexes shown in Fig. 3. The isomer shown in Fig. 3a positions the unique triazolyl donor arm in a *trans* orientation to the carbonato ligand, resulting in a five-membered chelate ring in the plane of the carbonato ligand. The two pyrazolyl substituents are also in a *trans* relationship. We refer to this isomer as the *trans*-isomer of the complex that has C_s symmetry. The other two isomers are a pair of enantiomers that have the two pyrazolyl rings *cis* to one another, with one of these *trans* to the carbonato ligand (these *cis*-isomers have C_1 symmetry). Six distinct peaks are observed for the pyrazolyl protons (H$_{a–c}$) of the complexes, indicating that the two pyrazole rings are in different environments. This suggests that the complexes **3a–c** have formed stereoselectively as a racemic mixture of the *cis*-isomer (Fig. 3), and this is confirmed in the solid state structures (see below).
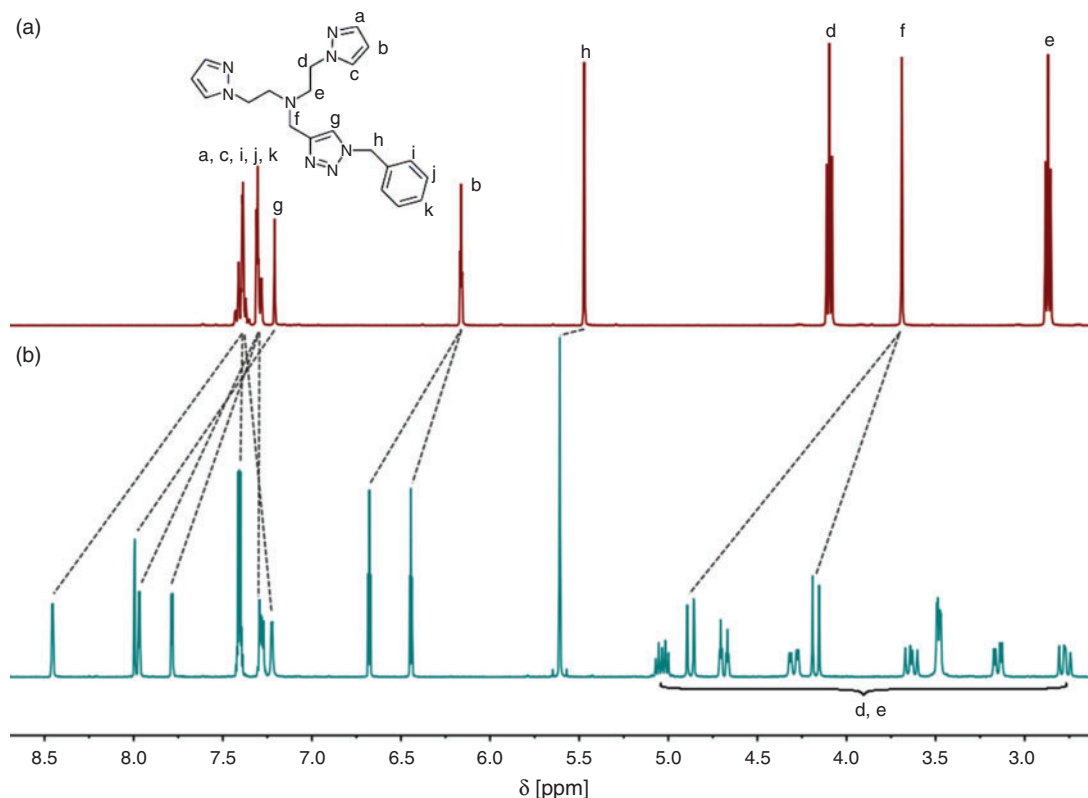

Fig. 2. ^{1}H NMR spectra (CD$_3$CN, 400 MHz, 298 K) of (a) ligand **2a** and (b) complex **3a** with peaks and peak shifts (dashed lines) indicated.
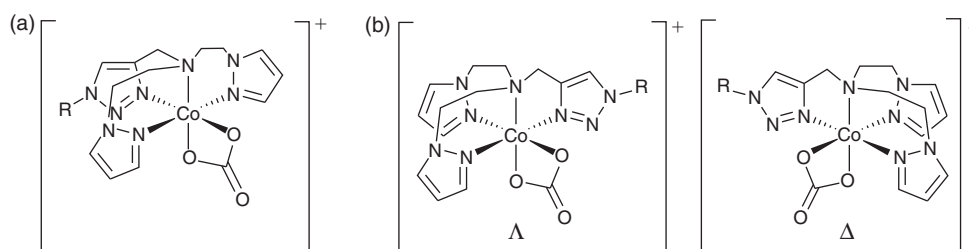

Fig. 3. Isomeric possibilities for complexes **3a–c**: (a) *trans*-isomer and (b) enantiomers (Λ and Δ) of the *cis*-isomer.

Mass spectra of complexes **3a**–**c** (Supplementary Material) display peaks assigned to the $[Co(\mathbf{L})CO_3]^+$ cations, confirming that the complexes are stable. Peaks resulting from loss of CO_2 to form the $[Co(\mathbf{L})O]^+$ cations are also apparent. Further fragmentation of complexes, most prominently loss of a pyrazolylethyl arm, was also observed.

The complexes are red solids, with an absorption in the visible region at ~500 nm. This corresponds to a $^1A_{1g} \rightarrow {}^1T_{2g}$ metal-centred electronic transition,[18] as observed in similar cobalt(III) complexes.[9c] The position of this metal-centred electronic transition in the mono-metallic complex is unaffected by the different triazole substituents in the complexes **3a**–**c**.[10d]

X-Ray quality crystals of complexes **3a** and **3b** were isolated from aqueous solutions of the compounds containing ~1 M $NaClO_4$. Crystals of **3c** were obtained by slow diffusion of diethyl ether into a CH_3CN solution of the complex. The complexes **3a** and **3b** crystallize as dark red, irregular crystals in the space group $P2_1/c$, whereas complex **3c** crystallizes as dark red block-shaped crystals in the space group P-1. *ORTEP* plots of the cations of the complexes **3a**–**c** are shown in Fig. 4. In each case the asymmetric unit consists of a $[Co(\mathbf{L})O_2CO]^+$ cation, a perchlorate counterion, and solvate molecules. The Co^{III} ions in the cations are bound to the four nitrogen donor atoms of the appropriate tetraamine ligand and one bidentate carbonato ligand with the triazole unit coordinated to the metal through the more electron rich N3 nitrogen as expected.[2] Consistent with the NMR data, the complexes **3a**–**c** crystallize as racemic (*rac*) mixtures of the *cis*-isomers.

