

## 21. Metal Complexes with Macrocyclic Ligands

Part XLIII<sup>1)</sup>

### Tetraazamacrocyclic Nickel(II) and Copper(II) Complexes with Aliphatic Methylthio- and Methoxy-Substituted Pendant Chains

by Claudio L. Schmid, Markus Neuburger, Margareta Zehnder, and Thomas A. Kaden\*

Institute of Inorganic Chemistry, Spitalstrasse 51, CH-4056 Basel

and Krzysztof Bujno and Renata Bilewicz

Department of Chemistry, University of Warsaw, ul. Pasteura 1, PL-02-093 Warsaw

(13.VIII.96)

The 14-membered tetraazamacrocyclic Ni<sup>2+</sup> and Cu<sup>2+</sup> complexes of **4** (1,4,8-trimethyl-11-[(2-methylthio)ethyl]-1,4,8,11-tetraazacyclotetradecane), **5** (1,4-dimethyl-8,11-bis[2-(methylthio)ethyl]-1,4,8,11-tetraazacyclotetradecane), and **7** (1,4,8,11-tetrakis[2-(methylthio)ethyl]-1,4,8,11-tetraazacyclotetradecane), with one, two, and four methylthio-substituted pendant chains, respectively, and the Ni<sup>2+</sup> complex of **6** (1,4-dimethyl-8,11-bis(2-methoxyethyl)-1,4,8,11-tetraazacyclotetradecane), with two methoxy-substituted pendant chains, were synthesized and their chemistry studied with regard to modelling F430. Solution spectra in H<sub>2</sub>O, MeCN, and DMF indicate participation of the side chain in metal coordination when the donor group is a thioether, whereas no coordination with the metal ion is observed with the ether group. Similarly the X-ray structures of the thioether-containing compounds [Ni(**5**)](ClO<sub>4</sub>)<sub>2</sub>, [Cu(**5**)](ClO<sub>4</sub>)<sub>2</sub>, and [Cu(**7**)](ClO<sub>4</sub>)<sub>2</sub> show a coordination number of 5, whereas that of [Ni(**6**)](ClO<sub>4</sub>)<sub>2</sub> with ether pendant chains, shows a coordination number of 4. Cyclic voltammetry of these complexes in MeCN reveals that Ni<sup>2+</sup> is reversibly reduced to Ni<sup>+</sup> between – 0.64 and – 0.77 V vs. SCE, the potential being influenced by the nature and number of the pendant chains. At more negative potentials, the thioether is cleaved, whereby a thiol is formed; the thiol is then oxidized at ca. + 0.8 V vs. SCE, when a glassy carbon electrode is used, or at ca. 0 V vs. SCE at a dropping Hg electrode. No cleavage of the ether bond in [Ni(**6**)](ClO<sub>4</sub>)<sub>2</sub> is observed under similar conditions.

**Introduction.** – The functionalization of polyazamacrocycles with pendant chains containing donor atoms, which can coordinate, is a powerful technique to modify the chemical and physical properties of the metal ion [2]. Whereas this aspect has been studied in great detail, much less has been done to investigate how the metal ion modifies the properties and reactivity of the side-chain functional group. Such systems are good models for metalloenzymes, since through the side chain, the reactive group is brought close to the metal center, which can activate it in a similar way as in an enzyme-substrate complex. Examples of enhanced hydrolytic reactions of esters [3] and nitriles [4] have been observed.

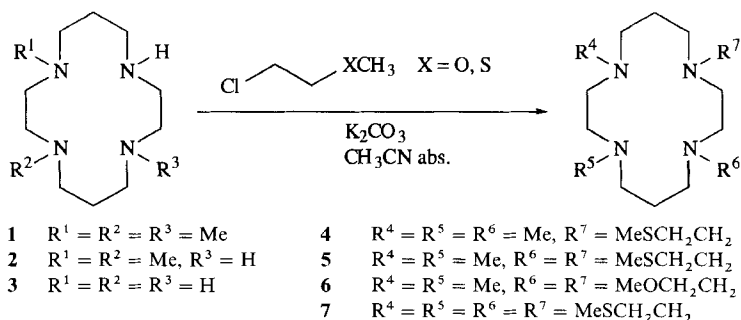
In contrast, nearly no mimicking of redox processes has been reported in the literature, although many redox-active metalloproteins are known [5]. One interesting system

<sup>1)</sup> Part XLII [1].

is F430, the cofactor of methyl-coenzyme-M reductase, which catalyzes the reductive cleavage of a methyl-thioether bond in the catabolic pathway of methanogenic bacteria [6].

