1366 *Inorg. Chem.* **1994**, *33*, 1366–1375

Nickel(II) Complexes of Azacyclams: Oxidation and Reduction Behavior and Catalytic Effects in the Electroreduction of Carbon Dioxide

Fabio Abbà,[1] Giancarlo De Santis,[1] Luigi Fabbrizzi,[*,1] Maurizio Licchelli,[1] Anna Maria Manotti Lanfredi,[*,2] Piersandro Pallavicini,[1] Antonio Poggi,[1] and Franco Ugozzoli[2]

Dipartimento di Chimica Generale, Università di Pavia, 27100 Pavia, Italy, and the Istituto di Chimica Generale and the Centro di Studio per la Strutturistica Diffrattometrica CNR, Università di Parma, 43100 Parma, Italy

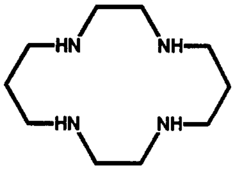
Received July 21, 1993[•]

A wide range of functionalized *azacyclam* complexes of Ni^{II} have been prepared through a template reaction which involves the open-chain tetramine complex $[Ni^{II}(2{\cdot}3{\cdot}2\text{-tet})]^{2+}$, formaldehyde, and a locking fragment which is a primary carboxamide or sulfonamide, either aliphatic or aromatic (RNH_2). The crystal and molecular structure has been determined for the low-spin [3-(4-tolylsulfonyl)-1,3,5,8,12-pentaazacyclotetradecane]nickel(II) complex. The crystal structure consists of three crystallographycally indipendent cationic complexes. Single-crystal X-ray diffraction data were collected with the use of Ni-filtered Cu Kα radiation: space group *Pbca* with $a = 23.128(3)$ Å, $b = 22.891(3)$ Å, $c = 27.595(4)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$; $V = 14609(3)$ Å^3, and $Z = 24$ ($R = 0.051$, $R_w = 0.059$). All the investigated azacyclam derivatives display the typical solution behavior of the Ni^{II} macrocyclic complexes: inertness toward demetalation by strong acids and the blue-to-yellow interconversion in coordinating media. Electrochemical investigations in acetonitrile have shown that $E_{1/2}$ values associated with Ni^{III}/Ni^{II} and Ni^{II}/Ni^{I} couples are influenced by the nature of the substituent appended to the azacyclam ring: such an effect is interpreted on the basis of a π interaction between the metal center and the fifth nitrogen atom inserted in the azacyclam ring. Water soluble Ni^{II}–azacyclam complexes catalyze the electroreduction of CO_2, as indicated by cyclic voltammetry investigations and controlled-potential coulometry studies, with an efficiency comparable to that of $[Ni^{II}(cyclam)]^{2+}$. Such a high efficiency is strictly related to the structural features of the cyclam and azacyclam framework: a 14-membered cycle forming a 5,6,5,6 sequence of chelate rings. Even small deviations from such a geometrical arrangement cause the electrocatalytic effect to be drastically reduced or completely lost.

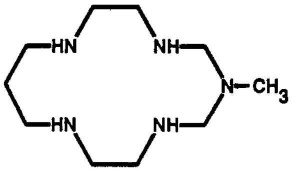
Introduction

Encircling a Ni^{II} center by the 14-membered tetraamine macrocycle cyclam I allows the access to the otherwise unstable Ni^{III} and Ni^{I} oxidation states. Interestingly, both trivalent and monovalent species have been shown to display unusual reactivity. In particular, (i) Ni^{III} complexes of cyclam and cyclam-like ligands play a catalytic role in DNA modification under oxidative conditions[3] and in the homogeneous oxidation of cyclohexene and arylalkenes to epoxides,[4] and (ii) the Ni^{I} complex of cyclam has been proven to mediate the electrochemical reduction of CO_2[5–9] and alkyl halides.[10,11] In any case, the ligand structure appears to be strictly critical, and any modification of the 14-membered framework (variation of the ring size, introduction of alkyl substituents, introduction of variable degrees of unsaturation, etc.) drastically reduces the catalytic efficiency in both processes of types i and ii.

On the other hand, the 14-membered cyclam-like framework can be easily obtained through synthetic template procedures, which have been documented since the very beginning of macrocyclic chemistry.[12] In particular, cyclam can be conveniently prepared in multigram amounts through an easy route, whose first step is the Ni^{II} template Schiff base condensation of the open-chain tetraamine 3·2·3-tet and glyoxal.[13] Noticeably, if the same template procedure is attempted to obtain tetraaza macrocycles of different atomicity than cyclam, yields decrease drastically, often to zero. We have recently reported the Ni^{II} template synthesis of the 14-membered pentaaza macrocycle II, which has been called *azacyclam* as it can be virtually obtained from cyclam by replacing a $-CH_2-$ group of the aliphatic backbone by a nitrogen atom.[14] X-ray diffraction studies on the $[Ni^{II}(\mathbf{II})](ClO_4)_2$ complex have shown that only the four secondary amine nitrogen atoms of the potentially quinquedentate ligand are bound to the metal center, according to the coordination mode of cyclam. The fifth (tertiary) amine nitrogen atom is not involved at all in the coordination and plays a purely structural role. Synthesis of the macrocycle **II** involves the cyclization of the open-chain tetraamine 2·3·2-tet, coordinated to the Ni^{II} ion,



I



II

[•] Abstract published in *Advance ACS Abstracts*, February 15, 1994.

(1) Università di Pavia.

(2) Università di Parma.

(3) Chen, X.; Rokita, S. E.; Burrows, C. J. *J. Am. Chem. Soc.* **1991**, *113*, 5884.

(4) Kinneary, J. F.; Albert, J. S.; Burrows, C. J. *J. Am. Chem. Soc.* **1988**, *110*, 6124.

(5) Fisher, B.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 7361.

(6) Beley, M.; Collin, J.-P.; Ruppert, R.; Sauvage, J.-P. *J. Chem. Soc., Chem. Comm.* **1984**, 1315.

(7) Beley, M.; Collin, J.-P.; Ruppert, R.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1986**, *108*, 7461.

(8) Fujihira, H.; Hirata, Y.; Suga, K. *J. Electroanal. Chem.* **1990**, *292*, 199.

(9) Taniguchi, I. In *Modern Aspect of Modern Electrochemistry 20*; Bockris, J. O'M., White, R. E., Conway, B. E., Eds.; Plenum Press: New York, 1989; p 327.

(10) Gosden, C.; Healy, K. P.; Pletcher, D.; Rosas, R. *J. Chem. Soc., Dalton Trans.* **1978**, 972.

(11) Gosden, C.; Kerr, J. B.; Pletcher, D.; Rosas, R. *J. Electroanal. Chem.* **1981**, *117*, 101.

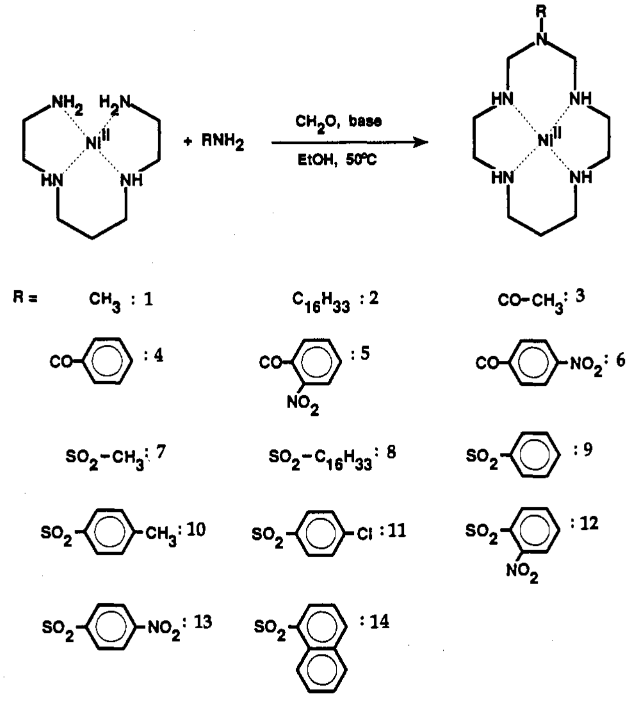
(12) Lindoy, L. F. *The Chemistry of Macrocyclic Ligands Complexes*; Cambridge University Press: Cambridge, U.K., 1989.

(13) Barefield, E. K.; Wagner, F.; Herlinger, A. W.; Dahl, A. R. *Inorg. Synth.* **1976**, *16*, 220.

(14) Fabbrizzi, L.; Manotti Lanfredi, A. M.; Pallavicini, P.; Perotti, A.; Taglietti, A.; Ugozzoli, F. *J. Chem. Soc., Dalton Trans.* **1991**, 3263.