Metal–ligand bond lengths are reported in Table 1, and ligand–metal–ligand bond angles are reported in Table 2. There is no significant variation of the metal–heterocycle nitrogen bond lengths between the different complexes. However, the central aliphatic nitrogen donor of ligands **2a**–**c** coordinates with a bond distance that is roughly 0.1 Å longer than the heterocyclic donor bond distances, a phenomenon that is common among tripodal tetraamine ligands. Cobalt–oxygen bonds also do not exhibit significant variations between complexes. All

Co^{III}–$N_{triazole}$,[3a,19] Co^{III}–$O_{carbonate}$,[9b,9d,9,g,9h] Co^{III}–$N_{pyrazole}$,[9c,20] and Co^{III}–$N_{apical}^{[9e,9i]}$ distances are typical of similar moieties observed in previously reported compounds. While N–Co–N bond angles generally exhibit limited distortion from perfect octahedral geometry (average N–Co–N angles across the complexes is 91.8°), the O–Co–O angle between the chelating oxygen atoms of the carbonato ligand are ~20° smaller than the ideal 90° angle (69.59(9)°, 69.57(9)°, 69.17(17)° for **3a**, **3b**, and **3c**, respectively). This is unsurprising for a species forming a four-membered chelate ring, and is observed in previous examples of cobalt(III) carbonato complexes.[9b,9d,9,g,9h] The plane of the benzyl ring in **3a** lies at an angle of 87.96° to the triazole ring, whereas the phenyl ring in **3b** lies at an angle of only 22.36°, and in **3c** the pyridyl ring, which adopts a transoid disposition with respect to the triazole nitrogen atoms, is almost coplanar with the triazole ring, with an angle of 6.09°.

The extended structure of **3a** shows a solvent water molecule being hydrogen bonded to O(3) of the carbonate ligand ($O_{water} \cdots O(3)$ 2.772 Å, O–H$\cdots$O(3) 169.81°), while the ClO_4^- anion forms several weak hydrogen bonding interactions with methylene and aromatic CH protons, as well as to the water molecule. In **3b**, a solvent water molecule forms a bridging hydrogen bond between the O(3) of the carbonate (2.809 Å, 179.59°) and the (coordinated) O(1) of a second molecule (2.990 Å, 161.87°). Such hydrogen bonding generates chains of cations (of alternating chirality) and water molecules, running along the crystallographic *b*-axis (Fig. 5). Additionally, phenyl

Table 1. Selected bond lengths in the solid state structures of complexes 3a–c

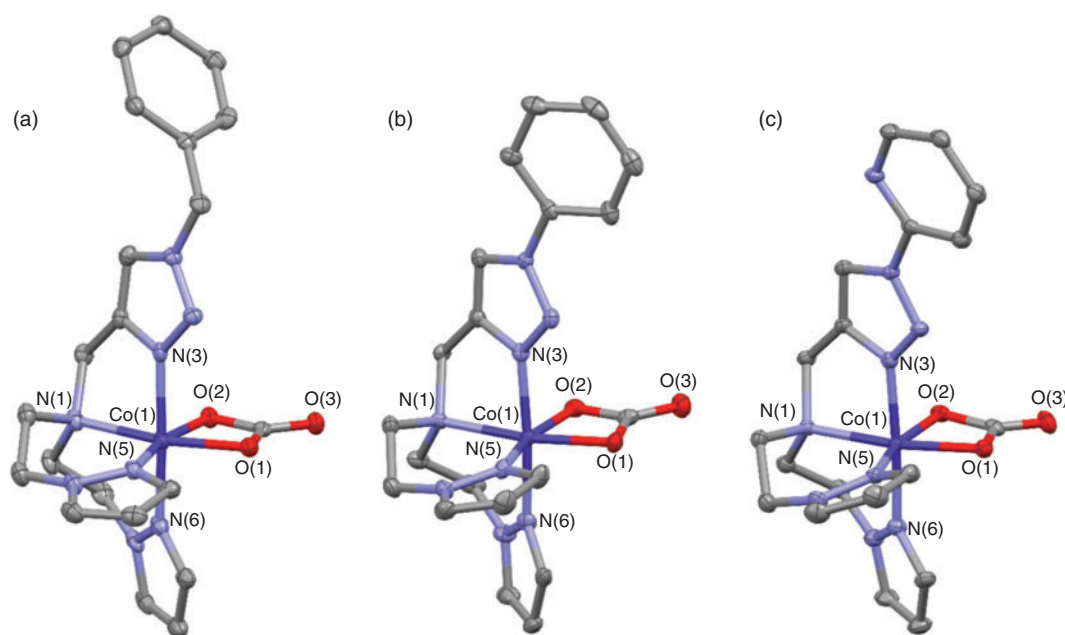| Complex	Co–N(1) [Å]	Co–N(3) [Å]	Co–N(5) [Å]	Co–N(6) [Å]	Co–O(1) [Å]	Co–O(2) [Å]
3a	2.022(3)	1.919(3)	1.916(3)	1.925(3)	1.897(2)	1.890(2)
3b	2.027(3)	1.918(3)	1.916(3)	1.906(3)	1.901(2)	1.888(2)
3c	2.035(3)	1.901(3)	1.910(3)	1.915(3)	1.885(2)	1.896(2)

Fig. 4. *ORTEP* representations of the solid state structures of (a) **3a**, (b) **3b**, and (c) **3c**. Ellipsoids are drawn at the 50 % probability level and counter-anions and solvent molecules have been omitted for clarity. The Δ enantiomer is shown in each case.

rings of neighbouring cations exhibit offset π–π stacking interactions, with a closest C···C distance of 3.345 Å and a centroid–centroid distance of 3.908 Å. Complex **3c** crystallizes with two acetonitrile molecules rather than water molecules and these, along with the coordinated carbonate and the ClO_4^- anion, form only weak hydrogen bonding interactions with various aromatic and methylene CH groups. An offset π–π stacking interaction also exists between the pyridyl–triazole ring systems of adjacent molecules – the closest C···N distance is 3.387 Å and centroid–centroid distance is 3.581 Å.

Multi-Metallic Complexes

Efforts to obtain X-ray quality crystals of the di- (**3d**) and tri- (**3e**) metallic complexes were unsuccessful. However, as mentioned above, elemental analyses and IR data were consistent with the formation of the di- and tri- cobalt carbonato complexes. UV-Visible and mass spectral data of the complexes **3d** and **3e** were also consistent with the formation of the multi-metallic architectures.

The ESI-MS spectrum of the complex **3d** displayed two isotopically resolved peaks at $m/z = 1011.1577$ and 456.1058, which correspond to the $[Co_2(\mathbf{2d})(CO_3)_2(ClO_4)]^+$ and $[Co_2(\mathbf{2d})(CO_3)_2]^{2+}$ ions, respectively. Similarly, the tri-metallic complex **3d** displayed two isotopically resolved peaks at $m/z = 1528.1930$

and 714.1223, which correspond to the $[Co_3(\mathbf{2e})(CO_3)_3(ClO_4)_2]^+$ and $[Co_3(\mathbf{2e})(CO_3)_3(ClO_4)]^{2+}$ ions, respectively. The spectra of both complexes also display additional peaks due to fragmentation of the parent complexes (Supplementary Material).

UV-Visible spectra of complexes **3d** and **3e** are shown in Fig. 6, with a comparison to complex **3a** provided. The $^1A_{1g} \rightarrow {}^1T_{2g}$ metal-centred electronic transitions were observed at 498 ± 1 nm. That these complexes exhibit almost exactly the same energy transition suggests that the cobalt(III) ions in the complexes **3a**, **3d**, and **3e** are in the same ligand environment. An additive relationship between the molar absorptivity at λ_{max} and number of cobalt centres in the complex was observed, with $\varepsilon = 115\,M^{-1}\,cm^{-1}$ for complex **3a**, $\varepsilon = 224\,M^{-1}\,cm^{-1}$ for complex **3d**, and $\varepsilon = 344\,M^{-1}\,cm^{-1}$ for complex **3e**, providing further support for the formation of the di- and tri- metallic systems.

