A macrobicyclic cage incorporating selenium donor atoms: synthesis and structure of [Co^{III}L]Cl$_3$ (L = 1-nitro-8-methyl-6,10,19-triselena-3,13,16-triazabicyclo[6.6.6]icosane)

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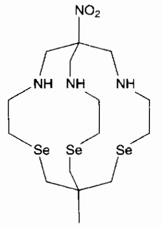
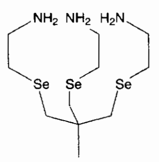
One of a new series of complexes of mixed selenium–nitrogen donor atom cage ligands is presented; X-ray structural analysis of the cobalt complex, [Co^{III}L]Cl$_3$·5H$_2$O 1 is described together with redox, NMR and electronic spectroscopic data.

Since the initial discovery of the capping procedures which led to the synthesis of macrobicyclic cages such as sepulchrate[1] and sarcophagine,[2] numerous variations of these ligands have been reported. The modifications typically involve changes in the capping groups[3] and variations of the donor atoms or donor atom set.[4–6] As part of our research into the design and synthesis of novel mixed donor N, S/Se cages and *molecular tubes*,[7] we have synthesised a new variation of the sarcophagine theme, a nitro-capped cage, L, with an N$_3$Se$_3$ donor set derived from the tripodal ligand L^1.[8]



L



L^1

Incorporation of the larger Se atom (covalent radius 1.17 Å, *cf.* N 0.73, S 1.04 Å) should result in a change in the size of the cage cavity and hence allow for some interesting coordination behaviour. In addition, the greater σ-donating ability of Se would facilitate the complexation of a variety of metal ions. To this end we are also currently investigating mixed nitrogen–selenium donor macrocycles and their complexation preferences.

To our knowledge, there are no reported examples of mixed selenium–nitrogen donor or all-selenium containing cages. The closest examples would be the tetraselena-macrocyclic complexes of Rh^{III} (ref. 9) and Pd^{II}, Pt^{II},[10] and earlier work regarding complexes of Cu^{I}, Cu^{II} and Hg^{II}.[11] The selenium–nitrogen donor ligand aminoethaneselenol, complexed with a variety of first-row transition metal ions, has been reported,[12] however there has only been one structural description of a mixed Co^{III}Zn^{II} polynuclear species.[13] The only other structure found in the literature involves a Co^{III} complex of the methylated ligand '(methylseleno)ethylamine'.[14]

Complex **1** was prepared by treating [Co^{III}L^1]Cl$_3$ with HCHO and MeNO$_2$ in water. The reaction mixture was chromatographed on Dowex 50W-X2 and the single product was isolated using HCl as the eluent.[8] The presence of seven resonances in the ^{13}C NMR spectrum† indicates that the Co^{III} ion is fully encapsulated and that the molecule, on the NMR timescale, exhibits C_3 symmetry. The ^{1}H NMR spectrum exhibits a complicated splitting pattern for the CH$_2$ protons in the aminoethaneseleno fragment of the cage; the protons in the methyl cap appear as a singlet at δ 1.5. In the ^{77}Se NMR spectrum of **1** in D$_2$O,‡ a single resonance is observed at δ 563 (*vs.* Me$_2$Se), which is expected owing to the symmetry of the molecule. Also, the appearance of selenium satellites in the ^{13}C and ^{1}H spectra allow unequivocal assignment of nuclei adjacent to selenium atoms; values of $^1J_{\text{CSe}}$, $^2J_{\text{CSe}}$ are secondary indicators of carbon atoms in α or β positions to selenium. In addition, microanalytical and IR data confirm the formulation of the nitro-capped cage.§

X-Ray quality crystals of **1** were obtained by vapour diffusion of ethanol into an aqueous solution of the complex. The cation from the single-crystal X-ray structure of [Co^{III}L]Cl$_3$·5H$_2$O is shown in Fig. 1.¶

