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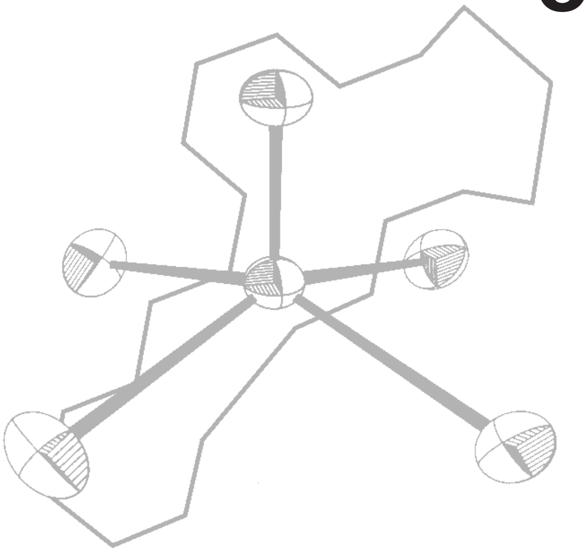

Volume 52, 1999

A journal for the publication of original research
in all branches of chemistry and chemical technology

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Aust. J. Chem., 1999, **52**, 817–822

The Preparation of a Mixed-Ligand Cobalt(III) Complex of DPPZ and Ethylenediamine: Crystal Structures of $[\mathrm{Co(en)_2(DPPZ)}](\mathrm{ClO_4})_3.0\cdot5\mathrm{H_2O}$, $[\mathrm{Co(en)_2(bpy)}]\mathrm{Br(ClO_4)_2}$ and $[\mathrm{Co(en)_2(phen)}]\mathrm{Br_3}$

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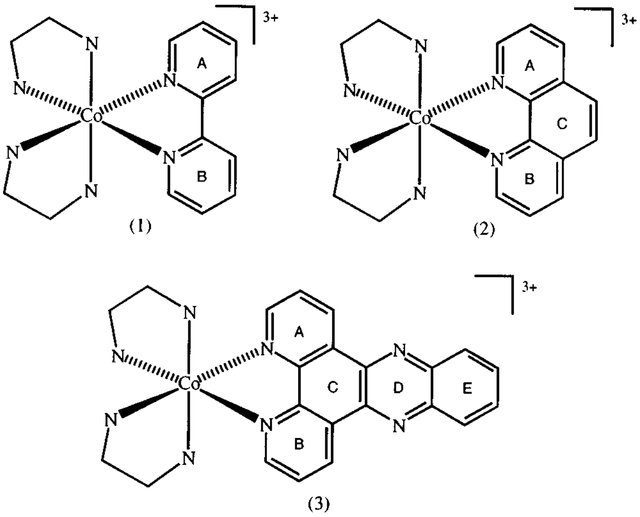
The complex $[\mathrm{Co(en)_2(DPPZ)}](\mathrm{ClO_4})_3$ (3) has been synthesized, and the crystal structures of this complex and those of $[\mathrm{Co(en)_2(bpy)}]\mathrm{Br(ClO_4)_2}$ (1) and $[\mathrm{Co(en)_2(phen)}]\mathrm{Br_3}$ (2) have been determined. Crystal data for (1): M 614·13, monoclinic, space group $C2/c$ (No. 15), a 16·7834(16), b 16·308(3), c 8·3167(15) Å, β 104·932(11)°, V 2199·4(6) Å, $F(000)$ 1240, Z 4, D_c 1·855 g cm^{-3}, μ 2·895 cm^{-1}, Mo K$\bar{\alpha}$ (graphite monochromatized) radiation, λ 0·71073 Å, T 293(1) K. Crystal data for (2): M 599·07, triclinic, space group $P\bar{1}$ (No. 2), a 7·7113(11), b 10·633(2), c 12·9884(18) Å, α 85·745(15), b 78·258(11), γ 74·967(16)°, V 1006·7(3) Å, $F(000)$ 588, Z 2, D_c 1·976 g cm^{-3}, μ 6·819 cm^{-1}, Mo K$\bar{\alpha}$ (graphite monochromatized) radiation, λ 0·71073 Å, T 293(1) K. Crystal data for (3): M 773·44, monoclinic, space group $P2_1/c$ (No. 14), a 20·296(2), b 9·6197(11), c 15·725(2) Å, β 92·850(10)°, V 3066·4(6) Å, $F(000)$ 1579, Z 4, D_c 1·675 g cm^{-3}, μ 0·898 cm^{-1}, Mo K$\bar{\alpha}$ (graphite monochromatized) radiation, λ 0·71073 Å, T 293(1) K. In all three complexes the cobalt is in the usual octahedral environment, with the cations being linked by hydrogen bonds between the amine hydrogens and the anions into extended structures.

