Diminution of the Macrocyclic Effect for Nickel(II) Complexes of Thioethers in Nonaqueous Solvents

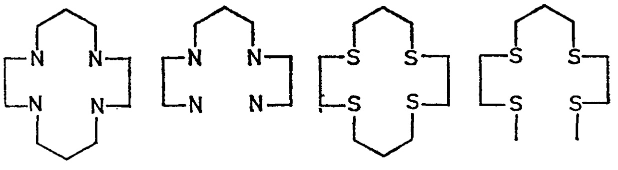
By Gregory F. Smith and Dale W. Margerum*

(Department of Chemistry, Purdue University, West Lafayette, Indiana 47907)

Summary The ratio of stability constants for 14-membered macrocyclic *vs.* open-chain tetrathia complexes of Ni^{II} in nitromethane is only 180, whereas the corresponding ratio for tetramine complexes in water is $10^{6.4}$, lending support to the hypothesis that (in addition to contributions from configurational entropy) the differing degree of ligand solvation by hydrogen bonding in water is a major source of the macrocyclic effect.

Macrocyclic ligands with four amine donor groups, such as cyclam, form much more stable complexes than the corresponding open-chain ligands, such as 2,3,2-tet.[1,2] This macrocyclic effect has been shown in the case of the nickel(II) complexes to be largely due to differences in the $\Delta H°$ of complexation and has been attributed to differences in ligand solvation.[2,3] We have now compared the stability of the nickel complex with the macrocyclic ligand containing four thioether donor groups (TTP), with that of the corresponding open-chain ligand (TTT). The relative stabilities of the $Ni(TTP)^{2+}$ and $Ni(TTT)^{2+}$ complexes were determined in nitromethane solvent. In this situation the difference in ligand solvation is small because there are no hydrogen bonding effects between the ligands and the solvent. Hence this system serves as a test for the hypothesis that ligand solvation is a predominant factor in cases when there is a very large macrocyclic effect.

The nickel tetrafluoroborate complexes of 1,4,8,11-tetrathiacyclotetradecane, $Ni(TTP)(BF_4)_2$, and of 2,5,9,12-tetrathiatridecane, $Ni(TTT)(BF_4)_2$ were prepared by Rosen and Busch.[4] The complexes are diamagnetic, 2:1 electrolytes, and exhibit electronic spectra in nitromethane solution typical of square-planar nickel complexes. We observed a λ_{max} at 494 nm for both complexes with molar absorptivities of 336 M^{-1} cm^{-1} for $Ni(TTP)^{2+}$ and 259 M^{-1} cm^{-1} for $Ni(TTT)^{2+}$. The addition of H_2O, MeOH, Me_2SO, DMF, or MeCN cause the complexes to dissociate.



Cyclam 2,3,2-tet TTP TTT

The nitromethane solvent was purified by the method of Olah *et al.*[5] The relative stabilities of $Ni(TTP)^{2+}$ and $Ni(TTT)^{2+}$ were determined spectrophotometrically by reacting 1,11-dioxa-4,8-dithiaundecane $[HO(CH_2)_2S(CH_2)_3S(CH_2)_2OH$ or L] with $Ni(TTP)^{2+}$ or $Ni(TTT)^{2+}$. If T stands for TTP or TTT then equations (1) and (2) describe the system.

$$NiT^{2+} + L \rightleftharpoons NiL^{2+} + T \qquad K_1 \qquad (1)$$

$$NiL^{2+} + L \rightleftharpoons NiL_2{}^{2+} \qquad K_2 \qquad (2)$$

The NiL^{2+} and $NiL_2{}^{2+}$ complexes are not square planar and have very low molar absorptivities at 494 nm. The source of Ni^{II} and TTP or TTT is either $Ni(TTP)(BF_4)_2$ or

$Ni(TTT)(BF_4)_2$ and L is present in excess. Therefore equation (3) can be derived and plots for this equation with TTP and with TTT give the equilibrium constants reported

$$\frac{[T]^2}{[NiT][L]_T} = K_1 + K_1K_2[L]_T \qquad (3)$$

in the Table. The K_1 values are significantly different for TTP and TTT. The K_2 values should be the same and they do agree within experimental error.