The structure of F430 has been elucidated and shows that the  $\text{Ni}^{2+}$  ion is coordinated by the four pyrazole N-atoms of the hydrocorphinoid ligand [7]. It has also been demonstrated that the redox step  $\text{Ni}^{\text{II}} \rightarrow \text{Ni}^{\text{I}}$  is of paramount importance for the whole process and that the redox potential of  $-0.89 \text{ V vs. SCE}$  [8] is close to the end of the range of potentials reachable under physiological conditions. Comparative studies of F430 with  $\text{Ni}^{\text{II}}/\text{Ni}^{\text{I}}$  complexes of tetraazamacrocycles have shown that these compounds can be used as models to study the reaction mechanism of the methyl transfer [9].

We have previously reported that the  $\text{Ni}^{2+}$  complexes of tetraazamacrocycles with an appended aromatic MeS group can be reduced to  $\text{Ni}^+$  and that at negative potentials the Me–S bond is cleaved forming a thiol [1]. In continuation of such studies, we have now prepared a series of similar compounds with one, two, or four aliphatic side chains carrying a MeS or a MeO group, *i.e.* 4–7, and studied their  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  complexes.



**Experimental.** – *General.* Compounds 1,4,8-trimethyl-1,4,8,11-tetraazacyclotetradecane (**1**) [10], 1,4-dimethyl-1,4,8,11-tetraazacyclotetradecane (**2**) [10], and 1,4,8,11-tetraazacyclotetradecane (**3**) [11] were prepared according to the literature. UV/VIS Spectra: *Perkin-Elmer-Lambda-9* spectrometer; 0.2 mm solns. for  $\text{Cu}^{2+}$  complexes and 0.8 mm solns. for  $\text{Ni}^{2+}$  complexes in  $\text{H}_2\text{O}$ , MeCN, or DMF (*Merck, Uvasol*) in 1-cm cells. IR Spectra: *Perkin-Elmer-1600* spectrophotometer; KBr pellets.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR Spectra: *Varian-Gemini-300* or *-400* instrument;  $\delta$  rel. to  $\text{SiMe}_4$  as internal standard (= 0 ppm). GC/MS: *Hewlett-Packard* (mass selective director 5971 series; gas chromatograph 5890 series II; column *HP-1, SE-30*, 25 m). MS: *VG 70-250*, FAB. Elemental analyses were performed by the analytical laboratory of *Ciba AG*, Basel.

*General Alkylation Procedure.* To a mixture of **1** or **2** (1 mmol), dissolved in abs. MeCN, or **3**, suspended in abs. MeCN, and  $\text{K}_2\text{CO}_3$  (2 mmol/NH; finely pulverized and dried for 1 h at  $100^\circ$ ), 2-chloroethyl methyl thioether or 2-chloroethyl methyl ether (1.1 mmol/NH), was added dropwise under  $\text{N}_2$ . The soln. was stirred for 1 h at r.t. and then refluxed for 40 h.  $\text{K}_2\text{CO}_3$  was removed by filtration, the soln. evaporated, and the resulting oil dried under high vacuum and purified by FC (MeOH/ $\text{NH}_3$  soln. (25%)).

*1,4,8-Trimethyl-11-[2-(methylthio)ethyl]-1,4,8,11-tetraazacyclotetradecane (4).* Yield 68%.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ): 1.56–1.72 (*quint.*,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ); 2.12 (*s*, MeS); 2.20, 2.21, 2.22 (*3s*, MeN); 2.40–2.50, 2.52–2.74 (*2m*,  $\text{CH}_2\text{N}$ ,  $\text{NCH}_2\text{CH}_2\text{SMe}$ ).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ): 15.79 (MeS); 24.48, 24.55 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ); 31.46 ( $\text{NCH}_2\text{CH}_2\text{SMe}$ ); 43.39, 43.67, 43.72 (MeN); 51.03, 51.21, 53.82, 53.95, 53.99, 54.51, 54.67, 54.71, 54.96 ( $\text{CH}_2\text{N}$ ). MS: 316 ( $M^+$ ). Anal. calc. for  $\text{C}_{16}\text{H}_{36}\text{N}_4\text{S} \cdot 0.18\text{H}_2\text{O}$  (319.80): C 60.09, H 11.46, N 17.52, S 10.03,  $\text{H}_2\text{O}$  1.01; found: C 60.34, H 11.50, N 17.84, S 9.65,  $\text{H}_2\text{O}$  0.99.