Introduction

We are presently interested in mixed-ligand cobalt(III) complexes of aromatic nitrogen donors and ethylenediamine (en) for their potential use as electron acceptor units in bridged electron donor–acceptor complexes. The ligands 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) and dipyrido[3,2-*a*:2′,3′-*c*]phenazine (DPPZ) have been chosen for this work as it is relatively straightforward to prepare functionalized derivatives of these which may then be coupled to electron donor groups. The complexes $[\mathrm{Co(en)_2(bpy)}]\mathrm{Br(ClO_4)_2}$ (1) and $[\mathrm{Co(en)_2(phen)}]\mathrm{Br_3}$ (2) are well known[1–3] (Fig. 1) but hitherto the DPPZ analogue has not been prepared. Herein we describe the synthesis of the new complex $[\mathrm{Co(en)_2(DPPZ)}](\mathrm{ClO_4})_3.0\cdot5\mathrm{H_2O}$ (3) via the precursor $[\mathrm{Co(en)_2(dione)}](\mathrm{ClO_4})_3$,* and its characterization by single-crystal X-ray diffraction. It is of note that despite the interesting properties and the large amount of work that has been performed on complexes of DPPZ[4–6] there are relatively few reports on the crystal structure of these complexes.[6–7] Furthermore, no crystal structure of a cobalt(III) complex of this ligand has been reported. We also describe single-crystal X-ray diffraction studies of the related analogues $[\mathrm{Co(en)_2(bpy)}]\mathrm{Br(ClO_4)_2}$ (1) and $[\mathrm{Co(en)_2(phen)}]\mathrm{Br_3}$ (2).



(1) (2) (3)

Fig. 1. Series of cobalt(III) cations studied: $[\mathrm{Co(en)_2(bpy)}]^{3+}$ (1), $[\mathrm{Co(en)_2(phen)}]^{3+}$ (2) and $[\mathrm{Co(en)_2(DPPZ)}]^{3+}$ (3).

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* The ligand represented as 'dione' is 1,10-phenanthroline-5,6-quinone.

Manuscript received 13 May 1999

10.1071/CH99060 0004-9425/99/080817$05.00

Experimental

Preparations

The complexes $[Co(en)_2(bpy)]\,Br(ClO_4)_2$ (1) and $[Co(en)_2(phen)]\,Br_3$ (2) were synthesized according to literature methods.[8,9] Ultraviolet/visible spectra were recorded on aqueous solutions by means of a Hewlett–Packard 8452A diode array spectrophotometer. ^1H n.m.r. spectra were recorded on a Varian Unity-300 spectrometer with D_2O as solvent. Chemical shifts (δ, positive downfield) are given in ppm and sodium 3-trimethylsilylpropanesulfonate was used as an internal standard. ^1H chemical shift data are not given for exchangeable (amine) protons due to the variance between samples in position and intensity of these signals. Elemental analysis was performed by the Microanalytical Laboratory, Department of Chemistry, University of Otago, Dunedin, New Zealand. All reagents used were of A.R. grade.

*Bis(ethylenediamine)(1,10-phenanthroline-5,6-quinone)-cobalt(*III*) Perchlorate, $[Co(en)_2(dione)]\,(ClO_4)_3$*