The ^{1}H NMR spectra (Supplementary Material) of the complexes **3d** and **3e**, though consistent with metal complexation to the ligands, were more complicated than initially expected. This suggested that the di- and tri-metallic compounds were isolated as mixtures of stereoisomers. As the mono-metallic complexes (**3a**–**c**) were isolated as *rac* mixtures (Δ, Λ) of the *cis*-isomer, then it could be envisioned that analogous complexes of the di-tripodal ligand **2d** would generate a mixture of ($\Delta\Delta$) and ($\Lambda\Lambda$) enantiomers and the corresponding *meso* ($\Delta\Lambda$ or $\Lambda\Delta$) diastereomers in a

Table 2. Selected bond angles in the solid state structures of complexes 3a–c

Complex	O(2)–Co(1)–O(1) [°]	O(2)–Co(1)–N(5) [°]	O(2)–Co(1)–N(3) [°]	O(2)–Co(1)–N(1) [°]	O(1)–Co(1)–N(5) [°]	O(1)–Co(1)–N(3) [°]
3a	69.59(9)	89.46(10)	87.16(10)	97.73(10)	90.64(10)	92.56(9)
3b	69.57(9)	90.94(10)	87.24(10)	98.86(10)	92.08(10)	93.46(10)
3c	69.72(10)	89.59(11)	88.83(11)	98.35(11)	90.60(11)	93.58(11)

Complex	O(1)–Co(1)–N(6) [°]	N(5)–Co(1)–N(6) [°]	N(3)–Co(1)–N(6) [°]	N(5)–Co(1)–N(1) [°]	N(3)–Co(1)–N(1) [°]	N(6)–Co(1)–N(1) [°]
3a	96.00(10)	88.70(11)	95.74(11)	93.51(11)	82.32(10)	96.78(10)
3b	94.37(10)	91.17(11)	92.41(11)	91.55(11)	82.22(11)	97.07(11)
3c	94.38(11)	92.61(12)	90.29(12)	92.17(12)	83.07(11)	97.43(11)

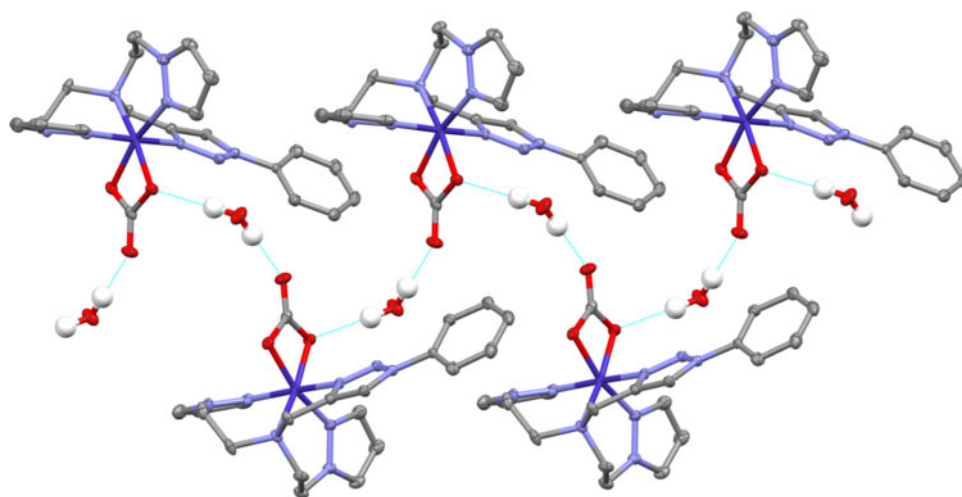| Complex	O(2)–Co(1)–N(6) [°]	O(1)–Co(1)–N(1) [°]	N(5)–Co(1)–N(3) [°]
3a	165.45(10)	166.65(10)	174.22(11)
3b	163.86(10)	167.92(10)	173.16(11)
3c	163.98(11)	167.73(11)	174.72(12)

Fig. 5. Extended structure of **3b** showing hydrogen-bonded chains of cations and water molecules running along the *b*-axis.
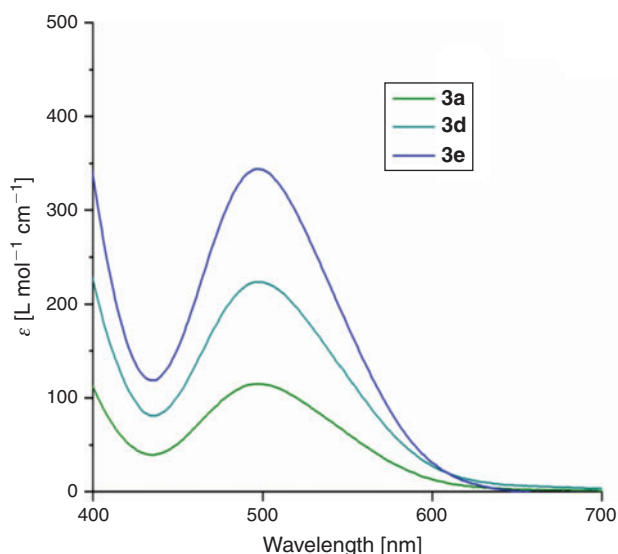
Fig. 6. UV-Visible spectra of mono- (**3a**), di- (**3d**), and tri- (**3e**) metallic complexes in CH$_3$CN.

1:1 ratio. Likewise, the tri-metallic cobalt(III) complex could form a range of stereoisomers (e.g. ΔΔΔ, ΛΛΛ, ΔΔΛ, ΔΛΛ) in a 1:3 ratio of homochiral-to-heterochiral isomers. The ^{1}H NMR spectra of **3d** and **3e** (Supplementary Material) were consistent with the formation of mixtures of these stereoisomers in exactly these ratios. ^{1}H DOSY spectra of **3d** and **3e** were also consistent with this postulate. All the individual proton resonances in the spectrum of ^{1}H DOSY spectra of **3d** display the same diffusion coefficient ($D = 8 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$) suggesting that the protons are associated with molecules of identical size (i.e. isomers) rather than constitutionally different compounds. A similar behaviour is observed in the DOSY spectrum of **3e** ($D = 7 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$). Consistently, the diffusion coefficient of **3e** is smaller than that of **3d** indicating that the tri-metallic complex has a larger size in solution.

Density functional theory (DFT) calculations were used to examine the relative energetics of the potential (*cis,cis*, *cis,trans*, and *trans,trans*) isomers of the di-metallic complex **3d**. DFT calculations have been previously exploited to predict structures of cobalt complexes[21] and provide an insight into the properties associated with triazole containing systems.[10d,10e,10,g] Optimization calculations (Supplementary Material) showed that the *cis,cis* isomer was the most stable (by 19 kJ mol^{-1} relative to *cis,trans*, and 56 kJ mol^{-1} relative to *trans,trans*). These findings provide further support for the proposed interpretation of the NMR data of the multi-metallic complexes.

The isomerism observed in complexes **3d** and **3e** is most likely the major reason that X-ray crystals of the complexes could not be obtained. However, despite a lack of crystallographic data, NMR, infrared, and UV-visible spectroscopic data suggest that the coordination environments in these multi-metallic complexes are analogous to the mono-cobalt compounds.

