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The Slow Isomerisation of a High-Spin $[Ni(tetraamine)(DMSO)_2]^{2+}$ Cation

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In DMSO solution the $[Ni(2,3,2\text{-}tet)DMSO)_2]^{2+}$ *cation (2,3,2-tet = 1,4,7,11-tetraazaundecane) undergoes a remarkably slow* trans ⇄ cis *isomerisation: the initially* trans *cation converts to an equilibrium mixture which is mainly* cis. $k_{obs}(298) = 1.92 \times 10^{-5}$ sec^{-1} ($t_{1/2} \approx 14$ *hr*), $K_{eq} \approx 5$, $k_{obs}(318) = 4.89 \times 10^{-5}$ sec^{-1}, $\Delta H^{\ddagger} = 8.2$ (±0.5) *kcal mol*$^{-1}$, $\Delta S^{\ddagger} = -52.0$ (±2.0) *cal deg*$^{-1}$ *mol*$^{-1}$, *and* $E_a = 8.8$ (±0.5) *kcal mol*$^{-1}$. *Added water or dimethylsulphone accelerate the reaction, which seems to be unique among such tetraamine compounds. The slowness probably results from a uniquely ordered solvent shell.*

Introduction

High-spin nickel(II) compounds, especially those with aliphatic amines, are generally quite labile. Among the few slow reactions of Ni^{II} are the racemisations of $[Ni(1,10\text{-phenanthroline})_3]^{2+}$ and related species [1]. Thus there is some surprise in the observation, which we report here, that $[Ni(2,3,2\text{-tet})(DMSO)_2]^{2+}$ (2,3,2-tet = 1,4,7,11-tetraazaundecane [2]) undergoes a slow *trans* ⇄ *cis* isomerisation in DMSO.

Results and Discussion

The Figure shows the sort of data on which we rely.

When $[Ni(2,3,2\text{-tet})]I_2$ or *trans*$[Ni(2,3,2\text{-tet})Cl_2]$ are dissolved in DMSO, an initial equilibrium mixture (1) is obtained. This is a labile equilibrium [2–4], and we estimate relative amounts of each species present

$$\underset{\text{high spin (80\%)}}{trans\text{-}[Ni(2,3,2\text{-tet})(DMSO)_2]^{2+}} \xrightleftharpoons[k_{-1}]{k_1}$$

$$\underset{\text{low spin (20\%)}}{[Ni(2,3,2\text{-tet})]^{2+} + 2\,DMSO} \qquad (1)$$

using [3] an ϵ_{max}(low spin) at 22,000 cm^{-1} of 60.

Then a slow reaction ensues as equilibrium (2) is approached:

$$trans\text{-}[Ni(2,3,2\text{-tet})(DMSO)_2]^{2+} \xrightleftharpoons[k_{-2}]{k_2}$$

$$cis\text{-}[Ni(2,3,2\text{-tet})(DMSO)_2]^{2+} \qquad (2)$$

This equilibrium is defined by, and the approach to equilibrium is studied using, the electronic absorption spectra (Figure).

In these spectra the band at 22,000 cm^{-1} arises entirely from the low-spin $[NiN_4]^{2+}$ species. High spin nickel(II) compounds of the sort studied here show no significant absorption in this region. They are instead characterised by bands centred at ~10,000, 18,000, and 29,000 cm^{-1}, with the *cis* and *trans* isomers distinguishable from the differences