Concentrated H_2SO_4 (12 ml) followed by concentrated HNO_3 (6 ml) was slowly added to $[Co(en)_2(phen)]\,Br_3$ (1·89 g, $3{\cdot}2\times10^{-3}$ mol) and NaBr (1·07 g, $1{\cdot}0\times10^{-2}$ mol) with cooling. The mixture was heated to boiling and refluxed for 40 min. Heating was then reduced and the condenser removed to allow the bromine vapours to escape during 5 min of gentle boiling. The resultant orange-yellow solution was removed from the heat and cooled to 0°C, then added dropwise, with stirring, to a solution of $NaClO_4.H_2O$ (4·26 g, $3{\cdot}0\times10^{-2}$ mol) in H_2O (40 ml). Upon cooling overnight at −20°C fine yellow crystals were deposited. These were collected, washed with ice-cold 0·1 M HCl (2×5 ml), then with ice-cold ethanol (1×5 ml) and dried under vacuum to give a yellow powder (1·79 g). N.m.r. indicated this material to be a mixture of $[Co(en)_2(dione)]\,(ClO_4)_3$ (70%) and $[Co(en)_2(5\text{-}NO_2phen)]\,(ClO_4)_3$ (30%). ^1H n.m.r. δ (D_2O) of major component: 2·87, br, 4H, en CH_2; 3·08, br, 4H, en CH_2; 8·05, dd, 2H, dione CH; 8·71, d, 2H, dione CH; 8·69, d, 2H, dione CH. Minor component: 2·87, br, 4H, en CH_2; 3·08, br, 4H, en CH_2; 8·16, dd, 1H, 5-NO_2phen CH; 8·23, dd, 1H, 5-NO_2phen CH; 8·79, d, 1H, 5-NO_2phen CH; 8·82, d, 1H; 5-NO_2phen CH; 8·86, d, 1H, 5-NO_2phen CH; 9·1, m, 2H, 5-NO_2phen CH.

This material was used without further purification in the next step.

*(Dipyrido[3,2-*a*:2′,3′-*c*]phenazine)bis(ethylenediamine)-cobalt(*III*) Perchlorate, $[Co(en)_2(dppz)]\,(ClO_4)_3.0{\cdot}5H_2O$ (3)*

Crude $[Co(en)_2(dione)]\,(ClO_4)_3$ (1·00 g) was dissolved with warming in deaerated (by flushing with N_2) H_2O (40 ml) and concentrated HCl (1 ml). A solution of benzene-1,2-diamine (0·16 g, $1{\cdot}5\times10^{-3}$ mol) in EtOH (20 ml) was flushed with N_2 gas for a period of 5 min. This solution was then added to the still warm $[Co(en)_2(dione)]\,(ClO_4)_3$ solution under a nitrogen atmosphere. The yellow cobalt solution immediately turned a dark orange-red. Upon heating to reflux the solution became light orange in colour. Reflux was continued for a further 5 min, then the solution was cooled gradually to −20°C under N_2 whereupon an orange precipitate formed. The precipitate was collected under a nitrogen atmosphere and washed with ice-cold H_2O (2×2 ml), then EtOH (1×2 ml), and dried at the pump. The product was recrystallized twice from the minimum amount of acidified (1% $HClO_4$ (70%)) warm water to yield *$[Co(en)_2(dppz)]\,(ClO_4)_3.0{\cdot}5H_2O$* (0·32 g) (Found: C, 34·4; H, 3·4; Cl, 13·8; N, 14·6. $C_{22}H_{27}Cl_3CoN_8.\frac{1}{2}H_2O$ requires C, 34·4; H, 3·5; Cl, 13·8; N, 14·6%). Visible λ_{max} 464 nm, ϵ_{max} 121 l. mol^{-1} cm^{-1}. ^1H n.m.r. δ (D_2O) 2·97, br, 4H, en CH_2; 3·26, m, 4H, en CH_2; 8·25, dd, 2H, dppz CH; 8·52, dd, 2H, dppz CH; 8·9, dd, 2H, dppz CH; 9·27, d, 2H, dppz CH; 10·12, d, 2H, dppz CH.

Crystallography

Crystal Data

$[Co(en)_2(bpy)]\,Br(ClO_4)_2$ (1); M 614·13, monoclinic, space group $C\,2/c$ (No. 15), a 16·7834(16), b 16·308(3), c 8·3167(15) Å, β 104·932(11)°, V 2199·4(6) Å^3, $F(000)$ 1240, Z 4, D_c 1·855 g cm^{-3}, μ 2·895 cm^{-1}, Mo $K\bar{\alpha}$ (graphite monochromatized) radiation, λ 0·71073 Å, T 293(1) K.

$[Co(en)_2(phen)]\,Br_3$ (2); M 599·07, triclinic, space group $P\,\bar{1}$ (No. 2), a 7·7113(11), b 10·633(2), c 12·9884(18) Å, α 85·745(15), β 78·258(11), γ 74·967(16)°, V 1006·7(3) Å^3, $F(000)$ 588, Z 2, D_c 1·976 g cm^{-3}, μ 6·819 cm^{-1}, Mo $K\bar{\alpha}$ (graphite monochromatized) radiation, λ 0·71073 Å, T 293(1) K.

