# Synthesis and *X*-Ray Crystal Structure of a C-Spiro-bi-[cyclam nickel(II)] Complex (cyclam = 1,4,8,11-tetra-azacyclotetradecane)

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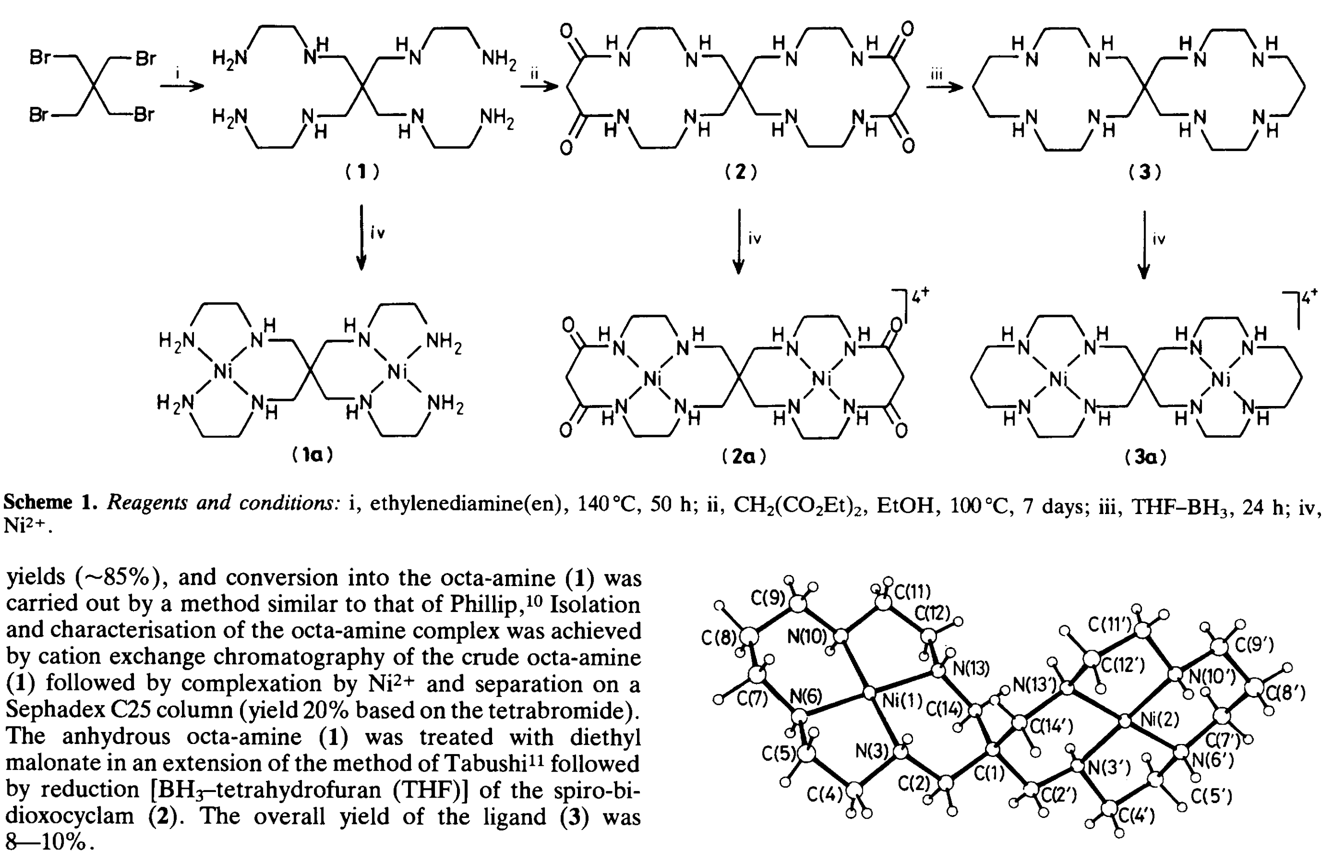
The salt 6,6′-spirobi[1,4,8,11-tetra-azacyclotetradecane]nickel(II) tetraperchlorate {C-spiro-bi-[cyclam nickel(II)]} was isolated as single crystals and the *X*-ray crystal structure obtained; a deviation in orthogonality of the macrocyclic rings, resulting in possible Ni–Ni interaction, is deduced from the e.s.r. spectra of the oxidised forms of the complex.

