

Synthesis and structural characterisation of a series of cobalt complexes of N-appended anthracenyl cyclam

Simon Boyd, W. David McFadyen*, Brendan F. Abrahams, Martin J. Grannas, Kenneth P. Ghiggino

School of Chemistry, University of Melbourne, Vic. 3010, Australia

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Abstract

The synthesis and structural characterisation of a series of cobalt complexes of 1-(anthracen-9-ylmethyl)-1,4,8,11-tetraazacyclotetradecane (hereafter **L2**) is described. The complexes, of the type $trans\text{-[CoL2X}_2\text{]}^+$ in which $X = \text{Cl}^-$, NCS^- and NO_2^- were synthesised for their use in photoactivated ligand release studies. X-ray crystal structures show that the macrocycle in all three complexes of the series adopts a *trans*-(*III*) configuration. Both thiocyanato ligands were found to be N-bound in $trans\text{-[CoL2(NCS)}_2\text{]}^+$ while $trans\text{-[CoL2(NO}_2\text{)}_2\text{]}^+$ contained both a nitro and nitrito ligand in the one complex. The synthesis of the complex $cis\text{-[CoL2(NO}_2\text{)}_2\text{]}^+$ from sodium hexanitrocobaltate(III) is also described. This complex also contains both a nitro and nitrito ligand in the one complex, with the cyclam in a *cis*-(*V*) arrangement about the metal centre.

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1. Introduction

A considerable range of systems has been developed which utilise the electron and energy transfer processes occurring in linked donor–acceptor molecules for particular applications. The scope of this work encompasses the use of transition metal complexes and a number of potential uses of metal-based systems are being realised. Fabrizzi's group have described several molecular systems in which a fluorescent chromophore has been covalently linked to a cyclic or open quadridentate ligand [1–7]. Such systems can be used for a variety of applications such as molecular thermometers [1], molecular switches of fluorescence [2–4] or sensitive metal ion sensors [5–7] when triggered by complexation with a transition metal ion. De Rosa et al. describe a range of Cr(III) cyclam complexes in which pendant chromophores could serve as sensitizers

for metal centred photoreactions [8,9]. Complexes involving a coordinated nitrite ligand were found to be capable of photoactivated nitric oxide generation [9]. Compounds of this type could enable delivery of the biologically important NO within a well-defined volume when coupled with a focussed excitation source [9]. We are interested in similar donor–acceptor complexes containing a Co(III) metal centre coupled to a range of ligands for future use in photoactivated ligand release studies. Towards this end we have previously described the synthesis and characterisation of the ligand 6-(anthracen-9-ylmethyl)-1,4,8,11-tetraazacyclotetradecane (hereafter **L1**) in which an anthracene moiety is appended to the apical carbon of the cyclam framework by a methylene bridge (Fig. 1) [10]. Subsequent metallation with cobalt was also described to yield the complex $trans\text{-[CoL1Cl}_2\text{]}^+$ and some of its photochemical properties were examined. Excitation of a solution of the complex in DMF led to spectral changes consistent with substitutions at the Co(III) centre [10].

* Corresponding author. Tel.: +61 3 8344 4222; fax: +61 3 9347 5180.
E-mail address: wdmf@unimelb.edu.au (W.D. McFadyen).

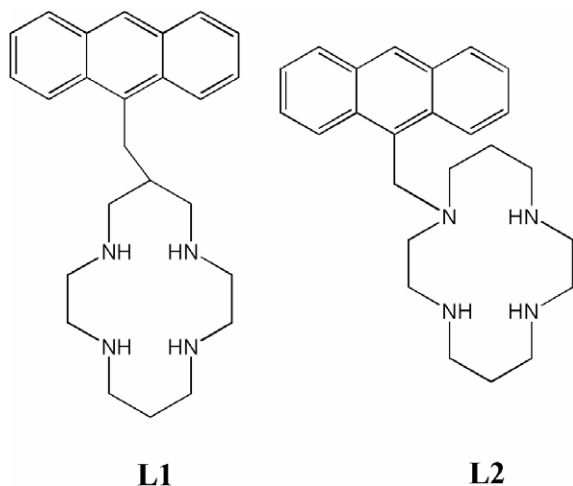


Fig. 1. Structures of the **L1** and **L2** ligands.