Conclusions

We have synthesized a novel family of tripodal, tetraamine ligands incorporating two pyrazolyl donors and one 1,2,3-triazolyl donor using the efficient and versatile CuAAC reaction. These ligands can be generated in high yields generally without the need to isolate potentially explosive azide intermediates. Mono-, di- and tri- cobalt(III) carbonato complexes

of these tripodal ligand scaffolds were readily generated in poor-to-modest yields. X-Ray crystallography and NMR spectroscopy of the mono-metallic complexes indicated that these systems selectively formed racemic mixtures of the *cis*-isomer. The corresponding di- and tri-metallic systems were isolated as mixtures of stereoisomers.

The mild functional group tolerant CuAAC methodology used to generate these tripodal ligand scaffolds could be exploited to rapidly generate families of poly-tripodal ligand systems. Access to these types of poly-tripodal ligands could potentially allow the facile synthesis of a range of well-defined multi-metallic[22] complexes, which could be of use in the development of new catalysts[23] as well as materials for biological[24] and electronic[25] applications.

Experimental

All chemicals were used as received. Solvents used were LR (laboratory reagent) grade or better. Bis(pyrazolylethyl)amine and pyridotetrazole were prepared by previously reported methods.[9a,12] ^{1}H NMR and ^{13}C NMR spectra were collected at 25°C on a Varian 400 MHz NMR spectrometer in either d_6-DMSO, CD$_3$CN, or CDCl$_3$; chemical shifts are reported relative to the appropriate solvent peak (^{1}H NMR spectra: d_5-DMSO = 2.50 ppm, CD$_2$HCN = 1.94 ppm, CHCl$_3$ = 7.26 ppm; ^{13}C NMR spectra: d_6-DMSO = 39.5, CD$_3$CN = 1.3 ppm, CDCl$_3$ = 77.2 ppm). DOSY spectra and the ^{1}H NMR spectrum of complex **3e** were collected on a Varian 500 MHz NMR spectrometer in CD$_3$CN, with other conditions as described above. Microanalyses were conducted by the Campbell Microanalytical Laboratory, University of Otago, and are accurate to ± 0.4%. UV-Visible spectroscopic measurements were carried out on a Perkin–Elmer Lambda 950 UV-visible spectrometer. IR spectra were collected in the solid state on a Bruker Alpha FT-IR spectrometer with an attenuated total reflection (ATR) module, and characteristic bands are reported in wavenumbers as broad (br), weak (w), medium (m), or strong (s). Mass spectra were collected on a micrOTOF-Q (Bruker Daltonics, Bremen, Germany) mass spectrometer using electrospray ionization in the positive mode (ESI$^+$).

N,N-Bis[2-(1H-pyrazol-1-yl)ethyl]prop-2-yn-1-amine (1)

Bis(pyrazolylethyl)amine (3.31 g, 15.4 mmol) was dissolved in CH$_3$CN (50 mL). K$_2$CO$_3$ (8.37 g, 60.6 mmol) was added, and then 3-bromopropyne (80% w/w in toluene, 17 mmol, 1.8 mL) was added dropwise. The resulting yellow suspension was heated at reflux for 20 h, over which time it became dark brown. K$_2$CO$_3$ was filtered off, and the resulting dark brown solution was filtered through a plug of basic alumina. Solvent was removed to yield a light brown oil (3.48 g, 93%). ν_{max} (ATR)/cm^{-1} 2946w (C–H$_{sat}$), 2844w (C–H$_{sat}$), 2038w (C≡C), 750s (γ pz), 618s (pz). δ_H (CDCl$_3$, 400 MHz) 7.49 (2H, d, J 1.3, H$_a$), 7.23 (2H, d, J 1.7, H$_c$), 6.19 (2H, m, H$_b$), 4.09 (4H, t, J 6.2, H$_d$), 3.32 (3H, d, J 2.4, H$_f$), 2.98 (4H, t, J 6.2, H$_e$), 2.20 (1H, t, J 2.4, H$_g$). δ_C (CDCl$_3$) 139.2, 129.7, 105.2, 78.2, 73.2, 53.8, 50.4, 42.7. *m/z* (HRMS ESI; CH$_3$CN) 266.1359; [Na**1**]$^+$ requires 266.1376.

N-[(1-Benzyl-1H-1,2,3-triazol-4-yl)methyl]-2-(1H-pyrazol-1-yl)-N-[(2–1H-pyrazol-1-yl)ethyl]ethanamine (2a)

Benzyl bromide (0.775 g, 4.52 mmol), NaN$_3$ (0.295 g, 4.53 mmol), CuSO$_4$·5H$_2$O (0.415 g, 1.66 mmol), and sodium ascorbate (0.815 g, 4.11 mmol) were combined in DMF/H$_2$O (4:1, 10 mL). Compound **1** (1.00 g, 4.12 mmol) was added and the resulting

brown solution was stirred at room temperature for 20 h. An aqueous solution of 0.1 M ethylenediaminetetraacetic acid (EDTA)/1 M NH$_4$OH (50 mL) was then added and the resulting green solution was stirred at room temperature for 1 h. The product was extracted with CHCl$_3$ (3 × 25 mL) and washed with water (5 × 150 mL) and brine (150 mL), dried with MgSO$_4$ and filtered. Solvent was removed to yield a yellow oil (1.33 g, 86 %) from which colourless crystals formed on standing. ν_{max} (ATR)/cm^{-1} 3130w, br (C–H pz), 2951w (C–H$_{sat}$), 2827m (C–H$_{sat}$), 775s (γ pz), 620s (pz). δ$_H$ (CDCl$_3$, 400 MHz) 7.42 (2H, d, J 1.9, H$_a$), 7.38 (3H, m, H$_i$ and H$_k$), 7.23 (2H, dd, J 7.4, 2.2, H$_j$), 7.07 (2H, d, J 2.3, H$_c$), 6.76 (1H, s, H$_g$), 6.11 (2H, t, J 2.1, H$_b$), 5.42 (2H, s, H$_h$), 4.07 (4H, m, H$_d$), 3.70 (2H, s, H$_f$), 2.93 (4H, m, H$_e$). δ$_C$ (CDCl$_3$) 145.5, 139.2, 134.8, 130.2, 129.1, 128.7, 128.0, 122.2, 105.0, 54.2, 54.0, 50.5, 49.4. m/z (HRMS ESI; CH$_3$CN) 399.2013; [Na**2a**]$^+$ requires 399.2016, 377.2183; [H**2a**]$^+$ requires 377.2197. Found: C 63.9, H 6.6, N 29.7. C$_{20}$H$_{28}$N$_8$ requires C 63.8, H 6.4, N 29.8 %.