Although novel binuclear complexes involving nickel(II) and copper(II) have been reported recently, these species either have pendant arms,[1—3] or possess two macrocyclic units joined by an ethylene (linking two triazacyclononane rings[4]) or longer chains with terminal tetra-azacyclotetradecane macrocycles.[5] In only a very few cases have bis-macrocycles been prepared where the linking takes place *via* the carbon–carbon bonds of the macrocycles. This is observed in bis-oxocyclam and bis-cyclam nickel(II) complexes (cyclam = 1,4,8,11-tetra-azacyclotetradecane).[6]

We report here the preparation of a bis-macrocyclic complex where the two 14-membered cyclam units are joined at a single quaternary carbon centre forming a C-spiro-bicyclam. The binuclear complex formed exhibits a robustness characteristic of the parent nickel(II) cyclam complex[7] and the orientation of the two rings is close to pependicular. The synthetic route differs from that to an open chain binuclear copper(II) complex[8] prepared recently which is built on a framework similar to the octa-amine precursor species also described in this paper. The preparation of the ligands and complexes is shown in Scheme 1.

Pentaerythrityl tetrabromide was prepared[9] in excellent



**Scheme 1.** *Reagents and conditions:* i, ethylenediamine(en), 140 °C, 50 h; ii, $CH_2(CO_2Et)_2$, EtOH, 100 °C, 7 days; iii, THF–$BH_3$, 24 h; iv, $Ni^{2+}$.

yields (~85%), and conversion into the octa-amine (**1**) was carried out by a method similar to that of Phillip,[10] Isolation and characterisation of the octa-amine complex was achieved by cation exchange chromatography of the crude octa-amine (**1**) followed by complexation by $Ni^{2+}$ and separation on a Sephadex C25 column (yield 20% based on the tetrabromide). The anhydrous octa-amine (**1**) was treated with diethyl malonate in an extension of the method of Tabushi[11] followed by reduction [$BH_3$–tetrahydrofuran (THF)] of the spiro-bi-dioxocyclam (**2**). The overall yield of the ligand (**3**) was 8—10%.

Ligands (**1**), (**2**), and (**3**) were characterized by $^{13}C$, $^1H$ n.m.r., and mass spectroscopy. Excellent microanalytical data have been obtained for the amine hydrochlorides and the nickel(II) complexes.†

The structures of various nickel(II) cyclam complexes have been reported recently,[12—14] and it is of interest to compare these with the present species. In Ni$^{II}$ cyclam perchlorate[13b] the average Ni–N distance is 1.955 Å and average N–Ni–N bond angles for the 5- and 6-membered rings are 86 and 94°, respectively. For the spiro ion (**3a**), the corresponding values are 1.941 Å, and 86.8 and 93.2° (Figure 1). The implication is that in terms of geometry around the metal centre, the two complexes are isostructural and hence, complex (**3a**) might be expected to behave as two nickel cyclam complexes. The structure of the octa-amine precursor, (**1a**) has also been determined in our laboratory (Ni–N 1.926 Å, N–Ni–N 86.4, 93.6°, respectively). Since the ligand is acylic, the complex should be relatively free of steric constraints and hence might represent an ideal geometry for a square planar nickel(II) complex. However, the values for the bis-macrocycle are not significantly different, suggesting that they represent 'strain-free' geometries in all cases. Interestingly, the bond lengths are slightly longer than the ideal distance (Ni–N *ca.* 1.89 Å) suggested by Fabbrizzi[15] and, in accordance with molecular mechanics calculations,[14] a *trans* III geometry is observed for (**3a**).

