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Evidence for the R,S,R,R Isomer of (1,4,8,11-Tetramethyl-1,4,8,11-tetra-azacyclotetradecane)nickel(II) Ion

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The R,S,S,R (A) and R,S,R,S (B) isomers of (1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) nickel(II) ion, $[Ni(TMC)]^{2+}$, shown in Fig. 1, were first reported [1–3] several years ago, but it is only recently that some evidence for the existence of the R,S,R,R isomer (C) has been adduced [4]. Whilst (C) has yet to be separated from admixture with (B) in the solid state our preparative, ^{13}C NMR, and kinetic studies of the $[Ni(TMC)]^{2+}$ system indicate that mixtures of (B) and (C) are readily prepared, and that (C) isomerises to (B) in solution.

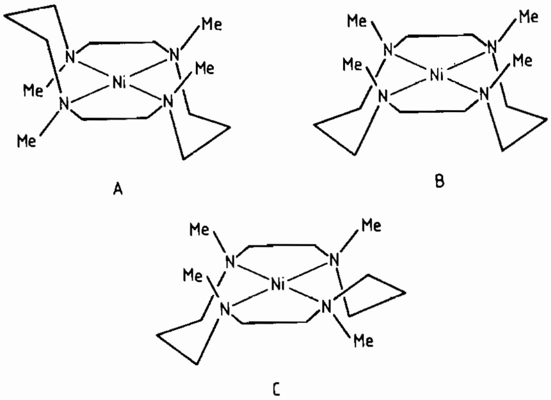

Fig. 1. The R,S,S,R (A), R,S,R,S (B), and R,S,R,R (C) isomers of $[Ni(TMC)]^{2+}$.

Experimental

Hydrated nickel(II) triflate ($CF_3SO_3^-$) or perchlorate (0.010 mol) was reacted with triethylorthoformate (0.14 mol) for 2hr at 320 K and, after cooling to 300 K, solid TMC (0.011 mol) was added with vigorous stirring whereupon a red precipitate was obtained. This product was thoroughly washed with dry ether and dried under vacuum. Good analyses were obtained for $[Ni(TMC)](CF_3SO_3)_2$ and its perchlorate analogue. The yield was essentially quantitative. The ^{13}C NMR spectrum of the triflate product (Fig. 2(i)) showed (B) and (C) to be present in similar amounts whilst that of the perchlorate product indicated the presence of a markedly smaller proportion of (C). Recrystallisation of these products in CH_3NO_2 converts (C) almost entirely to (B). It was found that the published methods [1] for the preparation of (B) also produce small amounts of (C) in the crude product.

NMR spectra were run on Bruker CXP300 and WP80 spectrometers. The exchange rate of N,N-dimethylformamide (DMF) on $[Ni(TMC)DMF]^{2+}$ was determined from 300 MHz ^1H NMR spectra obtained in the temperature range 190–300 K using standard procedures [5–7]. The high-spin/low-spin equilibrium constant characterising (B) in DMF was determined spectrophotometrically in the wavelength range 400–510 nm and the temperature range 280.7–355.7 K. The isomerisation of (C) to (B) at 298.2 K in DMF was followed at 400 and 510 nm.

All solvents were distilled, dried and stored over Linde 4A molecular sieves.

Results and Discussion

The broad band ^1H decoupled ^{13}C NMR spectrum of a CH_3NO_2 solution of an isomeric mixture of $[Ni(TMC)](CF_3SO_3)_2$ is shown in Fig. 2(i). Isomer

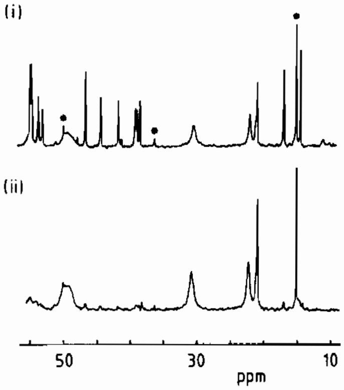

Fig. 2. The broad band ^1H decoupled ^{13}C (75.47 MHz) NMR spectra of (i) a freshly prepared CH_3NO_2 solution of a mixture of the (B) and (C) isomers of $[Ni(TMC)])CF_3SO_3)_2$ and (ii) the same solution after heating at 373 K for 22 hr. The two small resonances and the larger one (15.02 ppm) indicated by asterisks arise from minor impurities in the CH_3NO_2 solvent.

