Inorganica Chimica Acta, 24 (1977) L21–L23
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Does a Macrocyclic Effect Exist in the Blue-to-Yellow Conversion of Nickel(II) Complexes with Tetra-aza Ligands?

A. ANICHINI, L. FABBRIZZI, P. PAOLETTI

Istituto di Chimica Generale dell'Università e Laboratorio CNR, via Jacopo Nardi 39, 50132 Florence, Italy

R. M. CLAY

Department of Chemistry, University of Stirling, Stirling, Scotland, U.K.

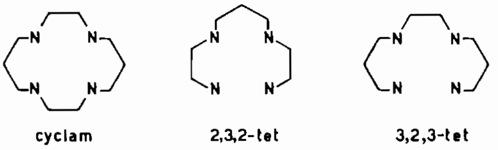
Received April 18, 1977

The effect of ligand cyclization on the properties of metal complexes with multidentate ligands has been thoroughly explored in the past years. It has been shown that cyclic tetramines form more stable metal complexes than their linear counterparts, both from a thermodynamic [1] and kinetic [2] point of view. Furthermore, tetra-aza macrocycles are able to induce strong ligand-field effects [3] and stabilize unusually high oxidation states of metals [4].

In aqueous solutions, tetra-aza complexes of Ni(II) exist in equilibrium as a mixture of the blue (paramagnetic, octahedral) and yellow (diamagnetic, square planar) forms [5].

$$\underset{\text{blue}}{\mathrm{NiL(H_2O)_2^{2+}}} \rightleftharpoons \underset{\text{yellow}}{\mathrm{NiL^{2+}}} + 2\mathrm{H_2O} \qquad (1)$$

With linear tetramines the blue species strongly predominates at equilibrium [6], whereas it has been reported that for the cyclic tetramine 1,4,8,11-tetra-aza-tetradecane (cyclam) only the yellow form is present in solution [7]. We wished to ascertain whether, and to what extent, the cyclic nature of the ligand might affect the position of equilibrium (1) and we have made a thermodynamic study of the blue-to-yellow conversion of the Ni(II) complexes of cyclam and its linear analogues 1,4,8,11-tetra-aza-undecane (2,3,2-tet) and 1,5,8,12-tetra-aza-dodecane (3,2,3-tet).



Equilibrium (1) is displaced to the right by increasing either the temperature (the formation of the yellow species is endothermic) or the ionic strength (ions of the inert electrolyte are thought to compete for the water molecules coordinated to the Ni(II) ion) [8, 9].

The equilibrium (1) can be monitored spectroscopically using the absorption band at about 22,000 cm^{-1}, which is due to the yellow diamagnetic chromophore. We have found that a solution of Ni(cyclam)$^{2+}$, while appearing yellow, has a molar extinction coefficient (ϵ) of 46 mol^{-1} l at ν_{max} = 445 mμ; this value of ϵ is somewhat smaller than that found for solutions of Ni(II) tetramines exclusively in the yellow form: Ni(2,3,2-tet)$^{2+}$ (yellow), ϵ = 67 mol^{-1} l; Ni(3,2,3-tet)$^{2+}$ (yellow), ϵ = 63 mol^{-1} l. Furthermore, either increasing temperature or adding small amounts of the inert electrolyte $NaClO_4$ strengthens the band intensity. Contrary to a previous report [7], these data suggest that Ni(cyclam)$^{2+}$ exists in aqueous solution as a mixture of blue and yellow forms. Direct evidence for the octahedral blue form is two-fold: i) in the visible spectrum of an aqueous solution of Ni(cyclam)$^{2+}$ a sharp band at 30,300 cm^{-1} (ν_3) and a shoulder at about 15,000 cm^{-1} (ν_2) are evident. These features disappear on the addition of the inert electrolyte; ii) PMR spectra at 35 °C of D_2O solutions of Ni(cyclam)$^{2+}$ show resonance signals which are intermediate between those expected for fully paramagnetic octahedral complexes and square planar diamagnetic complexes. Concerning the electronic spectra, the addition of an inert electrolyte eventually causes no further increase in ϵ, demonstrating that 100% conversion to the yellow form has taken place and allowing the determination of the limiting spectrum. The limiting value of the band at 22,470 cm^{-1} in 6*M* $NaClO_4$ is 64.5 mol^{-1} l and this cannot be increased by raising the temperature. The equilibrium constant (K) for reaction (1) at 25 °C in 0.1 *M* $NaClO_4$ was calculated ($K = \epsilon/\epsilon_{limit} - \epsilon = 2.47$). Thus Ni(cyclam)$^{2+}$ exists under these conditions as 71% of the yellow square-planar and 29% of the blue octahedral forms. Temperature dependence of logK in the range 19 - 49 °C allowed the determination of ΔH° and ΔS° values. The complexes Ni(2,3,2-tet)$^{2+}$ (22% of the yellow form in 0.1 *M* $NaClO_4$, at 25 °C) and Ni(3,2,3-tet)$^{2+}$ (8% of the yellow form in 0.1 *M* $NaClO_4$, at 25 °C) were investigated in a similar manner over the temperature ranges 19 - 56 °C and 20 - 45 °C, respectively. The limiting ϵ values for these two complexes were determined in 7 *M* $NaClO_4$ solutions and checked for temperature dependence. All the determined thermodynamic functions are reported in the Table.