There is extensive hydrogen bonding between the amino nitrogens and the chloride anions (N···Cl 3.08–3.14 Å), the water molecules and chloride anions (O···Cl 3.07–3.17 Å) and between the water molecules (O···O 2.74–2.87 Å). Notable features of the structure include the Co–Se mean bond length of 2.340 Å compared to 2.33, 2.386(3) Å in the structures of sodium bis[2,2′-selenodiphenolato(2−)-*O,O,Se*]cobalt(III) and [(2-methylseleno(ethylamine)bis(ethylenediamine)]-cobalt(III)[14] respectively. In the aza-capped thia analogue|| of **1**, the Co–S distance is 2.24 Å.[4]

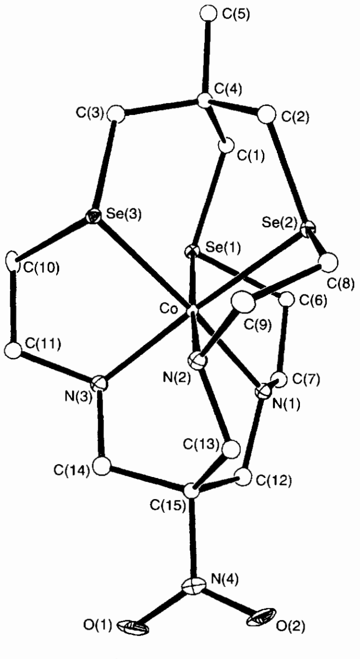


Fig. 1 Structure of the [Co^{III}L]$^{3+}$ cation with thermal ellipsoids at the 30% probability level.[22] Numbered atoms are carbons. Bond lengths (Å) Co–Se(1), Se(2), Se(3) 2.363(2), 2.336(1), 2.321(1); Co–N(1), N(2), N(3) 2.005(7), 1.989(7), 2.008(7); Se(1)–C(1), C(6) 1.977(8), 1.963(8); Se(2)–C(2), C(8) 1.974(9), 1.941(9); Se(3)–C(3), C(10) 1.952(9), 1.953(8).

The longer metal to selenium bonds are accompanied by long C_{cap}–Se bond lengths (mean 1.968 Å, *cf.* 1.84, 1.80, 1.96 in S structure) and longer Se–$C_{methylene}$ distances (mean 1.952 Å; *cf.* 1.79, 1.85, 1.81 Å in S structure). The corresponding bond angles around the methyl cap reflect some degree of strain, 105–108° between the methyl cap, the quaternary carbon and the methylenes, ≈113° from the methylene–quaternary carbon–methylene parts of the cap and 114–117° between the selenium–methylene–quaternary carbon units. These values can be understood in terms of the methyl cap of the cage adjusting to accommodate the larger Se atoms. The cobalt atom lies rigorously in the mean planes defined by each set of four bonding atoms [mean deviation 0.006(3) Å].

The Co–N and NH–CH_2 (cap) bond distances are comparable to those found in the aza-capped thia structure and the dinitro-capped sarcophagine complex of Co^{III}.[16] The chelate rings containing the aminoethaneselenol fragment are in the $(lel)_2ob$ conformation,[17] with N–C–C–N dihedral angles −55.8(8), −51.2(8) and 42.0(9)° respectively.

In the electronic spectrum of **1**, intense absorption bands are apparent at λ_{max} 210, 234 and 310 nm (ε = 9680, 9400 and 10 840 $dm^3\ mol^{-1}\ cm^{-1}$ respectively). These are attributed to Se–Co charge-transfer bands.[18] The weaker d–d transitions are observed at λ_{max} 388, 512, nm (ε = 909 and 746 $dm^3\ mol^{-1}\ cm^{-1}$ respectively), corresponding to the spin-allowed ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transitions. The positions of these transitions are at lower energies than those reported for the nitro-capped N_3S_3 sarcophagine analogue, and a variety of other related cage complexes.[6]

Cyclic voltammetry in acetonitrile solution reveals a well behaved quasi-reversible (ΔE = 70 mV) Co^{III}–Co^{II} couple at $E_{1/2}$ = −130 mV.** This value is in contrast to that observed for the analogous nitro-capped N_3S_3 cage (+170 mV),[19] suggesting that the process $Co^{III} \rightarrow Co^{II}$ is less favourable and that the Co^{III} oxidation state is stabilised by the selena cage, relative to the thia analogue.