$[Co(en)_2(dppz)]\,(ClO_4)_3.0{\cdot}85H_2O$ (3); M 773·44, monoclinic, space group $P\,2_1/c$ (No. 14), a 20·296(2), b 9·6197(11), c 15·725(2) Å, β 92·850(10)°, V 3066·4(6) Å^3, $F(000)$ 1579, Z 4, D_c 1·675 g cm^{-3}, μ 0·898 cm^{-1}, Mo $K\bar{\alpha}$ (graphite monochromatized) radiation, λ 0·71073 Å, T 293(1) K.

Data Collection and Structure Solution

Single X-ray quality crystals of (1) and (2) were grown by the slow evaporation of aqueous solutions of the complexes. The data for (1) were collected from a light orange-brown needle of approximate dimensions 0·09 by 0·19 by 0·37 mm and for (2) from an irregular brown prism of approximate dimensions 0·24 by 0·41 by 0·39 mm. Single X-ray quality crystals of (3) were grown by the slow diffusion of ethanol into an aqueous solution of the complex and data were collected from an orange plate of approximate dimensions 0·13 by 0·16 by 0·23 mm in a sealed capillary tube in the presence of mother liquor.

Details of the data collection refer to $[Co(en)_2(bpy)]\,Br(ClO_4)_2$ (1). The corresponding details for $[Co(en)_2(phen)]\,Br_3$ (2) and $[Co(en)_2(dppz)]\,(ClO_4)_3$ (3), respectively, are given in parentheses. Accurate unit cell parameters were calculated by a least-squares procedure from the setting angles of 25 reflections. Intensity data were collected on an Enraf–Nonius CAD4-MachS single-crystal X-ray diffractometer. The $\omega:2\theta$ scan method and graphite monochromatized Mo $K\bar{\alpha}$ radiation, λ 0·71073 Å, were used. During collection three intensity control reflections were monitored every 9600 s of X-ray exposure time. These showed no deterioration in intensity for all complexes. A total of 2567 (5384, 6791) reflections were measured, $2 \leq 2\theta \leq 26°$ ($2 \leq 2\theta \leq 27°$, $2 \leq 2\theta \leq 25°$), of which 2162 (4390, 5388) were unique (R_{int} 0·0133 (0·0122, 0·0321)) and 1799 (3601, 3317) considered observed ($I \geq 2\sigma(I)$). Corrections were applied for Lorentz and polarization effects as well as for absorption, the corrections being evaluated by Gaussian integration.[10] The maximum and minimum transmission factors were 0·7755 and 0·6085 (0·3545 and 0·0801; 0·9099 and 0·8439).

