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# Mixtures obtained by reacting *trans*-(±)-1,2-diaminocyclohexane with acetylacetone in the presence of simple cobalt(II) salts

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**Abstract**

In the absence of a metal ion, racemic *trans*-1,2-diaminocyclohexane (*trans*-(±)DCH) reacts with acetylacetone (acacH) (1:2.5 mole ratio) to form the bisoxoenamine condensation product, boe (**1**). $CoCl_2{\cdot}6H_2O$ and $Co(ClO_4)_2{\cdot}6H_2O$ each react with *trans*-(±)DCH in air to give complexes containing the oxidised Co(III) ion, $[Co((\pm)DCH)_3]^{3+}$, which does not subsequently react with added acacH to give a Schiff base complex. Mixtures of complexes are obtained from one-pot reactions involving *trans*-(±)DCH, a simple Co(II) salt and acacH (1:1:2.5 mole ratio). When $CoCl_2{\cdot}6H_2O$ is used, the mixed-ligand Co(II) complex $[Co((\pm)DCH)Cl_2]$ (**4**) precipitates first and, after a period of weeks, the Co(II) complex $(diazH)_2[CoCl_4]$ (**5**) ($diazH^+$ is a diazepinium cation), the Co(II) complex $[Co(boe)Cl_2]_n$ (**6**) and the Co(III) complex $[Co(acac)_3]$ (**7**), co-crystallise from the mother liquor. Using $Co(ClO_4)_2{\cdot}6H_2O$ in the reaction with *trans*-(±)DCH and acacH also gives a mixture of products. Complexes **7**, the Co(II) complex $[Co_2(acac)_4(H_2O)_2][Co(acac)(H_2O)_4]ClO_4{\cdot}EtOH$ (**8**) and the Co(III) complex $[Co(acac)_2(\pm)DCH]ClO_4$ (**9**) co-crystallise. Complexes **1**, **5**, **7**, **8** and **9** were characterised using X-ray crystallography. The major difference between using $CoCl_2{\cdot}6H_2O$ and $Co(ClO_4)_2{\cdot}6H_2O$ in reactions involving (±)DCH and acacH is that no DCH/acacH condensation products are identified in the product mixtures when the perchlorate salt is employed. 

*Keywords:* *trans*-(±)-1,2-Diaminocyclohexane; Acetylacetone; Cobalt(II) salts; Schiff base complexes

## 1. Introduction

Condensation reactions involving β-diketones and α,ω-diamines can give a range of products depending on the experimental conditions [1,2].[1] For example, in Scheme 1, formation of the bisoxoenamine (a) is favoured in the pH range 6–10, whereas diazepine (b) production occurs under either more acidic or more alkaline conditions. In Scheme 2 the anil (a) is stabilized when $R = CH_3$ because of steric effects.

Diazepines are of significance in relation to the medicinally important 1,4-benzodiazepine tranquillizers [3]. *trans*-1,2-Diaminocyclohexane (*trans*-DCH) has frequently been used as the diamine in the production of diazepines and Schiff bases. For example, the structurally characterised compound, (5a*R*,9a*R*)-2,4-dimethyl-5a,6,7,8,9,9a-hexahydro-1*H*-1,5-benzodiazepine (Fig. 1), forms from the condensation of (1*R*,2*R*)-*trans*-1,2-diaminocyclohexane with 4-amino-3-penten-2-one [4]. Furthermore, chloride [5] and perchlorate [6] salts of 2,3-dihydro-1*H*-1,4-diazepinium cations have been prepared by condensing 1,2-diamines with acetylacetone (acacH). Ultraviolet spectral measurements on the chloride salt, synthesised from *trans*-(±)DCH and acacH, indicated planarity of the two fused rings in the cation and suggested delocalisation of the 6 π electrons (Scheme 3).

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[1] Representations of the keto-enol tautomers of diketones and imino enol-amino ketone tautomers of the Schiff bases are given in the forms presented in the various literature citations.

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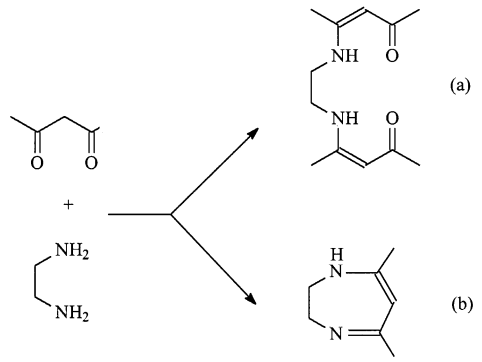
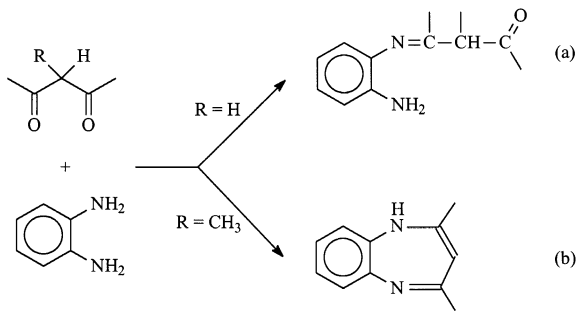
Condensing acacH with either *trans*-(+)-DCH or *trans*-(*meso*)-DCH in a 2:1 mole ratio gives the respective Schiff base ligands (Scheme 4) [7]. In the absence of X-ray crystallographic studies, structural assignment of the product was based on spectroscopic data.




