DALTON
FULL PAPER

Preparation, structures and reactions of isomeric [Co(cyclen)-$(O_2C_2O_2)$]$^+$ and [Co(cyclen)$(O_2CCH_2CO_2)$]$^+$ complexes (cyclen = 1,4,7,10-tetraazacyclododecane) †

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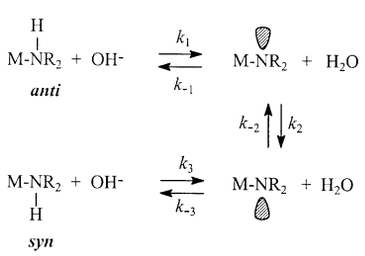
The *syn*,*anti* and *syn*,*syn* forms of the complexes [Co(cyclen)$(O_2C_2O_2)$]ClO_4 **1** and **2** respectively and [Co(cyclen)-$(O_2CCH_2CO_2)$][ClO_4]·H_2O **3** and **4** respectively (cyclen = 1,4,7,10-tetraazacyclododecane) have been prepared and their single crystal structures determined. Protonated forms of **3** and **4** are obtained as their ClO_4^- salts on crystallisation of the parent complexes from aqueous $HClO_4$, and a crystal structure of the former shows protonation occurs on a carbonyl O atom in the malonato bidentate ligand. Proton exchange (D_2O, 25.0 °C, I = 1.0 M) of the equatorial NH protons (*syn* and *anti*) in **1**, **2**, **3** and **4** is first order in [OD^-], with k_H values in the range (1–8) × 10^7 M^{-1} s^{-1}. Equilibration between the *syn*,*anti* and *syn*,*syn* forms of the complexes follows the rate equation $k_{obs} = k_{isom}[OH^-]$ with k_{isom} = (1.3 ± 0.1) × 10^5 M^{-1} s^{-1} (25.0 °C, I = 1.0 M NaCl) for both systems, and with final equilibrium distributions of **[2]**/**[1]** = 0.100 ± 0.005 and **[4]**/**[3]** = 0.057 ± 0.002. The various equatorial NH sites are very susceptible to inversion, with rate constants for lone pair inversion of the deprotonated centres being in the range 2 × 10^6 to 1 × 10^8 s^{-1} at 25 °C. Alkaline hydrolysis (25.0 °C, 1.0 M, $NaClO_4$) of [Co(cyclen)$(O_2CCH_2CO_2)$]$^+$ gives [Co(cyclen)$(OH)_2$]$^+$ in a biphasic reaction, with both paths first order in [OH^-], $k_{OH(1)}$ = 26.9 ± 0.6 M^{-1} s^{-1}, $k_{OH(2)}$ = 4.9 ± 0.6 M^{-1} s^{-1}, whereas alkaline hydrolysis of [Co(cyclen)$(O_2C_2O_2)$]$^+$ gives [Co(cyclen)$(OH)_2$]$^+$ in one step, k_{OH} = 0.114 ± 0.009 M^{-1} s^{-1}. Mechanisms for the reactions are discussed.

Introduction

Many of the important properties of octahedral anionocobalt(III) amines relate to the acidity of the bound amine groups. It is a controlling factor in alkaline hydrolysis reactions, where generation of the conjugate base precedes rate-determining loss of the anionic leaving group (S_N1CB mechanism)[1] and, for complexes containing coordinated *sec*-NH centres, it mediates inversion at these sites.[2] In disymmetric systems it is the stepwise processes of H^+ dissociation from a bound *sec*-amine, inversion of the resultant lone pair and subsequent reprotonation by H_2O which results in generation of the alternative configuration, *e.g.* the interconversion between *syn* (*endo*) and *anti* (*exo*) forms, *cf.* Scheme 1.



Scheme 1 Mechanism for inversion at a co-ordinated amine centre.

In a series of recent papers we have explored the influence of NH lability on the reactivity of cobalt(III) cyclen complexes (cyclen = 1,4,7,10-tetraazacyclododecane).[2k,3] [Co(cyclen)-(X)Y]$^{n+}$ species exhibit exclusive *cis* stereochemistry, but exist as various isomeric forms depending on the orientation (*syn* or *anti*) of the *sec*-NH protons at the two equatorial sites, *cf.* Fig. 1. The C–N–C bond angles about these (*ca.* 118–120 *syn*, 113–116° *anti*, irrespective of the nature of X and Y)[4] are considerably distorted from the tetrahedral value (109.5°), which indicates considerable strain in both. This translates to unusually fast rates of proton exchange, often at the diffusion controlled limit ($k_H \approx 10^{10}$ M^{-1} s^{-1}), and to rapid inversion at

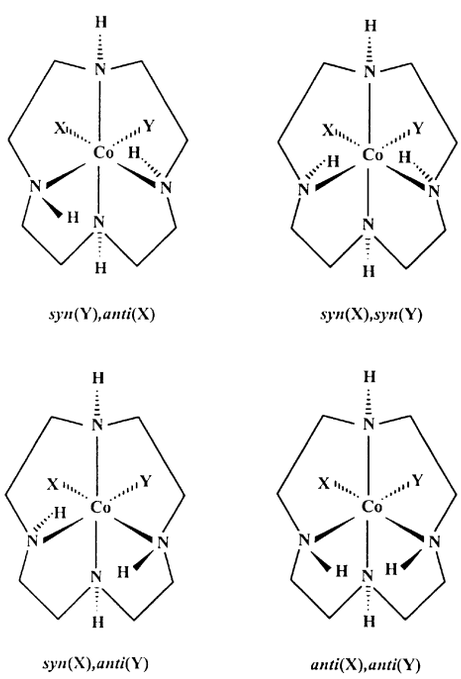


Fig. 1 Isomer possibilities in the [Co(cyclen)(X)Y]$^{n+}$ system.

† Electronic supplementary information (ESI) available: observed and calculated rate constants for exchange of the *sec*-NH protons. See http://www.rsc.org/suppdata/dt/b0/b008350j/

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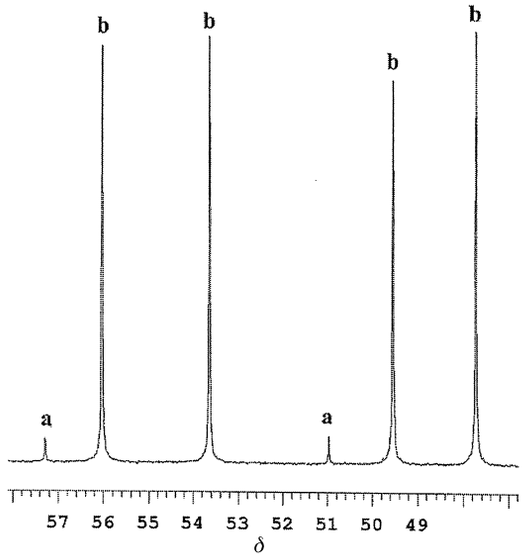


Fig. 2 ^{13}C NMR spectrum (methylene region) for *syn,anti*-[Co(cyclen)-$(O_2C_2O_2)]^+$ in water following equilibration at pH 6.7 for 24 h. Peaks **a** and peaks **b** are respectively associated with the *syn,syn* and *syn,anti* isomers.

these sites (note that the apical NH centres cannot invert).[2k] The effect of proton orientation and lability on alkaline hydrolysis reactivity can be profound. For example, OH^- induced loss of the first NH_3 ligand from *syn,anti*-$[Co(cyclen)(NH_3)_2]^{3+}$ is at least 3×10^{10} more rapid than from the more weakly acidic $[Co(NH_3)_6]^{3+}$ ion.[3e]

Herein we investigate the influence of NH lability on the aqueous solution chemistry of the chelate species [Co(cyclen)-$(O_2C_2O_2)]^+$ and $[Co(cyclen)(O_2CCH_2CO_2)]^+$, and report crystal structures of isomeric forms. We also report the structure of an unusual protonated form of the malonato complex. As will be shown below, the oxalato and malonato complexes undergo facile isomer interconversion (*syn,anti* $\rightleftharpoons$ *syn,syn*) and are hydrolysed rapidly in alkali to produce $[Co(cyclen)(OH)_2]^+$. The processes are discussed in relation to those previously observed for the higher charged chelates [Co(cyclen)-(*S*-AlaO)]$^{2+}$ (*S*-AlaO$^-$ = *S*-alaninate),[2k,3a] [Co(cyclen)(en)]$^{3+}$,[3e] and [Co(cyclen)(tn)]$^{3+}$ [3e] (tn = trimethylenediamine).

