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1-(4-Tolylsulfonyl)-1,4,8,11-tetraazacyclotetradecane (Tscyclam): A Versatile Ligand for Nickel(II) and Nickel(III) Cations

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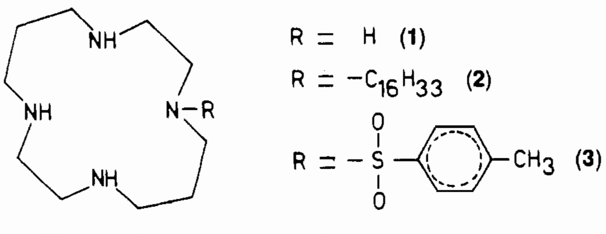
1-(4-Tolylsulfonyl)-1,4,8,11-tetraazacyclotetradecane (Tscyclam, **3**) forms complexes with Ni^{II} of stoichiometry: Ni(Tscyclam)$X_2 \cdot 2H_2O$ (X = Cl, ClO_4). The crystal structure has been determined for the chloride complex salt, which indicates that the complex is better described by the formula $[Ni(Tscyclam)(H_2O)_2]Cl_2$. The salt crystallizes in the monoclinic space group $P2_1/n$, with $a = 13.030$ (5) Å, $b = 7.859$ (3) Å, $c = 22.640$ (9) Å, $\beta = 93.17$ (3)°, $V = 2315$ (2) Å^3, and $Z = 4$. The structure was solved by using 3062 unique reflections with $I_0 > 3\sigma(I_0)$. Anisotropic least squares refinement gave $R = 0.11$. The tetraaza macrocycle is folded and the two water molecules occupy two cis positions of a distorted octahedron. Average distance for the Ni^{II}(high spin)–N(amine) bonds is 2.08 (2) Å, whereas the Ni^{II}(high spin)–N(amide) distance is 2.36 (1) Å. The $[Ni(Tscyclam)(H_2O)_2]^{2+}$ chromophore keeps intact its stereochemical arrangement on dissolution both in water and in noncoordinating solvents (e.g. CH_2Cl_2). Tscyclam has been used as a carrier for the transport of Ni^{II} across a bulk liquid membrane, displaying a much greater efficiency than the lipophilic version of cyclam (*N*-cetylcyclam, **2**). The aqueous $[Ni^{II}(Tscyclam)(H_2O)_2]^{2+}$ complex, in the presence of Cl^- ions, is oxidized by persulfate to give the species $[Ni^{III}(Tscyclam)Cl_2]^+$, in which two equivalent chloride ions lie on the *z* axis and the tetraaza macrocycle is coplanarly chelated, as shown by the ESR of the frozen solution. Coplanar coordination of Tscyclam is now allowed due to the smaller dimensions of the Ni^{III} metal center compared to high-spin Ni^{II}. The Ni^{III}/Ni^{II} redox change could not be characterized through voltammetric investigations at the platinum electrode, but it was possible, through chemical evidence, to locate the potential for the $[Ni^{III}(Tscyclam)Cl_2]^+/[Ni^{II}(Tscyclam)(H_2O)_2]^{2+}$ couple at an especially low value (<0.42 V vs NHE), much lower than that determined for the $[Ni^{III}(cyclam)Cl_2]^+/[Ni^{II}(cyclam)]^{2+}$ redox couple.

Introduction

Much attention has been devoted during the past decade to ligands able to transport metal ions across an organic layer (*a liquid membrane*) from an aqueous phase to another one. The ligand has to be lipophilic and should bind the cation strongly enough to extract it from the aqueous source phase, but not too strongly to prevent its release to the receiving aqueous phase, the process being driven by a concentration gradient.[1] In the case of block s cations, crown ethers and cryptands (made lipophilic through the insertion on the ligand framework of carbon chains of appropriate length) satisfy the required conditions, and very selective three-phase separations of mixtures of alkaline and alkaline-earth ions have been achieved by matching the size of the ligand cavity with that of the wanted cation.[2] For the block d metals, principles of coordination chemistry would simply suggest replacement of the ethereal oxygen donor atoms by amine nitrogen atoms. However, nitrogen analogues of crown ethers and cryptands, i.e. polyamine macrocycles and sepulchrands, cannot be recommended as carriers for the transport of 3d metal ions across liquid membranes.

As a matter of fact, the lipophilic version of the champion of tetraaza macrocycles—cyclam (**1**)—e.g. 1-hexadecyl-1,4,7,10-tetraazacyclotetradecane, *N*-cetylcyclam (**2**), can extract aqueous 3d metal ions under two-phase conditions, but the macrocyclic complexes that form in the liquid membrane are so stable, in a *thermodynamic* and, in particular, in a *kinetic* sense, that the metal center (e.g. Ni^{II}) is not released at all to the aqueous receiving phase, even if this has been made strongly acidic or contains strong complexing agents such as EDTA. Thus, we thought that reduction of the strong donating properties of the cyclam ligating array could afford a ligand of intermediate binding properties, suitable for fast metal-exchange processes at the membrane/water interface. The way we chose to weaken cyclam donicity was to transform one of its four *amine* groups into an *amide* group. Amide groups are considered noncoordinating or very poorly coordinating systems and, for instance, through equilibrium studies on the complexation of Cu^{II} by some diamine–diamide macrocycles in aqueous solution, the binding constant for the metal/amide interaction was estimated to be approximately nil.[3] In particular, we have prepared the molecule 1-(4-tolylsulfonyl)-1,4,8,11-tetraazacyclotetradecane, Tscyclam (**3**), which contains three amine nitrogen atoms and a *p*-toluenesulfonamide group. The $-SO_2-$ group is thought to drastically reduce the donating tendencies of the adjacent nitrogen atom. Moreover, the pendant aromatic ring is expected to impart some lipophilicity to the system.



This work describes the solution chemistry of the Ni^{II} complexes of Tscyclam both in aqueous and organic phases. Very surprisingly, the Ni^{II} complex can be easily oxidized, in aqueous solution, to an authentic stable Ni^{III} species. This contrasts with the current belief that only strongly coordinating multidentate amine systems allow the attainment of the unusually high oxidation states of the encircled metal center.[4]

Experimental Section

Synthesis of Tscyclam and of Its Nickel(II) Complexes. Tscyclam has been prepared through reaction of tosyl chloride (TsCl) with cyclam. We found it more convenient to purify the crude ligand through the formation of its Ni^{II} complex, which can be more easily separated from the side products originating from tosylation of cyclam. Tscyclam in its pure form was then obtained through demetalation in acidic solution of the fairly labile Ni^{II} complex.

Synthesis of Crude Tscyclam. In a three-neck round-bottom flask, equipped with a mechanical stirrer, 250 mL of a $CHCl_3$ solution 0.015 M in TsCl were dropped, over a period of 6 h, on 1 L of a vigorously stirred $CHCl_3$ solution 0.0075 M in cyclam[5] and 0.004 M in triethylamine, under a nitrogen atmosphere, at room temperature. After addition, stirring under nitrogen was continued overnight. The $CHCl_3$ solution was treated with two 100-mL portions of 1 M NaOH and then dried over anhydrous sodium sulfate. The solution was then rotovaped to give a white solid, which contained Tscyclam, unreacted cyclam, and, eventually, polytosylated cyclam derivatives. The solid was treated with two 100-mL portions of diethyl ether: cyclam is poorly soluble in ether, and most of the unreacted material was recovered upon filtration.

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[1] Behr, J.-P.; Kirch, M.; Lehn, J.-M. *J. Am. Chem. Soc.* **1985**, *107*, 241.

[2] Lamb, J. D.; Christensen, J. J.; Izatt, S. R.; Bedke, K.; Astin, M. S.; Izatt, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 3399.

[3] Fabbrizzi, L.; Forlini, F.; Perotti, A.; Seghi, B. *Inorg. Chem.* **1984**, *23*, 807. Buttafava, A.; Fabbrizzi, L.; Perotti, A.; Poggi, A.; Seghi, B. *Inorg. Chem.* **1984**, *23*, 3917.