Scheme 1.




Scheme 2.

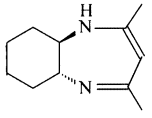
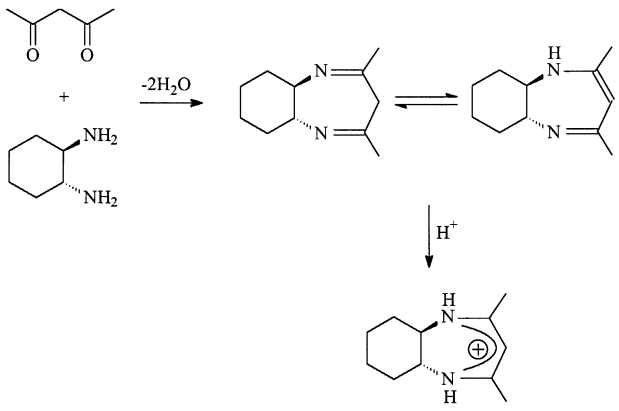
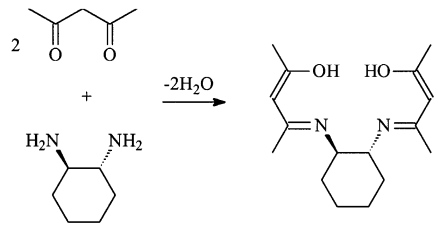



Fig. 1. (5a*R*,9a*R*)-2,4-Dimethyl-5a,6,7,8,9,9a-hexahydro-1*H*-1,5-benzodiazepine.




Scheme 3.




Scheme 4.

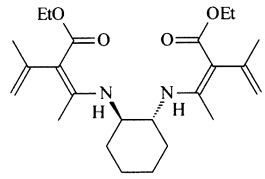



Fig. 2. Schiff base made from *trans*-1*S*,2*S*-(+)-DCH and ethyl (ethoxymethylene)acetoacetate.

A family of Schiff bases was generated by reacting *cis*-1,2-diaminocyclohexane and resolved forms of *trans*-DCH with ethoxymethylene-β-carbonyls in a 1:2 mole ratio [8]. The Schiff base formed using *trans*-1*S*,2*S*-(+)-DCH and ethyl (ethoxymethylene)acetoacetate was structurally characterised (Fig. 2) and a variety of Ni(II) and Cu(II) complexes was also prepared using the various bases.

Bailey et al. [1] noted that with Schiff bases derived from *trans*-DCH the bite sizes limit complex formation because of the steric constraint introduced by an unfavourable overlap between the cyclohexane bridge protons (on C3 and C4) and the methyl groups adjacent to the nitrogen of the Schiff base. With this in mind these workers used *cis*-DCH in preference to the *trans* isomer for the preparation of compartmental Schiff base ligands from β-triketones.

The present work focuses on the reactions of *trans*-(±)DCH with acacH in the absence of and in the presence of Co(II) ions.

## 2. Results and discussion

*trans*-(±)DCH reacts with acacH in a 1:2.5 mole ratio to give the bisoxoenamine condensation product boe (**1**) in good yield. The X-ray crystal structure of **1** is shown in Fig. 3 (Table 1). Compound **1** is the keto form of the Schiff base enol tautomer illustrated in Scheme 4. The basic structural framework of **1** is similar to that of the condensation product shown in Fig. 2. The asymmetric unit contains two molecules and although the molecules are very similar, a search using PLATON [9] did not reveal any extra symmetry. Each molecule has two internal hydrogen bonds linking the amines to the terminal oxygen atoms on the same acac 'arm'.

The reactions of *trans*-(±)DCH with $CoCl_2 \cdot 6H_2O$ and $Co(ClO_4)_2 \cdot 6H_2O$ in a 3:1 mole ratio in air gave the respective oxidised Co(III) tris–DCH chloride and perchlorate salts, $[Co((\pm)DCH)_3]Cl_3 \cdot H_2O$ (**2**) and $[Co((\pm)DCH)_3](ClO_4)_3$ (**3**). The anhydrous form of **2**, $[Co((\pm)DCH)_3]Cl_3$, has previously been reported to form in a reaction in which $H_2O_2$ was employed as the metal oxidant [10]. Racemic and resolved forms of *trans*-DCH have been used as a bidentate ligand for the synthesis of $[Ir(DCH)_3]^{3+}$ and $[Co(DCH)_3]^{3+}$ [10], whilst the racemic diamine was used to make the copper(II) complexes $[Cu((\pm)\text{-}DCH)_3](ClO_4)_2 \cdot H_2O$ [11], $[Cu((\pm)\text{-}DCH)_2(ClO_4)_2]$ [11], $[Cu((\pm)\text{-}DCH)_2(H_2O)_2]Cl_2$ [12] and $[Cu((\pm)\text{-}DCH)_2(NO_3)_2]$ [12]. The copper(II) complexes and some of the iridium(III) and cobalt(III) complexes were structurally characterised.