Results and discussion

Syntheses and isomer distributions

The direct reaction of $[Co(cyclen)Cl_2]Cl$ with sodium oxalate in aqueous solution results in mainly *syn,anti*-[Co(cyclen)-$(O_2C_2O_2)]^+$, with lesser quantities of the *syn,syn* isomer. The corresponding reaction with sodium malonate also produces large amounts of *syn,syn*-$[Co(cyclen)(O_2CCH_2CO_2/H)]^{+,2+}$ in addition to the *syn,anti* isomer, and up to 30% recovered yields of the *syn,syn* forms of the complexes as their ClO_4^- salts are obtained. Isomer separation and isolation is easily carried out using ion-exchange chromatography (Dowex 50W × 2, HCl eluent, both systems) and structures were assigned by crystallography (see below). pH Measurements on 0.010 M solutions of $[Co(cyclen)(O_2CCH_2CO_2H)]^{2+}$ species show these protonated forms to be strongly acidic (pH 2). Also, the above isomer ratios are indicative of kinetic control during synthesis since OH^--catalysed equilibration leads to much lower proportions of the *syn,syn* forms. Fig. 2 gives the ^{13}C NMR spectrum (methylene region) obtained for *syn,anti*-$[Co(cyclen)(O_2C_2O_2)]^+$ following equilibration at pH 6.7 for 24 h. Peaks **a** (two) and peaks **b** (four) are respectively associated with the *syn,syn* and *syn,anti* isomers in this system (as shown by comparison with spectra of the pure compounds) and integration, obtained under conditions of full relaxation, gave the thermodynamic isomer distribution, *syn,syn*:*syn,anti*, as $K_{isom} = 0.100 \pm 0.005$. An identical result was obtained on equilibration starting with *syn,syn*-$[Co(cyclen)(O_2C_2O_2)]^+$. Parallel studies using [Co-(cyclen)$(O_2CCH_2CO_2)]^+$ (both isomers) similarly established the equilibrium isomer distribution for this species, *syn,syn*:*syn,anti*, as $K_{isom} = 0.057 \pm 0.002$. As with all other cobalt(III) cyclen complexes examined to date[2k,3a,b,e,4g] we could find no evidence for the presence of *anti,anti* isomers in the equilibrium mixtures (<1% of $[Co]_T$), and the reduced amounts of the *syn,syn* isomers compared to their *syn,anti* counterparts also accords with earlier observations.[2k,3e]

Crystal structures

Structural studies were undertaken principally as a means of isomer assignment. Representations of the *syn,anti*-$[Co(cyclen)(O_2C_2O_2)]^+$ **A**, *syn,syn*-$[Co(cyclen)(O_2C_2O_2)]^+$ **B**, *syn,anti*-$[Co(cyclen)(O_2CCH_2CO_2)]^+$ **C**, *syn,syn*-[Co(cyclen)-$(O_2CCH_2CO_2)]^+$ **D** and *syn,anti*-$[Co(cyclen)(O_2CCH_2CO_2H)]^{2+}$ **E** cations are shown in Fig. 3. In all cases the structures involve a central Co coordinated in a distorted octahedral fashion to all four, mutually *cis*, nitrogen atoms of a cyclen ligand and to two oxygen atoms of the chelating dicarboxylate. One or two perchlorate counter ions balance the charge on the cation. Bond lengths and angles for the complexes are given as supplementary information. The Co–N bond lengths involving *ap* nitrogen atoms are consistently longer (by *ca.* 0.02 Å) than those involving equatorial nitrogen atoms and this follows the pattern observed in other cobalt(III) cyclen complexes.[3e,4] Also, the Co–N and Co–O bonds in *syn,anti*-$[Co(cyclen)(O_2C_2O_2)]ClO_4$ are significantly longer (by *ca.* 0.02–0.05 Å) than the corresponding bonds in the other complexes. Chelate bite angles (O1–Co–O4, Fig. 3, **A**, **B**) of *ca.* 86° in the oxalato chelates are not too different from the bite angles (*ca.* 83°) in *syn,anti*-[Co(cyclen)-(diamine)]$^{3+}$ ions (diamine = en or tn), and are similar to the corresponding angle (84.2°) in *syn,anti*-$[Co(cyclen)(NH_3)_2]^{3+}$.[3e] In these species the geometry around the central Co is fixed mainly by the constraints imposed by the cyclen macrocycle. However, the malonato chelates (Fig. 3, **C**–**E**) display considerably larger bite angles (90.3 to 93.7°), in keeping with the tendency of the six-membered ring systems to flatten as a consequence of substantial sp^2 character in the central methylene (C9–C10–C11 bond angles of 116.5 to 120.5°). Similarly, an almost planar geometry is seen in the potassium hydrogenmalonate structure.[5] The cobalt(III) hydrogenmalonato complex *syn,anti*-$[Co(cyclen)(O_2CCH_2CO_2H)][ClO_4]_2 \cdot 2H_2O$ crystallises with two independent molecules in the asymmetric unit. They are distinguished by having either *syn*(C=OH$^+$) or *anti*(C=OH$^+$) stereochemistry, and each has the proton on carbonyl O oriented *syn* to equatorial NH. The structures feature hydrogen bonding of the protonated carbonyl O atoms to an adjacent H_2O of crystallisation (O · · · O distances of 2.489 and 2.528 Å), and a longer C–O bond for the protonated carbonyl group (1.285 and 1.303 Å) compared to unprotonated carbonyl C–O in the same complex (1.254 and 1.225 Å). The carbonyl C–O bond lengths in the neutral forms of the malonato complex (*cf.* Fig. 3, **C**, **D**) range from 1.235 to 1.241 Å. There are few other fully characterised complexes containing chelated hydrogenmalonato ligands, with only the structures of $Mg(O_2CCH_2CO_2H)_2 \cdot 2H_2O$[6] and its isomorph $Zn(O_2CCH_2CO_2H)_2 \cdot 2H_2O$[7] having been described.