[4] Fabbrizzi, L. *Comments Inorg. Chem.* **1985**, *4*, 33.

[5] Barefield, E. K.; Wagner, E.; Herlinger, A. W.; Dahl, A. R. *Inorg. Synth.* **1976**, *16*, 220.

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Table I. Crystallographic Data for $[Ni(Tscyclam)(H_2O)_2]Cl_2$

chem formula	$C_{17}H_{34}Cl_2N_4NiO_4S$
fw	520.1
space group	$P2_1/n$
a, Å	13.030 (5)
b, Å	7.859 (3)
c, Å	22.640 (9)
β, deg	93.17 (3)
V, Å^3	2315 (2)
Z	4
T, K	293
radiation	Mo Kα (λ = 0.7107 Å), graphite monochr
ρ_{calcd} g cm^{-3}	1.492
μ(Mo), cm^{-1}	11.9
transm coeff, %	96.8–99.8
$R(F_o)$	0.11
$R_w(F_o)$ ($w = 1/\sigma(F_o)^2$)	0.13

Table II. Final Fractional Coordinates and Isotropic Equivalent Displacement Parameters of $[Ni(Tscyclam)(H_2O)_2]Cl_2$ with Estimated Standard Deviations in Parentheses

atom	x/a	y/b	z/c	B_{eq},[a] Å
Ni	−0.0153 (1)	0.2596 (2)	−0.32682 (8)	2.69 (3)
Cl(1)	−0.7057 (3)	−0.0687 (6)	−0.9096 (2)	5.05 (9)
Cl(2)	−0.1384 (3)	0.2009 (5)	−0.6348 (2)	5.0 (1)
S	0.0043 (3)	0.4002 (4)	−0.1850 (2)	2.87 (6)
O(1)	0.0883 (7)	0.506 (1)	−0.1987 (4)	3.5 (2)
O(2)	−0.0992 (7)	0.455 (1)	−0.1977 (4)	3.9 (2)
O(3)	0.0014 (9)	0.523 (1)	−0.3237 (5)	4.3 (2)
O(4)	−0.1735 (7)	0.321 (1)	−0.3112 (4)	4.3 (2)
N(1)	0.0169 (8)	0.216 (1)	−0.2243 (5)	2.9 (2)
N(2)	−0.0337 (9)	0.273 (2)	−0.4183 (5)	3.8 (3)
N(3)	0.1408 (9)	0.212 (1)	−0.3268 (4)	3.0 (2)
N(4)	−0.0726 (9)	0.011 (2)	−0.3391 (5)	3.3 (2)
C(1)	0.127 (1)	0.154 (2)	−0.2218 (6)	3.4 (3)
C(2)	0.1880 (9)	0.237 (2)	−0.2682 (7)	4.1 (3)
C(3)	0.197 (1)	0.290 (2)	−0.3734 (9)	4.8 (4)
C(4)	0.154 (1)	0.257 (2)	−0.4356 (7)	5.0 (3)
C(5)	0.054 (1)	0.337 (3)	−0.4516 (8)	5.5 (4)
C(6)	−0.073 (1)	0.111 (3)	−0.4399 (7)	5.7 (4)
C(7)	−0.134 (1)	0.025 (3)	−0.3930 (8)	5.4 (4)
C(8)	−0.130 (1)	−0.065 (2)	−0.2943 (7)	3.9 (3)
C(9)	−0.068 (1)	−0.078 (2)	−0.2371 (7)	3.8 (3)
C(10)	−0.054 (1)	0.081 (2)	−0.1996 (7)	3.8 (3)
C(11)	0.017 (1)	0.347 (2)	−0.1092 (6)	2.9 (3)
C(12)	−0.072 (1)	0.312 (2)	−0.0802 (6)	3.2 (3)
C(13)	−0.061 (1)	0.269 (2)	−0.0218 (7)	4.2 (3)
C(14)	0.036 (1)	0.260 (2)	0.0084 (7)	4.6 (3)
C(15)	0.122 (1)	0.291 (2)	−0.0229 (7)	4.6 (4)
C(16)	0.113 (1)	0.337 (2)	−0.0809 (6)	3.7 (3)
C(17)	0.048 (2)	0.207 (2)	0.0709 (9)	6.6 (5)

[a] Defined as $^4/_3\ [a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table III. Selected Interatomic Distances and Angles for $[Ni(Tscyclam)(H_2O)_2]Cl_2$ with Estimated Standard Deviations in Parentheses

Distances (Å)			
Ni–N(1)	2.36 (1)	Ni–N(2)	2.07 (1)
Ni–N(3)	2.07 (1)	Ni–N(4)	2.11 (1)
Ni–O(3)	2.08 (1)	Ni–O(4)	2.166 (9)
S–N(1)	1.71 (1)	S–O(1)	1.42 (1)
S–O(2)	1.43 (1)	S–C(11)	1.77 (1)
N(1)C(1)	1.51 (2)	N(1)–C(10)	1.53 (2)
N(2)–C(5)	1.49 (2)	N(2)–C(6)	1.44 (2)
N(3)–C(2)	1.45 (2)	N(3)–C(3)	1.45 (2)
N(4)–C(7)	1.49 (2)	N(4)–C(8)	1.42 (2)
C(1)–C(2)	1.50 (2)	C(3)–C(4)	1.51 (2)
C(4)–C(5)	1.48 (2)	C(6)–C(7)	1.47 (3)
C(8)–C(9)	1.49 (2)	C(9)–C(10)	1.52 (2)
Angles (deg)			
N(1)–Ni–N(2)	173.4 (4)	N(1)–Ni–N(3)	81.4 (4)
N(1)–Ni–N(4)	92.1 (4)	N(1)–Ni–O(3)	95.7 (4)
N(1)–Ni–O(4)	89.6 (4)	N(2)Ni–N(3)	94.0 (4)
N(2)–Ni–N4)	83.9 (5)	N(2)–Ni–O(3)	89.5 (5)
N(2)–Ni–O(4)	95.2 (4)	N(3)–Ni–N(4)	100.0 (4)
N(3)–Ni–O(3)	94.6 (4)	N(3)–Ni–O(4)	170.3 (4)
N(4)–Ni–O(3)	164.4 (4)	N(4)–Ni–O(4)	83.9 (4)
O(3)–Ni–O(4)	82.6 (4)	Ni–N(1)–S	111.7 (5)
Ni–N(1)–C(1)	101.6 (8)	Ni–N(1)–C(10)	112.5 (8)
C(1)–N(1)–C(10)	111 (1)	Ni–N(2)–C(5)	118.2 (9)
Ni–N(2)–C(6)	108 (1)	C(5)–N(2)–C(6)	113 (1)
Ni–N(3)–C(2)	110.2 (8)	Ni–N(3)–C(3)	117.1 (8)
C(2)–N(3)–C(3)	114 (1)	Ni–N(4)–C(7)	102 (1)
Ni–N(4)–C(8)	119.5 (9)	C(7)–N(4)–C(8)	112 (1)
N(1)–C(1)–C(2)	112 (1)	N(3)–C(2)–C(1)	111 (1)
N(3)–C(3)–C(4)	116 (1)	C(3)–C(4)–C(5)	116 (1)
N(2)–C(5)–C(4)	115 (1)	N(2)–C(6)–C(7)	112 (1)
N(4)–C(7)–C(6)	110 (1)	N(4)–C(8)–C(9)	111 (1)
C(8)–C(9)–C(10)	118 (1)	N(1)–C(10)–C(9)	115 (1)

Evaporation of diethyl ether gave an oily material, which contained Tscyclam, some polytosylated cyclam derivatives, and some cyclam, as indicated by the ^{1}H NMR spectrum.