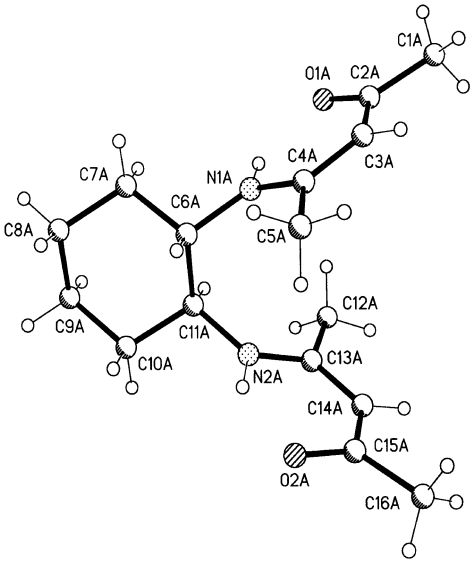



Fig. 3. Structure of boe (**1**).

Table 1
Selected bond lengths (Å) and angles (°) for **1**

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| O(1A)–C(2A) | 1.249(3) | C(11A)–N(2A) | 1.452(3) |
| C(4A)–N(1A) | 1.336(3) | N(2A)–C(13A) | 1.335(3) |
| N(1A)–C(6A) | 1.451(3) | C(15A)–O(2A) | 1.249(3) |
| *Bond angles* | | | |
| O(1A)–C(2A)–C(3A) | 121.8(3) | C(13A)–N(2A)–C(11A) | 129.9(2) |
| O(1A)–C(2A)–C(1A) | 119.5(3) | O(2A)–C(15A)–C(14A) | 122.9(3) |
| C(4A)–N(1A)–C(6A) | 129.4(2) | O(2A)–C(15A)–C(16A) | 118.9(3) |

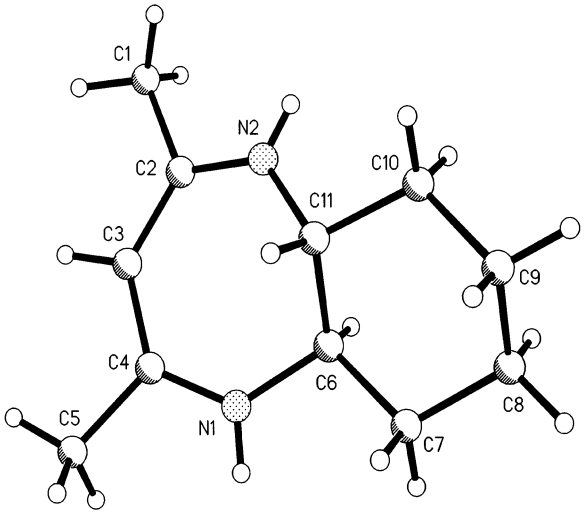



Fig. 4. Detailed structure of one of the $diazH^+$ cations in **5**.

Table 2
Selected bond lengths (Å) and angles (°) for **5**

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| C(2)–N(2) | 1.313(3) | N(1)–C(6) | 1.459(3) |
| C(2)–C(3) | 1.387(4) | C(6)–C(11) | 1.536(4) |
| C(3)–C(4) | 1.385(4) | C(11)–N(2) | 1.456(4) |
| C(4)–N(1) | 1.316(4) | | |
| *Bond angles* | | | |
| N(2)–C(2)–C(3) | 125.0(3) | N(1)–C(6)–C(11) | 111.1(2) |
| C(4)–C(3)–C(2) | 131.1(3) | N(2)–C(11)–C(6) | 111.7(2) |
| N(1)–C(4)–C(3) | 126.8(3) | C(2)–N(2)–C(11) | 126.7(2) |
| C(4)–N(1)–C(6) | 128.0(3) | | |

Unsuccessful attempts were made to use the DCH complexes **2** and **3** in the template synthesis of Schiff base complexes by subsequent condensation with acacH. Only unreacted starting materials were recovered when **2** and **3** were treated with acacH (1:6 mole ratio), emphasising the slow ligand exchange kinetics of Co(III) complexes containing N-donor ligands [10]. In contrast to the kinetic inertness of such Co(III) complexes the nickel(II) ethylenediamine (en) complex, $[Ni_2(en)_4Cl_2]Cl_2$, reacts with a β-diketone in the presence of a catalytic amount of pyridine to form a precipitate of the respective Schiff base complex [13].

A one-pot reaction involving *trans*-(±)DCH, $CoCl_2 \cdot 6H_2O$ and acacH (1:1:2.5 mole ratio) produced firstly a precipitate of $[Co((\pm)DCH)Cl_2]$ (**4**) followed by the co-crystallisation of $(diazH)_2[CoCl_4]$ (**5**), $[Co(boe)Cl_2]_n$ (**6**) and $[Co(acac)_3]$ (**7**). When the experiment was repeated using a smaller amount of acacH (9.37 mmol instead of 23.67 mmol) the yield of **4** increased substantially and the yield of the mixture **5**–**7** decreased dramatically. Whereas samples **4**–**6** are Co(II) complexes, **7** is a Co(III) species. It is noteworthy that $[Co((\pm)DCH)_3]Cl_3 \cdot H_2O$ (**2**) was not recovered from reactions in which acacH featured as a starting material.