H/D exchange

The two equatorial (*eq*) NH protons in *syn,anti*-[Co(cyclen)-$(O_2C_2O_2)]^+$ give rise to separate signals in the ^{1}H NMR spectrum (δ 6.7, 6.4), but we have not been able unequivocally to determine which corresponds to *syn*-NH and which to *anti*. However, exchange data (25 °C, $I = 1.0$ M (NaCl), supplementary information) show that both these *eq*-NH protons decay at similar rates by processes strictly first order in [OD$^-$],

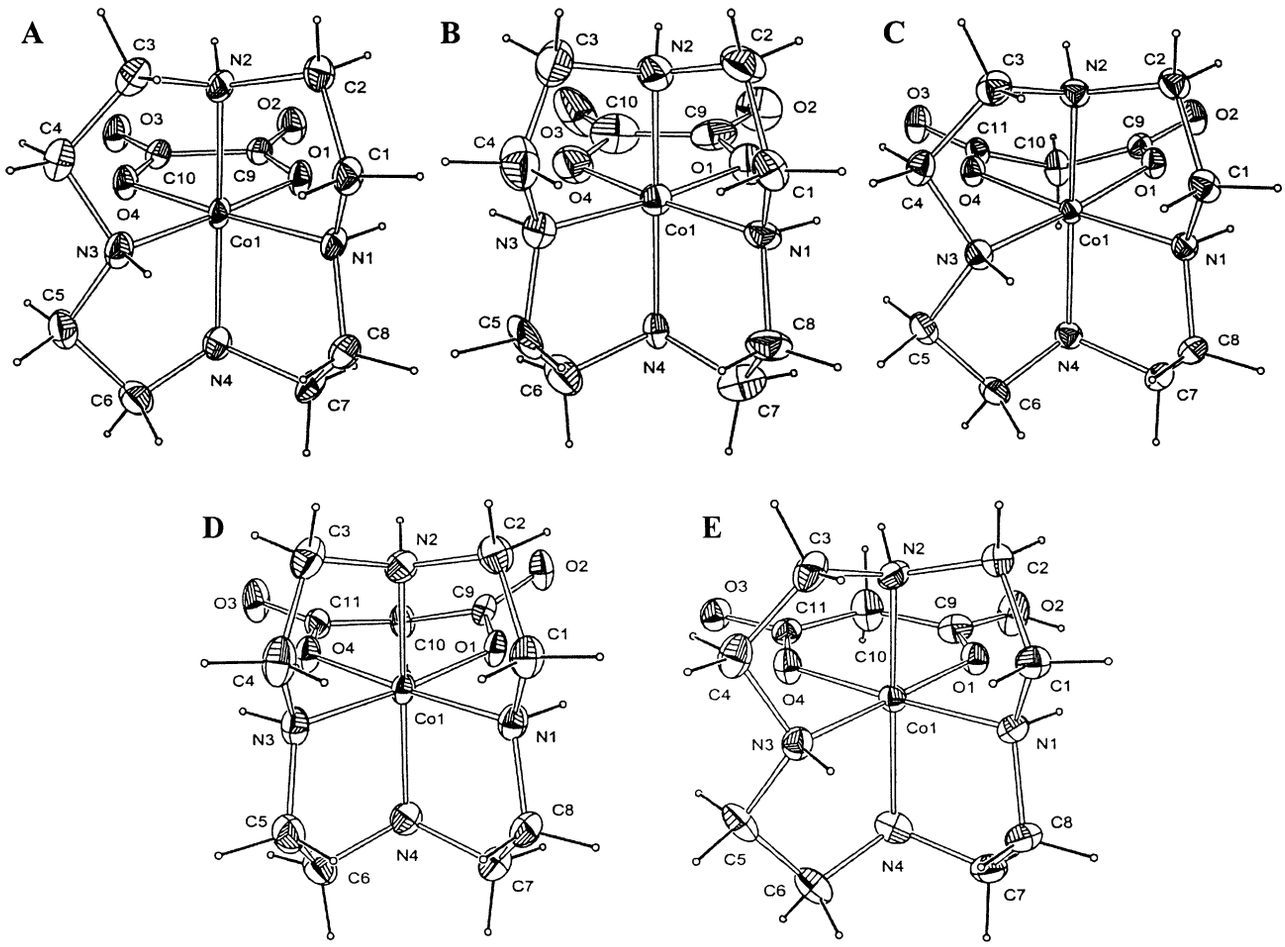


Fig. 3 Structures of *syn,anti*-[Co(cyclen)$(O_2C_2O_2)]^+$ **A**, *syn,syn*-[Co(cyclen)$(O_2C_2O_2)]^+$ **B**, *syn,anti*-[Co(cyclen)$(O_2CCH_2CO_2)]^+$ **C** and *syn,syn*-[Co(cyclen)$(O_2CCH_2CO_2)]^+$ cations, and of one of the two *syn,anti*-[Co(cyclen)$(O_2CCH_2CO_2H)]^{2+}$ isomers **E** (with, in this case, the protonated carbonyl O *cis* to *syn*-NH). Thermal ellipsoids are drawn at the 50% confidence level.

$k_H = (2.8 \pm 0.3) \times 10^7$ and $(5.4 \pm 0.5) \times 10^7$ M^{-1} s^{-1} for the signals at δ 6.7 and 6.4 respectively. The corresponding data for *syn,syn*-[Co(cyclen)$(O_2C_2O_2)]^+$ (*syn*-NH signal at δ 6.5) give $k_H = (8.8 \pm 0.9) \times 10^7$ M^{-1} s^{-1}. The apical (*ap*) NH protons in *syn,anti*-[Co(cyclen)$(O_2C_2O_2)]^+$ (δ 6.89 signal) exchange some 200–400 times slower than the equatorial protons, $k_H = (1.2 \pm 0.2) \times 10^5$ M^{-1} s^{-1}, *cf.* supplementary information, but observation of the corresponding process in the *syn,syn* species is complicated by the occurrence of comparably rapid equilibration between the *syn,syn* and *syn,anti* forms of the complex. Equilibration favours formation of the latter by a large margin (10 : 1, see later), and its production was evidenced in an H-exchange experiment at pD 6.0 by the growth and subsequent decay of a signal at δ 6.89, during which time the *ap* NH signal of the reactant (δ 6.82) decayed monotonously. Rates of isomer interconversion in both the oxalato and malonato systems were subsequently determined using UV-vis spectroscopy, see below.

Rate constants for H/D exchange in *syn,anti*-[Co(cyclen)$(O_2CCH_2CO_2)]^+$ and *syn,syn*-[Co(cyclen)$(O_2CCH_2CO_2)]^+$ (25 °C, $I = 1.0$ M, $NaClO_4$) are given in the supplementary information. As was the case in the oxalato system the equatorial NH protons of the *syn,anti* isomer were unable to be assigned to particular configurations despite being distinguished in the ^1H NMR spectrum (δ 6.2, 5.9) and exhibiting differing exchange rates ($k_H = (3.1 \pm 0.3) \times 10^7$ and $(1.1 \pm 0.1) \times 10^7$ M^{-1} s^{-1} respectively). The *eq* NH protons in *syn,syn*-[Co(cyclen)$(O_2CCH_2CO_2)]^+$ undergo exchange with $k_H = (2.1 \pm 0.2) \times 10^7$ M^{-1} s^{-1}. Taken overall, the results from both systems make it clear that OD^--catalysed exchange at the equatorial NH sites is insensitive both to proton orientation (*syn* or *anti*) and O–O chelate ring size (O–O = dicarboxylate chelate, five- and six-membered rings) and the k_H values lie in the relatively narrow range (1–4) $\times 10^7$ M^{-1} s^{-1} (a statistical factor of two has been applied in the case of the *syn,syn* isomers).