TABLE

Equilibrium constants obtained from the competition of L with the TTP and TTT complexes at 25·0 °C

	K_1	K_2/M^{-1}
$Ni(TTP)^{2+}$	$(1{\cdot}2 \pm 0{\cdot}5) \times 10^{-4}$	144 ± 70
$Ni(TTT)^{2+}$	$(2{\cdot}17 \pm 0{\cdot}06) \times 10^{-2}$	172 ± 6

ratio $\dfrac{K_{Ni(TTP)}}{K_{Ni(TTT)}} = 180 \pm 70$

The macrocyclic ligand containing only thioether donor atoms forms a slightly more stable complex with nickel(II) in nitromethane than does the corresponding open-chain ligand. It has been suggested that for a series of complexes with the same geometry, the wavelength of maximum absorbance correlates with the strength of the metal ligand interaction.[6] Both the $Ni(TTP)^{2+}$ and $Ni(TTT)^{2+}$ complexes have the same λ_{max}.[4] The macrocyclic ligand structure cannot be imposing a geometry which forces the donor sites closer to the nickel(II) ion such that the nickel–sulphur bond strengths are increased. Any increase in the strength of the metal-sulphur interaction due to a constrictive effect of the macrocyclic ligand would probably be offset by an increase in the strain energy of the ligand.[7]

The $Ni(TTP)^{2+}$ complex is found to be about 180 times more stable than the $Ni(TTT)^{2+}$ complex which is in contrast to the case of $Ni(cyclam)^{2+}$ and $Ni(2,3,2\text{-tet})^{2+}$ where the stability ratio is $10^{6\cdot4}$ for the square-planar complexes in aqueous solution.[3] We attribute this diminished macrocyclic effect to the lack of difference in ligand solvation of TTP and TTT in nitromethane. The extent to which the stability constant for $Ni(TTP)^{2+}$ is larger than that of $Ni(TTT)^{2+}$ can be assigned to differences in the configurational entropy of the free ligands. The cyclic ligand will have a smaller loss of configurational entropy than the open-chain ligand upon co-ordination to the nickel ion. The magnitude of the effect for the tetrathia ligands is consistent with the behaviour of the tetramine ligands in water where the effects of configurational entropy tend to be obscured by other entropy changes due to differences in ligand solvation.

Other factors can give a diminished macrocyclic effect, such as that found[8] for $Cu(cyclen)^{2+}$ where a change in co-ordination geometry forced by a 12-membered ring prevents formation of a square-planar complex.

We thank the National Science Foundation for support.

(*Received*, 1*st July* 1975; *Com.* 748.)

---

[1] D. K. Cabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, 1969, **91**, 6540.

[2] F. P. Hinz and D. W. Margerum, *J. Amer. Chem. Soc.*, 1974, **96**, 4993.

[3] F. P. Hinz and D. W. Margerum, *Inorg. Chem.*, 1974, **13**, 2941.

[4] W. Rosen and D. H. Busch, *J. Amer. Chem. Soc.*, 1969, **91**, 4694.

[5] G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardin, *J. Amer. Chem. Soc.*, 1954, **86**, 1043.

[6] P. Paoletti, L. Fabbrizzi, and R. Barbucci, *Inorg. Chim. Acta Rev.*, 1973, **7**, 43.

[7] L. Y. Martin, L. J. DeHayes, L. J. Zompa, and D. H. Busch, *J. Amer. Chem. Soc.*, 1974, **96**, 4046.

[8] M. Kodama and E. Kimura, *J.C.S. Chem. Comm.*, 1975, 326.