The X-ray crystal structures of **5**, **6** and **7** were obtained. Complex **5** contains independent $diazH^+$ cations (Fig. 4, Table 2), formed from a 1:1 condensation of acacH with *trans*-(±)DCH, and tetrahedral $[CoCl_4]^{2-}$ anions. The charge on the cations is delo-

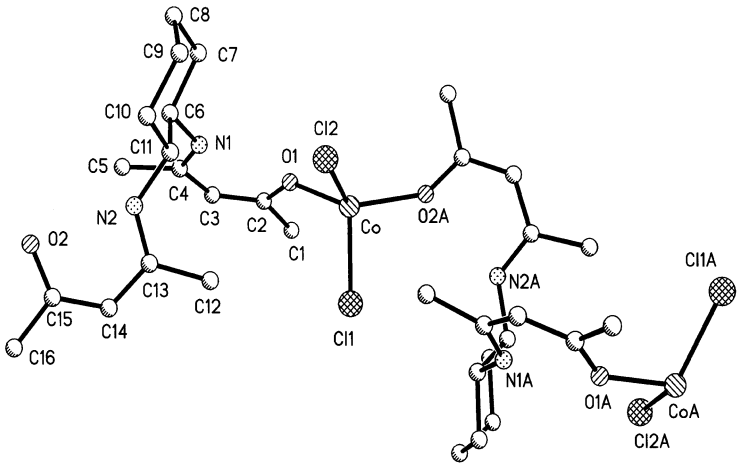



Fig. 5. A section of the polymer $[Co(boe)Cl_2]_n$ (**6**).

calised and the protons on both nitrogen atoms were located. Each proton is hydrogen-bonded to a $[CoCl_4]^-$ anion. All of the bonds in the vinamidine N1–C4–C3–C2–N2 moiety of the diazepine ring are shortened and this section of the ion is almost planar. Indeed, this portion of the ring is more planar than the corresponding section in the neutral diazepine illustrated in Fig. 1, the latter being described as 'pseudo-aromatic' [4]. There does not appear to be much difference in the apparent delocalisation between these cationic and neutral diazepine species. In contrast, for phenyl-substituted diazepines there is a striking difference between bond distances in neutral diazepine bases and in their corresponding cations [14]. Although the cations have a definite delocalised structure, the bonds in the vinamidine systems of the diazepine bases are alternatively single and double. Furthermore, whereas the cations are inherently symmetrical, the bases are not, and they can only achieve symmetry in solution by a very rapid 1,5-shift of a H atom between the 1- and 4-N atoms.

The bisoxoenamine Co(II) complex **6** is polymeric with the free oxygen donors of the neutral boe ligand **1** linking approximately tetrahedral cobalt ions, each also having two chloride ligands (Fig. 5, Table 3). The amine protons were located and their positions refined. As with the free ligand **1** there are hydrogen-bonds linking the amine and the neighbouring oxygen atoms (N1–O1 2.645(4), N2–O2 2.648(4) Å). The X-ray crystal structure of the tris(acac) Co(III) complex **7** was the same as that previously reported in the literature [15].

The use of $Co(ClO_4)_2{\cdot}6H_2O$ in a one-pot reaction mixture incorporating *trans*-(±)DCH and acacH (1:1:2.5 mole ratio) gave some different products than the same reaction involving $CoCl_2{\cdot}6H_2O$. These differences probably reflect the fact that $Cl^-$ is superior to $ClO_4^-$ as a competitive coordinating ligand. Complexes **7**, $[Co_2(acac)_4(H_2O)_2][Co(acac)(H_2O)_4]ClO_4{\cdot}EtOH$ (**8**) and $[Co(acac)_2(\pm)DCH]ClO_4$ (**9**) co-crystallised in the product mixture and single crystals of each were carefully separated and used for X-ray crystallographic studies.

In complex **8** (Figs. 6 and 7, Table 4) the asymmetric unit contains one $[Co(acac)(H_2O)_4]^+$ cation and half of each of two independent $[Co_2(acac)_4(H_2O)_2]$ species, one perchlorate anion and one ethanol solvate (both of which are disordered). The perchlorate anion was modelled with two sets of oxygen atoms about a common Cl position; and the central carbon of the ethanol molecule was disordered over two sites. All of the metal ions are six-coordinate and bond distances and stoichiometry are consistent with the Co(II) oxidation state. Each cobalt ion in the $[Co_2(acac)_4(H_2O)_2]$ dimers is coordinated to two *cisoid* bidentate $acac^-$ ligands and one water molecule; the coordination sphere is completed by a bridging oxygen atom from one of the bidentate $acac^-$ ligands coordinated to the second cobalt ion. Consequently, two of the $acac^-$ ligands are bidentate only while the other two also act as one-atom bridges between the metal ions. This is somewhat similar to the coordination found in the tetranuclear Co(II) complex $[Co_4(acac)_8]$ [16]. The Co–Co distances in $[Co_2(acac)_4(H_2O)_2]$ are 3.245(1) and 2.232(1) Å for Co(1)–Co(1A) and Co(2)–Co(2A), respectively. All of

Table 3
Selected bond lengths (Å) and angles (°) for **6**

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Co–O(1) | 1.955(3) | Co–Cl(2) | 2.2574(12) |
| Co–O(2) # 1 | 1.957(3) | Co–Cl(1) | 2.2595(12) |
| *Bond angles* | | | |
| O(1)–Co–O(2) # 1 | 131.78(11) | O(1)–Co–Cl(1) | 105.91(9) |
| O(1)–Co–Cl(2) | 97.49(9) | O(2) # 1–Co–Cl(1) | 97.39(9) |
| O(2) # 1–Co–Cl(2) | 105.94(9) | Cl(2)–Co–Cl(1) | 120.73(5) |