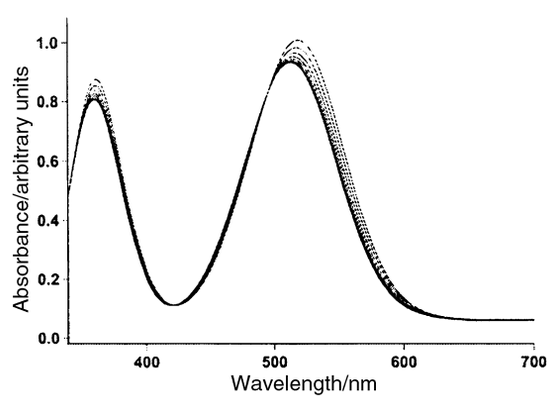


Fig. 4 UV-vis spectral changes accompanying isomerisation in the [Co(cyclen)$(O_2C_2O_2)]^+$ system, 25.0 °C, $I = 1.0$ M (NaCl), pH 5.74. 4.60 mg *syn,syn*-[Co(cyclen)$(O_2C_2O_2)$]Cl in 3.8 mL buffer, 5 min scan interval.

Isomerisation and inversion of coordinated *sec* amine centres

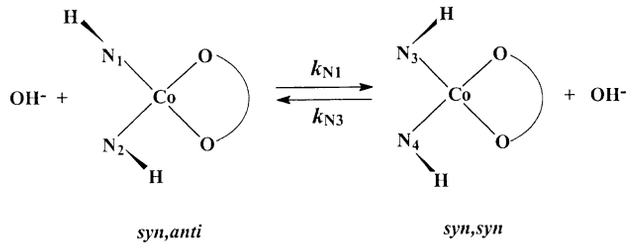
Isomerisation, *syn,syn* $\rightleftharpoons$ *syn,anti*, results in small changes in the UV-vis spectrum and these were utilised in the acquisition of rate data. Equilibration starting with the *syn,syn* isomers gives the greater spectral change, and absorbance–time traces for *syn,syn*-[Co(cyclen)$(O_2C_2O_2)$]Cl in pH 5.74 phosphate buffer, shown in Fig. 4, correspond to $t_{1/2} \approx 10$ min under this condition. First-order rate constants (25.0 °C, $I = 1.0$ M, NaCl)

Table 1 Rate constants for isomerisation, *syn*,*anti* $\rightleftharpoons$ *syn*,*syn*, in the $[Co(cyclen)(O_2C_2O_2)]^+$ and $[Co(cyclen)(O_2C_2O_2)]^+$ ions, 25.0 °C, $I = 1.0$ M NaCl

pH	$10^9[OH^-]$/M	$10^3k_{obs}/s^{-1}$	$10^3k_{calc}/s^{-1}$
$[Co(cyclen)(O_2C_2O_2)]^{+\,a}$			
5.13	2.01	0.252	0.261
5.58	5.67	0.690	0.737
5.81	9.94	1.19	1.29
6.04	16.4	2.04	2.13
6.24	25.9	3.28	3.34
6.41	38.4	5.30	4.99
6.61	60.8	8.38	7.90
$[Co(cyclen)(O_2CCH_2CO_2)]^{+\,b}$			
5.52	4.94	0.640	0.627
5.79	9.20	1.17	1.17
5.99	14.6	1.92	1.85
6.19	23.1	2.95	2.93
6.37	35.0	4.31	4.45
6.57	55.5	6.86	7.05

[a] Measurements at 520 nm, $k_{calc} = k_{isom}[OH^-]$, with $k_{isom} = 1.30 \times 10^5$ M^{-1} s^{-1}. [b] Measurements at 545 nm, with $k_{isom} = 1.27 \times 10^5$ M^{-1} s^{-1}.

were obtained as a function of pH (pH 5–6.5, both systems) and are given in Table 1. The rate equation $k_{obs} = k_{isom}[OH^-]$ holds, with $k_{isom} = (1.3 \pm 0.1) \times 10^5$ M^{-1} s^{-1} for $[Co(cyclen)(O_2C_2O_2)]^+$ and $k_{isom} = (1.27 \pm 0.05) \times 10^5$ M^{-1} s^{-1} for $[Co(cyclen)(O_2CCH_2CO_2)]^+$; thus the rate at which equilibrium is attained is the same for both. Isomerisation can be represented as in Scheme 2, with $k_{isom} = k_{N1} + k_{N3}$. Since $K_{isom} = k_{N1}/k_{N3}$ it



Scheme 2

follows that $k_{N1} = 1.2 \times 10^4$ M^{-1} s^{-1}, $k_{N3} = 1.2 \times 10^5$ M^{-1} s^{-1} for $[Co(cyclen)(O_2C_2O_2)]^+$ ($K_{isom} = 0.10$) and $k_{N1} = 0.72 \times 10^4$ M^{-1} s^{-1}, $k_{N3} = 1.2 \times 10^5$ M^{-1} s^{-1} for $[Co(cyclen)(O_2CCH_2CO_2)]^+$ ($K_{isom} = 0.057$).

The isomerisation processes, *cf*. Scheme 1, must involve ionisation at an equatorial NH centre (k_1, k_3), with inversion of the resulting nitrogen electron pair (k_2, k_{-2}) and reprotonation (k_{-1}, k_{-3}) generating the isomeric product. Accordingly, the relationships between inversion and isomerisation rate constants are: $k_2 = k_{N1}k_{-1}/k_1$ and $k_{-2} = k_{N3}k_{-3}/k_3$. The cobalt(III) amine conjugate base forms (*cf*. Scheme 1) should reprotonate (*via* k_{-1}, k_{-3}) at diffusion controlled rates since the acidity constants of the parent complexes are beyond the measurable range in aqueous solution ($pK_a > 14$, see below),[8] and for the present purpose we assume $k_{-1} = k_{-3} = 10^{10}$ s^{-1}. Also, the deprotonation rate constants should correspond closely to measured k_H values since only a small fractionation factor favouring OD^- over OH^- is expected[9] (*i.e.* $k_H = k_1, k_3$). However, a decision as to which k_H corresponds to k_1 is not possible since we are unable to distinguish between *syn*- and *anti*-NH deprotonation in the *syn*,*anti* isomers. Although the possible values are comparable (within a factor of 3, both complexes) the uncertainty makes the derived k_2 values correspondingly ambiguous. Thus $k_2 =$ (2 or 4) $\times 10^6$ s^{-1} with $k_{-2} = 3 \times 10^7$ s^{-1} for the oxalato complex, and $k_2 =$ (2 or 7) $\times 10^6$ s^{-1} with $k_{-2} = 1 \times 10^8$ s^{-1} for the malonato complex. However, despite the uncertainties in the above values it is clear that the observed isomer distributions result not from differences in rates of NH deprotonation, but from the ability of a *syn* lone pair in a deprotonated *syn*,*syn* isomer to invert more rapidly than the *anti* lone pair in its *syn*,*anti* congener.

Table 2 lists rate constants for proton exchange and, where applicable, for isomerisation and lone pair inversion at *sec*-NH centres in selected cobalt(III) cyclen complexes. It should be noted that, without exception, the various *syn*, *anti* and *ap* NH centres in these all have C–N–C bond angles of *ca.* 118, 115 and 110°, respectively, independent of complex charge (see below and refs. 3*a*, 3*e*), but there is no correlation between C–N–C bond angle and rate of exchange for *sec*-NH centres. It might be expected that strain, as indicated by the C–N–C bond angle, would be related to exchange rate,[10] but this appears not to be the case. Yet charge is clearly a factor in mediating rates of proton exchange at the *ap* centres, with approximately order of magnitude decreases in exchange rate as the charge reduces: $3+ \longrightarrow 2+ \longrightarrow 1+$, Table 2. Neither complex charge nor proton orientation (*syn* or *anti*) appears to be of significance in determining exchange rates at the *eq* NH sites. What seems to be important here is the nature of the other in-plane donor atoms, with exchange processes for *syn* and *anti* NH protons having k_H values in the range (1.5–6.6) $\times 10^9$ M^{-1} s^{-1} (*i.e.* at or near diffusion controlled rates) for sites *cis* to amine N (3+, 2+ charged complexes, NH_2R donors), and in the range (1–8.8) $\times 10^7$ M^{-1} s^{-1} for sites *cis* to carboxylate O (2+, 1+ charged complexes). These effects appear to be largely electronic in origin.