Synthesis of Ni(Tscyclam)Cl$_2$·2H$_2$O. The oil of crude Tscyclam was dissolved in the minimum volume of ethanol, until a clear solution was obtained. To this solution was added dropwise an aqueous standard solution of $NiCl_2 \cdot 6H_2O$; the solution took immediately a blue color, due to the formation of the high-spin $[Ni^{II}(Tscyclam)]^{2+}$ complex. On further addition, a blue precipitate formed. The aqueous ethanolic solution was rotovaped to dryness and the solid material was extracted five times with 50-mL portions of CH_2Cl_2, to eliminate excess $NiCl_2$. CH_2Cl_2 was rotovaped off, and the blue solid obtained was dissolved in 100 mL of water: some undissolved white powder (polytosylated cyclam derivatives) was filtered off. The blue aqueous solution was made 5 M in NaCl and equilibrated with 100 mL of CH_2Cl_2. The blue color passed into the organic layer, due to the presence of the $[Ni(Tscyclam)]^{2+}$ complex, while the aqueous layer took a pale yellow color, due to the presence of the $[Ni(cyclam)]^{2+}$ chromophore. Independent experiments indicated that, on equilibration of equal volumes of CH_2Cl_2 and aqueous 5 M NaCl, 100% of $[Ni(cyclam)Cl_2]$ goes in the aqueous layer. On concentration of the CH_2Cl_2 solution, a blue microcrystalline precipitate of $Ni(Tscyclam)Cl_2 \cdot 2H_2O$ formed, which was recrystallized from acetonitrile (1.2 g; yield 63% based on TsCl). Anal. Calcd for $C_{17}H_{34}Cl_2N_4O_4NiS$: C, 39.26; H, 6.59; N, 10.77. Found: C, 39.4; H, 6.7; N, 10.7. Through a similar procedure, but with $Ni(ClO_4)_2$ used in place of $NiCl_2$, the blue $Ni(Tscyclam)(ClO_4)_2 \cdot 2H_2O$ complex was obtained. Anal. Calcd for $C_{17}H_{34}Cl_2N_4O_{12}NiS$: C, 31.51; H, 5.29; H, 8.64. Found: C, 31.7; H, 5.4; N, 8.6.

Demetalation of the Ni(Tscyclam)Cl$_2$·2H$_2$O Complex and Extraction of Pure Tscyclam. A 0.5-g sample of $Ni(Tscyclam)Cl_2 \cdot 2H_2O$ was dissolved in 50 mL of water, and 10 mL of 6 M HCl was added. The blue solution turned pale green in a few minutes. Then 6 M NaOH was added until the pH = 11. The greenish suspension of $Ni(OH)_2$ was treated with an equal volume of CH_2Cl_2. The filtered organic layer was dried overnight on anhydrous sodium sulfate. After evaporation of the solvent, Tscyclam was obtained in form of a yellowish oil. The ligand was characterized through its trihydrochloride derivative, which was obtained by bubbling gaseous HCl in an ice-cold diethyl ether solution. The white precipitate was recrystallized from ethanol (yield 62%). Anal. Calcd for $C_{17}H_{33}Cl_3N_4O_2S$: C, 44.02; H, 7.17; N, 12.08. Found: C, 39.9; H, 7.3; N, 12.0.

Crystallographic Study. In spite of a great many attempts to grow single crystals suitable for an X-ray analysis, the size and quality of the crystals of $Ni(Tscyclam)Cl_2 \cdot 2H_2O$ and $Ni(Tscyclam)(ClO_4)_2 \cdot 2H_2O$ obtained were rather poor. In any case, in view of the importance of the structure determination for understanding the solution chemistry of the nickel(II) Tscyclam complexes, data were collected for the best available crystal of $Ni(Tscyclam)Cl_2 \cdot 2H_2O$. The data turned out to be good enough to allow an unequivocal determination of the overall molecular structure, even if the refinement accuracy is not too high. Data were collected on an Enraf-Nonius CAD4 diffractometer. Crystal data are reported in Table I. A total of 7334 reflections ($h,k,\pm l$) were collected by the $\omega/2\theta$ scan technique in the range 5° < 2 θ < 60°. Lorentz and polarization corrections were applied. The agreement between equivalent reflections was estimated as 0.040. All the calculations were performed with SDP programs[6] on a MICROVAX 2000 computer. The structure was solved with direct methods (MULTAN). Hydrogen atoms were entered in ideally calculated positions and held fixed. The water hydrogen atoms have not been considered. All the non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques with 3062 reflections having $I_0 > 3\sigma(I_0)$. Anomalous scattering terms were included.[7]

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(6) B. A. Frenz and Associates Inc., College Station, TX 77840, and Enraf-Nonius, Delft, The Netherlands, 1985.

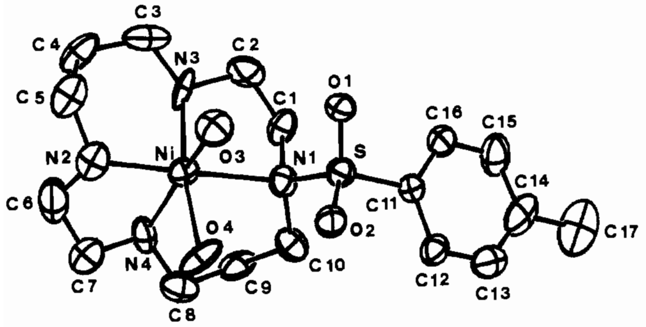

Figure 1. ORTEP view of the $[Ni^{II}(Tscyclam)(H_2O)_2]^{2+}$ complex cation present in the $Ni(Tscyclam)Cl_2{\cdot}2H_2O$ salt. Ellipsoids representing the thermal motions of the atoms are drawn at the 50% probability level. For the sake of clarity, hydrogen atoms are not shown.

The refinement gave final $R(F_o) = 0.11$, $R_w(F_o) = 0.13$. Atomic positional parameters are given together with their standard deviations in Table II. Selected bond lengths and angles are presented in Table III. The remaining bond lengths and angles, anisotropic thermal factors, hydrogen atom parameters, observed and calculated structure factors and experimental details are given as supplementary material.

Other Physical Measurements. Spectra in the UV–visible region were taken by means of a diode-array Model 8452A Hewlett-Packard spectrophotometer and of a Cary 2300 UV–vis–near-IR spectrophotometer (Varian). ESR spectra were obtained by using a Varian E-100 spectrometer and were calibrated vs DPPH.

Two- and Three-Phase Experiments. The tendency of Tscyclam to extract Ni^{II} from water into a CH_2Cl_2 layer and the rate at which the process takes place were investigated through the following experiment: a 1-cm-path quartz cuvette was filled by 2.0 cm^3 of a CH_2Cl_2 solution 2×10^{-3} M in Tscyclam (or the other investigated lipophilic ligand, *N*-cetylcyclam (**2**)[8] and by 1.0 cm^3 of an aqueous solution 1 M in $NaClO_4$ and 0.1 M in $Ni(ClO_4)_2$. The cuvette fitted the HP 89054A thermostatable cell holder, in which water thermostated at 25.00 ± 0.05 °C was circulated. The beam of light passed through the CH_2Cl_2 layer before being dispersed onto the diode array of the HP 8452A spectrophotometer. The organic layer was magnetically stirred with the HP 89055 stirring module, mounted inside the base of the thermostatable cuvette holder, which was driven by compressed air. Extraction of the metal into the CH_2Cl_2 phase was monitored through the appearance of the spectrum of the $[Ni^{II}(Tscyclam)(H_2O)_2](ClO_4)_2$ complex. In a similar way the extraction by aqueous Y^{4-} (H_4Y = EDTA) of Ni^{II} from the lipophilic complex dissolved in the CH_2Cl_2 layer was investigated (2.0 cm^3 of a CH_2Cl_2 solution 2×10^{-3} M in $[Ni^{II}(Tscyclam)(H_2O)_2](ClO_4)_2$ + 1.0 cm^3 of 0.1 M Na_2H_2Y, 1 M in $NaClO_4$, buffered at pH = 10 with borate buffer).