0020-1669/94/1333-1366$04.50/0

Scheme 1



in the presence of excess formaldehyde and methylamine (but any other primary amine can be used). The primary amine RNH_2 is the *locking fragment*; i.e., it behaves as a sort of *molecular padlock*, which firmly shuts the metal center inside the macrocylic framework. We have subsequently observed that *primary amides*, $RCONH_2$, can replace primary amines as locking fragments in the Ni^{II}-assisted synthesis of further azacyclam rings. In particular, the use of aromatic carboxamides opens the route to the design of azacyclam systems having the desired functionality appended.[15]

We report here the template synthesis of a complete class of Ni^{II}–azacyclam complexes obtained by using as locking fragments primary *carboxamides* and *sulfonamides*, both aliphatic and aromatic, as shown in Scheme 1. In particular, the complex $[\mathbf{10}](ClO_4)_2$ (locking fragment: 4-toluenesulfonamide) was obtained in a crystalline form and its structure was resolved from single-crystal X-ray diffraction data. Then, the redox behavior of all the synthesized complexes **1–14** was investigated by electrochemical techniques, and the $E_{1/2}$ values pertinent to the Ni^{II}/Ni^{III} and Ni^{II}/Ni^{I} reversible couples were shown to depend upon the nature of the locking fragment incorporated in the azacyclam ring. Moreover, the azacyclam Ni^{II} complexes were tested as catalysts for the reduction of CO_2 at a mercury cathode, following Sauvage's approach.[7] All the tested complexes displayed an electrocatalytic efficiency comparable to that of $[Ni^{II}(cyclam)]^{2+}$, indicating that replacement of a $-CH_2-$ group in the ligand backbone by an amide residue does not seriously alter the cyclam-like donor set (as far as the interaction with carbon dioxide is concerned) and does not disturb the catalytic process. Quite interestingly, as the electron-withdrawing effect exerted by the amido group anticipates the Ni^{II}/Ni^{I} potential, the CO_2 reduction to CO takes place at a distinctly less negative potential than observed when $[Ni^{II}(cyclam)]^{2+}$ is used as an electrocatalyst.

Experimental Section

Materials. Unless otherwise stated, commercial grade chemicals were used without further purification.

Table 1. Experimental Data for Nickel(II) Macrocyclic Complexes

		anal. found (calcd)			
complex	yield %	C	H	N	FAB[a]
$\mathbf{1}(ClO_4)_2$[b]	32	25.6 (25.4)	5.4 (5.3)	14.6 (14.8)	
$\mathbf{2}Cl_2$	29	53.9 (54.1)	9.8 (9.9)	12.8 (12.6)	
$\mathbf{3}(ClO_4)_2$	14	26.8 (26.4)	4.9 (5.0)	14.1 (14.0)	
$\mathbf{4}(ClO_4)_2$	13	33.9 (34.1)	4.6 (4.8)	12.7 (12.4)	363
$\mathbf{5}Cl_2$	82	39.7 (40.0)	5.6 (5.4)	17.2 (17.5)	408
$\mathbf{6}Cl_2$	52	39.6 (40.0)	5.5 (5.4)	17.3 (17.5)	408
$\mathbf{7}Cl_2$	42	29.0 (29.4)	6.3 (6.2)	16.8 (17.1)	337
$\mathbf{8}Cl_2$	21	48.2 (48.5)	8.9 (8.9)	11.0 (11.3)	547
$\mathbf{9}Cl_2$	27	38.0 (38.2)	5.6 (5.7)	14.6 (14.9)	
$\mathbf{10}Cl_2$	24	39.3 (39.6)	6.1 (6.0)	14.2 (14.4)	413
$\mathbf{11}(ClO_4)_2$	14	28.2 (28.4)	4.0 (4.1)	10.9 (11.1)	
$\mathbf{12}Cl_2$	17	34.6 (34.9)	5.1 (5.1)	16.0 (16.3)	444
$\mathbf{13}Cl_2$	61	34.5 (34.9)	5.2 (5.1)	16.1 (16.3)	444
$\mathbf{14}Cl_2$	62	43.5 (43.8)	5.5 (5.6)	13.2 (13.4)	449

[a] m/Z data are referred to monopositive complex cations (C^+) although the more abundant peaks corresponds to $(C - H)^+$ or $(C + Cl)^+$ ions. [b] Data from ref 20.

1,9-Diamino-3,7-diazanonane (2·3·2-tet) was prepared as described for the analogous tetraamine 1,10-diamino-4,7-diazadecane,[13] distilled at reduced pressure (125 °C; 5×10^{-2} Torr), and stored over NaOH in the refrigerator.

1-Hexadecanesulfonamide. Hexadecanesulfonyl chloride (3 mmol) was dissolved in acetone (30 cm^3), and 10 cm^3 of aqueous 30% NH_3 was slowly added under magnetic stirring. The mixture was refluxed for 1 h, and a white precipitate formed on cooling. The product was filtered off, washed with water, and recrystallized from ethanol. Yield: 61%. Anal. Calcd for $C_{16}H_{35}NO_2S$: C, 62.9; H, 11.55; N, 4.6. Found: C, 62.6; H, 11.7; N, 4.6.

Naphthalene-2-sulfonamide. Naphthalene-2-sulfonyl chloride (10 mmol) was dissolved in diethyl ether (25 cm^3) and treated, under magnetic stirring, with 32% aqueous NH_3 (80 cm^3). A white precipitate formed overnight, which was filtered off, washed with water, and dried *in vacuo*. Yield: 72%. Anal. Calcd for $C_{10}H_9NO_2S$: C, 58.0; H, 4.3; N, 6.8. Found: C, 58.1; H, 4.4; N, 6.8%.

Synthesis of Macrocyclic Ni^{II} Complexes. Method A. A 5-mmol sample of $NiCl_2{\cdot}6H_2O$ was dissolved in ethanol (30 cm^3) in a round-bottom flask equipped with a reflux condenser, a thermometer, and a dropping funnel. A solution of 2·3·2-tet (5 mmol) in ethanol (20 cm^3) was added dropwise to the magnetically stirred solution of the metal salt. The solution was warmed to 50 °C, and an equimolecular amount of the chosen amide (dissolved in the minimum amount of ethanol, typically 20–100 cm^3) was added dropwise. Then, triethylamine (0.5 cm^3, in one portion) and 40% aqueous formaldehyde (5 cm^3, in 3–4 portions during the reaction) were added through the dropping funnel. Heating and magnetic stirring were maintained for 12–24 h. After the mixture was cooled to room temperature, the violet precipitate was filtered through a sintered glass funnel, washed with cold ethanol, dried *in vacuo*, and recrystallized. In some preparations, the complex salt did not precipitate during the reaction: in this case the solution was filtered to eliminate small amounts of metal hydroxide, and aqueous 70% $HClO_4$ (or saturated $NaClO_4$) was slowly added to obtain the precipitation of the metal complex as the yellow-orange perchlorate salt.

Method B. All the reagents mentioned in the method A were mixed in a stoppered bottle which was heated to 50 °C in a termostatted bath for one night. The workup of the reaction mixture was performed as described for method A. Yields, which were found almost to be independent of the synthetic method, A or B, elemental analyses, and FAB mass spectroscopy results are summarized in Table 1.

---

(15) De Blas, A.; De Santis, G.; Fabbrizzi, L.; Licchelli, M.; Manotti Lanfredi, A. M.; Pallavicini, P.; Poggi, A.; Ugozzoli, F. *Inorg. ;Chem.* **1993**, *32*, 106.

Table 2. Experimental Data for the X-ray Diffraction Studies

formula	$C_{16}H_{29}N_5NiO_2S(ClO_4)_2$
cryst syst	orthorhombic
space group	*Pbca*
cell params at 295 K[a]	
a, Å	23.128(3)
b, Å	22.891(3)
c, Å	27.595(4)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	14 609(3)
Z	24
D_{calcd}, g cm^{-3}	1.673
$F(000)$	7632
mol wt	613.109
linear abs coeff, cm^{-1}	45.457
diffractometer	Siemens AED
scan type	$\theta/2\theta$
scan speed, deg/min	3–12
scan width, deg	$(\theta - 0.65)$, $[\theta + (0.65 + \Delta\lambda\lambda^{-1} \tan\theta]$
radiation	Cu Kα (1.541 78 Å)
2θ range, deg	6–120
reflcns measd	$+h,+k,+l$
no. of tot. data measd	11 770
criterion for obsn	$I \geq 2\sigma(I)$
no. of obsd data measd	5585
no. of unique obsd data	5559
agreement between equiv obsd reflcns	0.01
no. of variables	1040
max Δ/σ on last cycle	0.09
$R = \sum\lvert\Delta F\rvert/\sum\lvert F_o\rvert$	0.051
$R_w = \sum w^{1/2}\lvert\Delta F\rvert/\sum w^{1/2}\lvert F_o\rvert$	0.059
GOF = $[\sum w\lvert\Delta F\rvert^2/(NO - NV)]^{1/2}$	0.33

[a] Unit cell parameters were obtained by least-squares analysis of the setting angles of 41 carefully centered reflections chosen from diverse regions of reciprocal space.

Caution! Perchlorate salts are potentially explosive and should be handled with care. In particular, they should never be heated as solids.

Crystal Structure Determination of [10]($(ClO_4)_2$). Crystal data and the most relevant parameters in the crystallographic study are reported in Table 2. X-ray diffraction measurements were performed at room temperature on a Siemens AED diffractometer, using Ni-filtered Cu Kα radiation. The cell parameters were obtained from 41 $(\theta, \chi, \phi)_{h,k,l}$ reflections found in a random search in the $26.85 \leq \theta \leq 38.40°$ range of the reciprocal lattice. The intensities were determined by profile analysis, according to the method of Lehman and Larsen.[16] One standard reflection collected every 100 reflections showed no significant fluctuations. The intensities were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by direct methods and refined by a blocked full-matrix least-squares fit. Anisotropic thermal parameters were assigned to all the non-hydrogen atoms with the exception of the oxygen atom of the ClO_4^- anion, which was equally disordered between two different orientations with the chlorine atom and one hydrogen atom in common. All the hydrogen atoms were placed in their calculated positions and refined "riding" on the corresponding C or N atoms. The highest remaining peak in the final Fourier DF map was equivalent to 0.46 e Å^{-3}. A weighting scheme $w = k[\alpha^2(F_0) + gF_0^2]^{-1}$, with $k = 0.292$ and $g = 0.00945$, was used in the last cycles of refinement. Atomic scattering factors, corrected for anomalous dispersion, were taken from ref 17. The structure was solved and refined with the SHELX86 and SHELX76 systems of computer programs.[18] Geometrical calculations were obtained by PARST.[19] Final atomic coordinates with the isotropic equivalent thermal parameters for the non-hydrogen atoms are listed in Table 3. All calculations were carried out on the GOULD ENCORE 91 computer of he Centro di Studio per la Strutturistica Diffrattometrica CNR, Parma, Italy.