The structures of (1) and (3) were solved by a combination of Patterson, direct methods and difference synthesis[11,12] whilst the structure of (2) was solved by a combination of direct methods and difference synthesis.[11,12] The structure of (3) was found to be disordered over two orientations related by an approximately 9° rotation about an axis perpendicular to the dppz ligand. This disorder was greatest for the atoms of the dppz farthest from the cobalt, while those atoms closest to the cobalt showed little evidence of disorder, as did the atoms of the ethylenediamine ligand. This disorder was modelled by including the atoms of the dppz ligand in two different positions, with both components constrained to have similar geometry and with the atoms of ring E constrained to ideal geometry. For (1) and (3) the perchlorate anions were found to be disordered and they were included in the refinement in two orientations constrained to geometrical estimates. The site of the water molecule in (3) was found to be partially occupied and also disordered, and hence was included as two components, each given a refinable occupancy factor. The three structures were refined by a full-matrix least-squares procedure based on F^2. Hydrogen atoms were located from the difference map and were constrained to geometrical estimates. Final refinement was carried out with anisotropic displacement parameters applied to all non-hydrogen atoms and isotropic displacement parameters for the hydrogen atoms; for (3) the displacement parameters of the disordered DPPZ ligand were constrained to be nearly isotropic. A weighting scheme of type $[\sigma^2(F_o{}^2)+(\mathsf{a}P)^2+\mathsf{b}P]^{-1}$ where $\mathsf{a} = 0\cdot0868$ and $\mathsf{b} = 29\cdot7652$ ($0\cdot0958$ and $3\cdot5531$; $0\cdot1289$ and $3\cdot0407$) was used where $P = (\max(F_o{}^2,0)+2F_c{}^2)/3$. At convergence, $R(I \geq 2\sigma(I))$ was $0\cdot0554$ ($0\cdot0524$, $0\cdot0722$), wR (all data) was $0\cdot1754$ ($0\cdot1556$, $0\cdot2226$), and S was $1\cdot075$ ($1\cdot070$, $1\cdot066$), where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR = (\Sigma(w(F_o{}^2-F_c{}^2)^2)/\Sigma w(F_o{}^2)^2)^{1/2}$. For (1) the final difference map showed a number of electron density peaks (maximum and minimum peak height $1\cdot26$ and $-1\cdot86$ e Å^{-3}) which suggested that the structure was disordered over two positions. Attempts to model this disorder, however, were not successful. For (2) the maximum and minimum peak heights were $1\cdot45$ and $-1\cdot98$ e Å^{-3}, close to the bromine atoms, either due to some disorder of the anions, or to inaccuracies in the absorption corrections as a result of measuring an irregularly shaped crystal. For (3) the maximum and minimum peak heights were $0\cdot688$ and $-0\cdot597$ e Å^{-3} respectively and were located close to the perchlorate anions. That only $0\cdot85$ mole equiv. of water was able to be located suggests either that some disordered components were not located, or that some loss of water occurred during data collection. On exposure to the atmosphere, the crystals lose water and microanalysis revealed only half the water remained.

The atomic scattering factors were those incorporated in the SHELXL-97 program system. Calculations were carried out on a Vaxstation 4000VLC computer system. Figs 2–5 were prepared from the output of ORTEPII.[13] Selected bond lengths and angles for complexes (1)–(3) are given in Tables 1–3. Material deposited* includes all atom coordinates, complete geometry, displacement parameters, and a listing of the observed and calculated structure factors.

Results and Discussion

Synthesis

Mixed-ligand complexes of cobalt(III) involving ethylenediamine with other ligands are often prepared by ligand exchange reactions using the precursor cations $[\mathrm{Co(en)_2Cl_2}]^+$ or $[\mathrm{Co(en)_2(OH)(OH_2)}]^{2+}$. This method was used to prepare the complexes $[\mathrm{Co(en)_2(bpy)}]\,\mathrm{Br(ClO_4)_2}$ and $[\mathrm{Co(en)_2(phen)}]\,\mathrm{Br_3}$.[8,9] Surprisingly, this approach could not be used to prepare the ion $[\mathrm{Co(en)_2(DPPZ)}]^{3+}$ as reaction between either the $[\mathrm{Co(en)_2Cl_2}]^+$ or $[\mathrm{Co(en)_2(OH)(OH_2)}]^{2+}$ ions and DPPZ in a variety of solvents led to the precipitation of dark brown insoluble products from the reaction mixture or an apparent lack of reaction over extended periods of time. The preparation of the related complex ion, $[\mathrm{Ru(bpy)_2(DPPZ)}]^{2+}$, has been successfully accomplished by the coupling of $[\mathrm{Ru(bpy)_2(dione)}]^{2+}$ with benzene-1,2-diamine.[5] A similar method proved successful for the synthesis of $[\mathrm{Co(en)_2(DPPZ)}]\,\mathrm{(ClO_4)_3}$. The precursor, $[\mathrm{Co(en)_2(dione)}]\,\mathrm{(ClO_4)_3}$, was prepared by using a modification of the method of Gillard.[9] The 1,10-phenanthroline ligand on the complex $[\mathrm{Co(en)_2(phen)}]\,\mathrm{Br_3}$ was oxidized to the coordinated 1,10-phenanthroline-5,6-quinone by refluxing the complex in a mixture of concentrated sulfuric acid, concentrated nitric acid and sodium bromide (conditions similiar to this are used to prepare free 1,10-phenanthroline-5,6-quinone directly from 1,10-phenanthroline[14]). The ^{1}H n.m.r. spectrum of the product indicated that the complex $[\mathrm{Co(en)_2(dione)}]\,\mathrm{(ClO_4)_3}$ was formed as the major component (*c.* 70%) with a minor impurity (presumably $[\mathrm{Co(en)_2(5\text{-}NO_2phen)}]\,\mathrm{(ClO_4)_3}$ (*c.* 30%)) being present. It was expected that it would be far easier to separate likely impurities (such as $[\mathrm{Co(en)_2(5\text{-}NO_2phen)}]\,\mathrm{(ClO_4)_3}$) from the DPPZ complex rather than from the dione complex. As a result the crude material was used without further purification. The coupling reaction of $[\mathrm{Co(en)_2(dione)}]\,\mathrm{(ClO_4)_3}$ with benzene-1,2-diamine to form the cation $[\mathrm{Co(en)_2(DPPZ)}]^{3+}$ was carried out under nitrogen in acidic conditions (reaction at neutral pH in solutions open to the air produced large amounts of a brown unidentified water-insoluble product). The DPPZ complex was isolated and recrystallized as a perchlorate salt.

