Preparation and Molecular and *X*-Ray Crystal Structure of $[NiC_{14}H_{34}N_6]$-$(ClO_4)_2\cdot Me_2NCHO$: a Nitrogen Analogue of a 20-Crown-6 Ether

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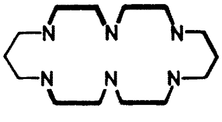
Summary *X*-Ray crystal structure of a complex containing a cyclic hexa-aza-alkane, 1,4,7,11,14,17-hexa-azaeicosane-nickel(II) $[Ni(haec)]^{2+}$, is reported and its electronic spectrum is presented and discussed.

During our studies of transition metal complexes of cyclic triaza-alkanes we have employed the non-high dilution synthetic methods of Richmann and Atkins[1] to prepare the ligands. In one attempt to prepare the nickel(II) complex of 1,4,7-triazacyclododecane, $[10]aneN_3$,[2] we isolated purple crystals and found surprisingly, that they were the nickel(II) complex of the cyclic dimer of $[10]aneN_3$, 1,4,7,11,14,17-hexa-azaeicosane (haec) (**1**). We now report the first definitive assignment of structure of a metal complex of a nitrogen analogue of a crown-6 ether.


(1)

Crystal data: violet crystals of $[NiC_{14}H_{34}N_6](ClO_4)_2\cdot$-$Me_2NCHO$, obtained by slow evaporation of a saturated dimethylformamide (DMF) solution, were sealed in a glass capillary to prevent loss of DMF. The crystals were monoclinic, $a = 13\cdot429(8)$, $b = 13\cdot484(8)$, $c = 15\cdot130(9)$ Å, $\beta = 93\cdot35(8)°$, space group $C2/c$, $Z = 4$, $D_m = 1\cdot55$, $D_c = 1\cdot50$ g cm^{-3}.†

Cell dimensions and intensity data were obtained with a Syntex $P2_1$ diffractometer using monochromated Cu-K_α *X*-rays ($\lambda = 1\cdot54178$ Å). The structure was determined by Patterson and Fourier techniques and refined by least-squares to a final value of $R = 0\cdot075$ for 1887 observed reflections. In the final cycles of refinement hydrogen atoms, located in a ΔF map, were included with isotropic temperature factors while all other atoms were refined anisotropically.

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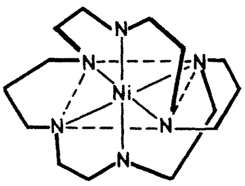
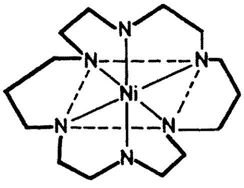
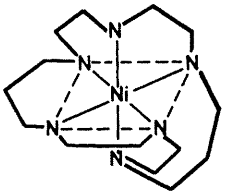
† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as a supplementary publication No. SUP 22575 (31 pp.) from the British Library. For details of obtaining this material, see Notice to Authors No. 7, *J.C.S. Dalton* or *Perkin I* and *II*, Index Issues.



(2)



(3)



(4)

The Ni^{2+} ion sits on a crystallographic 2-fold axis but the complex has no other symmetry. Complexes related by the *c* glide plane are enantiomers so that the crystals are racemic. Two other geometrical isomers, another racemic (**2**)‡ and a *meso* form (**3**), are possible when the hexadentate haec co-ordinates to a metal ion. The complex (**4**) isolated in this study is unique in that it does not contain *trans* trimethylene bridging groups. The Ni–N distances are equal within experimental error, averaging 2·12 Å, but the Ni–N$_6$ chromophore is significantly distorted from the octahedral symmetry with 4 of the 12 N–Ni–N bond angles being less than 83°. The conformations of the five-membered chelate rings for the enantiomer shown in the Figure are Ni–N(1)–C(1)–C(2)–N(2), λ, and Ni–N(2)–C(3)–C(4)–N(3), δ, while the six-membered rings are in the chair form.

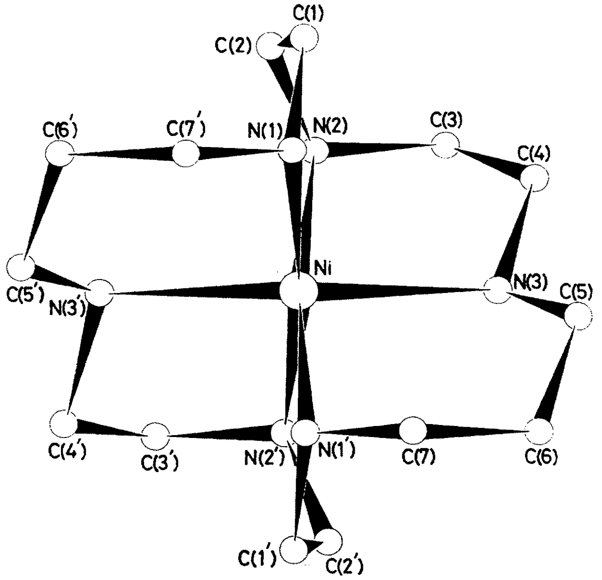


Figure. Molecular structure of [Ni(haec)]$^{2+}$. Pertinent bond angles (°) are as follows: chelate ring angles, N(1)–Ni–N(2), 82·0 (5-membered ring); N(2)–Ni–N(3), 82·2 (5-membered ring); N(3)–Ni–N(1′), 91·0 (6-membered ring); non-ring angles N(1)–Ni–N(3), 95·1; N(1)–Ni–N(1′), 96·9; N(2)–Ni–N(2′), 97·8; and N(2)–Ni–N(3′), 91·8. The uncertainty in the bond angles is *ca.* 0·8°.

Studies of one other cyclic alkyl hexa-aza-amine, 1,4,7,10,13,16-hexa-azaoctadecane (hexacyclen) have been reported.[3,4] Although we have only completed preliminary investigations on [Ni(haec)]$^{2+}$ it is apparent that its properties differ considerably from [Ni(hexacyclen)]$^{2+}$. [Ni(haec)]$^{2+}$ resembles macrocyclic and cyclic triaza-amine complexes of nickel(II) in that it hydrolyses slowly in aqueous acid solution. The hydrolysis of [Ni(hexacyclen)]$^{2+}$ in acid is rapid.[4] The presence of one or more six-membered chelate rings among five-membered rings in a complex tends to relieve strain energy.[5] This is in agreement with kinetic observations that the strained [Ni(hexacyclen)]$^{2+}$ complex is more rapidly hydrolysed than [Ni(haec)]$^{2+}$.

The electronic spectrum [solution and solid (Nujol mull)] of [Ni(haec)]$^{2+}$ is typical of a complex containing a NiN$_6$ chromophore which is distorted from octahedral symmetry, with band maxima at 11,400 cm^{-1}, ν_1, ($^3A_{2g} \rightarrow {}^3T_{2g}$); 19,000 cm^{-1}, ν_2, ($^3A_{2g} \rightarrow {}^3T_{1g}$); and 29,400 cm^{-1}, ν_3, [$^3A_{2g} \rightarrow {}^3T_{1g}$(P)]. The ν_1 band also contains a shoulder at 12,200 cm^{-1} of nearly the same intensity as the absorption maximum. This shoulder is assigned to the spin forbidden (^1E) transition since values of D_q (1140 cm^{-1}) and B (947 cm^{-1}) based upon the assignment above appear more consistent with the position of the ν_2 and ν_3 bands.

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‡ For an explanation of the configurational effect which leads to the dissymmetry of (**2**) see ref. 4.

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