Other Physical Measurements. UV–visible spectra were measured on a Hewlett-Packard 8452A diode-array spectrophotometer or on a Varian Cary 2300 spectrophotometer. ESR spectra were obtained by using a Varian E-100 spectrometer, and calibrated vs DPPH. Mass spectra (FAB) were obtained on a Finnigan TSQ700 instrument, by using an Ion Tech atom gun and 3-nitrobenzyl alcohol as matrix.

Electrochemical Experiments in Acetonitrile. MeCN was distilled over CaH_2 and stored under dinitrogen over molecular sieves. $[Bu_4N]ClO_4$ (Fluka, polarographic grade) was used without further purification. Electrochemical measurements (cyclic voltammetry, CV, and differential pulse voltammetry, DPV) were performed in a conventional three-electrode cell, using a PAR 273 potentiostat/galvanostat, controlled by an IBM AT personal computer. The working electrode was a platinum microsphere and the counter electrode was a platinum foil. A silver wire was used as a pseudoreference electrode and was calibrated using ferrocene as an internal standard. Thus, all the potentials reported in this work have been referred to the classical Fc^+/Fc standard couple. Controlled-potential coulometry experiments were performed on solutions 5×10^{-4} to 10^{-3} mol dm^{-3} in the complex, employing a platinum gauze as a working electrode.

Cyclic Voltammetry (CV) and Controlled-Potential Electrolysis (CPE) Experiments on the Electrochemical Reduction of CO_2 in Water. CV experiments were performed at 20 °C under either an N_2 or a CO_2 atmosphere, by using the same apparatus as in above-mentioned experiments performed in acetonitrile. The working electrode was a mercury pool electrode (Hg purity 99.999%), with a surface of 22.9 mm^2. The counter electrode was a platinum foil, and the reference was a NaCl saturated calomel electrode. The current–potential curves were obtained in nonbuffered solutions ($NaClO_4$); the pH was measured during the experiment and adjusted, if necessary, with small amounts of standard base (NaOH) or acid ($HClO_4$) at 5.0 ± 0.2 M. CPE experiments were carried out in a gastight cell, which was a three-necked, round-bottomed flask, assembled with a reference electrode, a gas bubbler, and a silicon rubber septum. The working electrode was a mercury pool (surface area = 22 cm^2), which was connected to the potentiostat by a platinum wire inserted through the cell bottom. The platinum counter electrode was dipped in a separate flask connected to the working cell through a salt bridge. The cell volume was 315 mL, 200 mL of which was occupied by the gases. The working cell contained 100 mL of an aqueous solution 10^{-4} M in the Ni^{II}–azacyclam complex. Before the experiment, CO_2 was bubbled in to the solution over a period of 30 min, and then the cell was dosed and the controlled-potential electrolysis was carried out. The turnover frequency (h^{-1}) was calculated as moles of CO produced in 1 h per mole of the Ni^{II} complex. Gas samples (0.5 mL) were taken through the silicon rubber septum at fixed time intervals with a gastight syringe (Dynatech). Gas samples were analyzed on a Varian 3400 gas-chromatograph with a thermal conductivity detector by using a Poraplot Q (10 μm) 50 × 0.32 mm column (Chrompack) at 50 °C.

Results and Discussion

Synthesis of Azacyclam Complexes. Azacyclam complexes were prepared by using the recently developed template procedure outlined in Scheme 1.[20] Such a synthetic route should be considered as an extension of the pioneering work by Sargeson.[21] Our one-pot synthesis is typically carried out in a EtOH/water solution (90/10 w/w), containing $NiCl_2 \cdot 6H_2O$, the open-chain tetraamine, and the *locking fragment* (RNH_2, $R'CONH_2$ or $R''SO_2NH_2$) in equimolecular amounts (*ca.* 10^{-2} mol dm^{-3}). The reaction mixture also contained 2 equiv of triethylamine and formaldehyde in a 13:1 excess. The blue-violet solution was warmed at 50–60 °C for 12–24 h, in a magnetically stirred round bottomed flash or in a stoppered bottle, under a dinitrogen atmosphere. In most cases, a violet precipitate (the [Ni^{II}(azacyclam)Cl_2] complex) formed during the reaction. Perchlorate salts could be obtained by treatment of the solution of

---

(16) Lehman, M. S.; Larsen, F. K. *Acta Crystallogr. Sect. A* **1974**, *30*, 580.

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

(18) (a) Sheldrick, G. M. SHELX86, Program for the solution of crystal structures. University of Gottingen, 1986. (b) Sheldrick, G. M. SHELX76, Program for Structure Determination. University of Cambridge, Cambridge, U.K., 1976.

(19) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.

(20) De Blas, A.; De Santis, G.; Fabbrizzi, L.; Licchelli, M.; Manotti Lanfredi, A. M.; Morosini, P.; Pallavicini, P.; Ugozzoli, F. *J. Chem. Soc. Dalton Trans.* **1993**, 1411.

(21) (a) Geue, R. J.; Hambley, J. M.; Harrowfield, J. M.; Sargeson, A. M.; Snow, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 5478. (b) Comba, P.; Curtis, N. F.; Lawrance, G. A.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1986**, *25*, 4260.

Table 3. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters (Å² × 10⁴) with Esd's in Parentheses for the Non-Hydrogen Atoms of **10**$(ClO_4)_2$

