Pendant Functional Group Control of Modes of Co-ordination of a Quinquedentate Macrocycle with an 'O_2N_3' Donor-set

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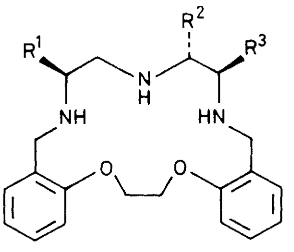
Apparently minor changes in methyl substitution in a 1,4,7-triazaheptane fragment of an O_2N_3-macrocycle are shown to have a significant influence on the modes of co-ordination of the ligand.

It has been shown[1] that the solution stability of nickel(II) complexes of a series of quadridentate macrocycles with O_2N_2-donor sets correlates with the 'hole-sizes' of the donor sets obtained from solid-state structure determinations. As an extension of this study, the interaction of nickel(II) chloride with a series of potentially quinquedentate ligands containing O_2N_3-donor sets has been investigated.[2] For the nickel chloride complexes of certain of these ligands, the stability constants show a dramatic dependence on the presence and position of methyl substituents on the macrocyclic backbone. In such cases, steric interactions involving the methyl substituents were postulated to control alternative modes of co-ordination of the ligand. *X*-Ray structural determinations are now reported for the isothiocyanatonickel(II) complexes of three macrocycles (**1a**—**c**) which show variations of this type.†

In the complex of the unsubstituted ligand (**1a**) the nickel atom achieves a pseudo-octahedral geometry [Figure 1(a)] in which the oxygen atoms of the O_2N_3-donor set are not co-ordinated. Six-co-ordination is completed by two *N*-co-ordinated thiocyanate ligands and the formation of a thiocyanato bridged dimeric unit (Figure 2). Similarly in the nickel complex of the unsymmetrical dimethyl derivative (**1b**) the oxygen atoms of the O_2N_3-ligand are unco-ordinated, a pseudo-octahedral co-ordination geometry being completed in this case by two thiocyanate ligands and a co-ordinated water molecule [Figure 1(b)]. It is significant that these structural arrangements both involve *fac*-co-ordination of the three nitrogen atoms of the 1,4,7-triazaheptane unit.



(**1**) **a**; $R^1 = R^2 = R^3 = H$
b; $R^1 = R^2 = Me, R^3 = H$
c; $R^1 = R^3 = Me, R^2 = H$

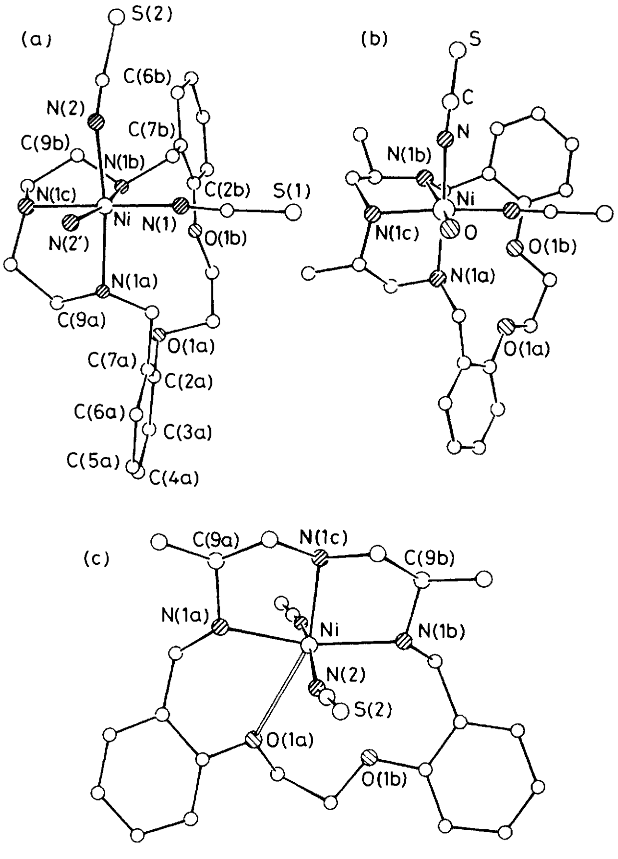


Figure 1. The structures of the pseudo-octahedral nickel(II) complexes (a) $[Ni(\mathbf{1a})(NCS)_2]_2$ (monomeric unit only) and (b) $[Ni(\mathbf{1b})(NCS)_2H_2O]$, and (c) of the five co-ordinate complex $[Ni(\mathbf{1c})(NCS)_2]$ [the ether oxygens O(1a) and O(1b) are 2.67 and 3.19 Å from the nickel atom in (c)]. The nickel to amine N(1a), N(1b), and N(1c) bonds in the three structures are (a) 2.128(9), 2.095(10), and 2.104(8); (b) 2.104(9), 2.195(10), and 2.081(9); and (c) 2.157(7), 2.189(6), and 2.069(7) Å, respectively.