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

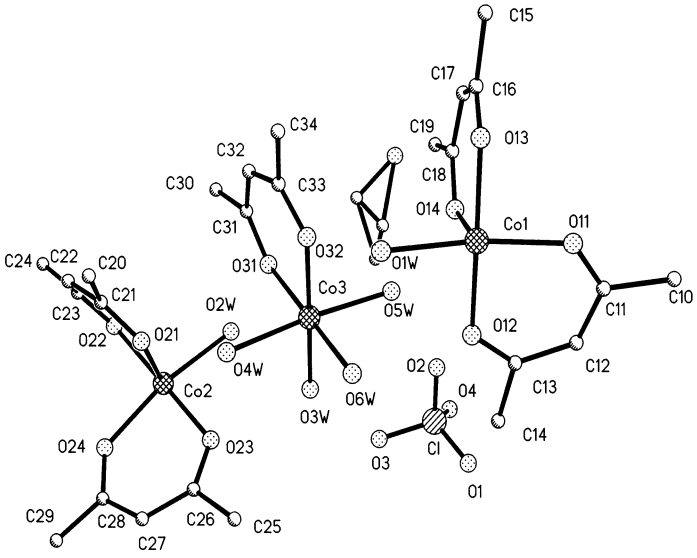



Fig. 6. Asymmetric unit of $[Co_2(acac)_4(H_2O)_2][Co(acac)(H_2O)_4]ClO_4{\cdot}EtOH$ (**8**).

the water molecule hydrogen atoms are involved in hydrogen-bonding. The cobalt complexes are linked into dimer–monomer–dimer H-bonded chains which in turn are linked by perchlorate and ethanol.

The asymmetric unit of the mixed ligand complex **9** contains one $[Co(acac)_2(\pm)DCH]^+$ cation and one perchlorate anion (Fig. 8, Table 5). The cobalt(III) ion is six-coordinate and is ligated by two *cisoid* $acac^-$ ions and a neutral DCH molecule. The Co–O(acac) bond distances in **9** are notably shorter than those in the Co(II) complex **8**. Apart from the weak hydrogen bond between one of the coordinated amine groups and the perchlorate counter ion (N2···O2 3.196(8) Å) there are no other striking interionic interactions.

In conclusion, it is seen that in the absence of a metal ion, *trans*-(±)DCH reacts with acacH (1:2.5 mole ratio) to form the bisoxoenamine condensation product, boe (**1**). The Co(II) salts, $CoCl_2{\cdot}6H_2O$ and $Co(ClO_4)_2{\cdot}6H_2O$, react with *trans*-(±)DCH in air to give complexes containing the oxidised Co(III) ion, $[Co((\pm)DCH)_3]^{3+}$. This ion does not react with added acacH to give a Schiff base complex. Mixtures of complexes are obtained from one-pot reactions involving *trans*-(±)DCH, a simple Co(II) salt and acacH (1:1:2.5 mole ratio). When $CoCl_2{\cdot}6H_2O$ is used, the mixed-ligand (DCH/chloride) Co(II) complex $[Co((\pm)DCH)Cl_2]$ (**4**) precipitates first and, after a period of weeks a myriad of complexes, $(diazH)_2[CoCl_4]$ (**5**), $[Co(boe)Cl_2]_n$ (**6**) and $[Co(acac)_3]$ (**7**), co-crystallise from the mother liquor. The interesting feature of **5** is the diazepinium cation, $diazH^+$, formed from the 1:1 cyclisation of *trans*-(±)DCH and acacH. These diazepinium cations act as counterions for the Co(II) complex ion, $[CoCl_4]^{2-}$. Complex **6** indicates formation of the bisoxoenamine ligand which ligates neighbouring Co(II) centre via its carbonyl oxygen atoms. Complex **7** comprises only $acac^-$ bidentate ligands chelated to an oxidised Co(III) centre. Using $Co(ClO_4)_2{\cdot}6H_2O$ in the reaction with *trans*-(±)DCH and acacH gives, again, a mixture of products. Complexes **7**, $[Co_2(acac)_4(H_2O)_2]$-$[Co(acac)(H_2O)_4]ClO_4{\cdot}EtOH$ (**8**) and $[Co(acac)_2(\pm)DCH]ClO_4$ (**9**) co-crystallise. Complexes **7** and **8** each contain $acac^-$ ligands (no DCH and no DCH/acacH condensation products) and the metal centres are Co(III) and Co(II), respectively. Both $acac^-$ and neutral (±)DCH ligands chelate to the oxidised Co(III) centre in **9**. The major difference between using $CoCl_2{\cdot}6H_2O$ and $Co(ClO_4)_2{\cdot}6H_2O$ in reactions involving (±)DCH and acacH is that no DCH/acacH condensation products are identified in the product mixtures when the perchlorate salt is employed.

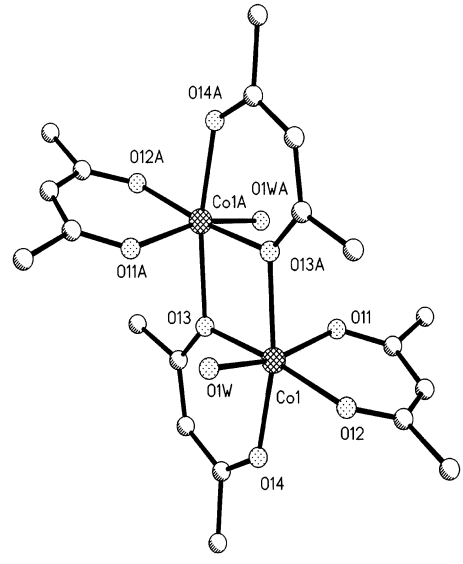



Fig. 7. One of the two independent $[Co_2(acac)_4(H_2O)_2]$ molecules in **8**.