For three-phase (transport) experiments a V-shaped glass cell was used.[9] In this vessel, the two aqueous layers (the metal source phase, 10^{-2} M in $Ni^{II}(ClO_4)_2$ and 1 M in $NaClO_4$, and the metal receiving phase, 0.1 M in Na_2H_2Y, 0.5 M in borate buffer, and 1 M in $NaClO_4$; 30 cm^3 each) were separated by a CH_2Cl_2 layer of 30 cm^3 (the bulk liquid membrane) and by a glass wall. The membrane, 2×10^{-3} M in $Ni^{II}L(ClO_4)_2$ (L = Tscyclam), was magnetically stirred at 200 rpm. The two aqueous layers were mechanically stirred by two glass rods driven by twin electrical motors, at a constant rate (200 rpm). During the transport experiments, dinitrogen saturated in CH_2Cl_2 flowed in both arms of the cell. The progress of the Ni^{II} transport experiment was monitored by syringing out, at selected time intervals, portions of the metal receiving aqueous layer (RP) and measuring the spectrum of the $[Ni^{II}Y]^{2-}$ complex. Three-phase experiments were carried out in a room thermostated at 25 ± 1 °C.

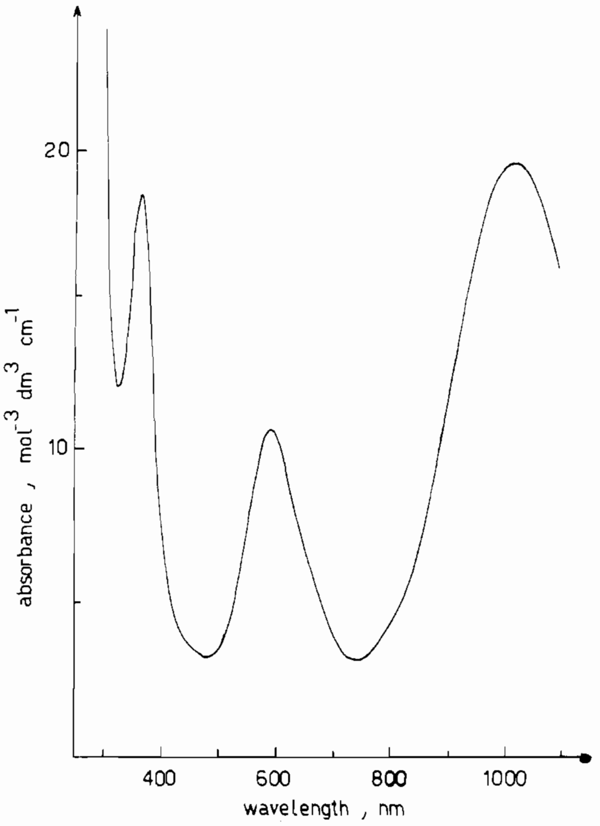

Figure 2. Electronic spectrum of an aqueous solution 5×10^{-3} M in $[Ni(Tscyclam)(H_2O)_2]Cl_2$.

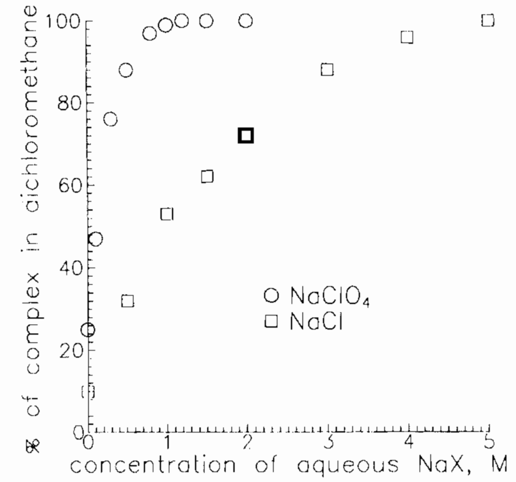

Figure 3. Partitioning of $[Ni^{II}(Tscyclam)(H_2O)_2]X_2$ complexes between water and CH_2Cl_2. Variation of the concentration of the $[Ni^{II}(Tscyclam)(H_2O)_2]X_2$ complex in a CH_2Cl_2 layer in equilibrium with an aqueous layer of increasing concentration of NaX (X = ClO_4, Cl).

Results

The crystal structure has been solved for the $Ni(Tscyclam)Cl_2{\cdot}2H_2O$ complex, which, on the basis of structural data, should be better written as $[Ni(Tscyclam)(H_2O)_2]Cl_2$ (vide infra). Figure 1 reports an ORTEP diagram of the Ni^{II} complex ion. Figure 2 reports the d–d absorption spectrum of an aqueous solution of the $[Ni(Tscyclam)(H_2O)_2]Cl_2$ complex. The effect of the X^- anion on the partitioning of $Ni(Tscyclam)X_2{\cdot}2H_2O$ complexes (X = Cl, ClO_4) between water and dichloromethane is illustrated in Figure 3. In the figure, the percent concentration of the $[Ni(Tscyclam)(H_2O)_2]Cl_2$ complex in the organic layer is plotted vs the molar concentration of NaX in the aqueous layer. The results of experiments on the transport of the $Ni(ClO_4)_2$ salt across a bulk CH_2Cl_2 membrane, mediated by Tscyclam, are illustrated in Figure 4. In those experiments, in the V-shaped glass cell, the CH_2Cl_2 layer (30 cm^3, 2×10^{-3} M in $[Ni(Tscyclam)(H_2O)_2](ClO_4)_2$, the *liquid membrane*) separated an aqueous layer 10^{-2} M in $Ni(ClO_4)_2$ and 1 M in $NaClO_4$ (30 cm^3, the source phase, SP) and an aqueous layer 0.1 M in the disodium salt of EDTA (Na_2H_2Y), 0.5 M in borate buffer (pH = 10) and 1 M in $NaClO_4$ (30 cm^3, the receiving phase, RP). The 1 M $NaClO_4$ concentration of both aqueous layers is sufficient to confine the [Ni-

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(7) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(8) Di Casa, M.; Fabbrizzi, L.; Mariani, M.; Seghi, B. *J. Chem. Soc., Dalton Trans.* **1990**, 55.

(9) De Santis, G.; Di Casa, M.; Mariani, M.; Seghi, B.; Fabbrizzi, L. *J. Am. Chem. Soc.* **1989**, *111*, 2422.

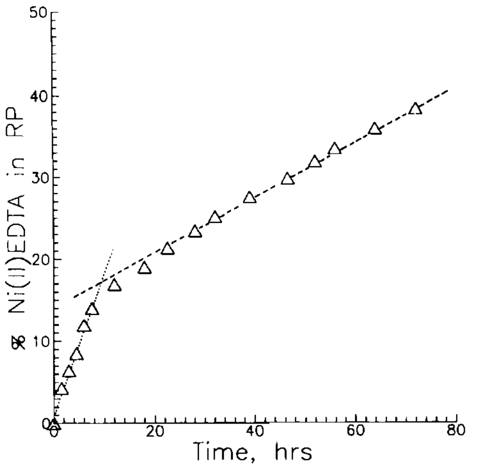

Figure 4. Variation with time of the concentration of the $[Ni^{II}Y]^{2-}$ complex that forms in the receiving phase, during the Tscyclam- (**3**-) mediated transport of $Ni(ClO_4)_2$ across a bulk CH_2Cl_2 membrane. The scheme of the transport is depicted in Figure 7. If the tetramine macrocycle *N*-cetylcyclam (**2**) is used as a carrier, no Ni^{II} transport takes place.