	x/a	*y/b*	*z/c*	U_{eq}[a]		*x/a*	*y/b*	*z/c*	U_{eq}[a]
Ni(1)[b]	598(1)	782(1)	3441(1)	440(3)	C(43)	4506(4)	2614(4)	3097(3)	718(34)
N(11)	1413(3)	1400(3)	2652(2)	669(25)	C(53)	3891(4)	2510(4)	3147(3)	853(38)
C(21)	953(4)	1048(4)	2452(3)	730(34)	N(63)	3794(3)	2193(3)	3612(2)	621(23)
N(31)	457(2)	1032(3)	2778(2)	540(22)	C(73)	3166(4)	2219(4)	3768(4)	850(39)
C(41)	−14(4)	682(4)	2563(3)	797(35)	C(83)	3042(4)	1862(4)	4192(4)	830(40)
C(51)	−446(4)	591(4)	2950(3)	776(37)	C(93)	3338(3)	2067(4)	4649(4)	784(36)
N(61)	−138(3)	390(3)	3406(2)	596(23)	N(103)	3979(3)	2026(3)	4612(2)	640(24)
C(71)	−532(4)	445(4)	3839(3)	748(37)	C(113)	4252(4)	2192(4)	5078(3)	778(37)
C(81)	−270(4)	230(4)	4290(3)	769(37)	C(123)	4870(4)	2303(4)	4986(3)	777(35)
C(91)	241(4)	578(4)	4447(3)	751(35)	N(133)	4915(2)	2695(3)	4567(2)	543(21)
N(101)	728(2)	531(2)	4107(2)	495(21)	C(143)	5523(4)	2760(5)	4421(4)	837(39)
C(111)	1246(3)	826(4)	4304(3)	630(30)	S(13)	5944(1)	3741(1)	4009(1)	776(9)
C(121)	1666(3)	882(4)	3906(3)	624(30)	O(13)	5948(3)	3940(3)	4506(2)	1023(28)
N(131)	1355(2)	1158(3)	3492(2)	474(20)	O(23)	5733(3)	4106(3)	3621(2)	958(27)
C(141)	1718(3)	1154(4)	3059(3)	664(33)	C(153)	6650(4)	3553(4)	3865(3)	667(31)
S(11)	1586(1)	2019(1)	2411(1)	683(8)	C(163)	7441(5)	3540(5)	3283(5)	1164(57)
O(11)	1928(3)	2323(2)	2768(2)	888(24)	C(173)	7590(5)	3185(5)	4080(5)	1265(60)
O(21)	1057(2)	2258(3)	2232(2)	862(24)	C(183)	7816(5)	3312(5)	3616(5)	1049(51)
C(151)	2019(3)	1865(3)	1911(3)	614(30)	C(193)	7005(5)	3309(4)	4219(4)	1044(51)
C(161)	2612(4)	1823(4)	1966(4)	902(43)	C(203)	6853(5)	3662(5)	3407(4)	969(45)
C(171)	2945(4)	1678(4)	1549(4)	997(47)	C(213)	8418(5)	3223(6)	3502(6)	1429(67)
C(181)	2700(5)	1622(4)	1100(4)	902(42)	Cl(1)	3478(1)	593(1)	3199(1)	619(7)
C(191)	2121(4)	1674(4)	1066(4)	908(43)	O(1A)	3512(4)	1090(3)	2923(3)	1331(37)
C(201)	1781(4)	1783(4)	1460(3)	750(37)	O(2A)	3751(4)	705(4)	3653(3)	1522(42)
C(211)	3086(6)	1492(6)	670(4)	1463(67)	O(3A)	2919(3)	465(3)	3329(3)	1317(35)
Ni(2)	1230(1)	4135(1)	3780(1)	474(4)	O(4A)	3752(3)	117(3)	2990(3)	1392(37)
N(12)	1676(3)	4804(3)	4727(2)	707(26)	Cl(2)	3969(1)	4317(1)	2860(1)	721(8)
C(22)	2099(4)	4416(4)	4517(3)	685(34)	O(1B)	3764(3)	4798(3)	3141(3)	1117(30)
N(32)	1995(2)	4370(3)	3991(2)	502(21)	O(2B)	3608(4)	3834(3)	2898(4)	1567(44)
C(42)	2431(4)	3991(4)	3764(3)	729(34)	O(3B)	4528(3)	4152(3)	3017(3)	1240(33)
C(52)	2241(4)	3861(4)	3259(3)	824(38)	O(4B)	4013(3)	4498(3)	2369(2)	1217(33)
N(62)	1619(3)	3692(3)	3281(2)	614(23)	Cl(3)	1551(1)	2692(1)	4402(1)	703(8)
C(72)	1379(4)	3703(4)	2785(3)	738(35)	O(1C)	1336(4)	2186(3)	4618(3)	1304(34)
C(82)	741(4)	3515(4)	2771(4)	910(44)	O(2C)	2051(3)	2885(3)	4645(3)	1407(37)
C(92)	341(4)	3891(4)	3051(4)	838(39)	O(3C)	1702(3)	2550(3)	3919(2)	1094(30)
N(102)	471(2)	3889(3)	3559(2)	589(23)	O(4C)	1132(3)	3154(3)	4389(3)	1014(27)
C(112)	21(4)	4212(4)	3832(4)	851(41)	Cl(4)	5229(1)	1027(1)	4021(1)	634(7)
C(122)	228(3)	4308(4)	4327(4)	781(36)	O(1D)	5378(3)	580(3)	3697(3)	1214(33)
N(132)	822(2)	4565(3)	4286(2)	563(23)	O(2D)	5007(3)	1501(3)	3750(2)	1146(31)
C(142)	1096(4)	4574(4)	4764(3)	758(36)	O(3D)	5729(3)	1233(3)	4273(3)	1190(32)
S(12)	1857(1)	5409(1)	4996(1)	664(7)	O(4D)	4809(3)	831(3)	4341(3)	1316(36)
O(12)	1344(2)	5756(2)	5008(2)	826(23)	Cl(5)	3918(1)	3949(1)	4525(1)	652(7)
O(22)	2370(3)	5611(2)	4751(2)	888(24)	O(1E)	4253(3)	3763(3)	4916(3)	1236(32)
C(152)	2046(3)	5237(3)	5584(3)	555(26)	O(2E)	3565(3)	3487(3)	4377(3)	1383(37)
C(162)	1620(4)	5166(4)	5936(3)	770(36)	O(3E)	3611(3)	4456(2)	4636(3)	1148(31)
C(172)	1767(4)	5033(4)	6404(3)	845(39)	O(4E)	4316(4)	4090(4)	4149(3)	1622(45)
C(182)	2326(4)	4950(4)	6535(3)	772(36)	Cl(6)	4858(1)	2243(1)	1448(1)	770(8)
C(192)	2741(4)	4995(4)	6180(4)	973(44)	O(1F)	4788(3)	2819(3)	1289(2)	998(19)
C(202)	2613(4)	5138(4)	5710(3)	798(37)	O(2F)	4815(8)	2192(7)	1937(7)	1264(58)
C(212)	2487(6)	4833(5)	7056(3)	1174(51)	O(3F)	4386(7)	1950(6)	1192(5)	1094(43)
Ni(3)	4345(1)	2456(1)	4088(1)	498(4)	O(4F)	5314(7)	1900(7)	1270(6)	1241(48)
N(13)	5555(3)	3147(3)	4007(2)	809(29)	O(2′F)	5487(6)	2222(6)	1599(5)	1058(41)
C(23)	5338(4)	2914(5)	3551(3)	931(45)	O(3′F)	4872(8)	1820(7)	1072(6)	1365(53)
N(33)	4706(3)	2873(2)	3554(2)	549(22)	O(4′F)	4517(8)	2076(8)	1841(7)	1325(63)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Cations 1, 2, and 3 are identified by the last character in the atomic numbering. A single prime indicates and alternative position.

the chloride complex salt with aqueous 70% $HClO_4$. When precipitation of the chloride salts did not occur spontaneously during the reaction, excess aqueous 70% $HClO_4$ or a saturated $NaClO_4$ solution was added to the violet solution and an orange-yellow precipitate formed (the $[Ni^{II}(azacyclam)](ClO_4)_2$ complex salt). Perchlorate derivatives of complexes **2** and **8**, made lipophilic by the appended long aliphatic tail, were prepared by a two-phase anion exchange procedure: a CH_2Cl_2 solution of the chloride complex salt was vigorously shaken with an aqueous layer saturated in $NaClO_4$. Then [**3**]$(ClO_4)_2$ and [**8**]$(ClO_4)_2$ were obtained as yellow-orange solids, by separating the organic layer, which was dried over Na_2SO_4 and removed by evaporation.

Notice that yields vary over a rather wide range (from 13% to 82%). They are especially low when the chloride complex salt does not spontaneously precipitate during the reaction. In any case, the described synthetic route still appears covenient in view of the simple and inexpensive nature of the procedure. Most of the complexes were characterized by mass spectroscopy by using the FAB technique. In all cases results confirmed the expected stoicheiometry. Attempts to obtain the free ligand by extruding the metal ion from the complexes were unsuccessful. In particular, when an aqueous solution of a complex chloride salt was boiled in presence of cyanide, under the experimental conditions described for demetalation of $[Ni^{II}(cyclam)](ClO_4)_2$,[13] an oily product was isolated after multiple $CHCl_3$ extractions, which was proved to contain the open-chain tetraamine 2·3·2-tet and other unidentified decomposition products. Such an instability of the uncomplexed azacyclam molecule can be explained on the basis of the described poor stability of the 1,1-diamine groups[22] present in the azacyclam ligand framework.

Crystal and Molecular Structure of [10]$(ClO_4)_2$. The crystal structure of [**10**]$(ClO_4)_2$, **III**, consists of six perchlorate anions

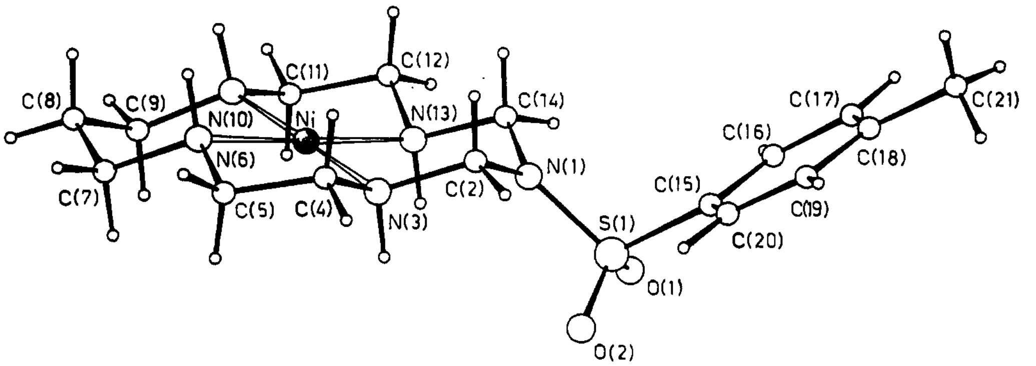


Figure 1. Perspective view of one independent [3-(4-tolylsulfonyl)-1,3,5,8,12-pentaazacyclotetradecane]nickel(II) cation, with the atomic numbering scheme.

and three crystallographically independent, although quite similar, [Ni^{II}]$^{2+}$ cationic complexes (L = (4-tolylsulfonyl)-1,3,5,8,12-pentaazacyclotetradecane). The perspective view of one of the three indipendent cations and the corresponding atomic numbering scheme are shown in Figure 1. Selected bond distances and angles for all the three complex cations are given in Table 4. The cations are characterized by an essentially square planar coordination around the metal centers, which are surrounded by the four secondary amine nitrogen atoms of the pentaaza macrocyclic moiety of the ligands. The displacements of the Ni^{II} ions, from the relative N_4 donor least-squares planes, range from 0.004(1) to 0.022(1) Å. The Ni^{II}–N bond distances in the three cationic complexes do not differ more than 0.029 Å from each other, range from 1.927(7) to 1.956(7) Å, and are those expected for the low-spin Ni^{II}–amine nitrogen bond. In particular, the Ni^{II}–N bond distances observed for the previously investigated low-spin azacyclam derivatives of Ni^{II} range in the 1.927(7)–1.949(9) Å interval in [Ni^{II}(3-(4-pyridiniumylcarbonyl)-1,3,5,8,12-pentaazacyclotetradecane)]$(ClO_4)_2$·$HClO_4$, IV,[15] and in the 1.921(6)–1.938(6) Å interval in [Ni^{II}(3-methyl-1,3,5,8,12-pentaazacyclotetradecane)]$(ClO_4)_2$, V.[14]

Moreover, the N–Ni^{II}–N bond angles, involved in the five- and six-membered rings, are quite comparable, ranging from 85.5(3) to 86.7(2)° and from 92.6(3) to 95.1(2)°, respectively. As found in the other azacyclam complexes IV and V, the six- and five-membered chelate rings adopt a *chair* and a *gauche* conformation, respectively, with two N–H bonds up and two down with respect to the plane of the four coordinated nitrogen atoms; a λ–δ configuration for the bis(ethylenediamine) nickel(II) moiety of each cation is allowed by the pseudo symmetry plane bisecting the N(3)–Ni^{II}–N(13) and N(6)–Ni^{II}–N(10) bond angles. In III the centrosymmetric space group allows the coexistence of both *RSRS* and *SRSR* configurations of the cations.