N-[(1-Phenyl-1H-1,2,3-triazol-4-yl)methyl]-2-(1H-pyrazol-1-yl)-N-[2–1H-pyrazol-1-yl)ethyl]ethanamine (2b)

Nitrogen was bubbled through a solution of DMSO/H$_2$O (9 : 1, 15 mL) for 15 min, and then iodobenzene (1.0 mL, 8.98 mmol), sodium azide (0.587 g, 9.02 mmol), CuSO$_4$·5H$_2$O (0.449 g, 1.80 mmol), sodium ascorbate (0.893 g, 4.51 mmol), and tetramethylethylenediamine (TMEDA) (0.54 mL, 3.59 mmol) were dissolved in the degassed solvent mixture. The solution was heated to 60°C for 5.5 h, and then allowed to cool to room temperature. Compound **1** (0.553 g, 2.27 mmol) was added, and the resulting brown solution was stirred at room temperature for 21 h. An aqueous solution of 0.1 M EDTA/1 M NH$_4$OH (50 mL) was then added and the resulting green solution was stirred at room temperature for 1 h. The product was then extracted with CHCl$_3$ (3 × 50 mL), and the combined organic fractions were washed with water (3 × 100 mL) and brine (100 mL). The organic layer was dried with MgSO$_4$, filtered, and solvent was removed. The resulting brown oil was loaded onto a neutral alumina gel column, and eluted with ethyl acetate. Removal of solvent resulted in a brown oil (0.383 g, 47 %). ν_{max} (ATR)/cm^{-1} 3117w (C–H pz), 2940w (C–H$_{sat}$), 2826m (C–H$_{sat}$), 752s (γ pz), 619s (pz). δ$_H$ (CDCl$_3$, 400 MHz) 7.66 (2H, dd, J 8.6, 1.2, H$_h$), 7.51 (2H, m, H$_i$), 7.46 (2H, d, J 1.3, H$_a$), 7.44 (1H, m, H$_j$), 7.25 (1H, s, H$_g$), 7.16 (2H, d, J 1.7, H$_c$), 6.18 (2H, t, J 2.1, H$_b$), 4.15 (4H, m, H$_d$), 3.80 (2H, s, H$_f$), 3.02 (4H, m, H$_e$). δ$_C$ (CDCl$_3$) 145.8, 139.3, 137.0, 130.3, 129.6, 128.6, 120.4, 122.3, 105.1, 54.3, 50.5, 49.4. m/z (HRMS ESI; CH$_3$CN) 363.2032; [H**2b**]$^+$ requires 363.2040.

2-(1H-Pyrazol-1-yl)-N-[2-(1H-pyrazol-1-yl)ethyl]-N-{[1-(pyridin-2-yl)-1H-1,2,3-triazol-4-yl]methyl} ethanamine (2c)

Pyridotetrazole (0.543 g, 4.52 mmol) was suspended in dry toluene (10 mL), and the mixture was degassed with argon. Compound **1** (0.989 g, 4.06 mmol) and copper(I) iodide (0.111 g, 0.583 mmol) were added, and the resulting suspension was heated to 100°C for 20 h, over which time the solution went a dark brown. Aqueous 0.1 M EDTA/1 M NH$_4$OH solution (50 mL) was added, and the mixture was stirred for 0.5 h. The organic fraction was separated, and the aqueous layer was washed with CHCl$_3$ (3 × 25 mL). The combined organic fractions were washed with water (150 mL) and brine (150 mL), dried with MgSO$_4$, and filtered, resulting in a brown solution. Solvent was removed, and the resulting brown oil was further purified by column chromatography on basic alumina gel with CH$_3$CN as the eluent. Solvent

was removed to yield a brown oil (1.07 g, 72 %). ν_{max} (ATR)/cm^{-1} 3109w, br (Ar–H), 2934w (C–H$_{sat}$), 2853m (C–H$_{sat}$), 753s (γ pz), 619s (pz). δ$_H$ (CDCl$_3$, 400 MHz) 8.50 (1H, ddd, J 4.9, 1.8, 0.8, H$_k$), 8.15 (2H, m, H$_g$ and H$_h$), 7.91 (1H, ddd, J 8.2, 7.5, 1.8, H$_i$), 7.46 (2H, d, J 1.3, H$_a$), 7.34 (1H, ddd, J 7.4, 4.9, 1.0, H$_j$), 7.24 (2H, d, J 2.2, H$_c$), 6.19 (2H, t, J 2.1, H$_b$), 4.13 (4H, t, J 6.0, H$_d$), 3.81 (2H, s, H$_f$), 3.00 (4H, t, J 6.0, H$_e$). δ$_C$ (CDCl$_3$) 148.5, 144.9, 139.3, 136.9, 130.1, 125.9, 123.5, 113.8, 105.2, 54.2, 50.6, 48.2. m/z (HRMS ESI; CH$_3$CN) 386.1810; [Na**2c**]$^+$ requires 386.1812, 380.1941; [(H$_3$O)**2c**]$^+$–H$_2$ requires 380.1947, 364.1994; [H**2c**]$^+$ requires 364.1993.

N-[(1-(4-(4-(N,N-Bis(2-(1H-pyrazol-1-yl)ethyl) aminomethyl)1H-1,2,3-triazol-1-ylmethyl)phenylmethyl)-1H-1,2,3-triazol-4-yl)methyl]-2-(1H-pyrazol-1-yl)-N-[(2–1H-pyrazol-1-yl)ethyl]ethanamine (2d)

1,4-Bis(bromomethyl)benzene (0.285 g, 1.08 mmol), NaN$_3$ (0.157 g, 2.41 mmol), CuSO$_4$·5H$_2$O (0.113 g, 0.451 mmol), and sodium ascorbate (0.236 g, 1.19 mmol) were combined in DMF/H$_2$O (4 : 1, 5 mL). Compound **1** (0.540 g, 2.22 mmol) was added and the resulting brown solution was stirred at room temperature for 20 h. An aqueous solution of 0.1 M EDTA/1 M NH$_4$OH (50 mL) was then added and the resulting green solution was stirred at room temperature for 1 h. The product was extracted with CHCl$_3$ (3 × 25 mL) and washed with water (5 × 150 mL) and brine (150 mL), dried with MgSO$_4$ and filtered. Solvent was removed to yield a yellow oil (0.644 g, 88 %). ν_{max} (ATR)cm^{-1} 2922m (C–H$_{sat}$), 2852m (C–H$_{sat}$), 750s (γ pz), 619s (pz). δ$_H$ (CDCl$_3$, 400 MHz) 7.41 (2H, d, J 1.9, H$_a$), 7.23 (2H, s, H$_i$), 7.09 (2H, d, J 2.2, H$_c$), 6.76 (1H, s, H$_g$), 6.12 (2H, m, H$_b$), 5.41 (2H, s, H$_h$), 4.07 (4H, m, H$_d$), 3.70 (2H, s, H$_h$), 2.92 (4H, m, H$_e$). δ$_C$ (CDCl$_3$) 145.5, 139.2, 135.9, 130.2, 127.9, 122.4, 105.1, 54.1, 53.5, 50.4, 49.3. m/z (HRMS ESI; CH$_3$CN) 697.3635; [Na**2d**]$^+$ requires 697.3671.

