Pendant Arm Encapsulated Complexes

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The synthesis and the *X*-ray crystal structure of the new encapsulated complex [{(4-amino-2-azabutyl)-8-nitro-3,6,10,13,16,19-hexa-azabicyclo[6.6.6]icosane}cobalt(III)] iodide, {[Co(NO$_2$asen)]I$_4$·3H$_2$O}, (**3**), bearing a functionalised five atom pendant arm, are reported.

The octa-amine (**1**) has attracted attention because of its capacity to complex two metal ions in a configuration where two MN$_4$$^{n+}$ (M = Cu^{2+}, Ni^{2+}) units are joined at a single C-spiro quaternary carbon centre.[1—3] In this configuration, metal complexes of (**1**) may be considered as dimeric analogues of the linear tetra-amine 1,9-diamino-3,7-diazanonane. Bis-macrocyclic nickel(II) complexes derived from (**1**), essentially dimeric analogues of the nickel(II) complexes of dioxocyclam (2,4-dioxo-1,5,8,12-tetra-azatetradecane)[4] and cyclam (1,4,8,11-tetra-azacyclotetradecane),[5] have also recently been reported.[3] Reaction of (**1**) with cobalt(II), and oxygen, in aqueous solution results in a mixture of products, predominantly a dimeric green *trans*-dichlorocobalt(III) species in which (**1**) again functions as a binucleating tetradentate ligand.[6]

Ligand (**1**) does, however, exhibit more versatile complexation behaviour. Under carefully controlled conditions (**1**) may function as a chelating hexa-amine ligand, co-ordinating in a configuration analogous to that displayed by the octahedral cobalt(III) complex of the hexa-amine 5-(4-amino-2-azabutyl)-5-methyl-3,7-diaza-1,9-nonanediamine, [Co(sen)]$^{3+}$.[7] Thus, under reaction conditions where the [(**1**): metal ion] ratio is maintained at slightly greater than 1, the hexa-amine complex (**2**)[†] has been isolated. Complex (**2**) possesses three facially

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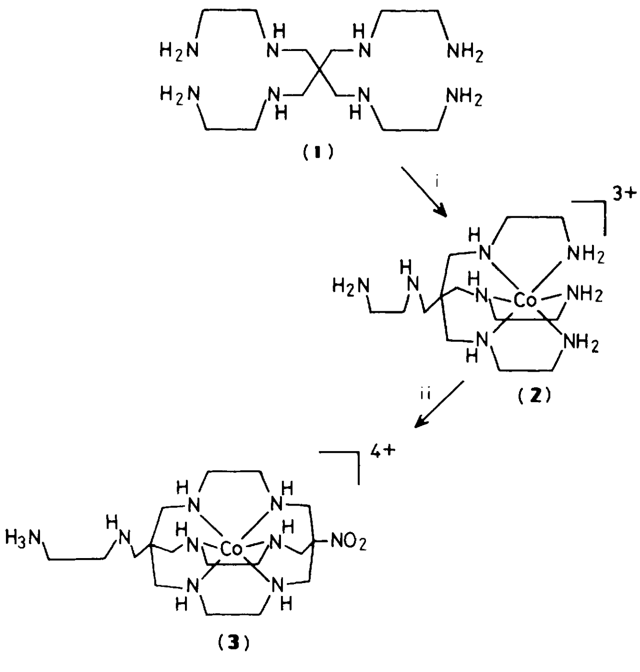
[†] *Spectroscopic data* for (**2**): ^{13}C n.m.r. (D$_2$O) δ 40.2 (CH$_2$), 43.5 (CH$_2$), 47.7 (Cq), 50.1 (CH$_2$), 52.8 (CH$_2$), 53.1 (CH$_2$), 56.9 (CH$_2$); $\lambda_{max.}$ (H$_2$O) 466 (ε 112 dm^3 mol^{-1} cm^{-1}), 337 (115). For (**3**): ^{13}C n.m.r. (D$_2$O) δ 36.1 (CH$_2$), 45.5 (Cq), 47.1 (CH$_2$), 51.3 (CH$_2$), 51.7 (CH$_2$), 51.9 (CH$_2$), 55.7 (CH$_2$), 55.8 (CH$_2$), 88.6 (Cq); $\lambda_{max.}$ (H$_2$O) 469 (148), 347 (689).

Crystal data for (**3**): $C_{17}H_{46}CoI_4N_9O_9$, M = 1023.2, monoclinic, space group $P2_1/c$, a = 12.524(2), b = 17.154(2), c = 15.376(5) Å, β = 97.14(2)°, D_x = 2.073 g cm^{-3}, U = 3278(1) Å^{-3}, Z = 4, μ(Mo-K_α) = 42.63 cm^{-1}, λ(Mo-K_α) = 0.71069 Å. Reflections were measured on an Enraf-Nonius CAD4-F four-circle diffractometer and were corrected for Lorentz, polarization, and absorption effects. The structure was solved by heavy atom methods and refined to R = 0.041, R_w = 0.044, on 3246 reflections [$F > 5\sigma(F)$, $2\theta \leqslant 48°$]. The nitro group was found to be rotationally disordered and I(3) was disordered over two sites. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1. *Reagents and conditions:* i, $CoBr_2 \cdot 6H_2O$, MeOH; ii, $MeNO_2$, HCHO 37% aq. solution, Na_2CO_3, stir 2 h.

arranged primary amine donors and is susceptible to reactions in which this trigonal face may be enclosed. Thus, (2) was treated with nitromethane and formaldehyde, in the presence of base, in an extension of previously described methods,[8,9] resulting in the isolation of (3)† in 60% yield, after chromatography on Dowex and Sephadex C25 cation exchange columns (Scheme 1). The encapsulated complex (3) possesses a 4-amine-2-azabutyl moiety occupying one trigonal cap, and a nitro- group the other. The pendant primary amine is readily reactive, being sufficiently removed from the neopentyl carbon atom, and alkylated and benzenesulphonated derivatives have been prepared. The preparation of the complexes is shown in Scheme 1 and Figure 1 shows an ORTEP drawing of the complex cation of (3).