Description of Crystal Structures

In each of the three structures the cobalt atom is in the usual octahedral environment, with all Co–N bond distances ($1\cdot94$–$1\cdot97$ Å range) and ligand bite angles typical of those found for other cobalt–nitrogen complexes.[15–17]

The crystal structure of (1) verifies the formation of this complex as a somewhat unusual mixed salt as first reported by Gillard *et al.*;[8] the cation is shown in Fig. 2. The cobalt atom lies on a twofold axis and in the least-squares plane of the bipyridine ligand (maximum deviation $0\cdot35$ Å for N(2)). The two rings of the bipyridine ligand are almost parallel, the dihedral angle being $0\cdot4(3)°$; however, they deviate somewhat from coplanarity with one ring lying approximately $0\cdot1$ Å above the other, giving rise to a slight S-bend along the ligand.

The structure of (2) (Fig. 3) is similar to that of (1); however, in this case the cobalt atom lies $0\cdot196(4)$ Å out of the plane of the phenanthroline ligand (maximum deviation $0\cdot063(5)$ Å for C(8)). The phenanthroline ligand itself is curved in a bowl-shaped manner with rings A and C at an angle of $1\cdot7(3)°$, and B and C at an angle of $2\cdot5(3)°$. This deviation from coplanarity in both structures (1) and (2) is presumably due to ring strain associated with coordination to the metal centre. In both structures the hydrogens on the amine nitrogens are involved in hydrogen bonds with the anions, these interactions linking the cations into linear chains which lie along the *c*-axis for (1), and the *a*-axis for (2).

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Table 1. Selected bond lengths and angles for $[\mathrm{Co(en)_2(bpy)}]\,\mathrm{Br(ClO_4)_2}$

Symmetry transformations used to generate equivalent atoms: $' -x,\ y, -z+1/2$

Bond lengths (Å)		Bond angles (degrees)	
Co–N(2)	1·950(5)	N(2)–Co–N(2′)	82·8(3)
Co–N(2′)	1·950(5)	N(2)–Co–N(3′)	88·6(2)
Co–N(3′)	1·967(5)	N(2)–Co–N(3)	94·1(2)
Co–N(3)	1·967(5)	N(3′)–Co–N(3)	176·4(3)
Co–N(1′)	1·970(5)	N(2)–Co–N(1′)	172·2(2)
Co–N(1)	1·970(5)	N(3)–Co–N(1′)	92·9(2)
		N(2)–Co–N(1)	93·8(2)
		N(3)–Co–N(1)	84·6(2)
		N(1′)–Co–N(1)	90·4(3)

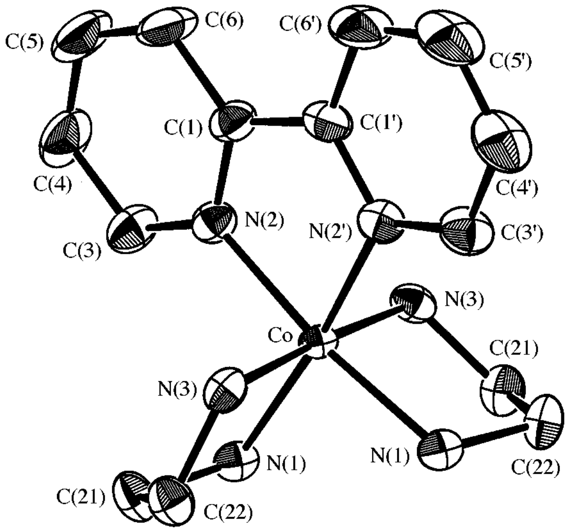

Fig. 2. Structure of the $[\mathrm{Co(en)_2(bpy)}]^{3+}$ cation. Displacement ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted. Symmetry code $'\ -x,\ y,\ -z+1/2$.