*1,4-Dimethyl-8,11-bis[2-(methylthio)ethyl]-1,4,8,11-tetraazacyclotetradecane (5).* Yield 58%.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ): 1.56–1.70 (*quint.*,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ); 2.11 (*s*, MeS); 2.22 (*s*, MeN); 2.40–2.50, 2.50–2.70 (*2m*,  $\text{CH}_2\text{N}$ ,  $\text{NCH}_2\text{CH}_2\text{SMe}$ ).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ): 15.82 (MeS); 24.51 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ); 31.75 ( $\text{NCH}_2\text{CH}_2\text{SMe}$ ) 43.80 (MeN);

51.21, 51.29, 54.24, 54.43, 54.58 (CH<sub>2</sub>N). MS: 376 (*M*<sup>+</sup>). Anal. calc. for C<sub>18</sub>H<sub>40</sub>N<sub>4</sub>S<sub>2</sub> · 0.16 H<sub>2</sub>O (379.57): C 56.96, H 10.71, N 14.76, S 16.90, H<sub>2</sub>O 0.76; found: C 57.12, H 10.52, N 14.86, S 16.64, H<sub>2</sub>O 0.76.

*1,4-Dimethyl-8,11-bis(2-methoxyethyl)-1,4,8,11-tetraazacyclotetradecane (6)*. Yield 70%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 1.56–1.70 (*quint.*, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 2.22 (*s*, MeN); 2.40–2.48, 2.56–2.68 (*2m*, CH<sub>2</sub>N); 3.36 (*s*, MeO); 3.40–3.48 (*t*, NCH<sub>2</sub>CH<sub>2</sub>OMe). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 24.35 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 43.87 (MeN); 51.50, 52.04, 54.15, 54.27, 54.65 (CH<sub>2</sub>N); 58.77 (MeO); 71.27 (NCH<sub>2</sub>CH<sub>2</sub>OMe). MS: 344 (*M*<sup>+</sup>).

*1,4,8,11-Tetrakis[2-(methylthio)ethyl]-1,4,8,11-tetraazacyclotetradecane (7)*. Yield 77%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 1.52–1.68 (*quint.*, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 2.11 (*s*, MeS); 2.48–2.56, 2.58–2.72 (*2m*, CH<sub>2</sub>N, NCH<sub>2</sub>CH<sub>2</sub>SMe). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 15.83 (MeS); 24.02 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 31.89 (NCH<sub>2</sub>CH<sub>2</sub>SMe); 51.32, 51.52, 54.82 (CH<sub>2</sub>N). CI-MS: 497 (*M*<sup>+</sup>).

*General Complexation Procedure.* To a soln. of the ligand **4**, **5**, **6**, or **7** in abs. EtOH, Ni(ClO<sub>4</sub>)<sub>2</sub> · 6 H<sub>2</sub>O or Cu(ClO<sub>4</sub>)<sub>2</sub> · 6 H<sub>2</sub>O (10% molar excess) was added. The soln. was refluxed during 30 min and then stirred overnight. The complex was collected by filtration, washed with abs. EtOH (4 ×) and Et<sub>2</sub>O (4 ×), and finally dried in the desiccator.

*{1,4,8-Trimethyl-11-[2-(methylthio)ethyl]-1,4,8,11-tetraazacyclotetradecane}nickel(II) Diperchlorate* ([Ni(**4**)](ClO<sub>4</sub>)<sub>2</sub>). Yield 99%. IR: 3428*m*, 2924*m*, 1468*m*, 1309*w*, 1089*s*, 1001*w*, 975*w*, 797*m*, 721*m*, 624*s*. FAB-MS: 473 ([*M* – ClO<sub>4</sub>]<sup>+</sup>). Anal. calc. for C<sub>16</sub>H<sub>36</sub>Cl<sub>2</sub>N<sub>4</sub>NiO<sub>8</sub>S (574.15): C 33.47, H 6.32, N 9.76, Ni 10.22, S 5.58; found: C 33.66, H 6.22, N 9.55, Ni 9.66, S 6.05.