Lone pair inversion at equatorial amine sites in the O–O (oxalato, malonato) and N–O ((*S*)-AlaO) chelates is very rapid ($k_2 = 10^6$–10^8 s^{-1}) and is at least as fast as inversion of simple uncoordinated amines.[11] However, site geometry is important, and in all the complexes the conformationally frozen *ap*-NH centres are unable to invert (*cf*. Table 2). Also, the fastest inversion rates involve *syn*(O) lone pairs and this may be a consequence of repulsive interactions between these and those on adjacent *cis* carboxylate O.[2k] Inversion of both *syn*(N) and *anti*(O) lone pairs in *syn*,*anti* isomers appears to be at least an order of magnitude slower than inversion of *syn*(O) lone pairs. However, just why the *syn*,*anti* isomers should predominate in the equilibrium mixtures (all complexes) is not entirely clear from the kinetic viewpoint. The *syn*,*syn* arrangement is least favourable for the $[Co(cyclen)(diamine)]^{3+}$ ions (<1% of $[Co]_T$, diamine = $(NH_3)_2$, en or tn)[3e] and it appears that in the chelates a *cis* carboxylate O atom is necessary in order to stabilise the *syn*,*syn* arrangement. This configuration respectively accounts for 5.0, 9.1 and 5.3% of $[Co]_T$ in equilibrium mixtures of the (*S*)-alaninato,[3a] oxalato and malonato complexes, with hydrogen bonding of the *syn* NH proton to the adjacent carboxylate O atom indicated as a major stabilising influence. The N1–O3 separation of between 2.53 to 2.69 Å for the five structures of Fig. 3 make this a real possibility. It is not known whether the essential absence of the *anti*,*anti* forms implies abnormally fast inversion rates for *anti* lone pairs in this situation, but there is no obvious reason why this should be so.

Alkaline hydrolysis

Rate constants for alkaline hydrolysis of $[Co(cyclen)(O_2C_2O_2)]^+$ and $[Co(cyclen)(O_2CCH_2CO_2)]^+$ are given in Table 3 (25 °C, $I = 1.0$ M, $NaClO_4$). These data refer to reaction of equilibrium mixtures of *syn*,*anti* and *syn*,*syn* forms since in both cases isomerism is much faster than hydrolysis. For $[Co(cyclen)(O_2C_2O_2)]^+$ hydrolysis leads directly to $[Co(cyclen)(OH)_2]^+$, without the accumulation of an intermediate and with $k_{obs} = k_{OH}[OH^-]$ ($k_{OH} = 0.114 \pm 0.009$ M^{-1} s^{-1}). Thus, k_{OH} must refer to the ring opening reaction. However, hydrolysis of $[Co(cyclen)(O_2CCH_2CO_2)]^+$ gives $[Co(cyclen)(OH)_2]^+$ in two steps with $k_{(1)obs} = k_{OH(1)}[OH^-]$ and $k_{(2)obs} = k_{OH(2)}[OH^-]$ ($k_{OH(1)} = 26.9 \pm 0.6$ M^{-1} s^{-1}, $k_{OH(2)} = 4.9 \pm 0.6$ M^{-1} s^{-1}), and with ring-opening

Table 2 Rate constants for proton exchange, isomerisation and lone pair inversion at coordinated *sec* amine centres in some cobalt(III) cyclen complexes containing bidentate ligands, 25 °C, $I = 1.0$ M (NaCl or $NaClO_4$)

Complex	NH centre	$10^{-7}k_H/M^{-1}\ s^{-1}$	$10^{-5}k_N/M^{-1}\ s^{-1}$	$10^{-6}k_2/s^{-1}$
syn,*anti*-[Co(cyclen)($NH_2(CH_2)_2NH_2$)]$^{3+}$ [a]	*syn*	300	—	—
	anti	300	—	—
	ap	1.6	—	—
syn,*anti*-[Co(cyclen)($NH_2(CH_2)_3NH_2$)]$^{3+}$ [a]	*syn*	330	—	—
	anti	620	—	—
	ap	8	—	—
syn(N),*anti*(O)-[Co(cyclen)((*S*)-AlaO)]$^{2+}$ [b]	*syn*(N)	250	—	—
	anti(O)	6.6	0.65	10
	ap	0.12 and 0.16	—	—
syn(O),*anti*(N)-[Co(cyclen)((*S*)-AlaO)]$^{2+}$ [b]	*syn*(O)	3.9	—	—
	anti(N)	150	8	5
	ap	0.09 and 0.12	—	—
syn,*syn*-[Co(cyclen)((*S*)-AlaO)]$^{2+}$ [b]	*syn*(O)	5.8	7.5	100
	syn(N)	660	50	7
syn,*anti*-[Co(cyclen)($O_2C_2O_2$)]$^{+}$ [c]	*anti*	3 or 5	0.12	2.4 or 4
	ap	0.012	—	—
syn,*syn*-[Co(cyclen)($O_2C_2O_2$)]$^{+}$ [c]	*syn*	8.8 (4.4)	1.2	27
syn,*anti*-[Co(cyclen)($O_2CCH_2CO_2$)]$^{+}$ [c]	*anti*	1 or 3	0.072	2.4 or 7.2
	ap	0.011	—	—
syn,*syn*-[Co(cyclen)($O_2CCH_2CO_2$)]$^{+}$ [c]	*syn*	2.0 (1.0)	1.2	120
syn,*anti*-[Co(cyclen)(O_2CO)]$^{+}$ [d]	*anti* (*syn*)	0.21 or 0.77	—	—

[a] Ref. 3(*e*). [b] Ref. 3(*a*). [c] This work. [d] Ref. 3(*d*).

Table 3 Observed and calculated rate constants[a] for alkaline hydrolysis of [Co(cyclen)($O_2C_2O_2$)]$^{+}$ and [Co(cyclen)($O_2CCH_2CO_2$)]$^{+}$, 25.0 °C, $I = 1.0$ M ($NaClO_4$)

$[OH^-]$/M	10^2k_{obs}[b]/s^{-1}	10^2k_{calc}[b]/s^{-1}	$10^2k_{(1)obs}$[c]/s^{-1}	$10^2k_{(1)calc}$[c]/s^{-1}	$10^2k_{(2)obs}$[c]/s^{-1}	$10^2k_{(2)calc}$[c]/s^{-1}
0.075	—	—	2.10	2.01	—	—
0.10	0.961	1.14	2.81	2.69	0.510	0.490
0.20	1.97	2.28	5.91	5.37	0.926	0.980
0.30	3.16	3.42	8.47	8.06	1.42	1.47
0.40	4.24	4.56	11.6	10.7	1.95	1.96
0.50	5.58	5.70	14.4	13.4	2.30	2.45
0.60	6.55	6.84	16.4	16.1	2.57	2.94
0.70	7.81	7.98	19.2	18.8	3.32	3.43
0.80	9.16	9.12	21.4	21.5	4.09	3.92
0.90	10.6	10.3	23.6	24.2	4.26	4.41
1.00	11.8	11.4	25.9	26.9	5.11	4.90