An interesting structural feature of azacyclam complexes is represented by the distance between the metal center and the noncoordinating tertiary nitrogen atom N(1). Table 5 reports the value of such a distance for the X-ray investigated low-spin Ni^{II}–azacyclam complexes obtained with varying locking fragments (an amine, an aromatic carboxamide, and an aromatic sulfonamide). For comparative purposes, structural parameters are also reported for a cyclam-like complex (whose locking fragment is $-CH_2-$). Table 5 shows that replacing the central $-CH_2-$ group of one of the trimethylene chain of cyclam by a $>NCH_3$ group does not induce any serious structural change: the Ni^{II}–R distance decreases only slightly. On the contrary, a drastic variation of the above parameter is observed when the locking fragment is an amide. In particular, the reduction of the Ni^{II}–R distance is distinctly more pronounced in the case of the toluenesulfonamide derivative. It is possible that the variation of the Ni^{II}–R distance is indicative of a metal–nitrogen interaction. However, such an interaction cannot be of the dipolar type. In this connection, it should be noted that a partial negative charge should reside on the nitrogen atom of the R group: due to the different withdrawing tendencies of the appended functionalities, this negative charge should be higher in the case of the methylamino fragment and should decrease along the series: $>NCH_3 > >NCO(R) > >NSO_2(R)$. Thus, the intensity of the electrostatic interaction between Ni^{II} and R should decrease along the same order, whereas the distance should increase. In fact, the sequence of the Ni^{II}–R distance is reversed, indicating that the intensity of the metal–nitrogen interaction decreases along the series: $>NSO_2(R) > >NCO(R) > >NCH_3$. Thus, we suggest that a completely different interaction exists and that the low-spin d^8 metal center interacts with the R group through a π mode. In particular, a filled d orbital may superimpose on an empty π^* molecular orbital of the amido group. Such a back-donation is enhanced in presence of the more efficient electron-withdrawing sulfonamide group. On the other hand, π-donation by the metal cannot take place in the case of the methylamino fragment which does not present (or presents to a much lower extent) an available empty π^* level. In particular, the Ni^{II}–NCH_3 distance is only slightly smaller than the corresponding Ni^{II}–CH_2 distance in a cyclam-like complex, in which any covalent (and even dipolar) interaction has to be ruled out. It should also be noted that the Ni^{II}–C(8) distance in the other side of the metallocyclam framework keeps in any case the normal value (3.33–3.35 Å). Thus, only the six-membered chelate ring containing the amido fragment is deformed with respect to the structure of the regular metallocyclam arrangement.

The crystal packing is built up by cations and perchlorate anions held together by electrostatic, hydrogen bond, and van der Waals interactions. Three perchlorate anions are axially packed with each cationic complex through hydrogen bonds involving coordinated secondary amine N–H groups. Two perchlorate anions lie on one side and only one ClO_4^- ion lies on the opposite side with respect to the N_4 coordination plane; the latter acts as a bridge between two neighboring cations. The former pair of perchlorate anions are quite far from the sulfonamido group, while the third ClO_4^- anion accommodated by a pair of N–H bonds, is in close proximity to the sulfonamido fragment [$O(ClO_4^-)\cdots O(>SO_2)$ = 3.48(1) Å]. The Ni$^{II}\cdots O(ClO_4^-)$ distances, which range from 2.76(2) to 3.13(1) Å, allow us to exclude any coordinative interaction of the ClO_4^- oxygen atoms with the metal center. The arrangement of the ClO_4^- anions, together with the rigidity of the sulfonamido group, prevents any axial coordination of the $>SO_2$ moiety oxygen atoms.

The geometrical parameters of the sulfonamido groups are as expected and agree well with those observed for similar portion in the 1-ethyl-5,5-pentamethylene-4-(1-naphthyl)-1,2,4-triazo-

---

(22) *Comprehensive Organic Chemistry*; Barton, D.; Ollis, W. D., Eds.; Pergamon Press: New York, 1979; Vol. 2, p 83.

(23) Barefield, E. K.; Chueng, D.; Van der Veer, D. G. *J. Chem. Soc., Chem. Commun.* **1981**, 302.

Table 4. Relevant Bond Distances (Å) and Angles (deg) of the Three Cations in **10**$(ClO_4)_2$[a]

	cation 1	cation 2	cation 3
Ni–N(3)	1.945(6)	1.939(5)	1.944(6)
Ni–N(6)	1.927(7)	1.932(6)	1.927(7)
Ni–N(10)	1.949(5)	1.942(5)	1.943(6)
Ni–N(13)	1.956(5)	1.952(6)	1.945(6)
N(1)–C(2)	1.444(11)	1.443(11)	1.456(11)
C(2)–N(3)	1.458(10)	1.475(10)	1.465(12)
N(3)–C(4)	1.477(11)	1.470(11)	1.468(10)
C(4)–C(5)	1.477(12)	1.491(12)	1.449(13)
C(5)–N(6)	1.517(11)	1.491(12)	1.491(10)
N(6)–C(7)	1.508(11)	1.477(10)	1.516(12)
C(7)–C(8)	1.469(12)	1.538(13)	1.456(15)
C(8)–C(9)	1.490(13)	1.481(14)	1.510(15)
C(9)–N(10)	1.470(10)	1.434(12)	1.489(10)
N(10)–C(11)	1.479(9)	1.482(11)	1.482(10)
C(11)–C(12)	1.472(11)	1.464(15)	1.474(13)
C(12)–N(13)	1.491(10)	1.499(9)	1.467(11)
N(13)–C(14)	1.460(9)	1.464(10)	1.470(11)
C(14)–N(1)	1.441(10)	1.445(12)	1.448(13)
N(1)–S(1)	1.616(7)	1.626(7)	1.630(7)
S(1)–O(1)	1.442(6)	1.428(5)	1.445(6)
S(1)–O(2)	1.428(6)	1.442(7)	1.443(7)
S(1)–C(15)	1.741(8)	1.726(9)	1.735(9)
N(3)–Ni–N(6)	86.7(2)	86.3(3)	85.5(3)
N(6)–Ni–N(10)	92.7(2)	92.6(3)	93.5(3)
N(6)–Ni–N(13)	178.0(3)	178.4(2)	178.0(2)
N(10)–Ni–N(13)	85.6(2)	86.2(2)	86.1(2)
N(13)–Ni–N(3)	95.1(2)	95.0(2)	94.9(2)
N(10)–Ni–N(3)	179.2(2)	178.8(2)	178.8(2)
C(2)–N(1)–C(14)	116.1(6)	115.7(7)	116.1(7)
N(1)–C(2)–N(3)	111.0(7)	109.2(6)	111.3(7)
C(2)–N(3)–C(4)	110.3(6)	110.5(6)	109.6(6)
N(3)–C(4)–C(5)	106.6(7)	108.3(7)	107.1(7)
C(4)–C(5)–N(6)	109.0(7)	107.3(7)	108.0(7)
C(5)–N(6)–C(7)	110.4(6)	108.7(6)	111.7(7)
N(6)–C(7)–C(8)	113.2(7)	112.3(7)	113.3(8)
C(7)–C(8)–C(9)	113.2(7)	115.1(8)	114.1(9)
C(8)–C(9)–N(10)	112.5(7)	112.2(8)	112.0(6)
C(9)–N(10)–C(11)	110.7(5)	110.4(7)	110.4(6)
N(10)–C(11)–C(12)	107.5(6)	108.6(8)	107.9(7)
C(11)–C(12)–N(13)	106.9(6)	106.8(6)	108.1(7)
C(12)–N(13)–C(14)	110.3(6)	109.5(6)	110.2(7)
C(14)–N(1)–S(1)	122.9(5)	121.1(6)	122.4(6)
C(2)–N(1)–S(1)	121.0(6)	122.2(6)	119.9(6)
N(13)–C(14)–N(1)	110.7(6)	110.1(7)	109.1(7)

Relevant Intermolecular Hydrogen Bonds

Cation 1					
N(3)···O(2F^{i})	3.14(1)	H(3A)···O(2F^{i})	2.24(2)	N(3)–H(3A)···O(2F^{i})	156(1)
N(6)···O(3B^{ii})	3.34(1)	H(8A)···O(3B^{ii})	2.47(1)	N(6)–H(8A)···O(3B^{ii})	150(1)
N(10)···O(4E^{ii})	3.30(1)	H(15A)···O(4E^{ii})	2.37(1)	N(10)–H(15A)···O(4E^{ii})	164(1)
N(13)···O(2′F^{i})	3.17(1)	H(20A)···O(2′F^{i})	2.38(2)	N(13)–H(20A)···O(2′F^{i})	139(1)
Cation 2					
N(3)···O(3A^{iii})	3.11(1)	H(3B)···O(3A^{iii})	2.21(1)	N(3)–H(3B)···(3A^{iii})	155(1)
N(6)···O(3C)	3.16(1	H(8B)···O(3C)	2.27(1)	N(6)–H(8B)···O(3C)	153(1)
N(10)···O(1F^{i})	2.95(1)	H(15B)···O(1F^{i})	2.19(1)	N(10)–H(15B)···O(1F^{i})	135(1)
N(13)···O(2A^{iii})	3.29(1)	H(20B)···O(2A^{iii})	2.43(1)	N(13)–H(20B)···O(2A^{iii})	149(1)
Cation 3					
N(3)···O(4E)	3.36(1)	H(3C)···O(4E)	2.49(1)	N(3)–H(3C)···O(4E)	151(1)
N(6)···O(2A)	3.41(1)	H(8C)···O(2A)	2.49(1)	N(6)–H(8C)···O(2A)	159(1)
N(10)···O(4D)	3.42(1)	H(15C)···O(4D)	2.58(1)	N(10)–H(15C)···O(4D)	146(1)
N(13)···O(1E)	3.04(1)	H(20C)···O(1E)	2.14(1)	N(13)–H(20C)···O(1E)	155(1)