Table 4
Selected bond lengths (Å) and angles (°) for **8**

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Co(1)–O(11) | 2.037(2) | Co(2)–O(21) | 2.065(2) |
| Co(1)–O(12) | 2.047(2) | Co(2)–O(2W) | 2.090(2) |
| Co(1)–O(13) | 2.058(2) | Co(2)–O(22) #2 | 2.150(2) |
| Co(1)–O(14) | 2.064(2) | Co(2)–Co(2) #2 | 3.2322(10) |
| Co(1)–O(1W) | 2.099(2) | Co(3)–O(32) | 2.055(3) |
| Co(1)–O(13) #1 | 2.164(2) | Co(3)–O(3W) | 2.064(3) |
| Co(1)–Co(1) #1 | 3.2449(10) | Co(3)–O(31) | 2.066(3) |
| Co(2)–O(23) | 2.039(2) | Co(3)–O(6W) | 2.080(3) |
| Co(2)–O(24) | 2.041(2) | Co(3)–O(5W) | 2.108(2) |
| Co(2)–O(22) | 2.055(2) | Co(3)–O(4W) | 2.132(2) |
| *Bond angles* | | | |
| O(11)–Co(1)–O(12) | 89.71(10) | O(22)–Co(2)–O(21) | 88.55(9) |
| O(13)–Co(1)–O(14) | 88.99(10) | O(21)–Co(2)–O(22) #2 | 167.08(9) |
| O(14)–Co(1)–O(13) #1 | 167.70(9) | O(32)–Co(3)–O(31) | 87.17(10) |
| O(23)–Co(2)–O(24) | 89.61(10) | | |

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z$; #2 $-x+1, -y+1, -z+1$.

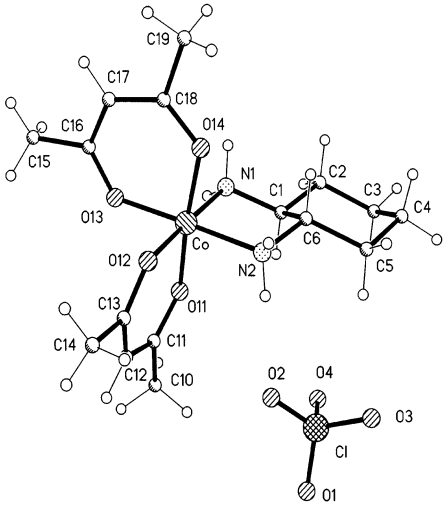



Fig. 8. Asymmetric unit of $[Co(acac)_2(\pm)DCH]ClO_4$ (**9**).

Table 5
Selected bond lengths (Å) and angles (°) for **9**

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Co–O(11) | 1.877(4) | Co–O(12) | 1.892(4) |
| Co–O(14) | 1.882(4) | Co–N(2) | 1.936(5) |
| Co–O(13) | 1.886(4) | Co–N(1) | 1.941(5) |
| *Bond angles* | | | |
| O(14)–Co–O(13) | 96.93(19) | N(2)–Co–N(1) | 86.7(2) |
| O(11)–Co–O(12) | 96.67(19) | | |

## 3. Experimental

Chemicals were purchased from commercial sources and used without further purification. Infrared spectra were recorded as KBr discs in the region 4000–400 $cm^{-1}$ on a Nicolet Impact 400D FT–IR Spectrometer. Electron impact mass spectra were measured using a Kratos Analytical Profile instrument. Elemental analyses were carried out by the Microanalytical Laboratory, Chemistry Department, National University of Ireland, Cork, Ireland.

### 3.1. boe (1)

To a solution of *trans*-($\pm$)-DCH (1.07 g, 9.37 mmol) in ethanol (20 $cm^3$) was added acacH (2.37 g, 23.67 mmol) and the resulting solution allowed to stir for 24 h. The mixture was rotary evaporated to dryness and the yellow solid recrystallised from hot ethanol. Colourless crystals of the product slowly formed and some of these in their mother liquor were used for X-ray structure determination. The remainder of the product was filtered from the mother liquor and washed with two small portions of cold ethanol. After a final washing with diethyl ether the solid was allowed to air-dry. The compound was soluble in ethanol and in chloroform and was insoluble in water. Yield 1.77 g (68%). *Anal.* Found: C, 69.02; H, 9.45; N, 10.20. Calc.: C, 69.03; H, 9.41; N, 10.07%. m.p. 146–148 °C. IR: 3076, 2944, 2856, 1603, 1576, 1300, 1150, 1119, 1026, 995, 816, 741 $cm^{-1}$. Mass spec.: $m/z = 279$, 278, 179, 136 (base peak).

### 3.2. $[Co((\pm)DCH)_3]Cl_3.H_2O$ (2)

To a stirred solution of *trans*-($\pm$)DCH (3.21 g, 28.11 mmol) in ethanol (20 $cm^3$) was added a solution of $CoCl_2.6H_2O$ (2.23 g, 9.37 mmol) in ethanol (10 $cm^3$). An immediate blue to green to light red colour change occurred and the light-red product precipitated. The mixture was stirred for 0.5 h, filtered and then washed with several portions of cold ethanol. After a final washing with diethyl ether the solid was allowed to air-dry. Yield 2.17 g (44%). *Anal.* Found: C, 41.37; H, 8.34; N, 15.31. Calc.: C, 41.11; H, 8.43; N, 15.99%. IR: 3440, 3140, 3070, 2940, 2860, 1590, 1450, 1159, 1059, 1030 $cm^{-1}$.

