Rapid Preparations of *trans*-$[CoX_2(L)]ClO_4$ Complexes (L = Me_2[14]dieneN_4, Me_4[14]dieneN_4 and Me_5[14]dieneN_4; X = Cl, Br) and Mechanistic Comments on Synthetic Routes

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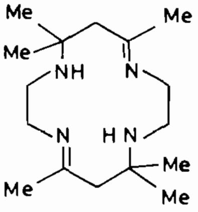
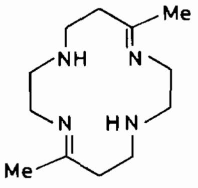
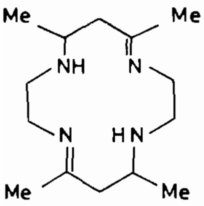
Complexes of the type $[CoX_2(L)]^+$ where L is a 14-membered macrocyclic tetra-aza ligand are generally prepared by methods developed by Sadasivan, Kernohan and Endicott [1] for complexes of Me_6-[14]dieneN_4 (I):



(I)



(II)



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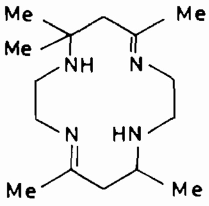

(IV)

We now describe rapid methods for the preparation of $[CoX_2(L)](ClO_4)$ complexes where L = Me_2-[14]dieneN_4 (II); Me_4[14]dieneN_4 (III); Me_5[14]dieneN_4 (IV) and X = Cl^-, Br^-.

Experimental

The dihydroperchlorate salts of the ligands were prepared as previously described Me_2[14]dieneN_4·$2HClO_4$ [2], Me_4[14]dieneN_4·$2HClO_4$ [3] and Me_5[14]dieneN_4·$2HClO_4$ [4].

Trans-*[$CoBr_2$(Me_2[14]dieneN_4] ClO_4*

The ligand dihydroperchlorate (4.20 g) was dissolved in hot aqueous methanol (145 cm^3 methanol and 5 cm^3 water). To this solution was added cobalt(II) bromide hexahydrate (3.2 g) in methanol (40 cm^3). The mixture was heated on a water bath for *ca.* 5 min, the solution became deep green and apple green crystals formed. After further heating (5 min) the solution was allowed to cool slowly and the complex was filtered off, washed with methanol then ethanol and dried *in vacuo* over silica gel (yield 2.1 g). *Anal.* Calc. for $C_{12}H_{24}Br_2ClCoN_4O_4$: C, 26.57; H, 4.46; N, 10.33. Found: C, 26.36; H, 4.38; N, 10.29%.

Trans-*[$CoBr_2$(Me_4[14]dieneN_4)] ClO_4*

A solution of cobalt(II) bromide hexahydrate (5.0 g) in hot methanol (50 cm^3) was added with stirring to the ligand dihydroperchlorate (7.2 g) in methanol (150 cm^3). The mixture was gently heated on a water bath for *ca.* 5 min and the resulting reddish brown solution filtered. The filtrate was heated for *ca.* 20 min when apple-green crystals formed. The solution was cooled slowly to room temperature and the crystals were removed by filtration, washed with methanol and dried (yield 3.6 g). A second crop (0.5 g) could be obtained by reducing the filtrate volume to *ca.* 50 cm^3. *Anal.* Calc. for $C_{14}H_{28}Br_2ClCoN_4O_4$: C, 29.47; H, 4.95; M, 9.82. Found: C, 29.32; H, 4.89; N, 9.82%.

Trans-*[$CoBr_2$(Me_5[14]dieneN_4)] ClO_4*

A filtered solution of $CoBr_2·6H_2O$ (3.25 g) in hot methanol (50 cm^3) was added to the ligand dihydroperchlorate (4.6 g) in methanol (100 cm^3). The mixture was heated on a water bath for *ca.* 1 hr, during which time the solution changed in colour from reddish-brown to green. The solution was allowed to stand (*ca.* 1.5 hr) and the resulting apple green crystals were filtered off, washed with methanol and dried (yield 2.0 g). A second crop (0.5 g) could be obtained by reducing the filtrate volume to 50 cm^3 and cooling. *Anal.* Calc. for $C_{15}H_{30}Br_2ClCoN_4O_4$: C, 30.82; H, 5.17; N, 9.58. Found: C, 30.67; H, 5.03; N, 9.66%.

Trans-*[$CoCl_2$(Me_4[14]dieneN_4)] ClO_4*

A solution of cobalt(II) chloride hexahydrate (0.48 g) in hot methanol (20 cm^3) was mixed with the ligadn dihydroperchlorate (0.9 g) in methanol (30 cm^3) and the mixture heated on a water bath for *ca.* 2 min during which time the solution rapidly changed in colour from blue to deep green. The solution was filtered hot and the filtrate heated on a water bath for a further 10 min, then allowed to cool. The green crystals obtained were filtered off and

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washed with methanol then ether (yield 0.3 g). Reduction of the filtrate volume to *ca.* 20 cm^3 gave a second crop (0.1 g). *Anal.* Calc. for $C_{14}H_{28}Cl_3CoN_4O_4$: C, 34.90; H, 5.85; N, 11.60. Found: C, 34.54; H, 5.74; N, 11.56%.

Trans-$[CoCl_2(Me_5[14]dieneN_4)]ClO_4$ was prepared similarly. *Anal.* Calc. for $C_{15}H_{30}Cl_3CoN_4O_4$: C, 36.34; H, 6.10; N, 11.30. Found: C, 36.37; H, 5.90; N, 11.21%.

