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^{13}C N.M.R. Evidence for a Dynamic Equilibrium Between Two Forms of (1,4,8,11-tetrathiacyclotetradecane)nickel(II) Fluoroborate in Nitromethane Solution

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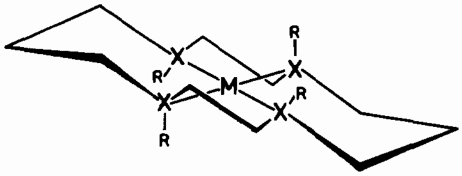
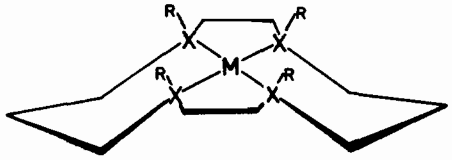
Previously we have shown how useful ^{13}C n.m.r. can be for probing the structures of diamagnetic metal complexes in solution [1]. A good example of how ^{13}C n.m.r. will sometimes reveal structural information with other techniques may fail to detect is shown by our studies of the nickel(II) complex of 1,4,8,11-tetrathiacyclotetradecane(TTP), [Ni(TTP]BF$_4$)$_2$, in nitromethane solution. A crystal structure of this complex shows that the nickel(II) ion is coordinated to the four sulphur atoms in a centrosymmetric square-planar structure (I; X = S, R = lone pair of electrons), with the tetrafluoroborate anions uncoordinated [2]. Four other structures are possible for square-planar complexes of TTP depending upon the relative positions of the lone pairs of electrons on each sulphur atom. The five possible structures are directly analagous to those of the related nitrogen-donor ligand, 1, 4, 8, 11-tetra-azacyclotetradecane (cyclam) in its square-planar or tetragonal complexes [3], in which the sulphur atoms of TTP are replaced by N–H groups, and the possible conformational arrangements of the N–H groups in cyclam are identical to those of the unco-ordinated lone pairs of electrons on the sulphur atoms of TTP. Of the five possible ligand conformations expected for cyclam and TTP in their tetragonal or square-planar complexes, only conformation (I) has been established so far, although conformation (II) is observed in [Ni(L)N$_3$]ClO$_4$ and [Ni(L)](ClO$_4$)$_2$, where L = 1,4,8,11-tetramethyl- 1,4,8,11-tetra-azacyclotetradecane (II; X = N, R = Me) [4, 5].

For the TTP, crystal structures of the tetragonal copper(II) complex [6], and the square-planar nickel(II) complex [2] have both been found with ligand conformation (I). Spectroscopic [7], thermodynamic [8, 9] and kinetic studies of these complexes have also failed to reveal the presence of more than one ligand conformation, although exo-conformations (where the ligand is turned 'inside-out') have been found for TTP in the binuclear complexes [(Cl$_5$Nb)$_2$TTP] [11] and [Cl$_2$Hg)$_2$TTP] [12]. Folded conformations for TTP and cyclam are also possible in complexes of the type *cis*-[MLX$_2$]Y (*e.g.* M = Co^{III}, Rh^{III}, Cr^{III}; L = TTP or cyclam; X = halide; Y = univalent counterion) [13, 14].



I



II

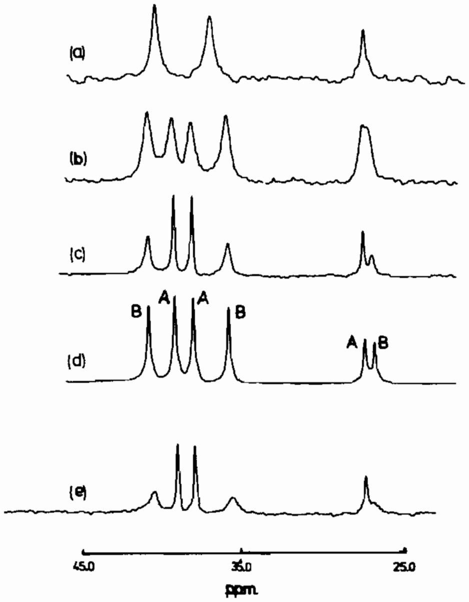


Figure 1. Variable temperature ^{13}C n.m.r. spectra of the complex [Ni(TTP)](BF$_4$)$_2$ at 0.202 mol dm^{-3} in [^{2}H$_3$]-nitromethane. a) 373 K, b) 323 K, c) 293 K, d) 253 K, e) 293 K, with H$_2$O present at 0.103 mol dm^{-3}.

A variable temperature ^{1}H-decoupled ^{13}C n.m.r. investigation of [Ni(TTP)](BF$_4$)$_2$ in [^{2}H$_3$]-nitromethane is shown in Figure 1. For the centrosymmetric structure (I) only three resonances are expected with relative peak areas 1:2:2. The low-temperature spectrum of [Ni(TTP)](BF$_4$)$_2$ reveals the presence of two sets of three resonances (A and B), each set having the expected intensity ratios 1:2:2. The relative populations of the two species

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are 50 ± 5% (A) and 50 ± 5% (B) at 283 K. As the temperature is increased, the two sets of resonances broaden and then merge, until a single set of three resonances appears at high temperatures. This behaviour is consistent with a dynamic equilibrium between two of the five possible ligand conformations predicted for square-planar or tetragonal complexes of TTP or cyclam [3], and we tentatively assign them to the two structures (I) and (II) (X = S, R = lone pair). The two conformations can interconvert by inversion at two of the four sulphur atoms, with or without metal–ligand bond cleavage. A complete line-shape analysis [15] of the spectrum at 301 K shows that the free energy of activation for this process is *ca.* 66.8 kJ mol^{-1} at this temperature. This can be compared with free energies of activation in the range 56–68 kJ mol^{-1} found for inversion at a single sulphur atom in platinum(II) complexes [16, 17]. Conformations (I) and (II) are preferred for solutions of $[Ni(TTP)](BF_4)_2$ by analogy with the known crystal structures [4, 5, 18], and because more than three ^{13}C resonances would be expected for at least two of the other three possible structures which are less symmetric [3].

The low-temperature ^{13}C n.m.r. spectrum of $[Ni(TTP)](BF_4)_2$ also changes upon addition of small amounts of donor solvents such as H_2O. This behaviour parallels that observed in earlier ^1H n.m.r. studies [13], large amounts of donor solvents causing complete dissociation of the complex. When only a small amount of water is added, the resonances B in the low-temperature ^{13}C n.m.r. spectrum are selectively broadened as shown in the figure. We attribute this broadening to the formation of a paramagnetic five or six co-ordinate complex, and by analogy with previous structure determinations [4, 5] it seems likely that this occurs preferentially with structure (II).

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