[a] Symmetry codes: (i) $-^1/_2 + x, y, ^1/_2 - z$; (ii) $^1/_2 - x, -^1/_2 + y, z$; (iii) $^1/_2 - x, ^1/_2 + y, z$;

lidin-3-one compound.[24] The S–C(*p*-tolyl) bond is in a staggered conformation with respect to the N–C bonds involving the N(1) tertiary amine nitrogen atom, the mean value of the C(*p*-tolyl)–S–N(1)–C torsion angles in the three cations ranging from 82.7(7) to 88.6(7)°. The *p*-tolyl moiety of the sulfonamido group is bent (through the steric control introduced by the >SO_2 fragment) by 48.4(2)° (average) with respect, to the N_4 coordination plane.

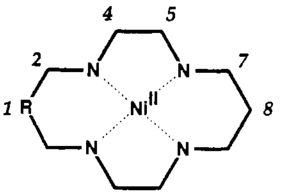
Solution Behavior of the Nickel(II) Complexes. All the investigated complexes **1–14** display the typical macrocyclic inertness toward demetalation by strong acids.[25] In this connection, it should be noted that most of the Ni^{II} complexes have been isolated as perchlorate salts upon addition of concentrated perchloric acid to the reaction solution. Moreover, the persistence in an acidic solution of those complexes, whose perchlorate salts are water soluble (e.g. **7**), was tested spectrophotometrically. In particular, the absorption spectra of an aqueous solution 5 × 10^{-3}

---

[24] Lehman, L. S.; Baclawsky, L. M.; Harris, S. A.; Heine, H. W.; Springer, J. P.; Van den Heuvel, W. J. A.; Arison, B. H. *J. Org. Chem.* **1981**, *46*, 320.

[25] Busch, D. H. *Acc. Chem. Res.* **1978**, *11*, 392.

Table 5. Structural Parameters for Low-spin Ni^{II} Complexes of Azacyclam Macrocycles Containing a Varying Locking Fragment R



	$-CH_2-$[a]	$-N(CH_3)$	$-N(CO)-$	$-N(SO_2)-$
Ni^{II}–R, Å	3.35	3.32	3.25	3.21
Ni^{II}–C(8), Å	3.35	3.35	3.34	3.33

[a] The $-CH_2-$ "locking fragment" refers to the cyclam macrocyle, taken as a reference.[23]. For atom indexes, see the formula shown above.

M in the complex and 5.5 M in $HClO_4$ were measured at 1-day intervals for 1 week. No significative decrease in the intensity of the absorption band centered at 458 nm was observed, demonstrating an extreme kinetic stability, in complete analogy with that found with the corresponding cyclam complex.

Another feature of the nickel(II) cyclam complex shared by the azacyclam analogues is the coexistence in solution of the high-spin and low-spin forms, according to the interconversion equilibrium reported below, where L is the macrocycle and S any solvent molecule displaying donor properties[26,27]

$$\underset{\text{octahedral, high-spin}}{[NiLS_2]^{2+}} \rightleftarrows \underset{\text{square, low-spin}}{[NiL]^{2+} + 2S} \qquad (1)$$

In the investigated solvents, water (when soluble) and acetonitrile, all the synthesized azacyclam complexes exist as a mixture of the two forms. This is demonstrated by the presence in the UV–vis spectrum (200–800 nm range) of an absorption band centered at *ca.* 450 nm (pertinent to the yellow, low-spin chromophore) and of two absorption bands centered at *ca.* 330 and *ca.* 520 nm (pertinent to the blue-violet, high-spin chromophore). A quantitative investigation on the blue-to-yellow equilibrium could be carried out only for water soluble complexes, e.g. **7**. Progressive addition of $NaClO_4$ to an aqueous 2×10^{-3} mol dm^{-3} solution of $[\mathbf{7}](ClO_4)_2$ caused the intensity of the band at 454 nm to increase: a limiting value (81.5 mol^{-1} L cm^{-1}) was reached for a 6–7 M perchlorate concentration, which corresponds to the formation of 100% of the yellow low-spin complex. The ability of the so-called inert electrolyte to compete for the water molecules and to displace to the right the spin interconversion equilibrium (1) of the nickel(II) complexes of cyclam and analogues is well documented.[27] Since the value of ϵ_{lim}(yellow) is known, the equilibrium constant for the blue-to-yellow conversion (1) can be calculated at any concentration of the background electrolyte: $K = \epsilon/(\epsilon_{lim} - \epsilon)$, where ϵ is the molar absorbance at given ionic strength. For instance, at $C_{NaClO_4} = 0.1$ M, $K = 0.734$, [yellow] = 42% and [blue] = 58% (compare to cyclam: [yellow] = 72% and [blue] = 28%).[27]

The same quantitative approach could not be employed to investigate the blue-to-yellow equilibrium in MeCN solutions, where the limited solubility of any background electrolyte prevented the determination of ϵ_{lim}(yellow). In this connection, we observed that all the investigated azacyclam complexes, as well as $[Ni^{II}(cyclam)](ClO_4)_2$, exist in an acetone solution as low-spin form at a concentrations ≥95%. Thus, taking the ϵ value measured in an acetone solution as ϵ_{lim} and assuming that its value does not vary too much with the solvent, we calculated the percent concentration of the yellow form in MeCN solution from the following ratio: $\epsilon_{MeCN}/\epsilon_{acetone}$. Complete data of the spectrophotometric investigations in acetone and acetonitrile are reported in Table 6.

Table 6. Spectral Data for Ni(II) Complexes

		acetonitrile[b]	
complex[a]	acetone λ_{max},[c] nm	λ_{max},[c] nm	% yellow[d]
1	456 (46.5)	464 (17.3)	37.1
2	462 (45.6)	480 (10.3)	22.8
3	460 (52.8)	468 (11.4)	21.6
4	458 (56.7)	470 (6.4)	11.3
5	462 (52.0)	474 (8.6)	16.6
6	460 (56.7)	478 (15.4)	27.1
7	462 (53.5)	480 (12.0)	22.5
8	462 (53.1)	478 (4.8)	9.1
9	456 (53.3)	482 (7.7)	15.1
10	458 (53.8)	482 (7.7)	14.4
12	460 (52.0)	482 (6.5)	12.5
13	462 (53.9)	486 (8.4)	15.6
14	462 (59.7)	486 (19.1)	32.3

[a] Spectra were registered on solutions *ca.* 10^{-3} mol dm^{-3} in perchlorate salts. [b] Only absorptions relative to yellow species are reported. Absorptions assigned to the blue species appears at *ca.* 320 nm as shoulders on the very intense UV bands. [c] ϵ values (dm^3 mol^{-1} cm^{-1}) are given in parentheses. [d] Yellow % values were determined by the ratio $\epsilon_{yellow}/\epsilon_{lim}$; as ϵ_{lim} values for the yellow species were not determinable in acetonitrile, the ones determined in acetone were used.

Table 7. Half-Wave Potential Values (V) Associated with the Oxidation and Reduction Processes of Ni(II) Complexes

Ni^{II} complex	$E_{1/2}(Ni^{III}/Ni^{II})$	$E_{1/2}(Ni^{II}/Ni^{I})$
$[Ni(cyclam)]^{2+}$	0.59	−1.82
1	0.58	−1.86
2	0.59	−1.85
3	0.70	−1.73
4	0.72	−1.74
5	0.74	*a*
6	0.73	*a*
7	0.75	−1.78
8	0.76	−1.78
9	0.76	−1.77
10	0.78	−1.76
11	0.77	−1.75
12	0.79	*a*
13	0.78	*a*
14	0.77	−1.75

[a] Two irreversible peaks which were attributed to reduction processes on the nitroaryl moiety.

Ni^{II}/Ni^{III} Oxidation Process. All of the investigated Ni^{II}–azacyclam complexes undergo a reversible one-electron oxidation process in MeCN solution, as indicated by voltammetry studies and controlled potential electrolysis experiments. Corresponding $E_{1/2}$ values are reported in Table 7. In the case of the cyclam precursor and other tetramine macrocycles, the authenticity of the Ni^{III} state has been demonstrated through the ESR investigation: the spectrum of a frozen MeCN solution of the oxidized complex typically displays axial symmetry and the $g_\perp$ value is substantially higher than $g_\parallel$, as expected for the formation of a low-spin d^7 cation in an octahedrally elongated environment.[28] In particular, apical positions are occupied by solvent molecules. Such a stereochemical arrangement has been confirmed in some cases by X-ray diffraction studies on a single crystal.[29,30] In presently investigated systems, the question can be raised whether the appended amide group, in particular the oxygen atom of the >NCOR function or one of the two oxygen atoms of the $>NSO_2R$ function, can be involved in the apical coordination to the Ni^{III} center, according to a *scorpiand* mode of coordination.[31] From

---

(26) Sabatini, L.; Fabbrizzi, L. *Inorg. Chem.* **1979**, *18*, 438.