[a] Calculated using $k_{OH} = 0.114\ M^{-1}\ s^{-1}$ (oxalato system) and $k_{OH(1)} = 26.9\ M^{-1}\ s^{-1}$, $k_{OH(2)} = 4.9\ M^{-1}\ s^{-1}$ (malonato system), see text. [b] *syn*,*anti*-[Co(cyclen)($O_2C_2O_2$)]$^{+}$ reactant. [c] *syn*,*anti*-[Co(cyclen)($O_2CCH_2CO_2$)]$^{+}$ reactant.

corresponding to the faster reaction. For either complex useful zero-time absorbance data could not be obtained prior to hydrolysis for OH^- concentrations in the range 0.025–1.0 M; only small, linear increases in absorbance with increasing $[OH^-]$ were observed. This implies that high concentrations of deprotonated species are not generated even at pH values approaching 14, since previous studies have shown that NH deprotonation leads to substantial changes in the visible spectra of cobalt(III) amines.[3a,e] The less than diffusion controlled rates of H/D exchange (*ca.* $10^7\ M^{-1}\ s^{-1}$, *cf.* Table 2) in [Co(cyclen)($O_2C_2O_2$)]$^{+}$ and [Co(cyclen)($O_2CCH_2CO_2$)]$^{+}$ also accord with $pK_a > 14$ for both species.[8] The faster to exchange ($k_H = 10^9$–$10^{10}\ M^{-1}\ s^{-1}$) and more highly charged *syn*,*anti*-[Co(cyclen)($NH_2(CH_2)_3NH_2$)]$^{3+}$ and *syn*,*anti*-[Co(cyclen)($NH_2(CH_2)_2NH_2$)]$^{3+}$ ions are substantially more acidic ($pK_a = 12.2$ and 12.9, respectively),[3e] and the situation is similar for [Co(cyclen)((*S*)-AlaO)]$^{2+}$ ($pK_a = 13.7$).[3a]

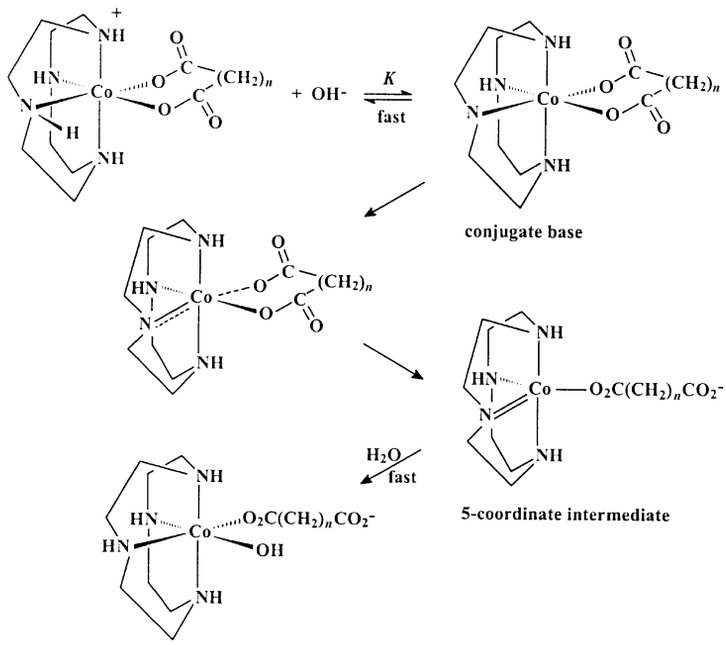
The rapid rates of OH^--catalysed ring opening in [Co(cyclen)($O_2C_2O_2$)]$^{+}$ and [Co(cyclen)($O_2CCH_2CO_2$)]$^{+}$ almost certainly imply that these species react *via* S_N1CB pathways, eqns. (1)–(3). Both Co–O and C–O bond cleavage is found

$$[(cyclen)Co(O\text{–}O)]^+ + OH^- \rightleftharpoons [(cyclen - H)Co(O\text{–}O)] + H_2O\ (K, \text{fast}) \quad (1)$$

$$[(cyclen - H)Co(O\text{–}O)] \longrightarrow [(cyclen - H)Co\text{–}O\text{–}O]\ (k_1, \text{r.d.s., 5-coord. int.}) \quad (2)$$

$$[(cyclen - H)Co\text{–}O\text{–}O] + H_2O \longrightarrow [(cyclen)Co(OH)\text{–}O\text{–}O]\ (\text{fast}) \quad (3)$$

for the ring-opening reaction of [Co(en)$_2$($O_2C_2O_2$)]$^{+}$ in alkali[11] but C–O fission, with its requirement for prior OH^- addition to carboxylate carbon, is much less likely for more reactive O–O chelates; [Co(cyclen)($O_2C_2O_2$)]$^{+}$ and [Co(cyclen)($O_2CCH_2CO_2$)]$^{+}$ base hydrolyse faster than their bis-ethylenediamine analogues[11,12] by factors of 1.6×10^3 and 9.5×10^4, respectively (1 M NaOH, 25.0 °C), and for the oxalato system the enhancement is 2.4×10^4 if just the S_N1CB contribution to the rate is considered. Since both complexes appear to be equally acidic (*cf.* the near identity in k_H values) the faster ring opening of [Co(cyclen)($O_2CCH_2CO_2$)]$^{+}$ compared to [Co(cyclen)($O_2C_2O_2$)]$^{+}$ (a ratio of 230:1 in k_{OH} values, $k_{OH} = k_1K$) must arise from differences in the rates of Co–O bond cleavage in the conjugate base species (k_1), *cf.* eqns. (1)–(3). The first Co–N bond fission in the [Co(cyclen − H)(tn)]$^{2+}$ and [Co(cyclen − H)(en)]$^{2+}$ ions exhibits a similar rate differential (ratio 140:1), and both sets of results reflect the greater stability of five- over six-membered chelate rings.[3e] In the mechanistic sense this is



Scheme 3 Ring opening mechanism for a $[(cyclen)Co(O–O)]^+$ chelate.

related to the ability of the system to modify its geometry on passing from the octahedral structure of the conjugate base derived from *syn*-NH deprotonation to the trigonal bipyramidal arrangement of the S_N1CB intermediate, *cf.* Scheme 3. Retention of chelate character in the dissociative transition state restricts the necessary bond angle expansion (from *ca.* 90 to *ca.* 120°), and this is more marked for the less flexible (*i.e.* five-membered) ring system. These aspects have been discussed previously [3e] and will be important for all chelate ring-opening reactions involving intermediates of reduced coordination number. Jordan [13] has recently commented on the unexpectedly slow rates of chelate ring opening in exchange labile nickel(II) species, and in these systems effects similar to those described above may well be operating.

Experimental

CAUTION: although no problems were encountered in the synthesis and handling of the materials described below, those containing perchlorate are potentially explosive and should be handled with great care.