In contrast, the symmetrically substituted dimethyl (*meso*) ligand (**1c**) gives a five co-ordinate complex $[Ni(\mathbf{1c})(NCS)_2]$ in which the nickel(II) ion has a very irregular co-ordination geometry. The triazaheptane unit has a *mer*-configuration, and as a consequence the ether oxygen atoms lie approximately in this co-ordination plane, but at distances which are too great to allow effective interaction with the nickel ion [see Figure 1(c)]. The resulting irregular geometry is presumably less favourable for the nickel ion than the pseudo-octahedral arrangements in the other two complexes, but is imposed upon the metal by the steric requirements of the pendant methyl groups. Molecular models show that if methyl groups are present in the 2,6-positions of the facially co-ordinated 1,4,7-

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† *Crystal data:* $[Ni(\mathbf{1a})(NCS)_2]_2 \cdot 3MeOH$, $C_{47}H_{66}N_{10}Ni_2O_7S_4$, triclinic, space group $P\bar{1}$, $a = 12.512(5)$, $b = 10.558(3)$, $c = 11.493(4)$ Å, $\alpha = 100.87(10)$, $\beta = 104.39(9)$, $\gamma = 100.23(11)°$, $Z = 1$, $I/\sigma(I) > 3.0$, present R value $= 0.0874$ for 2583 reflections (the methanol molecules are disordered). $[Ni(\mathbf{1b})(NCS)_2\text{-}H_2O]$, $C_{24}H_{33}N_5O_3NiS_2$, orthorhombic, space group *Pbca*, $a = 11.686(3)$, $b = 12.796(3)$, $c = 38.196(11)$ Å, $Z = 8$, $I/\sigma(I) > 2.5$, present R value $= 0.0672$ for 1501 reflections. $[Ni(\mathbf{1c})(NCS)_2]$, $C_{24}H_{31}N_5NiO_2S_2$, monoclinic, space group $P2_1/c$, $a = 10.333(3)$, $b = 15.811(5)$, $c = 16.238(5)$ Å, $\beta = 96.61(8)°$, $Z = 4$, $I/\sigma(I) > 3.0$, present R value $= 0.0754$ for 2438 reflections. 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.

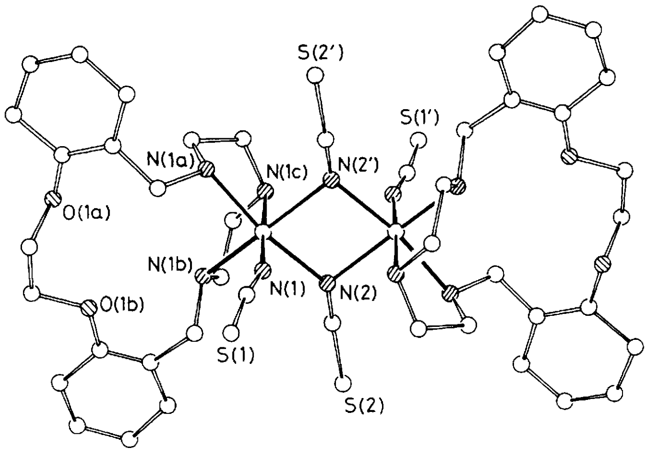

Figure 2. The structure of the dinuclear complex [Ni(**1a**)(NCS)$_2$]$_2$.

triazaheptane unit, then they will make unfavourable contacts with the adjacent *o*-benzyl groups.‡ These repulsive interactions presumably prevent (**1c**) adopting the ligand configurations observed in [Ni(**1a**)(CNS)$_2$]$_2$ or [Ni(**1b**)(NCS)$_2$H$_2$O] [Figure 1(a,b)].

Although the results may not be directly applicable to the solution studies mentioned previously, the *X*-ray determinations very clearly illustrate the manner by which ring substituents can influence the mode of macrocycle co-ordination to nickel(II). Further, the preference of high-spin nickel for octahedral co-ordination and the relative difficulty experienced by (**1c**) in presenting a facial arrangement of the N$_3$ donors to a pseudo-octahedral ion probably accounts for the significantly lower log *K* value found[2] for the nickel(II) chloride complex of this ligand relative to that of (**1a**).

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‡ These interactions can be defined more quantitatively by determining the intramolecular contacts experienced by methyl groups which are inserted on the C(9) atoms in [Ni(**1a**)(NCS)$_2$]$_2$ in calculated positions (assuming tetrahedral geometry and a C–C length of 1.54 Å). Such methyl groups are found to be either in close proximity to the adjacent ethane bridge (with several methyl H $\cdots$ ethane C contacts <2.2 Å), or to lie close to the C(6)–C(7)–C(2) portion of the benzene rings (with several methyl H $\cdots$ benzene C contacts <2.0 Å).

References

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