(27) Anichini, A.; Fabbrizzi, L.; Paoletti, P.; Clay, R. M. *Inorg. Chim. Acta* **1977**, *24*, L21.

(28) Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3109.

(29) Yamashita, M.; Toriumi, K.; Ito, T. *Acta Crystallogr.* **1985**, *C41*, 1607.

(30) Yamashita, M.; Miyamae, H. *Inorg. Chim. Acta*, **1989**, *156*, 71.

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

the ESR spectrum of a green MeCN solution of complex **10**, electrolyzed at the potential of 0.93 V (i.e. 150 mV above the $E_{1/2}$ value) an axial symmetry with $g_\perp > g_\parallel = 2.18$; $g_\perp = 2.02$) has been observed. Moreover, the $g_\perp$ feature is split into five lines with an intensity ratio of 1:2:3:2:1 ($A_\perp = 22$ G), due to the superhyperfine interaction of the metal center with two equivalent nitrogen atoms of the axially coordinated MeCN molecules. Such an evidence rules out the apical coordination by amide oxygen atom. As a matter of fact, if one of the axial positions were occupied by the amide oxygen atom of the $>NSO_2R$ group, a three-line splitting of $g_\perp$ should be observed. Axial coordination of the amido group has to be ruled out also for the Ni^{II} complex, obviously in the case of the low-spin form, as clearly indicated by X-ray data, but also in the case of the high-spin Ni^{II} center, which shows a much lower affinity than low-spin Ni^{III} toward the axial coordination. Thus, any observed effect on the electrochemical behavior, in particular on the $E_{1/2}(Ni^{III}/Ni^{II})$ values, cannot be ascribed to stereochemical changes involving the amido fragment of the azacyclam framework.

Electrochemical data in Table 7 indicate that replacing the middle $-CH_2-$ group of cyclam (six-membered chelate ring) by an R fragment may distinctly affect the $E_{1/2}(Ni^{III}/Ni^{II})$ value for azacyclam complexes. In particular, whereas replacing by the $N-CH_3$ group does not alter the $E_{1/2}(Ni^{III}/Ni^{II})$ value, insertion of a carboxamido group makes the potential substantially increase (by 100–130 mV). Such an increase is even more pronounced in presence of the sulfonamido group.

We suggest that such a behavior is related to the existence of a π-interaction between the metal center and the amido fragment of the azacyclam ligand. In this connection, it should be noted that a redox potential is related to the ratio of the stability of the two oxidation states involved. It has been pointed out in the section devoted to the structural features of azacyclam complexes that the Ni^{II} d^8 cation is able to transfer through a π mechanism electron charge on the π^* molecular orbital of the amido group, which accounts for the especially small $Ni^{II}-N(1)$ distance. On oxidation, the charge on the metal center decreases and the extent of the π donation to R decreases, too. This makes the overall stability of the trivalent complex decrease and the redox potential become more positive. Destabilization of the trivalent state is more pronounced and the $E_{1/2}(Ni^{III}/Ni^{II})$ value more positive in the case of the sulfonamido azacyclam complexes, where the metal-to-nitrogen π-donation is more important. Interestingly, for a given amido fragment, either carboxamido or sulfonamido, the destabilization of the Ni^{III} state is higher for the aromatic rather than the aliphatic derivative, which reflects the electron withdrawing tendencies.

Steric effects exerted by substituents on the ligand may also influence the oxidation of the metal center. Busch reported that for complexes of *C*-methyl substituted cyclam derivatives the Ni^{II}/Ni^{III} redox change occurred at a more positive potential than for the cyclam analogue.[28] This was ascribed to nonbonding interactions between the methyl groups on the carbon backbone and the axial ligands (i.e. solvent molecules) bound to the Ni^{III} ion. More recently, an analogous effect has been described for Ni^{II} complexes of 14-membered macrocycles in which one or two cyclohexane rings are fused to cyclam framework.[32] For the complexes investigated here (**1–14**) steric effects of this type are hardly predicatable. Although the substituent on the amido group (R′ or R″) can be very bulky, the large distance from the metal center and the relative rigidity of the amido group prevent any interaction with the axially coordinated solvent molecules. X-ray investigation performed on **10** actually showed that in the solid state the *p*-tolyl residue is quite far from the metal center (see Figure 1). In this connection, it should be noted that for the complexes of the sulfonamidocyclam macrocycles **7**, **9**, and **14** the $E_{1/2}(Ni^{II}/Ni^{III})$ value is nearly the same, independent of the bulkiness of the substituents (which vary from methyl to naphthyl).

Ni^{II}/Ni^{I} Reduction Process. All the investigated azacyclam complexes (with the exception of **5**, **6**, **12**, and **13**) undergo a reversible one-electron process at the platinum electrode, as shown by voltammetric investigations in MeCN. Corresponding $E_{1/2}$ values are reported in Table 7. The inserted amido fragment affects also the reduction process, although to a lesser extent than observed in the oxidation process: $E_{1/2}(Ni^{II}/Ni^{I})$ values for both carboxamido and sulfonamido derivatives are 50–90 mV less negative than in the case of the reference cyclam complex. Such a potential increase can again be ascribed to the variation of the intensity of the metal-to-ligand π interactions associated with the change of the oxidation state. In this case, the π contribution should stabilize the Ni^{I} state over the Ni^{II} state. As a matter of fact, the access to the Ni^{I} state is easier, and the $E_{1/2}(Ni^{II}/Ni^{I})$ value less negative, in the case of amido-containing azacyclam complexes. The less pronounced substituent effect on the $E_{1/2}(Ni^{II}/Ni^{I})$ potential compared to the $E_{1/2}(Ni^{III}/Ni^{II})$ potential would reflect a more drastic change of the π donor tendencies of the metal center moving from Ni^{III} to Ni^{II} than moving from Ni^{II} to Ni^{I}.

The four complexes **5**, **6**, **12**, and **13**, which contain in the azacyclam ring the nitrobenzamide and the nitrotoluenesulfonamide fragments showed two irreversible waves in the reduction scan. Such a process involves the nitro–amide subunit rather than the metal center. As a matter of fact, a similar two-wave profile is observed when the cyclic voltammetry experiment is carried out on a solution containing *o*-nitrobenzamide or *p*-nitrotoluenesulfonamide.

Electrochemical Reduction of CO_2 in the Presence of Ni^{II} Complexes. Carbon dioxide undergoes electrochemical reduction at highly negative potentials (*ca.* 2.0 V vs SCE or more negative.[9] Ni^{II} tetraaza macrocyclic complexes have been shown to display a catalytic effect in the electroreduction of CO_2. In particular, Sauvage has shown that the $[Ni^{II}cyclam)]^{2+}$ complex is a very efficient and selective catalyst in the reduction of CO_2 at a mercury electrode: in aqueous solution only CO is formed at the cathode.[7] In the proposed mechanism, the $[Ni^{I}cyclam]^{+}$ complex is assumed to play a crucial role, and in particular, a $[Ni^{I}cyclam(CO)]^{+}$ intermediate species has been detected in the course of the electrolysis experiment. Systems favoring the formation of the Ni^{I} state are expected to behave as efficient electrocatalysts for the CO_2 reduction. In this connection, the Ni^{II} complexes of some fluorinated cyclams, which exhibit a Ni^{II}/Ni^{I} potential less negative than $[Ni^{II}(cyclam)]^{2+}$, work well in the CO_2 reduction.[33]

We wished to test the efficiency of the Ni^{II} azacyclam complexes (those exhibiting a solubility in water of at least 10^{-4} M) as electrocatalysts for the reduction of CO_2, following Sauvage's approach, which involves both cyclic voltammetry and controlled-potential coulometry studies. In a typical CV experiment, a *catalytic* amount of the envisaged Ni^{II} complex was dissolved in an aqueous solution 0.1 M in $NaClO_4$. The concentration of the catalyst varied in the range 10^{-6}–10^{-4} M. A mercury pool having a surface of 22.9 mm^2 was used as a working electrode; the counter electrode was a platinum foil, and a sodium chloride saturated calomel electrode was used as a reference electrode. The solution was first degassed with dinitrogen, and then a cyclic voltammetry experiment was carried out under a dinitrogen atmosphere. In the case of the $[Ni^{II}cyclam]^{2+}$ complex, which was used as a standard, a quasi-reversible wave was observed with an $E_{1/2}$ value of -1.57 V vs SCE. Subsequently, carbon dioxide was bubbled in the solution, and then a CV scan was carried out under a CO_2 atmosphere. In the case of the cyclam complex, a very strong irreversible wave, whose peak intensity was about 2500 times larger than that recorded in the scan under N_2, was observed, in

---

(32) Kobiro, K.; Nakayama, A.; Hiro, T.; Suwa, M.; Tobe, Y. *Inorg. Chem.* **1992**, *31*, 676.

(33) Shionoya, M.; Kimura, E.; Iitaka, Y. *J. Am. Chem. Soc.* **1990**, *112*, 9237.