N-[(1-(Bis-3,5-(4-(N,N-bis(2-(1H-pyrazol-1-yl)ethyl) aminomethyl)1H-1,2,3-triazol-1-ylmethyl)phenylmethyl)-1H-1,2,3-triazol-4-yl)methyl]-2-(1H-pyrazol-1-yl)-N-[(2-1H-pyrazol-1-yl)ethyl]ethanamine (2e)

1,3,5-Tris(bromomethyl)benzene (0.778 g, 2.18 mmol), NaN$_3$ (0.471 g, 7.24 mmol), CuSO$_4$·5H$_2$O (0.221 g, 0.886 mmol), and sodium ascorbate (0.436 g, 2.20 mmol) were combined in DMF/H$_2$O (4 : 1, 10 mL). Compound **1** (1.63 g, 6.70 mmol) was added and the resulting brown solution was stirred at room temperature for 20 h. An aqueous solution of 0.1 M EDTA/1 M NH$_4$OH (50 mL) was then added and the resulting green solution was stirred at room temperature for 1 h. The product was extracted with CHCl$_3$ (3 × 25 mL) and washed with water (5 × 150 mL) and brine (150 mL), dried with MgSO$_4$, and filtered. Solvent was removed to yield a yellow oil (1.90 g, 90 %). ν_{max} (ATR)/cm^{-1} 3138w, br (pz), 2947w (C–H$_{sat}$), 2836m (C–H$_{sat}$), 751s (γ pz), 619s (pz). δ$_H$ (CDCl$_3$, 400 MHz) 7.39 (2H, d, J 1.9, H$_a$), 7.12 (2H, d, J 2.2, H$_c$), 7.01 (1H, s, H$_i$), 6.77 (1H, s, H$_g$), 6.14 (2H, t, J 2.1, H$_b$), 5.36 (2H, s, H$_h$), 4.09 (4H, m, H$_d$), 3.71 (2H, s, H$_f$), 2.92 (4H, t, J 5.8, H$_e$). δ$_C$ (CDCl$_3$) 145.7, 139.2, 137.0, 130.3, 126.9, 122.6, 105.1, 54.1, 53.1, 50.4, 49.3. m/z (HRMS ESI; MeOH) 995.5293; [Na**2e**]$^+$ requires 995.5325.

[Co(2a)(O$_2$CO)]ClO$_4$ (3a)

Ligand **2a** (0.405 g, 1.08 mmol) was dissolved in H$_2$O (10 mL) which had been adjusted to pH ~1 with concentrated HCl. Na$_3$[Co(CO$_3$)$_3$]·3H$_2$O (0.425 g, 1.17 mmol) was added,

resulting in evolution of CO_2. The mixture was heated to 60°C for 0.5 h, during which time more CO_2 evolved, and the dark red solution was allowed to cool to room temperature and filtered through Celite. The filtrate was diluted to 1 L and loaded onto a Sephadex SP C-25 cation exchange column, and eluted with 0.1 M $NaClO_4$ solution. The main band was collected as a fraction of 150 mL and concentrated to 20 mL. On standing at 4°C, red crystals (0.215 g, 33 %) formed, which were collected by filtration, washed with isopropanol and diethyl ether and air-dried. ν_{max} (ATR)/cm^{-1} 3470w, br (H_2O), 3116w (pz), 1670s (CO_3), 1086s, br (ClO_4), 771s (γ pz), 617s (pz). λ_{max}/nm (ε/L mol^{-1} cm^{-1}) 499 (115). δ_H (CD_3CN, 400 MHz) 8.46 (1H, d, J 2.2, H_a), 8.00 (1H, s, H_g), 7.97 (1H, d, J 2.6, H_c), 7.78 (1H, d, J 2.5, H_c), 7.41 (3H, m, H_i and H_k), 7.28 (2H, m, H_j), 7.22 (1H, d, J 1.9, H_a), 6.68 (1H, t, J 2.5, H_b), 6.44 (1H t, J 2.5, H_b), 5.61 (2H, s, H_h), 5.04 (1H, dt, J 13.9, 6.7, H_d or H_e), 4.88 (1H, d, J 15.4, H_f), 4.69 (1H, dt, J 15.1, 2.7, H_b), 4.29 (1H, dd, J 15.8, 4.3, H_d or H_e), 4.17 (1H, d, J 14.7, H_f), 3.64 (1H, dd, J 16.0, 11.0, H_d or H_e), 3.48 (2H, dd, J 7.2, 2.3, H_d or H_e), 3.15 (1H, dd, J 14.1, 4.3, H_d or H_e), 2.77 (1H, dd, J 14.6, 11.9, H_d or H_e). δ_C (CD_3CN) 145.4, 143.0, 137.2, 136.9, 133.8, 129.1, 129.0, 128.3, 124.9, 108.7, 108.2, 57.6, 57.3, 55.8, 47.4, 45.9. m/z (HRMS ESI; CH_3CN) 495.1316 [Co(**2a**)O_2CO]$^+$ requires 495.1298, 451.1421; [Co(**2a**)O]$^+$ requires 451.1400. Found: C 41.3, H 4.3, N 18.3. [Co($C_{20}H_{24}N_8$)(O_2CO)](ClO_4)·H_2O requires C 41.2, H 4.3, N 18.3 %.

[Co(**2b**)(O₂CO)]ClO₄ (**3b**)

Ligand **2b** (0.134 g, 0.370 mmol) and Co(ClO_4)$_2$·$6H_2O$ (0.156 g, 0.426 mmol) were dissolved in CH_3CN (10 mL). Then, 30 % H_2O_2 (0.076 mL, 0.74 mmol) and $NaHCO_3$ (0.033 g, 0.39 mmol) were added and the red solution was stirred overnight at room temperature. The solution was filtered through Celite, diluted to 1 L with H_2O, and loaded onto a Sephadex SP C-25 cation exchange column. Elution with 0.1 M aqueous $NaClO_4$ resulted in collection of a red band (150 mL), which was concentrated to 10 mL. Standing at 4°C overnight resulted in crystals (0.106 g, 42 %), suitable for X-ray diffraction, and were isolated by filtration and washed with isopropanol and diethyl ether and air-dried. ν_{max} (ATR)/cm^{-1} 3591w, br (H_2O), 3119w (pz), 1674s (CO_3), 1088s, br (ClO_4), 767s (γ pz), 621s (pz). λ_{max}/nm (ε/L mol^{-1} cm^{-1}) 498 (135). δ_H (CD_3CN, 400 MHz) 8.51 (1H, d, J 2.3, H_a), 8.48 (1H, s, H_g), 8.00 (1H, d, J 2.6, H_c), 7.80 (1H, d, J 2.5, H_c), 7.74 (2H, dd, J 8.3, 1.6, H_i), 7.63 (3H, m, H_h and H_j), 7.25 (1H, d, J 2.1, H_a), 6.68 (1H, t, J 2.5, H_b), 6.46 (1H, t, J 2.5, H_b), 5.09 (1H, ddd, J 14.3, 8.4, 5.3, H_d or H_e), 4.99 (1H, d, J 14.7, H_f), 4.73 (1H, dt, J 15.1, 2.7, H_d or H_e), 4.32 (2H, m, H_d or H_e and H_f), 3.66 (1H, dd, J 15.9, 11.0, H_d or H_e), 3.54 (2H, m, H_d or H_e), 3.21 (1H, dd, J 14.1, 4.3, H_d or H_e), 2.94 (1H, dd, J 14.5, 11.6, H_d or H_e). δ_C (CD_3CN) 146.0, 143.1, 143.0, 137.2, 136.9, 130.5, 130.1, 123.2, 121.0, 108.7, 108.2, 57.5, 57.4, 57.2, 47.4, 46.0. m/z (HRMS ESI; CH_3CN) 481.1123; [Co(**2b**)O_2CO]$^+$ requires 481.1141; [Co(**2b**)O]$^+$ requires 437.1249. Found: C 39.6, H 3.9, N 18.5. [Co($C_{24}H_{32}N_8$)(O_2CO)](ClO_4)·1.5H_2O requires C 39.5, H 4.2, N 18.4 %.