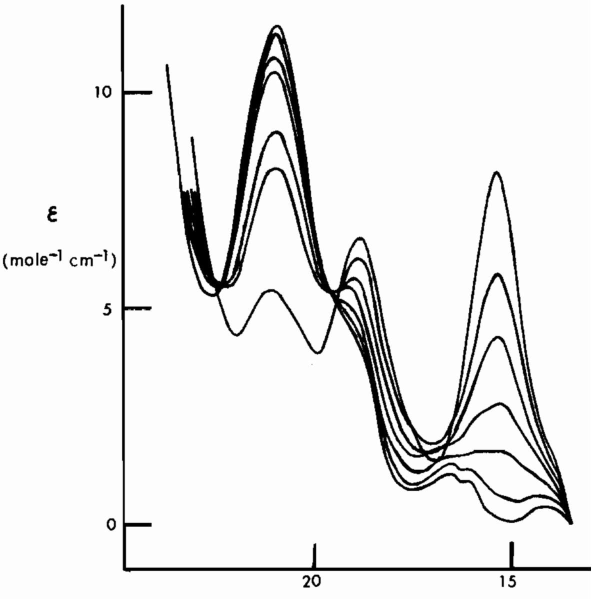

Figure. An example of the changing electronic absorption spectra which can be obtained when $[Ni(2,3,2\text{-tet})]I_2$ is dissolved in DMSO. With increasing time, intensity of absorption at ~10,000 cm^{-1} increases, whilst that at ~22,000 cm^{-1} decreases. The 'final' spectrum represents a solution left for 10 half-lives.

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in their spectra in the region 7,000–15,000 cm^{-1}. *Trans* isomers show a distinct 'splitting' of the 10,000 cm^{-1} band into two widely separated peaks – usually near 7,000 cm^{-1} and 13,000–15,000 cm^{-1}.

The present Figure gives a unique example of the spectra of *cis* and *trans* isomers of an $[Ni^{II}N_4O_2]$ chromophore. The 'initial' spectrum (neglecting the band at 22,000 cm^{-1}) is of almost pure *trans* isomer, and the 'final' one is that of nearly pure *cis* isomer. (Although up to 20% of the *trans* isomer remains at equilibrium, the extinction coefficients of the bands in its spectrum are so much smaller that the *cis* isomer completely dominates the spectrum).

At equilibrium ('final' spectrum) all three species are present: (i) the residual peak at 22,000 cm^{-1}, arising only from the low spin $[Ni(2,3,2\text{-}tet)]^{2+}$ species, indicates that 4(±1)% of this is present; (ii) from the data for equilibrium(1) in the 'initial' solutions, 16(±4)% of the high spin *trans*-$[Ni(2,3,2\text{-}tet)(DMSO)_2]^{2+}$ cation must also be present; and (iii) therefore the 'final' solution contains only ~80% of *cis**-$[Ni(2,3,2\text{-}tet)(DMSO)_2]^{2+}$.

Because we cannot isolate each of these three species separately in DMSO, we have no accurate determinations of extinction coefficients, and hence the equilibrium constants we have to use in the analysis of the data are but estimates. However, large variations in these values do not significantly alter the activation parameters obtained. Changes of K_{eq} over the temperature range studied also appear to be within the limits of the estimate.

For DMSO distilled from CaH_2 under N_2, $k_{obs}(298) = 1.92 \times 10^{-5}$ sec^{-1} ($t_{1/2} \approx 14$ hr), $k_{obs}(318) = 4.89 \times 10^{-5}$ sec^{-1}, $K_{eq} \approx 5$, $k_2(298) = 2.40 \times 10^{-5}$ sec^{-1}, $k_2(318) = 6.12 \times 10^{-5}$ sec^{-1}, $E_a = 8.8$ (±0.5) kcal mol^{-1}, $\Delta H^{\ddagger} = 8.2$ (±0.5) kcal mol^{-1}, $\Delta S^{\ddagger} = -52.0(\pm 2.0)$ cal deg^{-1} mol^{-1}.

The low value of E_a is compatible with the small increase of rate with temperature: an increment of 20° in temperature gives only a 2.5-fold increase in rate.

By contrast, all reactions of the nickel/2,3,2-tet species in water, DMF and $MeNO_2$, as well as those for the nickel compounds of the homologous ligands trien (2,4,7,10-tetraazadecane) and 3,2,3-tet (1,5,8,12-tetraazadodecane), in the same solvents appear to be unexceptionally fast [3]. Thus the slowness of the $[Ni(2,3,2\text{-}tet)(DMSO)_2]^{2+}$ isomerisation probably results from a rather unique solvent structure associated with the cation in the transition state. Whereas $\Delta H^{\ddagger}$ is normal for such nickel(II) reactions, $\Delta S^{\ddagger}$ is unusually large.