Complex (3) was crystallised from aqueous ethanol solution as the iodide salt. The structure consists of the complex cation, four iodide anions, and three water molecules. Microanalytical data was consistent with the observed structure. The absence of an expected fifth halide anion, for example chloride, was confirmed by *X*-ray photoelectron spectroscopy. This result suggests that either the nitrogen atoms on the pendant arm are protonated and one water molecule in the lattice is a hydroxide species, or that one of the amines is not protonated. There is extensive hydrogen bonding involving all amine groups, iodide anions, and water molecules. Three of the iodide anions are each hydrogen bonded to a pair of co-ordinated secondary amine groups, whilst the pendant arm amines are hydrogen bonded to both iodide anions and water molecules. It was not possible to locate the hydrogen atoms on the amine nitrogen atoms of the pendant arm or the lattice water molecules, therefore the degree of protonation of these atoms is unknown. The pendant arm adopts a configuration with the nitrogen atoms *cis* rather than the expected *trans* arrangements as previously observed in protonated ethylenediamine.[10] The complex cation adopts the D_3lel_3 conformation, observed for similar encapsulated complexes,[8] in which the ethylenediamine rings are parallel to the D_3 axis of the

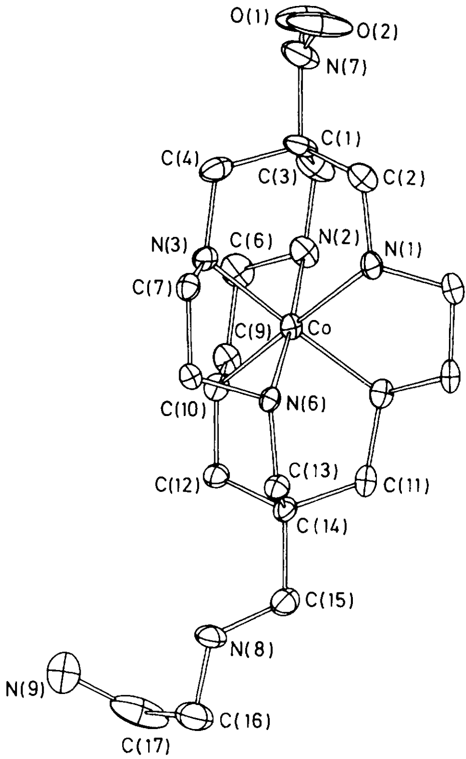


Figure 1. ORTEP[11] drawing of the cation $[Co(NO_2asen)]^{4+}$. Bond lengths to Co(III): N(1) 1.972(7), N(2) 1.983(8), N(3) 1.969(8), N(4) 1.964(8), N(5) 1.967(7), N(6) 1.960(7) Å; bond angles N(2)–Co–N(1) 90.5(3), N(3)–Co–N(2) 90.6(4), N(4)–Co–N(2) 92.6(4), N(5)–Co–N(1) 175.6(3), N(5)–Co–N(3) 92.6(3), N(6)–Co–N(1) 92.5(3), N(6)–Co–N(3) 86.4(3), N(6)–Co–N(5) 90.9(3), N(3)–Co–N(1) 90.4(3), N(4)–Co–N(1) 85.7(3), N(4)–Co–N(3) 174.9(3), N(5)–Co–N(2) 86.3(3), N(5)–Co–N(4) 91.5(3), N(6)–Co–N(2) 175.8(3), N(6)–Co–N(4) 90.6(3)°.

complex. Metal–ligand bond lengths are normal for such complexes.[8]

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References

1 A. T. Phillip, *Aust. J. Chem.*, 1968, **21**, 2301.
2 L. R. Gahan, K. E. Hart, C. H. L. Kennard, M. A. Kingston, G. Smith, and T. C. W. Mak, *Inorg. Chim. Acta*, 1986, **116**, 5.
3 A. McAuley, S. Subramanian, and T. W. Whitcombe, *J. Chem. Soc., Chem. Commun.*, 1987, 539.
4 I. Tabushi, Y. Taniguchi, and H. Kato, *Tetrahedron Lett.*, 1977, 1049.
5 R. M. Izatt and J. J. Christensen, 'Synthetic Multidentate Macrocyclic Compounds,' Academic, New York, 1978.
6 L. R. Gahan, K. E. Hart, and M. A. Kingston, unpublished work.
7 R. J. Geue and G. H. Searle, *Aust. J. Chem.*, 1983, **36**, 927.
8 R. J. Geue, T. W. Hambley, J. M. Harrowfield, A. M. Sargeson, and M. R. Snow, *J. Am. Chem. Soc.*, 1984, **106**, 5478.
9 U. Sakaguchi, S. Tamaki, K. Tomioka, and H. Yoneda, *Inorg. Chem.*, 1985, **24**, 1624.
10 P. C. Healy, J. M. Patrick, and A. H. White, *Aust. J. Chem.*, 1984, **37**, 1105.
11 C. K. Johnson, 'ORTEP, A Thermal Ellipsoid Plotting Program,' Oak Ridge National Laboratories, Oak Ridge, 1965.