At lower potentials, irreversible reductions are observed at −1.20 and −1.41 V. One is tentatively assigned as a reduction process for the nitro group, such reductions having been previously observed with other nitro-capped species.[20] In cyclic voltammetric studies of the remaining Co^{III} complexes of ligands in this new series, an irreversible reduction at lower potential is due to the Co^{II}–Co^{I} couple,[8,19] and thus we assign the other reduction wave to such a process. Comparison of the redox couples for the mixed selena–nitrogen and thia–nitrogen cages also gives some insight into the relative sizes of the cavities. It is not immediately obvious whether substitution of the nitrogen or sulfur atoms by the larger selenium atom would be accompanied by a decrease or an increase in the size of the coordination cavity. The present results show that the smaller Co^{III} ion is stabilised by the selena cage over the larger Co^{II} ion, compared to the thia analogue. Structural investigations of the other complexes in this series, including that of the open cage ligand L^1,[8] are currently in progress and they should provide further information about relative cavity sizes. Efforts are underway to expand this series to include copper and nickel complexes of L and related ligands.

Footnotes

† ^{13}C NMR (300 MHz, D_2O) δ (*vs.* internal dioxane at δ 69.26): 31.83 (CH_3), 38.68, 38.81 (CH_2Se), 42.88 (CCH_3), 56.08, 57.66 (CH_2NH), 89.21 (CNO_2). $^1J_{CSe}$ 49 Hz, $^2J_{CSe}$ 67 Hz. ^1H NMR (300 MHz, D_2O) δ (*vs.* internal dioxane at δ 3.74): 1.50 (s, 3H, CH_3), 2.86–3.42 (m, 18 H, CH_2 cage), 3.76–3.94 (m, CH_2 adjacent to CNO_2).

‡ Referenced relative to D_2SeO_3 in D_2O at 20 °C, δ 1301.4 *vs.* Me_2Se.[21]

§ Analysis: Calc. for $C_{15}H_{40}Cl_3CoN_4O_7Se_3$ C, 22.78; H 5.06; N 7.09; Cl, 13.46. Found: C, 23.36; H, 4.11; N, 7.09; Cl, 13.59%. IR ν/cm^{-1}: 3420, 3370 (N–H); 1545 (N=O) (KBr disc).

¶ *Crystal data* for $C_{15}H_{30}Cl_3CoN_4O_2Se_3 \cdot 5H_2O$: monoclinic, space group $P2_1/c$, a = 9.133(2), b = 19.269(4), c = 15.945(3) Å, β = 94.85(3)°, U = 2796.0(10) $Å^3$, Z = 4, D_c = 1.878 g cm^{-3}. 5222 reflections were collected at 130 K on a Siemens P3 diffractometer using Mo-Kα radiation (λ = 0.71073 Å, graphite monochromator), 4 < 2θ < 50°. The structure was solved by Patterson methods (SHELXS-90)[23] and refined using empirical absorption corrected data. Hydrogen atoms on the cation were held in calculated positions. All hydrogens were refined with an isotropic thermal parameter 1.2 times that of the heavy atoms; Co, Se, O, C(9) and C(10) atoms were refined anisotropically and the remaining C and N atoms were refined with isotropic thermal parameters.

Refinement (SHELXL-93)[24] on F_0^2 using all data (4872) converged to a conventional R of 0.056 [for 3292 $F_0 > 4\sigma(F_0)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, see Information for Authors, Issue No. 1.

|| Data quoted for the $S_2O_6^{2-}$ salt; a corresponding nitro-capped structure has not been reported.

** Measurements conducted in 0.1 mol dm^{-3} NBu_4BF_4 in acetonitrile, sample concentration 0.001 mol dm^{-3}, cell purged with argon between scans, Pt working electrode, Pt wire auxiliary electrode, Ag/AgCl reference electrode in 3 mol dm^{-3} KCl, scan rate 100 mV s^{-1}, internal standard Fc–Fc^+.

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