*{1,4,8-Trimethyl-11-[2-(methylthio)ethyl]-1,4,8,11-tetraazacyclotetradecane}copper(II) Diperchlorate* ([Cu(**4**)](ClO<sub>4</sub>)<sub>2</sub>). Yield 98%. IR: 3426*s*, 2929*m*, 1624*m*, 1465*m*, 1336*w*, 1290*w*, 1095*s*, 798*w*, 729*w*, 627*s*, 482*m*. FAB-MS: 478 ([*M* – ClO<sub>4</sub>]<sup>+</sup>). Anal. calc. for C<sub>16</sub>H<sub>36</sub>Cl<sub>2</sub>CuN<sub>4</sub>O<sub>8</sub>S (579.00): C 33.19, H 6.27, Cu 10.98, N 9.68, S 5.54; found: C 33.30, H 6.37, Cu 10.60, N 9.74, S 5.41.

*{1,4-Dimethyl-8,11-bis[2-(methylthio)ethyl]-1,4,8,11-tetraazacyclotetradecane}nickel(II) Diperchlorate* ([Ni(**5**)](ClO<sub>4</sub>)<sub>2</sub>). Yield 93%. IR: 3428*s*, 2921*m*, 2017*w*, 1637*m*, 1482*s*, 1444*s*, 1367*m*, 1308*m*, 1090*s*, 975*m*, 929*w*, 898*w*, 853*w*, 795*m*, 722*m*, 623*s*. FAB-MS: 533 ([*M* – ClO<sub>4</sub>]<sup>+</sup>).

*{1,4-Dimethyl-8,11-bis[2-(methylthio)ethyl]-1,4,8,11-tetraazacyclotetradecane}copper(II) Diperchlorate* ([Cu(**5**)](ClO<sub>4</sub>)<sub>2</sub>). Yield 90%. IR: 3427*s*, 2929*w*, 2072*m*, 1628*m*, 1399*m*, 1334*w*, 1288*w*, 1088*s*, 726*w*, 625*s*, 510*w*. FAB-MS: 538 ([*M* – ClO<sub>4</sub>]<sup>+</sup>).

*{1,4-Dimethyl-8,11-bis(2-methoxyethyl)-1,4,8,11-tetraazacyclotetradecane}nickel(II) Diperchlorate* ([Ni(**6**)](ClO<sub>4</sub>)<sub>2</sub>). Yield 92%. IR: 3434*m*, 2886*m*, 2026*w*, 1637*m*, 1476*s*, 1087*s*, 982*m*, 940*m*, 825*w*, 786*w*, 717*m*, 627*s*. FAB-MS: 501 ([*M* – ClO<sub>4</sub>]<sup>+</sup>).

*{1,4,8,11-Tetrakis[2-(methylthio)ethyl]-1,4,8,11-tetraazacyclotetradecane}nickel(II) Diperchlorate* ([Ni(**7**)](ClO<sub>4</sub>)<sub>2</sub>). Yield 94%. IR: 3428*s*, 2923*m*, 1627*m*, 1432*m*, 1289*w*, 1244*w*, 1091*s*, 776*w*, 717*w*, 625*s*, 461*w*. FAB-MS: 653 ([*M* – ClO<sub>4</sub>]<sup>+</sup>).

*{1,4,8,11-Tetrakis[2-(methylthio)ethyl]-1,4,8,11-tetraazacyclotetradecane}copper(II) Diperchlorate* ([Cu(**7**)](ClO<sub>4</sub>)<sub>2</sub>). Yield 85%. IR: 3420*m*, 2918*m*, 1638*w*, 1481*m*, 1432*m*, 1253*w*, 1090*s*, 775*w*, 720*w*, 625*s*, 556*w*. FAB-MS: 658 ([*M* – ClO<sub>4</sub>]<sup>+</sup>).

*Cyclic Voltammetry.* Voltammetric experiments were performed with a three-electrode cell composed of a saturated calomel reference electrode, a Pt-foil counter electrode, and either a static Hg drop electrode of 0.015 cm<sup>2</sup> drop area (*Laboratori Pastroje*), used in the hanging drop mode (HMDE), or a glassy C electrode (BAS) with a surface area of 0.07 cm<sup>2</sup>. Voltammograms were recorded with an *EG & G PARC model 273* potentiostat controlled via *EChem* software on a *PC 486* computer. The *COOL* algorithm (*PAR* software) was used to fit the experimental curves to a reversible one-electron process for the electrode reaction at the metal center. MeCN solns. of the compounds (**1** or **2** mM) were prepared daily, and tetrapropylammonium tetrafluoroborate (0.1M in MeCN) was used as supporting electrolyte. All electrochemical experiments were done at 25°, using variable scan rates, in solns. deaerated by passing Ar.