With a view to further developing these ideas, and to better understand the photochemistry of donor–acceptor complexes containing cobalt(III) as the acceptor group, we have prepared a series of cobalt(III) complexes of 1-(anthracen-9-ylmethyl)-1,4,8,11-tetraazacyclotetradecane (hereafter **L2**) in which anthracene (the donor) is appended to a nitrogen atom of the cyclam macrocycle (Fig. 1). The complexes are of the type $trans-[CoL2X_2]^+$ in which $X = Cl^-$, NCS^- , and NO_2^- . These anionic ligands were chosen to cover a broad range of the spectrochemical series and it is these ligands that may be lost following a photo-induced process, with the cobalt atom remaining bound to the cyclam macrocycle. Investigation of complexes of **L2** will also allow comparison of the photochemical properties of these N-appended complexes with those of their C-appended analogues derived from **L1**. In this paper we describe the synthesis and structural characterisation of a series of complexes derived from **L2**. The preparation

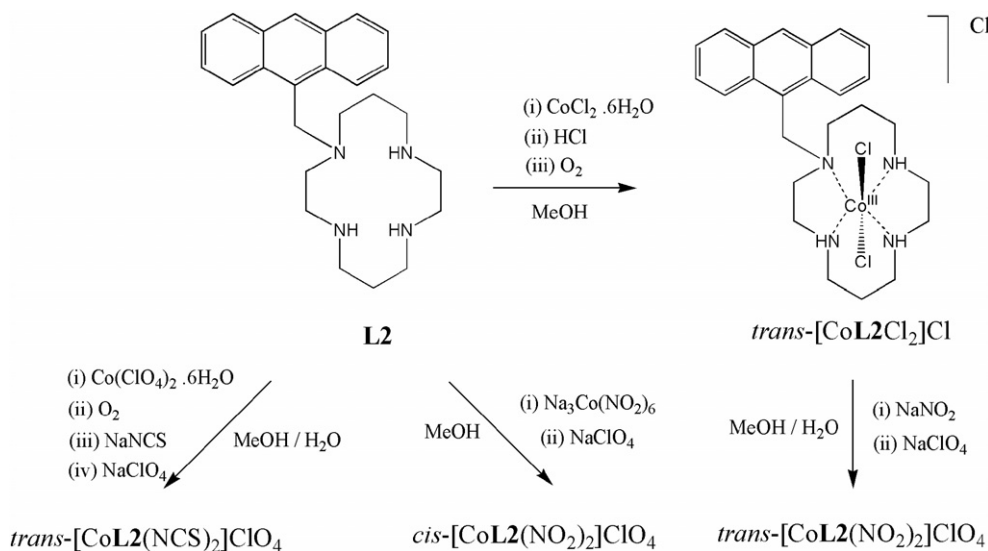
and structure of the complex $cis-[CoL2(NO_2)_2]^+$, which contains one N-bonded and one O-bonded nitrite ligand is also described.

2. Results and discussion

2.1. Synthesis

The synthesis of **L2** was accomplished by the N-alkylation of cyclam with 9-chloromethyl-anthracene following the method described by Fabrizzi et al. [7]. The synthetic route to the series of complexes $trans-[CoL2X_2]^+$ ($X = Cl^-$, NCS^- and NO_2^-) is summarised in Scheme 1.

The complex $trans-[CoL2Cl_2]^+$ was prepared by the addition of cobalt(II) chloride to **L2** in methanol. Subsequent addition of hydrochloric acid and aerial oxidation led to formation of the *trans*-dichloro cobalt(III) complex which was isolated as its green chloride salt. The complex $trans-[CoL2(NCS)_2]^+$ was prepared by first adding cobalt(II) perchlorate hexahydrate to **L2** in methanol. The resultant complex (presumably with water as the axial ligands) was oxidised to cobalt(III) in air and then an excess of sodium thiocyanate was added. The further addition of excess sodium perchlorate led to the isolation of the complex as its red/brown perchlorate salt. The complex $trans-[CoL2(NO_2)_2]^+$ was prepared via in situ generation of $trans-[CoL2Cl_2]^+$ followed by exchange of the chloride ions with nitrite following the addition of an excess of sodium nitrite. The complex was isolated as its orange perchlorate salt following the addition of $NaClO_4$. The complexes were characterised by elemental analysis, 1H NMR, ESI-MS and single crystal X-ray diffraction. ESI-MS of each of the complexes discussed in this work clearly displayed M^+ as the most abundant peak with $[M-HX]^+$ and $[M-2(HX)]^+$ peaks ($X = Cl^-$, NCS^- and NO_2^-) also clearly distinguishable. The bridging methylene protons in these complexes



Scheme 1. Reaction scheme for the synthesis of the series of cations $trans-[CoL2X_2]^+$ ($X = Cl^-$, NCS^- and NO_2^-) and the $cis-[CoL2(NO_2)_2]^+$ cation.

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