$(Tscyclam)(H_2O)_2](ClO_4)_2$ complex inside the membrane, as suggested by partition experiments illustrated by Figure 3 (vide supra). During the transport experiment, at selected time intervals, 3-cm^3 portions of RP were transferred in a 1-cm quartz cuvette, their spectra in the 300–800 nm range were measured, and then the portions were restored to RP. After some hours, the two bands pertinent to the $[NiY]^{2-}$ species, at 384 and 588 nm, began to develop. The course of the transport experiment is illustrated in Figure 4, in which the percent concentration of $[Ni^{II}Y]^{2-}$ in RP (=mol of $[Ni^{II}Y]^{2-}$ over mol of Ni^{2+} in SP at the beginning of the experiment) is plotted vs time. Kinetic aspects of the processes occurring at the membrane/SP and membrane/RP interfaces were investigated through two-phase experiments performed inside a spectrophotometric cuvette. In the first type of experiment, a 1-cm quartz cuvette was filled by 2.0 cm^3 of a CH_2Cl_2 solution 2×10^{-3} M in $[Ni(Tscyclam)(H_2O)_2](ClO_4)_2$ and by 1.0 cm^3 of an aqueous solution 0.1 M in Na_2H_2Y, 0.5 M in borate buffer (pH = 10) and 1 M in $NaClO_4$. Absorption spectra of the magnetically stirred CH_2Cl_2 layer were taken at fixed time intervals: the intensity of the bands of the $[Ni(Tscyclam)(H_2O)_2](ClO_4)_2$ chromophore was observed to decrease, due to the demetalation by EDTA. Figure 5 demonstrates the decrease with time of the percent concentration of the $[Ni(Tscyclam)(H_2O)_2](ClO_4)_2$ complex in the CH_2Cl_2 layer: the decrease was linear, and after 3 h 24% of the complex was demetalated by aqueous EDTA. In the second type of experiment, the cuvette contained 2.0 cm^3 of a CH_2Cl_2 solution 2×10^{-3} M in Tscyclam and 1.0 cm^3 of an aqueous solution 0.1 M in $Ni(ClO_4)_2$ and 1 M in $NaClO_4$. Spectra of the organic layer were taken at constant time intervals, looking at the appearance of the bands of the $[Ni(Tscyclam)(H_2O)_2](ClO_4)_2$ complex. Figure 6 shows the ESR spectrum of an aqueous solution of the $Ni(Tscyclam)Cl_2{\cdot}2H_2O$ complex that has been treated with $Na_2S_2O_8$ and frozen at 77 K.

Discussion

Synthesis of Tscyclam. The only previously known tosylated cyclam derivative was Ts$_3$cyclam, which was used as a very convenient intermediate for the synthesis of some functionalized cyclam molecules (e.g. *scorpiands*[10] and *bis(macrocycles)*.[11] The monotosylated derivative, Tscyclam, has been obtained through reaction of tosyl chloride on one of the four equivalent amine nitrogen atoms of cyclam. To minimize formation of *n*-tosylated derivatives (*n* = 2, 3, 4), reaction was carried out with an excess of cyclam. We found the 2:1 cyclam/TsCl molar ratio as the most convenient, since, under these conditions, formation of polytosylated derivatives is low enough and, on the other hand, not too much cyclam is consumed. Moreover, reaction of the crude product with a NiX_2 salt allows us to separate Tscyclam, which behaves as a ligand, from the noncoordinating polytosylated derivatives. The complexed material contains $Ni(Tscyclam)Cl_2{\cdot}2H_2O$ and some $Ni(cyclam)Cl_2$, (10% at most). However, the two salts can be conveniently separated on the basis of their different solubilities in water and CH_2Cl_2: when the mixture of the two salts is shaken with aqueous $NaCl/CH_2Cl_2$, $Ni(cyclam)Cl_2$ dissolves in water, whereas $Ni(Tscyclam)Cl_2{\cdot}2H_2O$ goes into the dichloromethane layer. The two Ni^{II} complexes could be also separated through elution on a Sephadex G25 column, using 0.5 M NaCl: the large blue band of the $Ni(Tscyclam)Cl_2{\cdot}2H_2O$ complex elutes first, whereas the yellow band of the $[Ni(cyclam)]^{2+}$ complex appears distinctly separate and elutes more slowly. However, it was found more convenient to use the much less time consuming two-phase separation procedure.

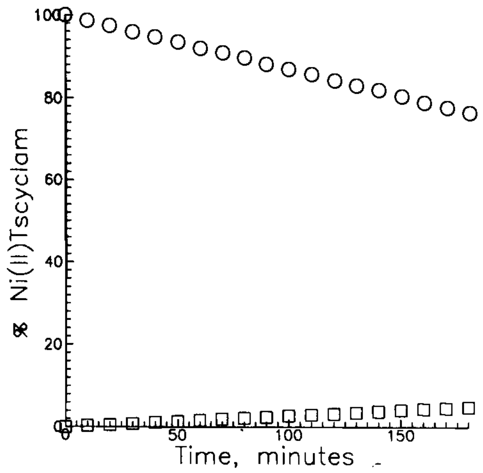

Figure 5. Time dependence of the concentration of $[Ni(Tscyclam)(H_2O)_2](ClO_4)_2$ in a stirred CH_2Cl_2 layer (2.0 cm^3, 10^{-3} M), in equilibrium with (○) an aqueous layer containing EDTA (1.0 cm^3, 0.1 M, pH = 10) or (□) an aqueous layer 0.1 M in $Ni(ClO_4)_2$ and 1 M in $NaClO_4$ (1 cm^3). Experiments were performed in a 1-cm quartz cuvette, and the $[Ni(Tscyclam)(H_2O)_2](ClO_4)_2$ concentration was monitored spectrophotometrically.

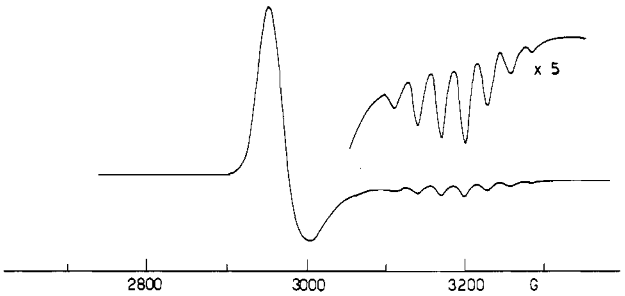

Figure 6. ESR spectrum of an aqueous solution of $[Ni(Tscyclam)(H_2O)_2]Cl_2$ oxidized with $Na_2S_2O_8$ and frozen at 77 K. The axial profile ($g_\perp$ = 2.18; $g_\parallel$ = 2.02) corresponds to that of an authentic Ni^{III} elongated octahedral complex, in which two equivalent chlorine atoms lie along the *z* axis: $[Ni^{III}(Tscyclam)Cl_2]^+$.

$Ni^{II}(Tscyclam)X_2{\cdot}2H_2O$ Complexes. Stereochemistry in the Solid State and in Solution. Both isolated $Ni(Tscyclam)X_2{\cdot}2H_2O$ complex salts are blue and high spin, independent of the nature of the counterion X^- (=Cl^-, ClO_4^-), in contrast with that observed with $Ni(cyclam)X_2$ complexes, which are high spin (blue-violet in color) in the presence of coordinating anions (X^- = Cl^-) but low spin (yellow in color) in the presence of poorly coordinating anions (X^- = ClO_4^-).

X-ray investigation has shown that the $Ni(Tscyclam)Cl_2{\cdot}2H_2O$ complex should be better written as $[Ni(Tscyclam)(H_2O)_2]Cl_2$. In this complex, the nickel(II) ion has a formal coordination number of 6, with a N_4O_2 donor set. In particular two water molecules, and not the chloride ions, are bound to the metal center.

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(10) Pallavicini, P. S.; Perotti, A.; Poggi, A.; Seghi, B.; Fabbrizzi, L. *J. Am. Chem. Soc.* **1987**, *109*, 5139.

(11) Ciampolini, M.; Fabbrizzi, L.; Perotti, A.; Poggi, A.; Seghi, B.; Zanobini, F. *Inorg. Chem.* **1987**, *26*, 3527.