### 3.3. $[Co((\pm)DCH)_3](ClO_4)_3$ (3)

This red solid was prepared by a similar procedure to that employed for the synthesis of $[Co((\pm)$-$DCH)_3]Cl_3{\cdot}H_2O$, but using $Co(ClO_4)_2{\cdot}6H_2O$ instead of $CoCl_2{\cdot}6H_2O$. Yield (25%). *Anal.* Found: C, 31.64; H, 6.15; N, 11.84. Calc.: C, 30.89; H, 6.05; N, 12.01%. IR: 3498, 3260, 2935, 2862, 1561, 1452, 1252, 1079, 922, 769, 625 $cm^{-1}$.

### 3.4. $[Co((\pm)DCH)Cl_2]$ (4), $(diazH)_2[CoCl_4]$ (5), $[Co(boe)Cl_2]_n$ (6) and $[Co(acac)_3]$ (7)

To a stirred solution of *trans*-($\pm$)DCH (1.07 g, 9.37 mmol) in ethanol (20 $cm^3$) was added $CoCl_2{\cdot}6H_2O$ (2.23

g, 9.38 mmol) and acacH (2.37 g, 23.67 mmol). As the mixture was stirred over a 3 h period it became dark blue in colour and the green powder **4** precipitated. Complex **4** was filtered off, washed with two small portions o f ethanol and then diethyl ether. Yield **4** 0.33g (14%). When the vessel containing the original blue mother liquor was sealed and set aside for 3 weeks, complexes **5**, **6** and **7** co-crystallised. Single crystals of each of the three complexes were carefully separated from the mixture and subjected to X-ray structural analysis. The remainder of the crystalline solid mixture was filtered off, washed with ethanol and dried in vacuo. Yield of mixture 1.39 g. *Anal*. Found: C, 31.08; H, 5.90; N, 11.66; Cl, 27.37. Calc. for **4**: C, 29.53; H, 5.78; N, 11.48; Cl, 29.05%. IR: 3460, 3270, 3215, 3140, 2940, 2860, 1580, 1445, 1150, 1135, 1059, 1035 $cm^{-1}$.

### 3.5. $[Co(acac)_3]$(**7**), $[Co_2(acac)_4(H_2O)_2]$-$[Co(acac)(H_2O)_4]ClO_4 \cdot EtOH$ (**8**) and $[Co(acac)_2(\pm)DCH]ClO_4$ (**9**)

*trans*-(±)DCH (1.14 g, 9.98 mmol) was dissolved in ethanol (20 $cm^3$) and added acacH (2.52 g, 25.17 mmol). Heat was evolved and the light yellow solution was stirred for 10 min. $Co(ClO_4)_2 \cdot 6H_2O$ (3.65 g, 9.97 mmol) was added and the solution immediately turned dark red and more heat was liberated. After standing for a few days **7**, **8** and **9** co-crystallised. Single crystals of each were carefully separated and each, suspended in a drop of the mother liquor, were analysed by X-ray crystallography.

### 3.6. X-ray crystallography

Crystal data for complexes **1**, **5**, **6**, **8** and **9** are summarized in Table 6. All the data sets were collected on a Bruker SMART diffractometer using Mo Kα radiation ($\lambda = 0.71071$ Å); **1** was collected at room temperature, the others were collected at 150(2) K. Each structure was solved by direct methods and refined on $F^2$ using SHELXTL [17]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters except for the disordered ethanol solvate and the minor component of the perchlorate disorder in **8**. Hydrogen atoms coordinated to carbon were inserted at calculated positions except for those of the ethanol molecule in **8**, which were not included. Hydrogen atoms bonded to oxygen atoms were located from difference maps and not refined. The positions of the amine protons were calculated for **9**, but for **1**, **5**

Table 6
Summary of crystal data, data collection, structure solution and refinement details for complexes **1**, **5**, **6**, **8** and **9**