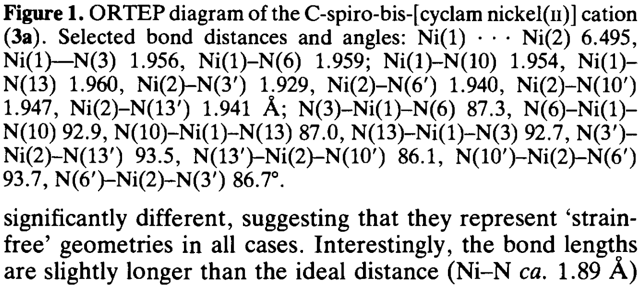


**Figure 1.** ORTEP diagram of the C-spiro-bis-[cyclam nickel(II)] cation (**3a**). Selected bond distances and angles: Ni(1) · · · Ni(2) 6.495, Ni(1)—N(3) 1.956, Ni(1)–N(6) 1.959; Ni(1)–N(10) 1.954, Ni(1)–N(13) 1.960, Ni(2)–N(3') 1.929, Ni(2)–N(6') 1.940, Ni(2)–N(10') 1.947, Ni(2)–N(13') 1.941 Å; N(3)–Ni(1)–N(6) 87.3, N(6)–Ni(1)–N(10) 92.9, N(10)–Ni(1)–N(13) 87.0, N(13)–Ni(1)–N(3) 92.7, N(3')–Ni(2)–N(13') 93.5, N(13')–Ni(2)–N(10') 86.1, N(10')–Ni(2)–N(6') 93.7, N(6')–Ni(2)–N(3') 86.7°.

A consequence of this ring geometry is that the six-membered chelate rings are in a chair conformation which has an effect on the orientation of the two 14-membered nickel–nitrogen rings. Ideally, these should be at 90° to each other. However, the chelate ring geometries result in a distortion to an angle of 84°. While this does not bring the axial co-ordination sites of the two nickel centres into contact, it does reduce the orthogonality of the $d_{z^2}$ orbitals suggesting that electronic interaction of the two metal centres might be possible. The spiro-bi-cyclam species may be oxidised ($Co^{3+}$ in aqueous acid media, electrochemically) to the Ni$^{III}$–Ni$^{III}$ complex. The e.s.r. spectra of these low spin $d^7$ centres differ significantly from the parent nickel(III) cyclam,[16] especially for the axially co-ordinated dichloro species where the septet deriving from hyperfine interaction with the two Cl atoms in the cyclam complex is not observed for the binuclear ion. Instead, a much simpler spectrum suggestive of a distorted triplet is obtained.‡ To date, we have not been able to isolate,

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† *Crystal data:* $Ni_2Cl_4O_{16}N_8C_{19}H_{44}$, $M = 899.83$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 12.447(3)$, $b = 16.667(4)$, $c = 8.328(2)$ Å, $\alpha = 76.49(2)$, $\beta = 92.57(3)$, $\gamma = 100.83(2)$°, $U = 1649.95$ Å$^3$, $D_c = 1.811$ g cm$^{-3}$, Mo-$K_\alpha$ radiation ($\lambda = 0.71069$ Å). 2206 Independent observed reflections with $I > 2\sigma(I)$ were obtained using a Picker four circle diffractometer. The structure was solved for the heavy atoms using MULTAN and refined by least squares using SHELX to a final conventional $R = 0.0487$. The Ni, Cl, and O atoms were refined anisotropically, while the C and N atoms were isotropic. The H atoms were observed and included in the final stages of refinement with a common thermal parameter. In addition, a blocked matrix was used in the final stages because of the large number of atoms (93) in the asymmetric unit. 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.

‡ At 77 K (3.2 M $HNO_3$) this feature may be due to an orthorhombic geometry ($g_{xx}$ 2.296, $g_{yy}$ 2.162, $g_{zz}$ 2.076). However, a change to an axial ($g_{\parallel}$ 2.025, $g_{\perp}$ 2.223) spectrum is observed on heating.

even as an intermediate, any mixed-valence $Ni^{II}$—$Ni^{III}$ ion. Oxidation–reduction kinetics and other aspects of the chemistry of these complexes are currently under investigation. It is of interest that a hexa-oxobimacrocycle, 18,18′-spirobi-(19-crown-6) is capable of dinuclear co-ordination of group 1 and 2 metals.[17] In the case of the $Li^+$ species, only three of the oxygens of each ring are involved in co-ordination.

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