The $[Ni(Tscyclam)(H_2O)_2]^{2+}$ complex exhibits a distorted octahedral stereochemistry with bond angles ranging from 81.4 (4) to 100.0 (4)°. The Ni–N(amine) bond distances average to 2.08 (2) Å, which compares well with the values typically observed in high-spin Ni^{II} complexes of tetramine macrocycles.[12] The Ni–N(1) bond distance, involving the sulfonamide group, is significantly longer: 2.36 (1) Å. The tetraaza macrocycle is in a folded configuration, and the two water molecules occupy cis coordination sites. A similar stereochemical arrangement has been previously described for the cyclam analogue: *cis*-$[Ni(cyclam)(H_2O)_2]Cl_2 \cdot 2H_2O$.[13] Both complexes present severe distortions from regular octahedral geometry. The more striking difference is that $Ni–OH_2$ distances are substantially shorter in the Tscyclam complex (2.07–2.08 Å) than in the cyclam analogue (2.13–2.14 Å). Moreover, in contrast to the *cis*-diaquo complex of cyclam, in the presently investigated complex the coordination number is only formally 6: the very large bond distance indicates that the interaction of the metal center with the amide nitrogen atom (N(1)) is extremely weak or nil. It is possible that the tetraaza macrocycle adopts the unusual folded configuration, rather than the most common and energetically favorable coplanar arrangement, in order to keep away the very poorly donating N(sulfonamide) atom. In particular, the high-spin Ni^{II} cation may be too large to be encompassed by the coplanar triamino–monoamido ring. It is also possible that the unusual coordination by the two water molecules, rather than by chloride ions, depends upon the enhanced "acidity" of the metal center, which is effectively coordinated by only three nitrogen atoms. In this connection, it should be noted that the *cis*-diaquo stereochemistry is rather unusual for cyclam complexes and it is unstable toward a coplanar coordination of the macrocycle.[13] It is noteworthy that it is only in the $[Ni(cyclam)(H_2O)_2]Cl_2 \cdot 2H_2O$ complex that water molecules are directly bound to the Ni^{II} cation. In all the other investigated high-spin Ni^{II} complexes coplanarly chelated by cyclam or derivatives, the remaining coordination sites are occupied by anions.[12]

$[Ni(Tscyclam)(H_2O)_2]Cl_2$ dissolves in water to give a bright blue solution whose absorption spectrum in the UV–visible region is reported in Figure 2. The spectrum displays the three typical transitions expected for high-spin Ni^{II} in an octahedral or distorted octahedral environment. The spectrum is very similar to that measured with the solid $[Ni(Tscyclam)(H_2O)_2]Cl_2$ complex (obtained on the powder spread on filter paper, in the absorption mode, range 300–700 nm). This suggests that the stereochemistry of the metal complex in the crystalline state is maintained after dissolution in water. Noticeably, the spectrum of the powder of the $Ni(Tscyclam)(ClO_4)_2 \cdot 2H_2O$ complex superimposes with that observed with $Ni(Tscyclam)Cl_2 \cdot 2H_2O$, suggesting the presence of the same chromophore: $[Ni(Tscyclam)(H_2O)_2]^{2+}$. In this case also, donor set and stereochemical arrangement are retained on dissolution in water. As a matter of fact, the spectrum of aqueous $Ni(Tscyclam)(ClO_4)_2 \cdot 2H_2O$ is exactly the same as observed with the $Ni(Tscyclam)Cl_2 \cdot 2H_2O$ salt. Moreover, due to their partially lipophilic nature, both complex salts dissolve well in apolar or poorly polar solvents such as benzene and dichloromethane. It is noteworthy that also in these media $Ni(Tscyclam)Cl_2 \cdot 2H_2O$ and $Ni(Tscyclam)(ClO_4)_2 \cdot 2H_2O$ display the same three-band absorption spectrum, and most surprisingly, the spectrum is coincident with that of the aqueous solutions. It derives that the $[Ni(Tscyclam)(H_2O)_2]^{2+}$ stereochemical arrangement is maintained in CH_2Cl_2, and in particular, water molecules are so strongly bound to Ni^{II} that they cannot be replaced by inorganic anions, even in a medium of low dielectric constant. Thus, Cl^- and ClO_4^- ions should be bound to the metal complexes merely electrostatically, as ion pairs.

The $[Ni(Tscyclam)(H_2O)_2]^{2+}$ species does not exhibit the inertness toward demetalation typically observed with cyclam complexes[14] and slowly decomposes in aqueous acidic solution to give the metal ion and the protonated ligand. The demetalation process can be followed by monitoring the intensity of the band at 1020 nm. In particular, it has been observed that in 0.1 M aqueous HCl demetalation takes place according to a first-order pattern, with $t_{1/2} = 35$ min. Persistence in solution reasonably decreases with the increasing concentration of the acid: for instance, in 1 M HCl, $t_{1/2}$ is 7 min. Notice that $Ni(cyclam)_2X_2$ complexes are indefinitely stable in acidic solutions of any concentration. This behavior is related to the rigid coplanar arrangement of the four strongly coordinating donor atoms of the cyclam ring. The relative lability of the $[Ni(Tscyclam)(H_2O)_2]^{2+}$ complex should be ascribed to the fact that only three donor atoms of the ring are tightly bound and the ligand is folded according to a cis configuration, an arrangement that is more prone to attack by H^+ ions.

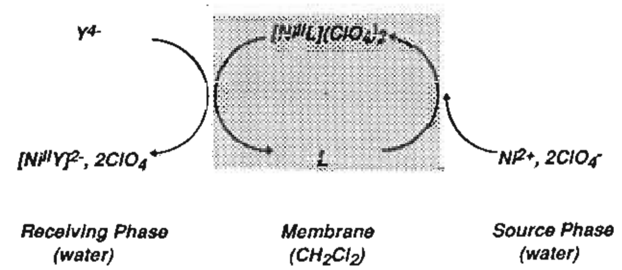

Figure 7. Scheme of the transport of the $Ni(ClO_4)_2$ salt across a bulk liquid membrane mediated by the Tscyclam ligand carrier. The driving force of the process is the complexation of Ni^{II} by the aqueous ethylenediaminetetraacetate ligand (Y^{4-}).

Partitioning of $Ni(Tscyclam)X_2 \cdot 2H_2O$ Complexes between Water and CH_2Cl_2. It has been mentioned in the previous paragraph that $Ni(Tscyclam)X_2 \cdot 2H_2O$ complexes dissolve both in water and CH_2Cl_2: this behavior results from the composite nature of the molecule, which presents a *hydrophilic* site on one side (the metal center) and a *lipophilic* moiety on the other side (the pendant toluene subunit). Quantitative studies on this double solvent affinity have been carried out equilibrating a CH_2Cl_2 layer 5×10^{-3} M in $Ni(Tscyclam)X_2 \cdot 2H_2O$ with an equal volume of water and comparing the absorption spectra in the UV–vis region of the CH_2Cl_2 layer before and after equilibration. The effect of the X^- anion on the partitioning of $[Ni(Tscyclam)(H_2O)_2]X_2$ complexes between a water and dichloromethane is illustrated in Figure 3. It can be seen that, for $X = ClO_4$, a 1 M electrolyte concentration is sufficient to push all the metal complex into the CH_2Cl_2 layer. On the other hand, in the case of chloride, a much higher concentration of aqueous NaCl (ca. 5 M) is required to prevent partitioning of the metal complex in the aqueous layer. The two-phase equilibrium, which may be described by

$$[Ni(Tscyclam)(H_2O)_2]X_2(org) = [Ni(Tscyclam)(H_2O)_2]^{2+}(aq) + 2X^-(aq) \quad (1)$$

is controlled by two main energy contributions: (i) the energy associated with the formation of the ion pair in CH_2Cl_2 and (ii) the hydration energies of either metal complex and anion X^-. It is probable that the ion-pair formation energy term is more favorable for the smaller chloride ion, compared to that for perchlorate. However, this contribution should be overwhelmed by the anion hydration term: the hydration energy of ClO_4^- is considerably smaller than that of Cl^-. Thus, the more favorable partitioning of the $[Ni(Tscyclam)(H_2O)_2](ClO_4)_2$ complex in CH_2Cl_2 should reflect the lower energy spent to dehydrate the ClO_4^- counterion, compared to Cl^- (ΔG°_{hydr}: ClO_4^-, 47.0 kcal mol^{-1}; Cl^-, 68.4 kcal mol^{-1}).[15]

$[Ni(Tscyclam)(H_2O)_2](ClO_4)_2$-Mediated Transport of Ni^{II} across a Bulk Liquid Membrane. Experiments have been performed to test the capability of Tscyclam to act as a *carrier* for the transport of Ni^{II} across a bulk liquid membrane. These experiments, whose

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(12) Henrik, K.; Tasker, P. A.; Lindoy, L. F. *Prog. Inorg. Chem.* **1985**, *33*, 1.