| Identification code | **1** | **5** | **6** | **8** | **9** |
|---|---|---|---|---|---|
| Complex | boe | $(diazH)_2[CoCl_4]$ | $[Co(boe)Cl_2]_n$ | $[Co_2(acac)_4(H_2O)_2]$-$[Co(acac)(H_2O)_4]ClO_4 \cdot EtOH$ | $[Co(acac)_2(\pm)DCH]ClO_4$ |
| Empirical formula | $C_{16}H_{26}N_2O_2$ | $C_{22}H_{38}Cl_4CoN_4$ | $C_{16}H_{26}Cl_2CoN_2O_2$ | $C_{27}H_{51}ClCo_3O_{21}$ | $C_{16}H_{28}ClCoN_2O_8$ |
| Formula weight | 278.39 | 559.30 | 408.22 | 923.92 | 470.78 |
| Temperature (K) | 298(2) | 150(2) | 150(2) | 150(2) | 150(2) |
| Space group | $P\bar{1}$ | *Pbcn* | *C*2/*c* | $P\bar{1}$ | *C*2/*c* |
| Unit cell dimensions | | | | | |
| *a* (Å) | 8.783(6) | 16.811(2) | 15.8275(19) | 9.5236(6) | 15.579(2) |
| *b* (Å) | 12.703(11) | 12.3038(15) | 17.263(2) | 10.2902(6) | 17.623(2) |
| *c* (Å) | 15.318(12) | 12.7329(16) | 15.865(2) | 23.6481(15) | 14.922(2) |
| *α* (°) | 81.36(4) | 90 | 90 | 90.6000(10) | 90 |
| *β* (°) | 88.74(5) | 90 | 119.856(2) | 98.5440(10) | 91.492(2) |
| *γ* (°) | 76.85(4) | 90 | 90 | 117.2070(10) | 90 |
| *Z* | 4 | 4 | 8 | 2 | 8 |
| Absorption coefficient ($mm^{-1}$) | 0.074 | 1.075 | 1.207 | 1.353 | 1.014 |
| *F*(000) | 608 | 1172 | 1704 | 958 | 1968 |
| Crystal size (mm) | $0.62 \times 0.22 \times 0.17$ | $0.33 \times 0.30 \times 0.15$ | $0.25 \times 0.13 \times 0.08$ | $0.45 \times 0.23 \times 0.12$ | $0.23 \times 0.20 \times 0.07$ |
| $2\theta$ Range (°) | 1.34–25.00 | 2.05–25.00 | 1.90–25.00 | 0.87–27.00 | 1.75–24.00 |
| Reflections collected | 16 189 | 17 832 | 9531 | 23 079 | 18 310 |
| Independent reflections ($R_{int}$) | 5786 (0.0629) | 2324 (0.0757) | 3300 (0.0759) | 8712 (0.0533) | 3219 (0.0994) |
| Max/min transmission | 1.00, 0.300 | 0.8554, 0.7181 | 0.9096, 0.7524 | 1.000, 0.828 | 1.000, 0.812 |
| Data/restraints/ parameters | 5786/0/381 | 2324/0/151 | 3300/0/218 | 8712/10/496 | 3219/0/257 |
| Final *R* indices $[I > 2\sigma(I)]$ | $R_1 = 0.0623$ $wR_2 = 0.1416$ | $R_1 = 0.0345$ $wR_2 = 0.0831$ | $R_1 = 0.0468$ $wR_2 = 0.0982$ | $R_1 = 0.0463$ $wR_2 = 0.1135$ | $R_1 = 0.0593$ $wR_2 = 0.1355$ |
| *R* indices (all data) | $R_1 = 0.1143$ $wR_2 = 0.1583$ | $R_1 = 0.0568$ $wR_2 = 0.0938$ | $R_1 = 0.0774$ $wR_2 = 0.1133$ | $R_1 = 0.0793$ $wR_2 = 0.1261$ | $R_1 = 0.1181$ $wR_2 = 0.1793$ |

and **6** they were located from difference maps and their positions allowed to refine.

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 159657–159661 for the five complexes. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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## References

[1] N.A. Bailey, K.C. Cox, C.P. Falshaw, D.E. Fenton, S.E. Grundy, P. Haigh, C.A. Phillips, T.J. King, J. Chem. Soc., Dalton Trans. (1983) 2241.
[2] (a) D. Lloyd, H.P. Cleghorn, D.R. Marshall, Adv. Heterocycl. Chem. 17 (1974) 1;
(b) D. Lloyd, H.P. Cleghorn, Adv. Heterocycl. Chem. 17 (1974) 27.
[3] The Complete Drug Reference, Consumer Reports Book, 1992 edn., Consumers Union, New York, p 218.
[4] R.F. Jordan, D.G. Black, D.C. Swenson, Acta Crystallogr. Sect. C 54 (1988) 1030.
[5] G.W. H. Potter, M.W. Coleman, A.M. Monro, J. Heterocycl. Chem. 12 (1975) 611.
[6] G. Swarzenbach, K. Lutz, Helv. Chim. Acta 23 (1940) 1139.
[7] M. Gullotti, A. Pasini, P. Fantucci, R. Ugo, R.D. Gillard, Gazz. Chim. Ital. 102 (1972) 855.
[8] E.G. Jager, K. Schuhmann, H. Gorls, Inorg. Chim. Acta 255 (1997) 295.
[9] A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, 1980–2000.
[10] D.J. Williams, J.S. Kruger, A.F. McLeroy, A.P. Wilkinson, J.C. Hanson, Chem. Mater. 11 (1999) 2241.
[11] C. Pariya, K. Panneerselvan, C.-S. Chung, T.-H. Lu, Polyhedron 17 (1998) 2555.
[12] C. Pariya, F.-L. Liao, S.-L. Wang, C.-S. Chung, Polyhedron 17 (1998) 547.
[13] D.F. Martin, E.J. Olszewski, Inorg. Synth. 8 (1966) 46.
[14] M. Brisander, S.G. Harris, D. Lloyd, H. McNab, S. Parsons, Chem. Res. 72 (1998) 526.
[15] (a) V.M. Padmanabhan, Proc. Ind. Acad. Sci. A 47 (1958) 329;
(b) P.K. Hon, C.E. Pfluger, J. Coord. Chem. 3 (1973) 67;
(c) G.J. Kruger, E.C. Reynhardt, Acta Crystallogr., Sect. B 30 (1974) 822.
[16] (a) F.A. Cotton, R.C. Elder, Inorg. Chem. 4 (1965) 1145;
(b) J.B. Ellern, R.O. Ragsdale, Inorg. Synth. 11 (1968) 84.
[17] SHELXTL Version 5.1, Bruker AXS, 1998.