[Co(**2c**)(O₂CO)]ClO₄ (**3c**)

Ligand **2c** (0.104 g, 0.285 mmol) was dissolved in H_2O (5 mL) which had been adjusted to pH ~1 with concentrated HCl. Na_3[Co(CO_3)$_3$]·$3H_2O$ (0.110 g, 0.304 mmol) was added. The mixture was heated to 60°C for 0.5 h, resulting in evolution of CO_2, and the dark red solution was allowed to cool to room temperature and filtered through Celite. The filtrate was diluted

to 100 mL and loaded onto a Sephadex SP C-25 cation exchange column, and eluted with 0.1 M $NaClO_4$ solution. The main band was collected as a fraction of 50 mL and concentrated to 5 mL. On standing at 4°C, red crystals (0.054 g, 30 %) formed, which were collected by filtration, washed with isopropanol and diethyl ether, and air-dried. ν_{max} (ATR)/cm^{-1} 3579w, br (H_2O), 3134w (Ar–H), 1663s (CO_3), 1062s, br (ClO_4), 761s (γ pz), 618s (pz). λ_{max}/nm (ε/L mol^{-1} cm^{-1}) 497 (131). δ_H (CD_3CN, 400 MHz) 8.83 (1H, s, H_g), 8.58 (1H, ddd, J 4.8, 1.7, 0.9, H_k), 8.54 (1H, d, J 2.2, H_a), 8.08 (2H, m, H_h and H_i), 8.00 (1H, d, J 2.5, H_c), 7.79 (1H, d, J 2.5, H_c), 7.57 (1H, ddd, J 7.1, 4.8, 1.3, H_j), 7.25 (1H, d, J 1.9, H_a), 6.69 (1H, t, J 2.5, H_b), 6.47 (1H, t, J 2.5, H_b), 5.09 (1H, ddd, J 14.3, 9.9, 3.6, H_d or H_e), 5.01 (1H, dd, J 14.8, 1.3, H_f), 4.74 (1H, dt, J 15.0, 2.5, H_d or H_e), 4.32 (2H, m, H_d or H_e and H_f), 3.66 (1H, dd, J 16.0, 11.0, H_d or H_e), 3.54 (2H, m), 3.22 (1H, dd, J 14.0, 4.3, H_d or H_e), 2.93 (1H, dd, J 13.7, 10.7, H_d or H_e). δ_C (CD_3CN) 152.1, 149.0, 146.0, 143.1, 143.0, 140.3, 137.3, 136.9, 125.7, 121.7, 113.9, 108.7, 108.3, 57.6, 57.4, 57.2, 47.4, 46.0. m/z (HRMS ESI; CH_3CN) 482.1137; [Co(**2c**)(O_2CO)]$^+$ requires 482.1094, 438.1255; [Co(**2c**)(O)]$^+$ requires 438.1201. Found: C 36.9, H 4.0, N 20.2. Co($C_{24}H_{32}N_8$)(O_2CO)](ClO_4)·2H_2O requires C 36.9, H 4.1, N 20.4 %.

[Co₂(**2d**)(O₂CO)₂](ClO₄)₂ (**3d**)

Ligand **2d** (0.553 g, 0.814 mmol) was dissolved in H_2O (10 mL) which had been adjusted to pH ~1 with concentrated HCl. Na_3[Co(CO_3)$_3$]·$3H_2O$ (0.742 g, 2.05 mmol) was added, resulting in evolution of CO_2. The mixture was heated to 60°C for 0.5 h, during which time more CO_2 evolved, and the dark red solution was allowed to cool to room temperature and filtered through Celite. The filtrate was diluted to 800 mL and loaded onto a Sephadex SP C-25 cation exchange column, and washed with 0.1 M $NaClO_4$ solution. The collected pink band was discarded, and the main fraction was eluted with 0.15 M $NaClO_4$. A fraction of 120 mL was collected and concentrated to 20 mL. On standing at 4°C, a red powder (0.104 g, 12 %) formed, which was collected by filtration, washed with isopropanol and diethyl ether, and air-dried. ν_{max} (ATR)/cm^{-1} 3560w, br (H_2O), 3121w (pz), 1658s (CO_3), 1070s, br (ClO_4), 750s (γ pz), 622s (pz). λ_{max}/nm (ε/L mol^{-1} cm^{-1}) 499 (224). δ_H (CD_3CN, 400 MHz) 8.42 (1H, d, J 2.4, H_a), 8.40 (1H, m, H_a), 8.05 (2H, m, H_g), 7.97 (2H, d, J 2.4, H_c), 7.84 (1H, dd, J 2.5, 0.7, H_c), 7.82 (1H, dd, J 2.5, 0.7, H_c), 7.22 (6H, dd, J 16.4, 0.5, H_a and H_i), 6.69 (1H, td, J 2.5, 0.5, H_b), 6.65 (1H, td, J 2.5, 0.6, H_b), 6.44 (2H, tt, J 2.6, 0.6, H_b), 5.59 (4H, m, H_h), 5.01 (2H, m, H_d or H_e), 4.85 (2H, m, H_f), 4.69 (2H, m, H_d or H_e), 4.34 (2H, d, J 15.8, H_d or H_e), 4.19 (2H, dd, J 14.8, 4.3, H_d or H_e), 3.62 (2H, ddd, J 16.6, 11.0, 6.2, H_d or H_e), 3.49 (4H, m, H_d or H_e), 3.16 (2H, dd, J 14.2, 4.4, H_d or H_e), 2.75 (2H, m, H_d or H_e). δ_C (CD_3CN) 145.5, 143.1, 143.0, 137.2, 137.0, 134.8, 128.8, 128.7, 128.3, 125.2, 108.7, 108.2, 57.6, 57.3, 57.7, 57.4, 57.3, 55.2, 47.4, 45.9. Diffusion coefficient (CD_3CN): 8×10^{-10} m^2 s^{-1}. m/z (HRMS ESI; CH_3CN) 1011.1577; {[Co$_2$(**2d**)(O_2CO)$_2$](ClO_4)}$^+$ requires 1011.1617. Found: C 35.8, H 4.2, N 18.6. [($C_{34}H_{42}N_{16}$)Co$_2$(O_2CO)$_2$](ClO_4)$_2$·5H_2O requires C 36.0, H 4.4, N 18.9 %.