When water or dimethylsulphone** are added to the DMSO, the reaction is markedly accelerated. For example, 0.5% H_2O doubles the rate; 0.5% Me_2SO_2 increases it 20 fold; and DMSO saturated with Me_2SO_2 gives a 300 fold increase over pure DMSO. Both additives can reasonably be expected to compete with the DMSO for positions in the solvation shell of the cation, and thus break down the unique structure formed by DMSO alone. DMSO hydrogen-bonds quite strongly to co-ordinated amines [5], and this would seem to play an important part in the formation of the unique solvation shell.

These additives do not appear to affect significantly the position of the final equilibrium. The solutions at equilibrium all have a peak in their spectra at 22,000 cm^{-1} which indicates the presence of ~4% of the low-spin $[Ni(2,3,2\text{-}tet)]^{2+}$ cation, and thus also 15–20% of *trans*-$[Ni(2,3,2\text{-}tet)(DMSO)_2]^{2+}$ [equil. (1)].

Qualitatively also it seems that the reaction

$$cis\text{-}[Ni(2,3,2\text{-}tet)Cl_2] \longrightarrow trans\text{-}[Ni(2,3,2\text{-}tet)Cl_2] \tag{3}$$

is slow in DMSO saturated with LiCl. When the reacted solution [equil. (2)] is treated with LiCl to saturation, fast anation gives *cis*-$[Ni(2,3,2\text{-}tet)Cl_2]$. This solution then slowly (over some hours) deposits crystals of *trans*-$[Ni(2,3,2\text{-}tet)Cl_2]$. Crystallisation cannot be induced by 'seeding' with the latter, so it seems that the slow rate of crystallisation is governed by a slow formation reaction. Thus, if an explanation is again to be given in terms of a tight solvation shell, it seems a remarkable coincidence that such solvation shells should be so effective for both *trans*-$[Ni(2,3,2\text{-}tet)(DMSO)_2]^{2+}$ in pure DMSO and *cis*-$[Ni(2,3,2\text{-}tet)Cl_2]$ in LiCl-saturated DMSO.

It will be interesting to see if some of the substituted 2,3,2-tet ligands also have slow reactions in DMSO.

Experimental

The reaction was followed spectrophotometrically on both Unicam SP700 and SP850 instruments, using DMSO solutions of the compound [2, 3] $[Ni(2,3,2\text{-}tet)]I_2$ [5×10^{-2} *M*]. The absorbance changes were followed *either* in the structurally significant region (7,000–15,000 cm^{-1}) *or* by measuring the decrease in the intensity of the band from the low-spin species at ~22,000 cm^{-1}. The latter was most convenient to use and, after several checks that either

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*The *cis* species can exist in a variety of configurations, but these cannot be distinguished with available data.

**Dimethylsulphone was originally added because we assumed that such a slow reaction could not involve the nickel spp. directly. One possible explanation seemed to be a catalysis of DMSO oxygenation to the sulphone, followed by the formation of $[Ni(2,3,2\text{-}tet)(Me_2SO_2)]^{2+}$, with a chelated sulphone and thus a non-planar tetraamine.

region gave the same results, was used predominantly. That is, approach to equil. (2) was followed indirectly through equil. (1).

Some problems were encountered initially with quantitative reproducibility. Attempts to use laboratory reagent DMSO, dried with molecular sieve (4Å) under N_2, led to quite variable rate data. The slowest observed rate, however, was in close agreement with the presently reported value obtained in DMSO freshly distilled from CaH_2 under N_2. The spectrophotometer cells were filled and sealed under N_2.

The data all gave good first-order plots for at least one-third reaction. Most of the reactions studied decelerated with time, but in several cases, straight line plots for up to three half-lives were obtained.

All data were analysed only in terms of first-order rate constants.

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