(13) Barefield, E. K.; Bianchi, A.; Billo, E. J.; Connolly, P. J.; Paoletti, P.; Summers, J. S.; Van Derveer, D. G. *Inorg. Chem.* **1986**, *25*, 4197.

(14) Busch, D. H. *Acc. Chem. Res.* **1978**, *11*, 392.

(15) Noyes, R. M. *J. Am. Chem. Soc.* **1962**, *84*, 513. Abraham, M. H.; Liszi, J. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1604.

progress is illustrated in Figure 4, indicate that transport of $Ni(ClO_4)_2$ from SP to RP, mediated by the Tscyclam carrier, is taking place, according to the scheme illustrated in Figure 7.

The driving force of the transport process is given by the complexation of Ni^{2+} by EDTA (at pH = 10) or, to be more precise, by the Ni^{2+} concentration gradient between SP and RP. Noticeably, the transport profile (see Figure 4) displays a two-rate pattern: a first, linear faster portion, which corresponds to the uptake of 60 μmol, and a second, slower portion. When the experiment was interrupted (after 72 h), the transport profile was still a straight line and 115 μmol of nickel had been transported, corresponding to about 40% of the Ni^{2+} present in SP at the beginning of the experiment.

To better understand the kinetic aspects of the Tscyclam-mediated $Ni(ClO_4)_2$ transport process, two-phase experiments in a spectrophotometric cuvette were carried out, whose results are illustrated in Figure 5. It was observed that, under analogous experimental conditions, the rate of the Ni^{II} decorporation from the $[Ni(Tscyclam)(H_2O)_2](ClO_4)_2$ complex by EDTA at the CH_2Cl_2/water interface (inside the cuvette) is remarkably faster than the two-phase process of Ni^{II} incorporation by Tscyclam. It is obvious that the two described two-phase experiments in the spectrophotometric cuvette do not exactly replicate the processes occurring at the two sides of the liquid membrane during the three-phase (transport) experiment. However, from these experiments, it can be reasonably assumed that the process at the RP/membrane interface (demetalation of $[Ni(Tscyclam)(H_2O)_2](ClO_4)_2$ by EDTA) is considerably faster than that occurring at the membrane/SP interface (uptake of Ni^{II} by Tscyclam). Thus, the first, higher rate portion of the transport profile (see Figure 4) should correspond to the demetalation of the complex dissolved in the liquid membrane. When the original complex has been depleted, the rate of the three-phase process is controlled by the slowest of the two two-phase processes, in the present case, than taking place at the SP/membrane interface. Therefore, the less positive slope of the second portion straight line is determined by the rate of this process.

For comparative purposes, an analogous transport experiment has been attempted by using $[Ni^{II}(N\text{-cetylcyclam})](ClO_4)_2$ as a carrier. Conditions were the same as described for the $[Ni(Tscyclam)(H_2O)_2](ClO_4)_2$ experiment. However, after 72 h no Ni^{II} was detected, in the form of the $[NiY]^{2-}$ complex, in RP. The sluggishness of demetalation of the $[Ni^{II}(N\text{-cetylcyclam})](ClO_4)_2$ complex at the membrane/RP interface was confirmed by two-phase experiments in the spectrophotometric cuvette: after 3 h of stirring, no decrease of the intensity of the absorption band of the low-spin complex in the CH_2Cl_2 layer was observed. Two-phase experiments in the cuvette showed also that after 3 h no uptake of Ni^{II} by *N*-cetylcyclam took place. However, in order to discriminate between the processes of metal incorporation and metal decorporation occurring at the dichloromethane/water interfaces, more drastic conditions have been explored: in particular, if a 10^{-3} M solution of *N*-cetylcyclam in CH_2Cl_2 is shaken for 2 h with an equal volume of an aqueous solution 10^{-3} M in $Ni(ClO_4)_2$ and 1 M in $NaClO_4$, 100% of the metal is extracted into the organic phase. On the other hand, when a CH_2Cl_2 solution 10^{-3} M in $[Ni^{II}(N\text{-cetylcyclam})](ClO_4)_2$ is shaken for days and days with an equal volume of an aqueous solution 0.1 M in EDTA, adjusted to pH = 10, no decomplexation takes place at all, as indicated by the persistence of the spectrum of the Ni^{II}(low spin) complex in the CH_2Cl_2 layer.

Thus, for Tscyclam, the demetalation process, under two-phase conditions, appears to be faster than the Ni^{II} complexation process. For *N*-cetylcyclam the opposite occurs, the metal incorporation process being faster than the metal decorporation by EDTA, a process which in practice does not take place. In any case, replacing an amine nitrogen atom of the cyclam ring by a sulfonamide group removes inertness toward demetalation, making the metal transport possible.

Formation of Nickel(III) Complexes in Organic and Aqueous Phases. A special feature of tetraaza macrocycles (in particular cyclam) is the capability to promote the oxidation of the encircled metal ion and to stabilize unusually high and otherwise unstable oxidation states.[16] The Ni^{II}/Ni^{III} oxidation process has been probably the most widely investigated and better characterized redox change for polyazamacrocyclic complexes, since the first isolation of an authentic trivalent nickel complex by Curtis[17] and the pioneering works on the electrochemical characterization by Olson and Vasilevskis[18] and on the spectromagnetic (ESR) authentication by Busch.[19]

We have found that also the poorly coordinating Tscyclam macrocycle favors the attainment of a trivalent species in aqueous solution. As a matter of fact, a blue aqueous solution of $[Ni(Tscyclam)(H_2O)_2]Cl_2$ turns yellow when treated by $Na_2S_2O_8$, a color typically observed with formation of trivalent nickel polyamine complexes. Substantial pieces of information on the authenticity and stereochemistry of the Ni^{III} complex can be obtained from the ESR spectrum of the solution frozen at 77 K (see Figure 6). The spectrum displays axial symmetry with $g_\perp$ considerably greater than $g_\parallel$ (2.18 and 2.02, respectively). This is consistent with the formation a d^7, low-spin metal center, in an octahedrally elongated environment. Noticeably, the $g_\parallel$ feature is split into *seven* lines ($A_\parallel$ = 22.6 G), which indicates the presence of two equivalent chloride ions along the *z* axis. Such a situation can be explained only by admitting that the Tscyclam macrocycle is coplanarly chelated and that the Ni^{III} cation lies in the plane of the four nitrogen atoms. The ESR response is very similar to that of the $[Ni^{III}(cyclam)Cl_2]^+$ complex;[20] however, for the latter system, the seven-line splitting of the $g_\parallel$ feature is obtained only in presence of extra added NaCl or HCl (>0.5 M). At lower concentrations of the background electrolyte, water molecules compete for the axial positions of the elongated octahedron of the cyclam complex. The extreme affinity of the $\{Ni^{III}(Tscyclam)\}$ fragment toward chloride ions may arise from the fact that the metal, even if coplanarly encircled by the tetraaza macrocycle, in practice profits only from the coordination of the three amine nitrogen atoms and is therefore especially prone to the binding of further donors (e.g. Cl^-), according to an axial mode. The special role of chloride is demonstrated by the fact that the $[Ni^{II}(Tscyclam)(H_2O)_2](ClO_4)_2$ complex is not oxidized by persulfate in aqueous solution, even in presence of excess of supporting NaX salts (X = ClO_4, NO_3).