*X-Ray Diffraction Measurements.* The crystal data and parameters of the data collection for [Ni(**5**)](ClO<sub>4</sub>)<sub>2</sub>, [Ni(**6**)](ClO<sub>4</sub>)<sub>2</sub>, [Cu(**5**)](ClO<sub>4</sub>)<sub>2</sub>, [Cu(**7**)](ClO<sub>4</sub>)<sub>2</sub>, and for **7**, are given in *Tables 1* and *2*. Unit-cell parameters were determined by accurate centering of 25 independent strong reflections by the least-squares method. Three standard reflections monitored every 2 h during data collection showed no significant variation of the intensity. The raw data set was corrected for polarization effects and X-ray diffraction absorption. The structure was solved by the direct method [12]. Anisotropic least-squares refinements were carried out on all non-H-atoms, using the program *CRYSTALS* [13]. The two ClO<sub>4</sub><sup>-</sup> ions are disordered. They were refined using two split positions per atom keeping the sum of their occupancy equal to 1. H-Atoms are in calculated positions with C–H and N–H distances of 0.96 Å and fixed isotropic thermal parameters. Scattering factors were taken from the 'International Tables for Crystallography' [14].

Table 1. *Crystal Data and Parameter of Data Collection for the Ni<sup>2+</sup> Complex with 5 and 6 and for the Cu<sup>2+</sup> Complex with 5*

|                                      | [Ni(5)](ClO <sub>4</sub> ) <sub>2</sub>  | [Cu(5)](ClO <sub>4</sub> ) <sub>2</sub>  | [Ni(6)](ClO <sub>4</sub> ) <sub>2</sub>  |
|--------------------------------------|--|--|--|
| Formula                              | (C <sub>18</sub> H <sub>40</sub> N <sub>4</sub> NiS <sub>2</sub> )(ClO <sub>4</sub> ) <sub>2</sub> | (C <sub>18</sub> H <sub>40</sub> CuN <sub>4</sub> S <sub>2</sub> )(ClO <sub>4</sub> ) <sub>2</sub> | (C <sub>18</sub> H <sub>40</sub> N <sub>4</sub> NiO <sub>2</sub> )(ClO <sub>4</sub> ) <sub>2</sub> |
| Mol. wt.                             | 634.27   | 639.10   | 602.16   |
| Crystal system                       | orthorhombic   | orthorhombic   | orthorhombic   |
| Space group                          | <i>Pbca</i>  | <i>Pbca</i>  | <i>Pc2<sub>1</sub>/n</i>   |
| <i>a</i> [Å]                         | 15.8776(6)   | 15.880(2)  | 9.7546(7)  |
| <i>b</i> [Å]                         | 17.7233(7)   | 17.553(1)  | 16.1011(15)  |
| <i>c</i> [Å]                         | 19.5738(24)  | 19.736(2)  | 33.8781(34)  |
| $\alpha$ [deg]                       | 90.000   | 90.000   | 90.000   |
| $\beta$ [deg]                        | 90.000   | 90.000   | 90.000   |
| $\gamma$ [deg]                       | 90.000   | 90.000   | 90.000   |
| Z                                    | 8  | 8  | 8  |
| Volume [Å <sup>3</sup> ]             | 5508.2(8)  | 5501.0(9)  | 5320.9(8)  |
| Density [g cm <sup>-3</sup> ]        | 1.53   | 1.54   | 1.50   |
| $\mu$ [mm <sup>-1</sup> ]            | 4.65   | 4.76   | 3.42   |
| <i>F</i> (000)                       | 2672   | 2680   | 2544   |
| Crystal size [mm]                    | 0.10 × 0.25 × 0.25   | 0.10 × 0.24 × 0.49   | 0.24 × 0.38 × 0.68   |
| Temperature [K]                      | 293  | 293  | 293  |
| $\theta_{\max}$ [deg]                | 77.50  | 77.50  | 77.50  |
| Radiation                            | CuK $\alpha$ ( $\lambda = 1.54180$ Å)  | CuK $\alpha$ ( $\lambda = 1.54180$ Å)  | CuK $\alpha$ ( $\lambda = 1.54180$ Å)  |
| Scan type                            | $\omega/2\theta$   | $\omega/2\theta$   | $\omega/2\theta$   |
| No. of measured refl.                | 4964   | 5167   | 5435   |
| No. of indep. refl.                  | 4792   | 4933   | 5238   |
| No. of refl. in ref.                 | 3846   | 4045   | 4247   |
| No. of variables                     | 317  | 317  | 669  |
| Final <i>R</i> value [%]             | 4.64   | 5.20   | 6.97   |
| Final <i>R<sub>w</sub></i> value [%] | 5.25   | 5.92   | 6.59   |
| Weighting scheme                     | <i>Chebychev</i> <sup>a)</sup>   | <i>Chebychev</i> <sup>a)</sup>   | <i>Chebychev</i> <sup>a)</sup>   |