Table 2. Selected bond lengths and angles for $[\mathrm{Co(en)_2(phen)}]\,\mathrm{Br_3}$

Bond lengths (Å)		Bond angles (degrees)	
Co–N(21)	1·943(5)	N(21)–Co–N(10)	93·01(9)
Co–N(10)	1·956(4)	N(21)–Co–N(1)	91·57(19)
Co–N(1)	1·959(4)	N(10)–Co–N(1)	83·80(19)
Co–N(22)	1·961(4)	N(21)–Co–N(22)	85·27(19)
Co–N(31)	1·963(4)	N(10)–Co–N(22)	93·16(19)
Co–N(32)	1·965(5)	N(1)–Co–N(22)	175·51(19)
		N(21)–Co–N(31)	92·4(2)
		N(10)–Co–N(31)	173·6(2)
		N(1)–Co–N(31)	92·7(2)
		N(22)–Co–N(31)	90·64(19)
		N(21)–Co–N(32)	176·39(19)
		N(10)–Co–N(32)	89·74(19)
		N(1)–Co–N(32)	91·06(19)
		N(22)–Co–N(32)	92·2(2)
		N(31)–Co–N(32)	85·0(2)

Table 3. Selected bond lengths and angles for $[\mathrm{Co(en)_2(dppz)}]\,\mathrm{(ClO_4)_3}$

Bond lengths (Å)		Bond angles (degrees)	
Co–N(21)	1·950(5)	N(21)–Co–N(32)	176·5(2)
Co–N(32)	1·954(5)	N(21)–Co–N(5)	90·6(7)
Co–N(5)	1·963(7)	N(32)–Co–N(5)	92·4(7)
Co–N(31)	1·966(6)	N(21)–Co–N(31)	91·7(2)
Co–N(22)	1·969(5)	N(32)–Co–N(31)	85·4(2)
Co–N(4)	1·979(7)	N(5)–Co–N(31)	177·7(7)
		N(21)–Co–N(22)	84·7(2)
		N(32)–Co–N(22)	93·4(2)
		N(5)–Co–N(22)	90·9(4)
		N(31)–Co–N(22)	89·7(3)
		N(21)–Co–N(4)	86·5(7)
		N(32)–Co–N(4)	95·7(7)
		N(5)–Co–N(4)	82·1(4)
		N(31)–Co–N(4)	97·6(4)
		N(22)–Co–N(4)	168·7(6)

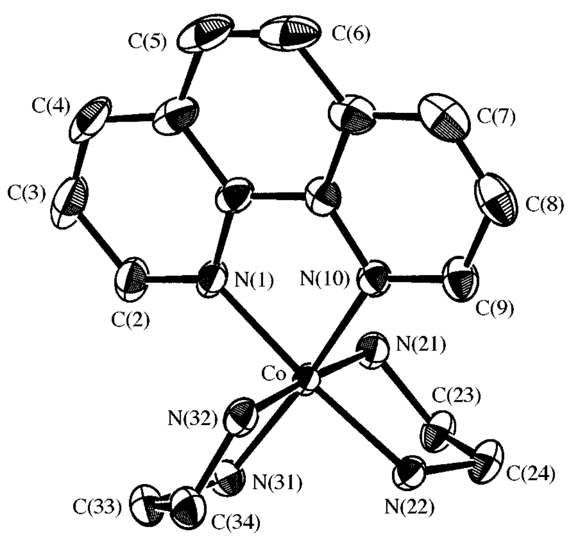

Fig. 3. Structure of the $[\mathrm{Co(en)_2(phen)}]^{3+}$ cation. Displacement ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted.