Materials

***syn*,*anti*-[Co(cyclen)($O_2C_2O_2$)]ClO_4 and *syn*,*syn*-[Co(cyclen)-($O_2C_2O_2$)]ClO_4.** A solution of $Na_2C_2O_4$ (0.20 g, 1.5×10^{-3} mol) in the minimum volume of warm water was added to [Co(cyclen)Cl_2]Cl [14] (0.50 g, 1.5×10^{-3} mol) in 25 mL water and stirred at 60 °C for two hours. The solution was sorbed onto a column of Dowex 50W × 2, washed with acidified water and the products eluted with 0.5–1.0 M HCl. The first (crimson) and second (red) bands were collected and evaporated to dryness (Rotavap). Each fraction was crystallised from acidified water by addition of $LiClO_4$ and the product obtained by filtration, washing with EtOH and drying in air. First fraction: 0.32 g (52%) of the *syn*,*anti* isomer. Calc. for $C_{10}H_{20}ClCoN_4O_8$: C, 28.69; H, 4.82; Cl, 8.47; N, 13.38. Found: C, 28.83; H, 4.72; Cl, 8.50; N, 13.31%. ^{1}H NMR (1.0 M DCl, 25 °C): δ 6.89 (br s, 2H, *ap*); 6.73 (br s, 1H); 6.34 (br s, 1H); 3.58–3.53 (m, 2H); 3.22–2.98 (m, 8H); 2.83–2.71 (m, 6H). ^{13}C NMR (1.0 M DCl, 25 °C): δ 169.0, 168.5, 55.8, 53.4, 49.3 and 47.5. Second fraction: 0.23 g (30%) of the *syn*,*syn* isomer. Calc. for $C_{10}H_{20}ClCoN_4O_8$: C, 28.69; H, 4.82; Cl, 8.47; N, 13.38. Found: C, 28.51; H, 4.98; Cl, 8.53; N, 13.58%. ^{1}H NMR (1.0 M DCl, 25 °C): δ 6.88 (br s, 2H, *ap*); 6.47 (br s, 2H, *syn*); 3.45–3.30 (m, 4H); 3.28–3.06 (m, 8H); 2.90–2.74 (m, 4H). ^{13}C NMR (1.0 M DCl, 25 °C): δ 168.5, 57.0 and 50.7.

***syn*,*anti*- and *syn*,*syn*-[Co(cyclen)($O_2CCH_2CO_2$)]$ClO_4\cdot H_2O$, *syn*,*anti*-[Co(cyclen)($O_2CCH_2CO_2H$)][ClO_4]$_2\cdot 2H_2O$ and *syn*, *syn*-[Co(cyclen)($O_2CCH_2CO_2H$)][ClO_4]$_2$.** To malonic acid (0.370 g, 3.55×10^{-3} mol) in two mole equivalents of aqueous NaOH (0.5 M, 7 mL) was added [Co(cyclen)Cl_2]Cl [14] (1.20 g, 3.55×10^{-3} mol) in the minimum volume of warm water and the mixture stirred at 60 °C for 2 hours. The resulting solution was sorbed onto a column of Dowex 50W × 2 which was then washed with slightly acidified water and the complexes were eluted with 0.2–1.0 M HCl. The first (purple) and second (purple-red) bands were collected and evaporated to dryness (Rotavap). The residue from the first band was taken up in the minimum volume of warm 1 M perchloric acid and $LiClO_4$ added. The deep maroon crystals were filtered off and allowed to air dry giving 0.63 g (32%) of *syn*,*syn*-[Co(cyclen)-($O_2CCH_2CO_2H$)][ClO_4]$_2$. A fraction of this material was converted into *syn*,*syn*-[Co(cyclen)($O_2CCH_2CO_2$)]$ClO_4\cdot H_2O$ on layering a concentrated aqueous solution with EtOH. After two days the crimson crystals were filtered off, washed with ice–water and dried in air. The residue from evaporation of the second band was dissolved in the minimum volume of acidified water, $LiClO_4$ was added and the solution cooled to give *syn*,*anti*-[Co(cyclen)($O_2CCH_2CO_2H$)][ClO_4]$_2\cdot 2H_2O$. The maroon crystals were filtered off, washed with ethanol and air dried, 0.84 g (43%). A fraction of this material was crystallised by layering a concentrated aqueous solution with EtOH to give *syn*,*anti*-[Co(cyclen)($O_2CCH_2CO_2$)]$ClO_4\cdot H_2O$. *syn*,*syn*-[Co(cyclen)($O_2CCH_2CO_2H$)][ClO_4]$_2$ (Calc. for $C_{11}H_{23}Cl_2CoN_4O_{12}$: C, 24.79; H, 4.35; N, 10.51. Found: C, 24.66; H, 4.60; N, 10.23%): ^{1}H NMR (1.0 M DCl, 25 °C) δ 7.13 (br s, 2H, *ap*); 6.17 (br s, 2H, *syn*); 3.54–3.42 (m, 4H); 3.29–3.08 (m, 8H); 2.73–2.65 (m, 4H); ^{13}C NMR (1.0 M DCl, 25 °C) δ 179.9, 58.4 and 52.1. *syn*,*syn*-[Co(cyclen)($O_2CCH_2CO_2$)]$ClO_4\cdot H_2O$ (Calc. for $C_{11}H_{22}ClCoN_4O_8\cdot H_2O$: C, 29.31; H, 5.37; Cl, 7.87; N, 12.43. Found: C, 29.34; H, 5.51; Cl, 7.75; N, 12.24%); ^{1}H NMR (1.0 M DCl, 25 °C) δ 7.13 (br s, 2H); 6.17 (br s, 2H); 3.54–3.41 (m, 6H); 3.29–3.08 (m, 8H); 2.75–2.66 (m, 4H); ^{13}C NMR (D_2O, 25 °C) δ 179.6, 58.3, 51.8 and 43.3, *syn*,*anti*-[Co(cyclen)($O_2CCH_2CO_2$)]$ClO_4\cdot H_2O$ (Calc. for $C_{11}H_{22}ClCoN_4O_8\cdot H_2O$: C, 29.31; H, 5.37; Cl, 7.87; N, 12.43. Found: C, 29.46; H, 5.45; Cl, 7.87; N,

Table 4 Crystal data and structural refinement for *syn*,*syn*-[Co(cyclen)($O_2C_2O_2$)]ClO_4, *syn*,*anti*-[Co(cyclen)($O_2C_2O_2$)]ClO_4, *syn*,*anti*-[Co(cyclen)($O_2CCH_2CO_2$)]$ClO_4\cdot H_2O$, *syn*,*syn*-[Co(cyclen)($O_2CCH_2CO_2$)]$ClO_4\cdot H_2O$ and *syn*,*anti*-[Co(cyclen)($O_2CCH_2CO_2H$)][ClO_4]$_2\cdot 2H_2O$

Empirical formula	$C_{10}H_{20}ClCoN_4O_8$	$C_{10}H_{20}ClCoN_4O_8$	$C_{11}H_{22}ClCoN_4O_9$	$C_{11}H_{24}ClCoN_4O_9$	$C_{11}H_{23}Cl_2CoN_4O_{14}$
Formula weight	418.68	418.68	448.71	450.72	565.16
T/K	163(2)	158(2)	158(2)	170(2)	168(2)
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	*Pna*2(1)	$P\bar{1}$	$P2_1/c$	$P2_1/c$	*Pbca*
a/Å	13.277(8)	7.406(4)	7.5762(5)	15.268(5)	18.022(4)
b/Å	13.314(7)	8.610(5)	14.3014(10)	7.616(2)	14.943(3)
c/Å	8.669(5)	14.305(10)	15.9803(12)	15.285(5)	32.020(8)
α/°		77.850(18)			
β/°		86.805(18)	91.505(1)	92.923(4)	
γ/°		68.773(11)			
V/Å^3	1532.5(15)	831.1(9)	1730.9(2)	1775.1(10)	8623(4)
Z	4	2	4	4	16
μ(Mo-Kα)/mm^{-1}	1.345	1.240	1.202	1.172	1.121
Reflections measured	18451	8909	11767	21855	105292
Unique reflections	3093	2986	3366	3659	8727
	[*R*(int) = 0.0451]	[*R*(int) = 0.0344]	[*R*(int) = 0.0187]	[*R*(int) = 0.0549]	[*R*(int) = 0.1454]
Final *R*1, *wR*2 [$I > 2\sigma(I)$]	0.0609, 0.1555	0.0480, 0.1412	0.0304, 0.0802	0.0369, 0.0934	0.0509, 0.0953
(all data)	0.0685, 0.1588	0.0513, 0.1453	0.0325, 0.0815	0.0446, 0.0974	0.1033, 0.1128