Interestingly, of the systems studied the Ni(cyclam)$^{2+}$ complex exhibits the greatest ability of the yellow form, while its formation from the blue form is the most endothermic. The enhanced stability must therefore depend on a very favourable entropy term.

During the conversion blue-to-yellow, the contraction and subsequent strengthening of in-plane Ni–N

TABLE. Thermodynamic Functions for the Blue-to-Yellow Conversion of Nickel(II) Complexes with the Ligands Cyclam, 2,3,2-Tet and 3,2,3-Tet, at 25 °C in 0.1 *M* $NaClO_4$.

Ligand	K[a]	ΔH° [b]	ΔS° [c]
Cyclam	$10^{0.39}$	5.4	20
2,3,2-Tet[d]	$10^{-0.54}$	3.4	9
3,2,3-Tet	$10^{-1.09}$	4.4	15

[a] Error within 0.05 log units. [b] kcal mol^{-1}, error within ± 0.4. [c] Cal K^{-1} mol^{-1}, error within ± 2. [d] Data in agreement with those previously reported on the same system [7].

bonds will be an exothermic contribution, which will be more than compensated for by the breaking of the axial Ni–OH_2 bonds [9]. The energy of the band in the 21,000–23,000 cm^{-1} region can be used as a measure of the Ni–N interaction [10] in the square planar complexes; the fact that both Ni(2,3,2-tet)$^{2+}$ and Ni(cyclam)$^{2+}$ absorb at almost the same frequency (22,420 and 22,470 cm^{-1}, respectively) suggests that the Ni–N in-plane bonds in both complexes have similar energies. A consideration of bond energies is, therefore, not sufficient to explain the different thermicity of the blue-to-yellow conversions. It has been demonstrated theoretically [11] that cyclam should adopt a configuration of minimum strain when it coordinates a metal ion with a M–N distance of 2.07 Å (with 4 coplanar nitrogens). Octahedral Ni(II) is one of the most appropriate metal ions to minimise configurational strain and a Ni–N of 2.06 Å has been found in Ni(cyclam)Cl_2 in the crystalline state [12]. However, the conversion to the diamagnetic yellow form is accompanied by a sharp reduction in Ni–N bond distance (1.90 to 1.91 Å has been found for diamagnetic tetramine complexes) [13, 14] and the ligand is required to re-arrange its donor atoms closer to the metal. Linear ligands as 2,3,2-tet will be able to adapt themselves more readily to the requirements of low-spin Ni(II) ion without expending large amounts of configurational energy than their cyclic counterparts, which, because of their lack of flexibility, must experience considerable mechanical resistance in contracting the size of their "hole". The greater endothermicity of the blue-to-yellow conversion in Ni(cyclam)$^{2+}$ is thus steric in origin. Although Ni(3,2,3-tet)$^{2+}$, from an enthalphic standpoint, falls between the other two complexes, a true comparison is more difficult since the Ni–N bonds in this complex are less strong (ν_{max} = 21,740 cm^{-1}). This results from the predominance of six- rather than five-membered chelate rings in Ni(3,2,3-tet)$^{2+}$, making the co-ordinative bonds intrinsically weaker [5].