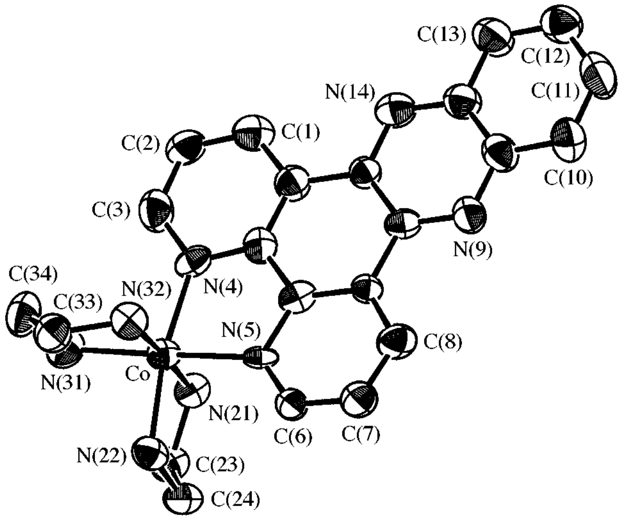

Fig. 4. Structure of the $[\mathrm{Co(en)_2(dppz)}]^{3+}$ cation. Displacement ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted.

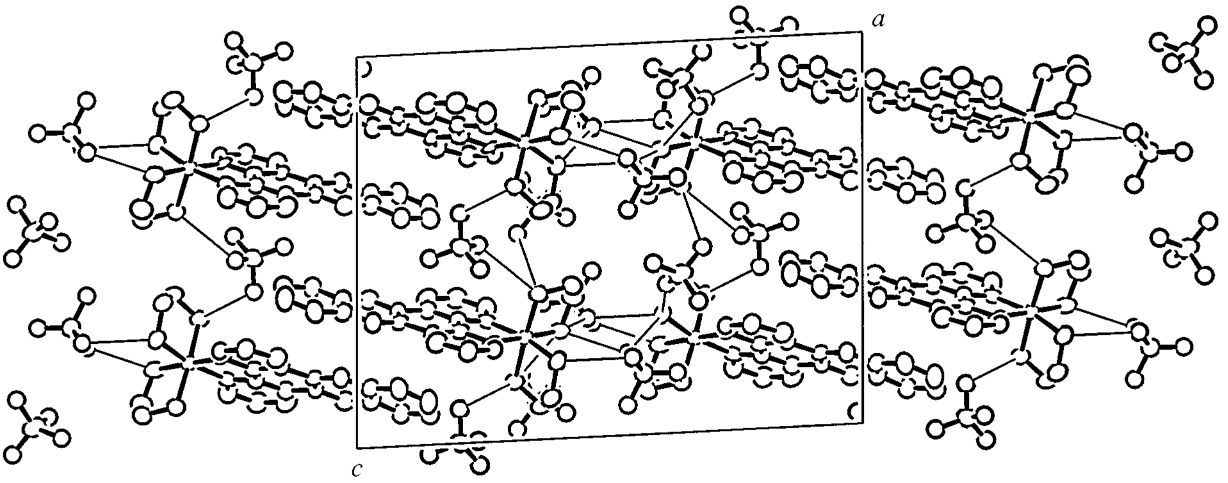

Fig. 5. View, down the *b* axis, of the packing and hydrogen bonding of $[Co(en)_2(DPPZ)](ClO_4)_3.0 \cdot 5H_2O$.

The crystal structure of (3), shown in Fig. 4, is of particular interest due to the extended π system of the DPPZ ligand. All previously reported structures containing the DPPZ ligand have shown crystal packing that appears to be driven by favourable π–π interactions of the extended conjugated systems of the ligands. The DPPZ ligands pack directly above one another, with a separation of about 3·5 Å, giving rise to ladder-type structures, where the DPPZ ligands form the rungs of the ladder and the metal atom and other ligands form the uprights. In (3) the DPPZ ligand is essentially planar (maximum deviation 0·104(9) Å for C(12)) with the cobalt atom lying in the ligand plane; the DPPZ has a bite angle of 82·1(4)°. However, the DPPZ ligands of adjacent molecules do not lie directly above each other (Fig. 5) but are displaced along the *b*-axis so that there is no overlap of any of the atoms of the ligands. This space is filled by the perchlorate anions which are involved in hydrogen bonds with the amine hydrogens of the ethylenediamine ligands; these interactions link the molecules into zigzag chains which lie along the *c*-axis. The other perchlorate anions are also involved in hydrogen bonds, further linking the cations into helical chains along the *b*-axis. It is possible that a change of anion, particularly to an anion not able to hydrogen bond, may result in a structure where significant π–π interactions of the DPPZ ligands occur.

Acknowledgments

The authors would like to acknowledge the financial support of the Australian Research Council, and A.M.F. the support of an AINSE scholarship.

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