The first structurally characterised perchlorato-cobalt(III) complexes, involving the C-bonded macrobicyclic ligand 1,4,8,11-tetraazabicyclo[9.5.2]octadecane†

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Two isomeric C-bonded complexes, *sym-anti*-[Co(L-C)(OH₂)]²⁺ and *sym-syn*-[Co(L-C)(OH₂)]²⁺ (L = 1,4,8,11-tetraazabicyclo[9.5.2]octadecane) when crystallised from aqueous NaClO₄ remarkably yielded the corresponding perchlorato complexes, confirmed by the single crystal X-ray structures.

As shown in Scheme 1, 1,4,8,11-tetraazabicyclo[9.5.2]octadecane (L) reacts with [Co(py)₄Cl₂]Cl·6H₂O under basic conditions and is dehydrogenated.[1] Regeneration of the amine function by BH₄⁻ reduction yields two symmetrical isomeric complexes in comparable amounts. These were separated and purified by column chromatography (Dowex, 50W-X2, H⁺ form, 200–400 mesh), in 62% total yield, and crystallised as their ClO₄⁻ salts. The faster eluted isomer has the newly generated *sec*-NH centre *anti* to the bound aqua group, the other *syn*. Crystals suitable for the crystal structural determinations were obtained by slow evaporation of the orange solutions of the individual complexes containing NaClO₄ (5 M). The resultant crystals were deep pink, yet their aqueous solutions were orange. The composition of both materials is [Co(L-C)(OClO₃)]ClO₄.‡

The molecular structures and the selected bond lengths and bond angles for both isomers, *sym-anti*- and *sym-syn*-[Co(L-C)(OClO₃)]ClO₄ and are presented in Figs. 1 and 2. Four octahedral sites are occupied by the nitrogen donors, one by the anionic γ-carbon of the dacn (1,4-diazacyclononane) ring, and one by an oxygen of a perchlorato group. In both complexes, the Co(1)–C(14) bond distance is 1.984 Å which is similar to that in [Co(L'-C)(OH₂)]ZnCl₄.[1] The *sym-anti* complex crystallises in the chiral space group P2₁, *i.e.*, it spontaneously resolves. The 6-membered ring adopts the preferred chair conformation in each structure.

The structural work confirms that the ligand L is as shown, saturated, *i.e.*, the imine has been hydrogenated. The generation of this additional bound *sec*-NH centre means that there are two adjacent *sec*-NH centres in a 'planar' arrangement of the 2223-N₄ portion of the bicyclic ligand. Fig. 3 shows that the original facial arrangement of one of these NH centres has become 'planar' in the BH₄⁻ reduction process, and it can invert under the mildly basic conditions to become *syn* or *anti* to the X
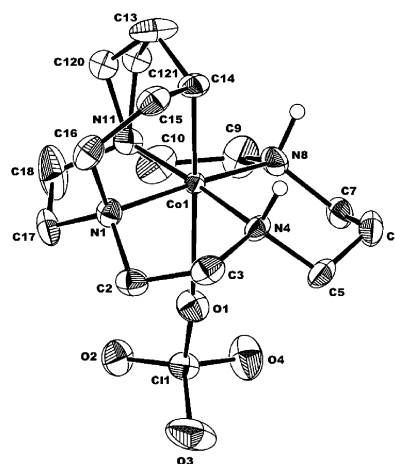