At its simplest, the entropy change can be estimated by considering two terms which should be common to all these complexes: a negative term due to the reduction of spin multiplicity (Rln3 = 2.2 cal K^{-1} mol^{-1}) and a positive term due to the release of the two co-ordinated water molecules. The increase in translational entropy resulting from the liberation of a water molecule in solution has been estimated to be between 7–10 cal K^{-1} mol^{-1} [7, 15, 16] and the value of ΔS° (+20 cal K^{-1} mol^{-1} for Ni(cyclam)$^{2+}$ fits this interpretation well. However, for Ni(2,3,2-tet)$^{2+}$ and Ni(3,2,3-tet)$^{2+}$, the ΔS° values are 9 and 15 cal K^{-1} mol^{-1} respectively, falling considerably short of the value found for Ni(cyclam)$^{2+}$ and required by the simple interpretation. It has previously been suggested [7] that the spin-state reduction of Ni(II) does not necessarily require a total release of apical water molecules to give a true square-planar species, but may occur by the extreme elongation of the axial bonds. If this happens, the water molecules will only be mobilised, not released, resulting in a smaller entropy gain. Further, as the size of the aliphatic part of the tetramine ligands increases, the larger steric repulsions between methylene groups and co-ordinated water molecules will favour the mobilisation–dehydration process and ΔS° should increase along the series 2,3,2-tet < 3,2,3-tet < cyclam, in reasonable agreement with the experimental results.

The correlation of non-bonded interactions between coordinated water molecules and the aliphatic part of the ligand is also evident in Nickel(II) complexes with bis-ethylenediamines; Ni(ethylenediamine)$_2^{2+}$ is blue, Ni(C,C-dimethyl-ethylenediamine)$_2^{2+}$ is a 50% blue–yellow mixture [17] and Ni(C,C,C′,C′-tetramethylethylenediamine)$_2^{2+}$ exists only in the yellow form [18].

In conclusion, the ability of cyclam to stabilise the square-planar yellow form relative to the linear analogues does not result from any special cyclic effect, but depends only on steric interactions which are also present in appropriate linear ligands. In fact, cyclisation and its mechanical consequences hinder the macrocyclic ligand in its coordination to the low-spin Ni(II) ion.

Acknowledgments

We thank Dr. Andrea Dei for his advice with the n.m.r. spectra, together with the Italian C.N.R. for financial support and the Royal Society for the award of a European Fellowship to R.M.C.

References

1 D. K. Cabbiness and D. W. Margerum, *J. Am. Chem. Soc., 91,* 6540 (1969).

2 C. T. Lin, D. B. Rorabacher, G. R. Cailey and D. W. Margerum, *Inorg. Chem., 14,* 919 (1975).

3 D. H. Busch, K. Farmery, V. L. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati and N. Tokel, *Adv. Chem. Ser., 100,* 44 (1971).

4 F. V. Lovecchio, E. S. Gore and D. H. Busch, *J. Am. Chem. Soc., 96,* 3109 (1974) and references therein.

5 P. Paoletti, L. Fabbrizzi and R. Barbucci, *Inorg. Chim. Acta Rev., 7,* 43 (1973).

6 R. G. Wilkins, R. Yelin, D. W. Margerum and D. C. Weatherburn, *J. Am. Chem. Soc., 91,* 4326 (1969); R. Barbucci, L. Fabbrizzi, P. Paoletti and A. Vacca, *J. Chem. Soc. Dalton,* (1973).

7 F. P. Hinz and D. W. Margerum, *Inorg. Chem., 13,* 2941 (1974).

8 C. K. Jorgensen, *Acta Chem. Scand., 11,* 399 (1957).

9 L. Fabbrizzi and P. Paoletti, *Gazzetta, 104,* 929 (1974).

10 C. J. Ballhausen and A. D. Liehr, *J. Am. Chem. Soc., 81,* 538 (1959).

11 L. Y. Martin, L. J. De Hayes, L. J. Zompa and D. H. Busch, *J. Am. Chem. Soc., 96,* 4046 (1974).

12 B. Bosnich, R. Mason, P. J. Pauling, G. B. Robertson and M. L. Tobe, *Chem. Comm.,* 97 (1965).

13 S. C. Nyburg and J. S. Wood, *Inorg. Chem., 3,* 468 (1964).

14 A. McPherson, Jr., M. G. Rossmann, D. W. Margerum and M. R. James, *J. Coord. Chem., 1,* 39 (1971).

15 G. Anderegg, "Coordination Chemistry", vol. 1, A. E. Martell ed., Van Nostrand Reinhold Company, New York (1971) p. 481.

16 L. Fabbrizzi and L. J. Zompa, to be published.

17 H. K. J. Powell and N. F. Curtis, *Aust. J. Chem., 26,* 977 (1973).

18 F. Basolo, Y. T. Chen and R. K. Murmann, *J. Am. Chem. Soc., 76,* 956 (1954).