[Co₃(**2e**)(O₂CO)₃](ClO₄)₃ (**3e**)

Ligand **2e** (0.428 g, 0.440 mmol) was dissolved in H_2O (25 mL) which had been adjusted to pH ~1 with concentrated HCl. Na_3[Co(CO_3)$_3$]·$3H_2O$ (1.45 g, 4.01 mmol) was added, resulting in evolution of CO_2. The mixture was heated to 60°C for 0.5 h, during which time more CO_2 evolved, and the dark red solution

was allowed to cool to room temperature and filtered through Celite. The filtrate was diluted to 1 L and loaded onto a Sephadex SP C-25 cation exchange column, and washed with 0.1 M $NaClO_4$ solution. The collected pink band was discarded, and the main fraction was eluted with 0.2 M $NaClO_4$. A fraction of 120 mL was collected and concentrated to 20 mL. On standing, at 4°C, a red powder (0.107 g, 14 %) formed, which was collected by filtration, washed with isopropanol and diethyl ether, and air-dried. v_{max} (ATR)/cm^{-1} 3436w, br (H_2O), 3049w (Ar–H), 1660s (CO_3), 1071s, br (ClO_4), 749s (γ pz), 621s (pz). λ_{max}/nm (ε/L mol^{-1} cm^{-1}) 497 (344). δ_H (CD_3CN, 500 MHz) 8.45 (1H, m, H_a), 8.41 (3H, d, J 2.3, H_a), 8.18 (1H, s, H_g), 8.10 (3H, m, H_g), 8.03 (3H, d, J 2.6, H_c), 8.01 (1H, d, J 2.7, H_c), 7.81 (4H, dt, J 2.6, 1.1, H_c), 7.25 (4H, s, H_a), 7.04 (2H, s, H_i), 6.95 (1H, s, H_i), 6.69 (5H, d, J 1.2, H_b), 6.49 (4H, m, H_b), 6.46 (1H, s, H_i), 5.57 (9H, m, H_h), 5.15 (3H, dd, J 19.7, 14.9, H_f), 5.07 (3H, m, H_d or H_e), 4.98 (4H, m, H_d or H_e and H_f), 4.89 (1H, m), 4.76 (4H, m, H_d or H_e), 4.29 (9H, m, H_d or H_e and H_f), 3.66 (4H, dd, J 16.4, 11.4, H_d or H_e), 3.55 (8H, m, H_d or H_e), 3.19 (3H, m, H_d or H_e), 2.85 (3H, t, J 5.2, H_d or H_e). δ_C (CD_3CN) 146.2, 146.1, 143.1, 142.9, 137.3, 137.0, 136.7, 136.3, 127.2, 126.4, 125.9, 125.8, 108.8, 108.3, 57.6, 57.3, 54.9, 54.6, 47.5, 46.0. Diffusion coefficient (CD_3CN): 7×10^{-10} m^2 s^{-1}. m/z (HRMS ESI; CH_3CN) 1527.1822; $\{[Co_3(2e)(O_2CO)_3](ClO_4)_2\}^+$ requires 1527.1936, 714.1165; $\{[Co_3(2e)(O_2CO)_3](ClO_4)\}^{2+}$ requires 714.1223. Found: C 34.2, H 4.0, N 18.9. $[(C_{48}H_{60}N_{24})Co_3(O_2CO)_3](ClO_4)_2 \cdot 8H_2O$ requires C 34.5, H 4.4, N 19.0 %.

Crystal Structure Data

X-Ray crystallographic data for complexes **3a** and **3b** were collected at 93 K on a Bruker Kappa APEX-II system using graphite-monochromated Mo$_{K\alpha}$ radiation with exposures over 0.5°, and were corrected for Lorentz and polarization effects using *SAINT*[26] and for absorption using *SADABS*.[27] Structures were solved with *SHELXS-97*[28] and refined using *SHELXL*[28] within the *WinGX*[29] package. All non-H atoms were assigned anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions. The perchlorate anion in the structure of complex **3b** was modelled in two disordered parts, and the thermal ellipsoids of the chlorine atom and one of the oxygen atoms in one of these parts were further restrained using the ISOR command.

X-Ray crystallographic data for complex **3c** were collected at 100 K on an Agilent Supernova system using mirrored Cu$_{K\alpha}$ radiation with exposures over 1°, and were corrected for Lorentz and polarization effects and for X-ray absorption using the *CrysAlisPro* package version 171.36.28.[30] The structure was solved with *OLEX-2*[31] within the *CrysAlisPro* package. All non-H atoms were assigned anisotropic thermal parameters, and hydrogen atoms were placed in calculated positions.

3a, $C_{21}H_{26}ClCoN_8O_8$, M 612.88, monoclinic, space group $P2_1/c$, a 11.230(2), b 22.277(4), c 10.409(2) Å, α 90°, β 110.529 (8)°, γ 90°, V 2438.6(8) Å^3, Z 4, crystal size 0.31 × 0.20 × 0.08 mm, colour red, collection temperature 93(2) K, Mo$_{K\alpha}$ radiation, λ 0.71073 Å, μ(Mo$_{K\alpha}$) 0.880 mm^{-1}, $T_{min,max}$ 0.7721, 0.9330, $2\theta_{max}$ 52.84, N 32366, N_{ind} 5000, N_{obs} 5000, R_{int} 0.1369, R_1 ($I > 2\sigma(I)$) 0.0540, $wR(F^2)$ ($I > 2\sigma(I)$) 0.1398, R_1 (all data) 0.0684, $wR(F^2)$ (all data) 0.1508, *GooF* (all) 1.044.

3b, $C_{25}H_{36}ClCoN_8O_9$, M 598.85, monoclinic, space group $P2_1/c$, a 16.9721(9), b 9.6280(5), c 15.6511(10) Å, α 90°, β 112.141(2)°, γ 90°, V 2368.9(2) Å^3, Z 4, crystal size 0.39 × 0.31 × 0.16 mm, colour red, collection temperature 93(2) K, Mo$_{K\alpha}$ radiation, λ 0.71073 Å, μ(Mo$_{K\alpha}$) 0.903 mm^{-1}, $T_{min,max}$

0.7196, 0.8689, $2\theta_{max}$ 52.82, N 11581, N_{ind} 4829, N_{obs} 4829, R_{int} 0.0518, R_1 ($I > 2\sigma(I)$) 0.0432, $wR(F^2)$ ($I > 2\sigma(I)$) 0.0853, R_1 (all data) 0.0707, $wR(F^2)$ (all data) 0.1057, *GooF* (all) 1.029.

3c, $C_{23}H_{28}ClCoN_{11}O_7$, M 664.94, triclinic, space group P-1, a 8.0665(2), b 11.9096(3), c 16.1450(4) Å, α 72.124(2)°, β 79.830 (2)°, γ 72.991(2)°, V 1405.15(7) (2) Å^3, Z 2, crystal size 0.18 × 0.07 × 0.07 mm, colour red, collection temperature 100.01(10) K, Cu$_{K\alpha}$ radiation, λ 1.54184 Å, μ(Cu$_{K\alpha}$) 6.228 mm^{-1}, $T_{min,max}$ 0.218, 0.598, $2\theta_{max}$ 154.08, N 23842, N_{ind} 5844, N_{obs} 5844, R_{int} 0.0657, R_1 ($I > 2\sigma(I)$) 0.0437, $wR(F^2)$ ($I > 2\sigma(I)$) 0.1185, R_1 (all data) 0.0533, $wR(F^2)$ (all data) 0.1137, *GooF* (all) 1.034.

Supplementary Material

Additional experimental procedures, ^{1}H and DOSY NMR spectra, HRMS ESI spectra and crystallographic data are available on the Journal's website. Details of the DFT calculations and the Cartesian coordinates for optimized structures of the binuclear isomers are also provided.

Acknowledgements

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[15] *This method gave complex **3b** in very low yield (7 %), and thus we used an alternative route to synthesize the compound. Ligand **2b** and cobalt(II) perchlorate hexahydrate were combined in CH$_3$CN, followed by addition of 30 % H$_2$O$_2$ and NaHCO$_3$. Stirring overnight gave a red solution, which was worked up as described above, giving complex **3b** in modest yield (42 %).*

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