Fig. 1 An ORTEP drawing of the cation *sym-anti*-[Co(L-C)(OClO₃)]⁺ with 30% probability ellipsoids. Atom C12 has been split over two sites. Hydrogen atoms (excluding the secondary amines) are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Co1–O1 2.452 (4), Co1–N1 1.943 (3), Co1–N4 1.964 (3), Co1–N8 1.968 (3), Co1–N11 1.926 (3), Co1–C14 1.984 (4), C13–C14 1.521 (7), C14–C15 1.532 (6); O1–Co1–N1 88.5 (1), O1–Co1–N11 92.7 (1), N1–Co1–N8 171.19 (17), N4–Co1–N11 176.29 (17).
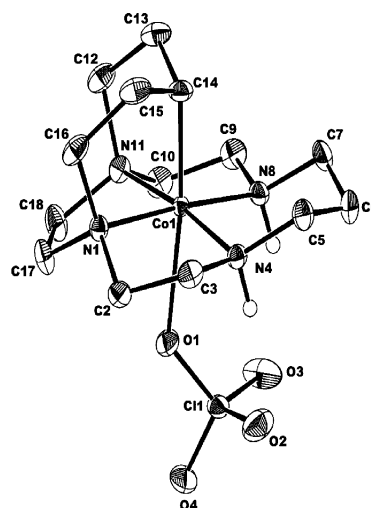

Fig. 2 An ORTEP drawing of *sym-syn*-[Co(L-C)(OClO₃)]⁺ with 30% probability ellipsoids. Hydrogen atoms (excluding the secondary amines) are omitted for clarity. Selected bond lengths (Å) and bond angels (°): Co1–O1 2.3557 (15), Co1–N1 1.9418 (15), Co1–N4 1.9503 (15), Co1–N8 1.9521 (16), Co1–N11 1.9389 (16), Co1–C14 1.9836 (19), C13–C14 1.514 (3), C14–C15 1.516 (3); O1–Co1–N1 86.32 (6), O1–Co1–N11 87.58 (6), N1–Co1–N8 173.32 (7), N4–Co1–N11 173.07 (7).

Scheme 1 Synthetic route to the Co(III) complexes of L.

group. Each such *sec*-NH centre can be *anti* or *syn* to the X group (aqua or perchlorate), and this gives rise to three isomers in principle for the *sym* configuration of the bicyclic ligand – both *sec*-NH centres can be *syn* or *anti*, or one *syn* and the other *anti*. We observe only two of these three possibilities.

The Co1–O1 bonds, in the *sym-anti*- and *sym-syn*-complexes are, respectively, 2.452 and 2.355 Å, which are rather long. The Cl–O1 bond lengths are 1.445 and 1.463 Å. These should be compared with the Cl–O bond lengths in the ClO_4^- counterions, which range from 1.407 to 1.442 Å, but which are on average shorter. Further, the Cl–O bonds lengths (excluding Co1–O1) in the bound ClO_4^- range from 1.401 to 1.463 Å. The expectation was for a metal ion bound O1–Cl1 to be longer than the others in the bound and free ligands but the ranges and other uncertainties do not permit meaningful comparisons.

The ^{13}C spectrum of each complex revealed the expected six CH_2 peaks, another peak due to the unique C6, while the supposed cobalt-bonded carbon was undetectable for the *sym*-anti complex. For the *sym-syn* complex, there is a small but broad peak at δ 40.82 ppm.‡ The weakness or absence of these carbon resonances is consistent with quadrupolar relaxation from the bonded ^{59}Co nucleus.

The proton on the Co(III)-bonded CH group is observed at δ 4.13 ppm in the ^1H spectrum of *sym-syn*-[Co(L-*C*)(OS(CD$_3$)$_2$)]$^{2+}$, generated by dissolution of the isolated perchlorato complex in (CD$_3$)$_2$SO. The significant ^1H–^1H through-space correlations are presented in Fig. 3. [Note that there are five other possible isomers, but all are asymmetric.] The DQCOSY and NOESY spectra of *sym-syn*-[Co(L-*C*)(OS(CD$_3$)$_2$)]$^{2+}$ are shown in the ESI† and Fig. 4. From the DQCOSY NMR spectrum the peaks at δ 4.12 and 3.96 ppm are assigned to the carbanion C*H* and N*H* protons respectively. From the NOESY spectrum, Fig. 4, the important cross peak (A) is observed, which is due to the H_1–H_3/H_4 interaction. This isomer can therefore be identified unambiguously as *sym-syn*-[Co(L-*C*)(OH$_2$)]$^{2+}$, so that the other must be *sym-anti*-[Co(L-*C*)(OH$_2$)]$^{2+}$. These conclusions are consistent with the crystal structural results for the perchlorato complexes chemically correlated to these DMSO complexes.
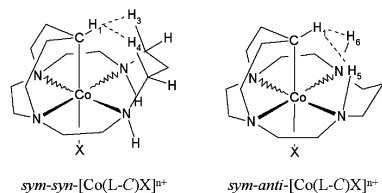