The oxidation half-reaction in water can be described by

$$[Ni^{II}(Tscyclam)(H_2O)_2]^{2+} + 2Cl^- = [Ni^{III}(Tscyclam)Cl_2]^+ + 2H_2O + e^- \quad (2)$$

and should involve the rearrangement of the macrocycle from a cis to the trans configuration and the replacement of the two coordinated water molecules by two chloride ions. The ligand rearrangement may be associated to the drastic variation of the ion size that occurs during the oxidation process: the Ni^{II} high-spin cation (the average Ni^{II}–N distance in paramagnetic octahedral polyamine complexes is 2.10 Å)[12] is probably too large to fit the coplanar tramine–amido ring, which is then forced to fold and to coordinate according to a cis mode. The one-electron oxidation reduces substantially the size of the metal center (as a matter of fact, the Ni^{III}(low spin)–N distance in tetraaza macrocyclic complexes ranges from 1.97 to 2.00 Å).[21] Thus, after oxidation, the metal center should be small enough to fit the macrocyclic ring and the ligand may relax to its more natural coplanar arrangement. Ni^{III}-promoted deprotonation of one of the amine nitrogen atom, as observed in complexes of cyclam and derivatives, seems to be ruled out. Addition of base to yellow solutions of Ni^{III}

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(16) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988; p 344.

(17) Curtis, N. F.; Cook, D. F. *J. Chem. Soc., Chem. Commun.* **1967**, 962.

(18) Olson, D. C.; Vasilevskis, J. *Inorg. Chem.* **1969**, *8*, 1611.

(19) LoVecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3110.

(20) Haines, R. I.; McAuley, A. *Coord. Chem. Rev.* **1982**, *39*, 77.

(21) Zeigerson, E.; Bar, I.; Bernstein, I.; Kirschenbaum, L. J.; Meyerstein, D. *Inorg. Chem.* **1982**, *21*, 73; Ito, T.; Sugimoto, K.; Toriumi, K.; Ito, H. *Chem. Lett.* **1981**, 1477; Yamashita, M.; Toriumi, K.; Ito, T. *Acta Crystallogr., Sect. C* **1985**, *41*, 1607; Yamashita, M.; Miyamae, H. *Inorg. Chim. Acta* **1989**, *156*, 71.

tetramine macrocyclic complexes produces a violet transient, which is ascribed to the formation of an unstable Ni^{III} complex in which an amine nitrogen atom has lost its proton.[22,23] A similar behavior was not observed with the $[Ni^{III}(Tscyclam)Cl_2]^+$ complex, whose yellow color and absorption spectrum are those expected for regular Ni^{III} polyazamacrocyclic complexes.

A voltammetric investigation was carried out on an aqueous solution 10^{-3} M in $[Ni^{II}(Tscyclam)(H_2O)_2]Cl_2$ and 0.1–5 M in NaCl by using a platinum or a carbon-paste working electrode, but no waves appeared within the entire potential scan, from the cathodic to the anodic discharge. This indicates that half-reaction (2), which occurs quickly in presence of $S_2O_8^{2-}$, does not take place at a platinum anode, even at very positive potential values. We are inclined to believe that failure in the electrochemical oxidation depends upon kinetic effects, rather than upon thermodynamic factors, i.e. on the fact that the Ni^{III}/Ni^{II} redox couple potential is more positive than that associated to the anodic discharge (Cl_2/Cl^-). As a matter of fact, chemical evidence allows us to locate the Ni^{III}/Ni^{II} potential at an especially low value; in particular, the yellow aqueous $[Ni^{III}(Tscyclam)Cl_2]^+$ species is not reduced by NO_2^- in neutral solution ($E° = 0.42$ V vs NHE),[24] which indicates that the Ni^{III}/Ni^{II} potential should be less positive than 0.42 V. Notice that NO_2^- does reduce $[Ni^{III}(cyclam)Cl_2]^+$, in agreement with the value of the Ni^{III}/Ni^{II} redox couple potential in the cyclam complex ($E° = 0.73$ V vs NHE, electrochemically determined). Moreover, on addition of the strong reducing agent $Na_2S_2O_4$, the yellow solution of the $[Ni^{III}(Tscyclam)Cl_2]^+$ species turns blue, due to the reduction to the divalent complex. It is noteworthy that it is possible to go back and forth from the blue to the yellow color through consecutive additions of persulfate, nitrite (to reduce the excess $S_2O_8^{2-}$), and dithionite.

It may be surprising that the aqueous $[Ni^{III}(Tscyclam)Cl_2]^+$ complex forms at a potential much lower than that observed for the formation of the $[Ni^{III}(cyclam)Cl_2]^+$ species, as judged from reactivity toward nitrite ion. However it should be considered that the electrode potential is not a measure of the *absolute* stability of the oxidized species, but is a measure of the *relative* stabilities of the oxidized and reduced forms. In the case of cyclam complexes, one moves from a rather stable reduced form, $[Ni^{II}(cyclam)]^{2+}$, in which a ligand able to exert strong in-plane interactions is coplanarly chelated, to an oxidized form, $[Ni^{III}(cyclam)Cl_2]^+$, in which the favorable ligand's arrangement is maintained. On the other hand, during the $[Ni^{II}(Tscyclam)(H_2O)_2]^{2+}/[Ni^{III}(Tscyclam)Cl_2]^+$ redox change, the macrocycle rearranges from a cis configuration to the more donating and more energetically favorable coplanar array. In this case, one moves from a poorly stable reduced form to a quite stable oxidized form. Thus, the easier formation of the $[Ni^{III}(Tscyclam)Cl_2]^+$ species does not depend on a high intrinsic stability of the trivalent complex, which is probably much lower than that of the cyclam analogue, but reflects the higher gain of ligand field energy associated with the $[Ni^{II}(Tscyclam)(H_2O)_2]^{2+}/[Ni^{III}(Tscyclam)Cl_2]^+$ half-reaction compared to that associated with the $[Ni^{II}(cyclam)]^{2+}/[Ni^{III}(cyclam)Cl_2]^+$ half-reaction.

Finally, if a CH_2Cl_2 layer containing $[Ni^{II}(Tscyclam)(H_2O)_2]Cl_2$ is equilibrated with an aqueous layer 5 M in NaCl containing excess $Na_2S_2O_8$, the blue organic phase decolorates, whereas the aqueous phase takes a bright yellow color. The ESR spectrum of the aqueous layer is similar to that reported in Figure 6 and indicates the presence of the $[Ni^{III}(Tscyclam)Cl_2]^+$ complex. If the aqueous solution contains less than 1 equiv of persulfate, the aqueous layer becomes yellow, but a blue color persists in the CH_2Cl_2 solution. Above evidences indicate that oxidation of $[Ni^{II}(Tscyclam)(H_2O)_2]Cl_2$ takes place also under two-phase conditions; the trivalent complex is so hydrophilic that it cannot be confined in the CH_2Cl_2 solution, even by aqueous 5 M NaCl (as occurs with the divalent complex). Notice that, on reduction with aqueous dithionite and after equilibration of the two phases, the divalent complex is extracted by the CH_2Cl_2 layer, which takes again its original blue color.

Conclusions

Tscyclam is a novel and versatile ligand for Ni^{II} and Ni^{III} cations, whose complexes display unprecedented solution chemistry, in particular as far as the redox behavior is concerned. The unusually rich reactivity mainly derives from the reduction (formally by one-fourth) of the strong coordinating properties of the precursor macrocycle cyclam, which has been obtained by substituting one amine group of the 14-membered fully saturated macrocycle by an amide group. This causes an extreme discrimination on the stabilities of the divalent and trivalent complexes, which is associated with the folded or coplanar mode of coordination of the tetraaza ligand. A further element of complexity is given by the presence of a pendant toluene moiety, which makes the divalent metal complex, but not the trivalent one, dissolve in organic solvents; thus, transfer of the metal center from the non-aqueous to the aqueous phase, and vice versa, may be driven by a gradient of redox potential, i.e., through consecutive oxidation and reduction processes.

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Supplementary Material Available: For $[Ni(Tscyclam)(H_2O)_2]Cl_2$, tables of bond distances and angles, fractional coordinates and thermal parameters of the hydrogen atoms, anisotropic displacement parameters, and full experimental details (6 pages); a table of structure factors (13 pages). Ordering information is given on any current masthead page.

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[22] Barefield, E. K.; Mocella, M. T. *J. Am. Chem. Soc.* **1975**, *97*, 4238.

[23] Ferri, E.; Fabbrizzi, L. Unpublished results.

[24] Bard, A. J.; Parsons, R.; Jordan, J. *Standard Potentials in Aqueous Solution*; Marcel Dekker: New York, 1985.