12.43%). ^{1}H NMR (1.0 M DCl, 25 °C) *δ* 7.19 (br s, 2H, *ap*); 6.72 (br s, 1H); 6.08 (br s, 1H); 3.70–3.60 (m, 2H); 3.35 (s, partially exchanged); 3.22–2.98 (m, 8H); 2.86–2.83 (m, 2H); 2.72–2.69 (m, 2H); 2.58–2.55 (m, 2H); ^{13}C NMR (1.0 M $NaClO_4$, 25 °C) *δ* 180.2, 179.7, 57.3, 54.8, 49.8, 48.6 and 43.7. *syn*,*anti*-[Co(cyclen)($O_2CCH_2CO_2H$)][ClO_4]$_2\cdot 2H_2O$ (Calc. for $C_{11}H_{23}Cl_2CoN_4O_{12}Cl_2\cdot 2H_2O$: C, 23.21; H, 4.78; Cl, 12.46; N, 9.84. Found: C, 23.67; H, 4.84; Cl, 12.72; N, 9.92%): ^{1}H NMR (1.0 M DCl, 25 °C) *δ* 7.17 (br s, 2H, *ap*); 6.71 (br s, 1H); 6.08 (br s, 1H); 3.78–3.60 (m, 2H); 3.18–3.03 (m, 8H); 2.86–2.83 (m, 2H); 2.72–2.69 (m, 2H); 2.58–2.55 (m, 2H); ^{13}C NMR (1.0 M DCl, 25 °C) *δ* 181.2, 179.2, 57.5, 54.8, 50.1 and 49.0.

Reagents were of AR grade. D_2O was obtained from Aldrich (99.9 atom% D) and Merck (99.8 atom% D).

Physical measurements

pH and pD measurements were made at 25.0 ± 0.1 °C using a Radiometer PHM 82 pH meter equipped with G2040B glass and K4040 calomel electrodes and a $NaNO_3$–NH_4NO_3 salt bridge. The system was calibrated using phosphate (0.025 M KH_2PO_4, 0.025 M Na_2HPO_4, pH 6.865), potassium hydrogenphthalate (0.05 M, pH 4.008) and $KH_3(C_2O_4)_2$ (0.05 M, pH 1.679) buffers.[15] pD was obtained from the relationship[16] pD = pH (meter reading) + 0.40. Values of [OD^-] were obtained from pD using [OD^-] = $10^{(pD\,-\,14.951)}/\gamma_{\pm}$, where $\gamma_{\pm}$ (1.0 M $NaClO_4$) = 0.67 M[17] and pK_w(D_2O) = 14.951 at 25 °C.[18]

Proton exchange studies were carried out using acidified ($DClO_4$ or DCl) or buffered, D_2O solutions. Formate buffers were prepared by taking D_2O, 1.0 M in $NaClO_4$ or NaCl (5 mL), and adding 18 μL formic acid to give [HCO_2D]$_T$ = 0.10 M. The pD was then adjusted to the required value by addition of 37% NaOD. Phosphate buffer solutions were prepared in a similar procedure using sodium dihydrogenorthophosphate (0.03 M) and 37% NaOD.

Rate data for proton exchange in the cobalt(III) cyclen complexes in D_2O were collected at 25 ± 0.5 °C using Varian VXR 300 MHz or Inova-500 2 Channel FT 500 MHz spectrometers. Reactions were carried out using *ca*. 20 mg of complex in 700 μL of buffer (*I* = 1.0 M) and the solution pD was measured at the completion of each experiment. Collected data from arrayed experiments were treated by least squares fitting[19] the time dependence of amine-NH signal area to a single exponential. Errors in the observed rate constants are estimated as ±10%.

Isomerisation rate measurements were made using a Cary 500 UV-vis spectrophotometer. Rate data for the alkaline hydrolysis of [Co(cyclen)($O_2C_2O_2$)]$^+$ were collected using a Cary 219 UV-vis instrument by following the decrease in absorbance at 300 nm. The biphasic reaction of [Co(cyclen)($O_2CCH_2CO_2$)]$^+$ in alkaline solution was followed using an OLIS stopped-flow instrument RSM-1000. The wavelength selected was in the range 500–580 nm where best definition of k^{fast} and k^{slow} was observed for a particular [OH^-] and absorbance–time traces were analysed using the appropriate double exponential expression[20] and least squares fitting.[19] Errors in observed rate constants obtained from spectrophotometric measurements are estimated as ±3%. For both complexes the final product of base hydrolysis was *syn*,*anti*-[Co(cyclen)($OH)_2$]$^+$ (λ_{max} = 547 (*ε* = 188 and 360 nm (166 M^{-1} cm^{-1})).[3d]

Crystal structures

Diffraction data for single crystals of *syn*,*syn*-[Co(cyclen)($O_2C_2O_2$)]ClO_4, *syn*,*anti*-[Co(cyclen)($O_2C_2O_2$)]ClO_4, *syn*,*anti*-[Co(cyclen)($O_2CCH_2CO_2$)]$ClO_4\cdot H_2O$, *syn*,*syn*-[Co(cyclen)($O_2CCH_2CO_2$)]$ClO_4\cdot H_2O$ and *syn*,*anti*-[Co(cyclen)($O_2CCH_2CO_2H$)][ClO_4]$_2\cdot 2H_2O$, isolated as described in the Experimental section, were collected on a Siemens SMART system using graphite monochromated Mo-Kα radiation with exposures over 0.3°. Data were corrected for Lorentz and polarisation effects using SAINT.[21] The structures were solved by direct methods using the TREF option in SHELXS 97[22] and weighted full-matrix refinement on F^2 was carried out using SHELXL 97.[23] With the exceptions described below, hydrogen atoms were included in calculated positions and refined as riding atoms with individual (or group, if appropriate) isotropic displacement parameters. The hydrogen atoms of the water molecule in *syn*,*syn*-[Co(cyclen)($O_2CCH_2CO_2$)]$ClO_4\cdot H_2O$ were located in the Fourier map and refined isotropically. The hydrogen atoms attached to O2 and O23 of the hydrogenmalonato ligands in *syn*,*anti*-[Co(cyclen)($O_2CCH_2CO_2H$)][ClO_4]$_2\cdot 2H_2O$ were similarly located, but attempts to refine these isotropically were unsuccessful. They were included in calculated positions as described above. The perchlorate oxygen atoms in all structures showed no disorder, with the exception of those attached to Cl1 in *syn*,*anti*-[Co(cyclen)($O_2CCH_2CO_2H$)][ClO_4]$_2\cdot 2H_2O$. This perchlorate was treated as being disordered over two sites, with almost equal (46 : 54) occupancy. Details of the crystals and structural refinements are given in Table 4.

CCDC reference number 186/2316.

See http://www.rsc.org/suppdata/dt/b0/b008350j/ for crystallographic files in .cif format.

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