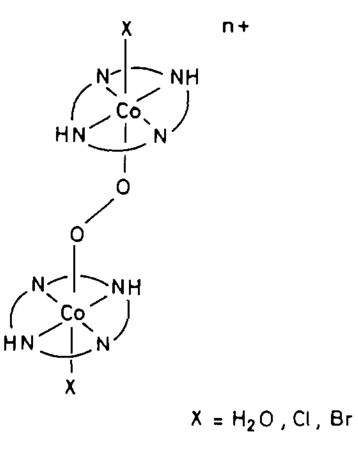
Trans-*[CoCl$_2$(Me$_2$[14]dieneN$_4$)]ClO$_4$*

A solution of $CoCl_2 \cdot 6H_2O$ (0.75 g) in methanol (10 cm^3) was added with stirring to a solution of aqueous methanol (60 cm^3, 90% methanol v/v) and the resulting mixture heated on a water bath (30 min), during which time the solution colour changed from brown to green. Initially some brown crystals, presumably the μ-peroxo species began to precipitate, but these disappeared on heating. After standing (1 hr) the pale green crystals were filtered off, washed with methanol then ether and dried *in vacuo* over silica gel (yield 0.5 g). *Anal.* Calc. for $C_{12}H_{24}Cl_3CoN_4O_4$: C, 31.77; H, 5.33; N, 12.35. Found: C, 31.51; H, 5.17; N, 12.11%.

Results and Discussion

The preparations of complexes of the present type have previously involved long periods of aeration of the ligand dihydroperchlorate and the appropriate cobalt(II) salt in methanol–water mixtures, or reaction of $Na_3[Co(CO_3)_3]$ with the ligand hydroperchlorate or hydrobromide in aqueous solution [1]. Such techniques are not required and the complexes can be readily isolated by the described methods in adequate yield.

The present complexes are almost certainly produced via the μ-peroxo species (V) and some of these can readily be isolated [3, 5–7].



(V)

The reaction of dissolved oxygen with the cobalt(II) complexes of the macrocycles is a rapid process (eqns. 1 and 2).

$$Co^{II}L + O_2 \overset{K_1}{\rightleftharpoons} Co^{III}LO_2^{\dot{-}} \tag{1}$$

$$Co^{III}LO_2^{\dot{-}} + Co^{II}L \overset{K_2}{\rightleftharpoons} [LCo^{III}O_2^{2-}Co^{III}L] \tag{2}$$

Kinetic work indicates that the μ-peroxo species decompose quite rapidly to $Co^{II}L$ and O_2. Thus $[(en)_2(NH_3)Co^{III}(\mu\text{-}O_2^{2-})Co^{III}(NH_3)(en)_2]^{4+}$ breaks down to Co^{II} and O_2 over the pH range 1.1–10.2 at a rate independent of $[H^+]$ [8]. Similar conclusions have been reached with the complex $[(tren)(NH_3)Co^{III}(\mu\text{-}O_2^{2-})Co^{III}(NH_3)(tren)]^{4+}$ [9].

Cobalt(II) complexes of 14-membered tetraaza macrocycles have been reported as low spin $[Co(N_4)(OH_2)_2]^{2+}$ species. Thus $[Co(Me_6[14]dieneN_4)(OH_2)]^{2+}$ is described as a yellow low spin species before oxygenation [10]. Low spin $t_{2g}^6e_g^1$ cobalt(II) complexes will be subject to Jahn–Teller distortion and the axial cobalt(II)–ligand bond lengths tend to be much longer than the corresponding axial Co^{III}–ligand bond lengths. The reorganisational barrier resulting from this difference in bond lengths is expected to be an important factor in determining rate patterns for electron transfer.

Wong *et al.* [11] have shown that the reaction of $[Co(Me_2[14]dieneN_4)(OH_2)_2]^{2+}$ with O_2 is rapid with apparently quantitative formation of the μ-peroxo complex in less than 1 minute. Breakdown of $[(H_2O)Co(Me_2[14]dieneN_4)]_2O_2^{4+}$ occurs in acidic media by a two step reaction, neither step showing a dependence on $[H^+]$ over the acidity range 0.05 to 0.5 *M* $[H^+]$. The products obtained are $[Co(OH_2)_6]^{2+}$ and LH_2^{2+} [12]. These reactions appear to involve the reverse of equations (1) and (2), coupled with the further reaction (3):

$$[CoL]^{2+} + 2H^+ \rightarrow [Co(H_2O)_6]^{2+} + LH_2^{2+} \tag{3}$$

Clearly strongly acidic conditions should be avoided in preparations of cobalt(III) complexes of macrocycles by aeration procedures.

Preparative methods using $[Co(CO_3)_3]^{3-}$ are likely to involve the intermediate formation of *cis*-$[CoL(CO_3)]^+$ which breaks down to *cis*-$[CoL(OH_2)_2]^{3+}$ under acidic conditions [13]. The aqua complex can then undergo isomerisation and anation to give the *trans* dihalo complex. *Cis*-complexes require the N-*racemic* stereochemistry of the chiral nitrogen centres of the macrocycle, and this stereochemistry will be retained in the dihalo-complex if acidic conditions are employed to prevent epimerisation.

As a result, different diastereoisomeric dihalo-complexes can be prepared by the aeration and [Co-$(CO_3)_3]^-$ routes [1, 3, 6]. The macrocycle has a planar configuration in the μ-peroxo intermediate and this reaction is expected to give mixtures of N-*meso* and N-*racemic* diastereoisomers, unless of course the N-*meso* diastereoisomer is much more thermodynamically stable than the N-*racemic*-derivative.

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