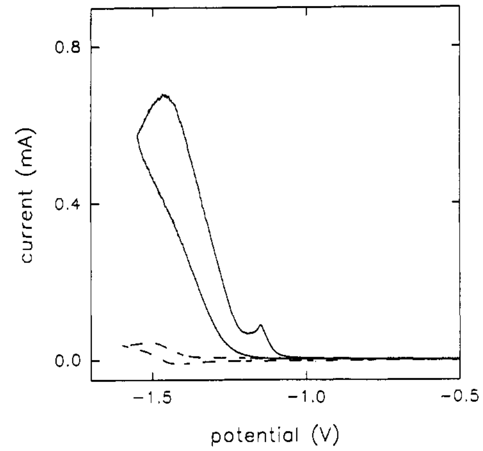


Figure 2. Cyclic voltammetry profiles for an aqueous solution 10^{-4} M in $4(ClO_4)_2$: (i) under a dinitrogen atmosphere (dashed line) and (ii) under a carbon dioxide atmosphere (continuous line). Conditions: $[NaClO_4]$ = 0.1 M; pH = 5; mercury pool electrode.

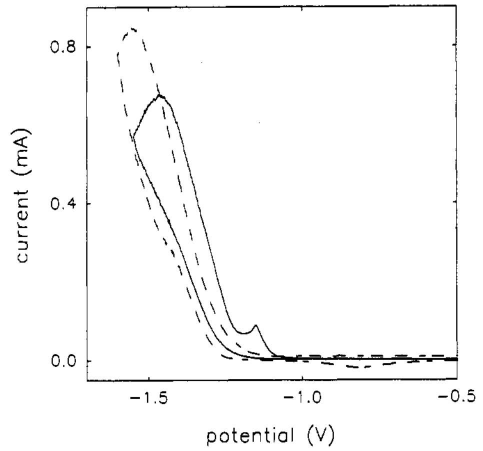


Figure 3. Cyclic voltammetry profiles in a carbon dioxide atmosphere for aqueous solutions 10^{-4} M in $[Ni^{II}cyclam]^{2+}$ (dashed line) and $[4]^{2+}$ (continuous line), under a carbon dioxide atmosphere ($[NaClO_4]$ = 0.1 M; pH = 5; mercury pool electrode).

complete agreement with Sauvage's experiment. It has been previously observed that even subtle modifications on the cyclam framework produce a drastic decrease of the catalytic current. Quite interestingly, all the investigated azacyclam complexes (**1**, **3**, **4**, **7**) produced a catalytic reduction wave of intensity comparable to that observed with the $[Ni^{II}cyclam]^{2+}$ complex.

In Figure 2 CV profiles obtained under N_2 (dashed line) and CO_2 for the nickel(II) complex **4** are superimposed: as in the case of $[Ni^{II}(cyclam)]^{2+}$ derivative the current intensity in presence of CO_2 is much greater than under N_2 (about 2000 times). Figure 3 compares the CV profiles observed with equimolar aqueous solutions of the complexes of cyclam and of benzamide–azacyclam (**4**) under the same experimental conditions.

Electrolysis experiments have been carried out on a CO_2-saturated solution of the complex **4** to verify the reduction pattern and to test the efficiency of the catalytic system. In particular, an aqueous solution 10^{-4} M in $[4](ClO_4)_2$, under a CO_2 atmosphere, was electrolyzed at a potential of 0.9 V vs SHE. Chromatographic analyses on gas samples showed that only CO_2 and CO were present in the mixture and that, in particular, H_2 was not present at all. After 4 h, 28% of the CO_2 was reduced to CO (56 cm^3) with an overall turnover number of 232, which corresponds to a turnover frequency of 57 h^{-1}. For comparative purposes, the same electrolysis experiment was carried out on a solution of the reference system, $[Ni^{II}(cyclam)](ClO_4)_2$, under the same conditions. It should be noted that the two systems display a very similar behavior and that, in particular, the electrocatalytic efficiency of the azacyclam complex (in terms of moles of CO produced) corresponds to the 80% of that of the cyclam reference complex. Noticeably, such a value agrees well with the ratio of the peak currents of the catalytic wave measured in the CV experiments.

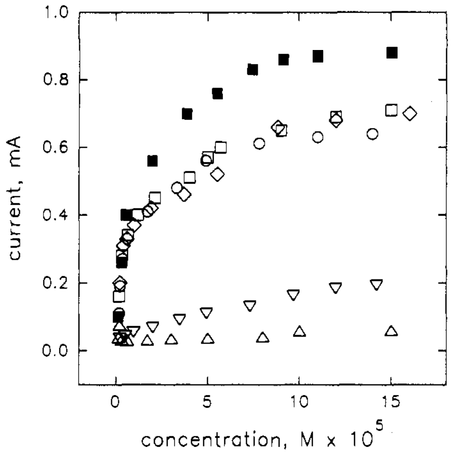


Figure 4. Effect of the concentration of the nickel(II) tetraaza macrocyclic complex on the intensity of the catalytic wave associated with the CO_2 reduction ($NaClO_4$ 0.1 M, pH = 5, mercury pool electrode). Key: (■) cyclam; (□) **4**; (○) **1**; (◇) **7**; (▽) isocyclam; (△) [15]aneN_4. The catalytic efficiency drastically decrease with the 5,6,5,6 sequence of the chelate rings of cyclam and azacyclam complexes is altered.

Comparison on the electrocatalytic efficiency of cyclam and all the investigated azacyclam complexes was made on the basis of CV data. In particular, the catalytic wave observed in the CV profile of the complex **4** displays a somewhat lower intensity as compared to the cyclam analogue, but it is anticipated to a less negative potential. The potential increase ΔE, *ca.* 100 mV, seems to reflect the increase of the $E_{1/2}(Ni^{II}/Ni^{I})$ value. Anticipation of the catalytic wave has been observed also for all the other investigated azacyclam complexes.

Figure 4 indicates how the intensity of the catalytic wave varies with the concentration of the Ni^{II}–macrocyclic complex. A typical saturation profile has been obtained for the cyclam complex and for its azacyclam analogues. Such a behavior has been interpreted assuming that the electroactive complex responsible for the CO_2 reduction is adsorbed on the mercury surface. When all the surface of electrode has been conveniently covered by the metal complex, a limiting current is obtained and a further increase of the concentration of the solution does not have any effect on the catalytic process. Quite interestingly, all the investigated azacyclam complexes display almost the same limiting current value, which is smaller than that observed with $[Ni^{II}(cyclam)]^{2+}$ (about 80%). Figure 4 reports also the profile observed for the $[Ni^{II}(isocyclam)^{2+}$ complex (isocyclam: 1,4,7,11-tetraazacyclotetradecane). Isocyclam is a 14-membered macrocycle, which forms with the encircled metal center a 5,5,6,6 sequence of the chelate rings (cyclam: 5,6,5,6). The limiting catalytic current observed with the isocyclam complex is much lower than that observed with the cyclam (4%) and azacyclam analogues (5%). Moreover, the Ni^{II} complex with the 15-membered tetraaza macrocycle 1,4,8,12-tetraazacyclopentadecane does not show any catalytic effect on the CO_2 electroreduction (see Figure 4).

Figure 4 clearly stresses that 14-membered cyclam framework is a crucial prerequisite for the encircled nickel center to act as catalyst in the CO_2 electroreduction. Replacing the middle $-CH_2-$ of one of the trimethylene chains of cyclam by an amido group (azacyclam complexes) does not alter the favorable structural features of the macrocycle, and the catalytic efficiency is only slightly reduced. On the other hand, other structural modifications of the cyclam framework drastically affect the metal ability to interact with CO_2 and to promote its cathodic reduction. Expansion of the tetraaza ring from the 14- to the 15-membered ring makes the complex lose its catalytic properties almost completely. Moreover, also the subtle rearrangement of the 14-membered ring from cyclam to isocyclam (which is not expected to alter significantly the ligand cavity size) causes a drastic reduction of the catalytic efficiency.

Conclusions

The $[Ni^{II}(cyclam)]^{2+}$ complex displays a very interesting solution chemistry, which is essentially related to the special features of the encircling macrocycle. In particular, cyclam imparts kinetic inertness to the bound metal center and promotes its redox activity. Ni^{II}–azacyclam derivatives represent a novel class of metal complexes displaying properties and reactivity very close to those of the cyclam analogue. In particular, (i) they can be obtained through a one-pot template synthesis from convenient reactants, (ii) they display a cyclam-like inertness toward demetalation, and (iii) they can easily achieve the Ni^{III} and the Ni^{I} states through reversible redox changes: noticeably, the amide fragment incorporated in the macrocyclic framework controls the redox activity of the metal center, introducing a new substituent effect on the electrode potential for the Ni^{III}/Ni^{II} and Ni^{II}/Ni^{I} redox couples. Such an effect seems related to a π-interaction between the nickel ion and the amido group and in any case favors the attainment of the lower oxidation state and disfavors access to the higher oxidation state. Interestingly, the insertion of an amido group does not substantially modify the unique structural features of the cyclam framework, in particular those related to the interaction with the CO_2 molecule and to its cathodic reduction.

Acknowledgment. This work was supported by grants from the National Council of Researches (CNR, Rome) and from the Ministry of the University (MURST, Rome). We are grateful to Dr. A. Guarini, Istituto G. Donegani, Novara, Italy, for assistance with FAB spectra.

Supplementary Material Available: Anisotropic thermal parameters for the non-hydrogen atoms (Table S1), hydrogen atom coordinates and isotropic thermal parameters (Table; S2), and a complete list of bond distances and angles (Table S3) (11 pages). Ordering information is given on any current masthead page.