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(B) is characterised by resonances at 49.97, 30.54 (both $-NH_2-\underline{C}H_2-$); 21.94 ($-\underline{C}H_3$); and 20.91 ppm ($-CH_2-\underline{C}H_2-CH_2$). Isomer (C) contains fourteen non-equivalent carbon atoms and its ^{13}C NMR spectrum exhibits thirteen resonances: 54.97, 54.79, 54.71, 53.71, 53.10, 46.69, 44.40 (all $-NH_2-\underline{C}H_2-$); 41.71, 39.15, 38.93, 38.51 (all $-\underline{C}H_3$); 16.87 and 14.37 ppm (both $-CH_2-\underline{C}H_2-CH_2-$); where that at 54.97 ppm appears to be twice the intensity of the other resonances. Chemical shifts are relative to TMS (that of $\underline{C}H_3NO_2$ is 57.30 ppm) and assignments were made from undecoupled spectra. On heating the solution at 320 K the (C) resonances lose intensity whilst the (B) resonances gain intensity to give the spectrum shown in Fig. 2(ii) consistent with isomerisation of (C) to (B) with a reaction half-time of *ca.* 30 hr. The resonances of both the triflate and perchlorate salts of (B) are broadened at 75.47 MHz by a factor of ≥ 5 by comparison to their width at 20.00 MHz, but the (C) resonances are not significantly broadened at either frequency. Whilst the chemical shifts of the resonances of (C) are virtually independent of the nature of the anion the (B) $-\underline{C}H_3$ and $-NH_2-\underline{C}H_2-$ resonances are shifted down-field and the $-CH_2-\underline{C}H_2-CH_2-$ resonance is shifted up-field in the presence of perchlorate by comparison to the shifts observed in the presence of triflate. It is also observed that the triflate ^{19}F resonances are broadened in the presence of (B). These observations suggest that the anions interact preferentially with (B) to produce a small amount of a high-spin species which is in rapid equilibrium with the predominant low-spin species, and which in turn produces the broadening of the isomer B resonances.

Dissolution of the triflate or perchlorate salts of (B) in DMF immediately produces a green solution consistent with substantial conversion of red low-spin $[Ni(TMC)]^{2+}$ to green high-spin $[Ni(TMC)DMF]^{2+}$ which is characterised by μ_{eff} = 3.24 BM [8]. ($K = [Ni(TMC)DMF^{2+}]/[Ni(TMC)^{2+}] = 10 \pm 1$ at 298.2 K characterises this facile equilibrium where k_{ex} (298.2 K) = $(1.6 \pm 0.2) \times 10^7$ s^{-1} characterises DMF exchange on $[Ni(TMC)DMF]^{2+}$ which species is assumed to possess the R,S,R,S configuration with the four methyl groups and DMF on the same side of the tetra-aza TMC plane as X-ray studies show to be the case in the crystalline state [9]). In contrast the dissolution of the triflate or perchlorate salts of the (B) and (C) isomeric mixture of $[Ni(TMC)]^{2+}$ in DMF immediately produces a red or brown solution (depending on the relative amounts of (B) and (C) in the sample) which slowly turns green at a rate characterised by a reaction half-time of *ca.* 25 min. at 298.2 K. This is consistent with the rate determining step for the colour change being the isomerisation of (C) to (B) with the high-spin species being more favoured for (B) as shown below. The isomerisation of (C) to (B) involves inversion about a nitrogen which probably requires the inverting nitrogen to detach from nickel(II) rendering

$$\begin{tikzcd}
\text{(red) } [Ni(TMC)]^{2+}(C) + DMF \arrow[r, shift left, dashed, "fast"] & {[Ni(TMC)DMF]^{2+}(C) \text{ (green?)}} \arrow[l, shift left, dashed] \arrow[d, shift left, "slow"'] \\
\text{(red) } [Ni(TMC)]^{2+}(B) + DMF \arrow[r, shift left, dashed, "fast"] & {[Ni(TMC)DMF]^{2+}(B) \text{ (green)}} \arrow[l, shift left, dashed] \arrow[u, shift left, dashed]
\end{tikzcd}$$

the previously quadridentate TMC temporarily terdentate. It has been observed that the isomerisation of (C) to (B) occurs more rapidly in the strong donor solvent DMF than in the weak donor solvent CH_3NO_2 for which the Gutmann donor numbers are 30.9 and 2.7, respectively [10]. Whilst there is no direct evidence for coordination of DMF to (C), this solvent is expected to show a greater tendency to coordinate than does CH_3NO_2 and thus if solvent coordination to (C) is important in the energetics of the nitrogen inversion process, the isomerisation of (C) to (B) should occur more readily in DMF than in CH_3NO_2.

Acknowledgements

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