sym-syn-[Co(L-*C*)X]$^{n+}$ *sym-anti*-[Co(L-*C*)X]$^{n+}$
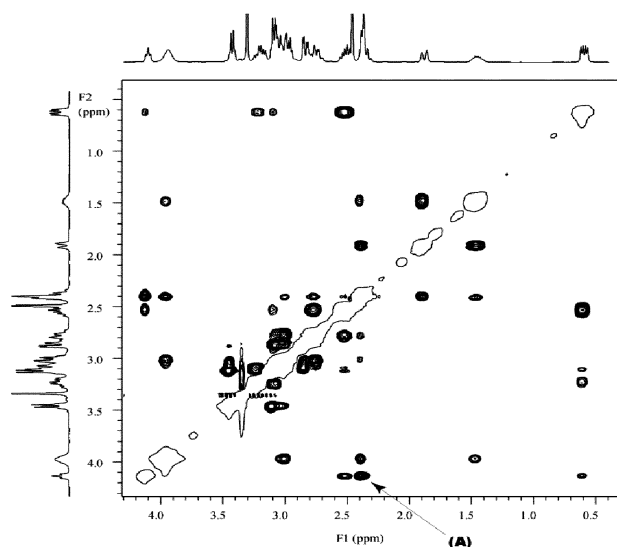
Fig. 3 Possible isomers of *sym*-[Co(L-*C*)X]$^{n+}$.

Fig. 4 ^1H NOESY spectrum of *sym-syn*-[Co(L-*C*)(OClO$_3$)]ClO$_4$ in Me$_2$SO-d_6; the complex in solution is [Co(L-*C*)(OS(CD$_3$)$_2$)]$^{2+}$.

The complex [(NH$_3$)$_5$Co(OClO$_3$)](ClO$_4$)$_2$ has been reported, although there are no X-ray structural data.[2] It hydrolyses completely in water within 1 min at 25 °C. Presumably in the case of such complexes in H$_2$O containing NaClO$_4$ there are very small but finite concentrations of the perchlorato species, and in the present cases of the macrocyclic species, it is clear that they selectively crystallise rather than the predominant aqua species simply because they are much less soluble (as ClO$_4^-$ salts). There are no clear indications of special lattice stabilising features in the crystallography. Alternative counterions, to selectively crystallise the aqua or perchlorato species, were not investigated.

This is the first report of perchlorate-bonded cobalt(III) complexes crystallised from aqueous solution, a fact quite remarkable. It is all the more remarkable where the group *trans* to the bound perchlorate is a *trans* activating carbanion, but this is only in a kinetic sense; both bound perchlorate and aqua groups are labilised to rapid substitution, but the equilibrium between the perchlorato and aqua ions may be unaffected, or even shifted to be more favourable towards perchlorate bonding. When the perchlorato ions are dissolved in D$_2$O or Me$_2$SO-d_6, the colour of both solutions is yellow rather than pink, as the D$_2$O or Me$_2$SO-d_6 substitutes 'instantly' the coordinated ClO$_4^-$ ligand to form the corresponding solvento complexes.

Notes and references

‡   *sym-anti*-[Co(L-*C*)(OClO$_3$)]ClO$_4$. Anal. Calcd for C$_{14}$H$_{29}$N$_4$Cl$_2$CoO$_8$: C, 31.77, H, 5.90, N, 10.59, Cl, 13.59. Found: C, 32.17, H, 5.74, N, 10.61, Cl, 13.55%. ^{13}C NMR δ (Me$_2$SO-d_6): 27.61, 38.69, 49.74, 52.79, 59.33, 59.55 and 60.78 ppm. ^1H NMR δ (Me$_2$SO-d_6): 0.85 (2H, m), 1.12 (1H, t), 1.71 (1H, d), 1.95 (2H, m), 2.43 (2H, m), 2.53–2.70 (6H, m), 2.94–3.10 (6H, m), 3.34–3.45 (4H, m), 4.61 (3H, s) ppm. *sym-syn*-[Co(L-*C*)(OClO$_3$)]ClO$_4$. Anal. Calcd for C$_{14}$H$_{29}$N$_4$Cl$_2$CoO$_8$: C, 31.77, H, 5.90, N, 10.59, Cl, 13.59. Found: C, 32.16, H, 5.57, N, 10.38, Cl, 13.76%. ^{13}C NMR δ (Me$_2$SO-d_6): 28.30, 40.85 (weak, br), 41.87, 46.71, 54.71, 63.44, 63.74 and 63.81 ppm. ^1H NMR δ (Me$_2$SO-d_6): 0.62 (2H, m), 1.48 (1H, t), 1.92 (1H, d), 2.40 (4H, t), 2.53 (2H, m), 2.75–2.89 (4H, m), 2.97–3.14 (8H, m), 3.23 (2H, m), 3.45 (2H, m), 3.97 (1H, t) ppm.

Crystal data: *sym-anti*-[Co(L-*C*)(OClO$_3$)]ClO$_4$, M = 511.24, purple, plate crystal (0.32 × 0.32 × 0.13 mm), monoclinic, space group $P2_1$, a = 8.1097 (1), b = 14.6807 (3), c = 8.7957 (2) Å, β = 108.442 (1)°, V = 993.40 (3) Å^3, Z = 2, D_c = 1.709 g cm^{-3}, μ = 1.185 mm^{-1}, 24988 reflections measured, 5778 independent. Atom C12 has been split over two isotropic sites. Refinement converged at a final R = 0.0368, wR = 0.0416, S = 1.0641 [for 3703 reflections with $I > 3.00\sigma(I)$] for 268 parameters. A final difference Fourier showed no residual outside −0.50 and 1.32 e Å^{-3}.

sym-syn-[Co(L-*C*)(OClO$_3$)]ClO$_4$, M = 511.24, orange, block crystal (0.47 × 0.36 × 0.23 mm), monoclinic, space group $P2_1/c$, a = 8.4196 (1), b = 16.6021 (2), c = 14.4434 (2) Å, β = 92.6915 (7)°, V = 2016.72 (3) Å^3, Z = 4, D_c = 1.684 g cm^{-3}, μ = 1.167 mm^{-1}, 47680 reflections measured, 5878 independent. Refinement converged at a final R = 0.0314, wR = 0.0371, S = 1.0616 [for 4106 reflections with $I > 3.00\sigma(I)$] for 268 parameters. A final difference Fourier showed no residual outside −0.55 and 0.82 e Å^{-3}.

For both structures $3 < \theta < 30°$, CCD scan, T = 200 K, Mo-Kα radiation, graphite monochromator, λ = 0.71073 Å) on an Enraf-Nonius CCD diffractometer. Analytical absorption and Lorentz polarisation corrections were applied to the data. The structure was solved by direct methods and refined by full-matrix least squares procedures based on *F*. Fully occupied non-H atoms were refined with anisotropic displacement parameters. The remaining non-H atoms were refined anisotropically. H atoms attached to N atoms were refined positionally, and those bonded to C atoms were included at calculated positions and ride on the atom to which they are bonded. CCDC 210479 (*sym-syn*) and 210480 (*sym-anti*); see http://www.rsc.org/suppdata/cc/b3/b305182j/ for crystallographic files in .cif format.

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