<sup>a)</sup> *Chebychev* polynomial weighting, see [15].

**Results and Discussion.** – We have synthesized mono-, di-, and tetrafunctionalized tetraazamacrocycles, carrying aliphatic pendant chains substituted with a MeO or a MeS group, by alkylation of the corresponding unsubstituted macrocycles, to study their metal complexes.

The spectra of the Ni<sup>2+</sup> complexes with **4**, **5**, and **7** (Table 3) show in H<sub>2</sub>O, MeCN, and DMF only small differences when the number of methyl-thioether pendant chains is increased (slight bathochromic shift). The typical bands for pentacoordinated species at *ca.* 390 nm and at 605–625 nm are observed [16], beside a strong charge-transfer absorption at 340–350 nm. The spectra of the Cu<sup>2+</sup> complexes (Table 3) also show a strong charge-transfer band at *ca.* 310 nm and sometimes at 375 nm, which are nearly not displaced when the solvent is changed. In contrast, the d-d\* band of the Cu<sup>2+</sup> chromophore is strongly dependent on the nature of the solvent. The shift to longer wavelengths with increasing donor properties of the solvent is a clear indication that the solvent binds axially, replacing the thioether group from the coordination sphere of the metal ion.

Pentacoordinated geometries are also observed in the solid state as confirmed by the X-ray structure of [Ni(5)](ClO<sub>4</sub>)<sub>2</sub> (Fig. 1) and of [Cu(5)](ClO<sub>4</sub>)<sub>2</sub> (Fig. 2). The Ni<sup>2+</sup> ion

Table 2. Crystal Data and Parameter of Data Collection for the  $\text{Cu}^{2+}$  Complex of **7** and for the Ligand **7** · 2H<sup>+</sup>

|                                      | [Cu( <b>7</b> )](ClO <sub>4</sub> ) <sub>2</sub>   | <b>7</b> · 2H <sup>+</sup>   |
|--------------------------------------|--|--|
| Formula                              | (C <sub>22</sub> H <sub>48</sub> CuN <sub>4</sub> S <sub>4</sub> )(ClO <sub>4</sub> ) <sub>2</sub> · 1.5H <sub>2</sub> O | (C <sub>22</sub> H <sub>50</sub> N <sub>4</sub> S <sub>4</sub> )(ClO <sub>4</sub> ) <sub>2</sub> |
| Mol. wt.                             | 786.35   | 697.82   |
| Crystal system                       | monoclinic   | monoclinic   |
| Space group                          | <i>P</i> 2 <sub>1</sub> / <i>n</i>   | <i>P</i> 2 <sub>1</sub> / <i>n</i>   |
| <i>a</i> [Å]                         | 21.515(1)  | 7.871(1)   |
| <i>b</i> [Å]                         | 8.301(1)   | 14.661(1)  |
| <i>c</i> [Å]                         | 21.612(2)  | 15.019(3)  |
| $\alpha$ [deg]                       | 90.000   | 90.000   |
| $\beta$ [deg]                        | 115.821(5)   | 97.94(1)   |
| $\gamma$ [deg]                       | 90.000   | 90.000   |
| <i>Z</i>                             | 4  | 2  |
| Volume [Å <sup>3</sup> ]             | 3474.5(5)  | 1716.5(5)  |
| Density [gcm <sup>-3</sup> ]         | 1.50   | 1.35   |
| $\mu$ [mm <sup>-1</sup> ]            | 4.99   | 4.36   |
| <i>F</i> (000)                       | 1656   | 748  |
| Crystal size [mm]                    | 0.08 × 0.26 × 0.44   | 0.25 × 0.28 × 0.45   |
| Temperature [K]                      | 293  | 293  |
| $\Theta_{\text{max}}$ [deg]          | 77.00  | 77.50  |
| Radiation                            | CuK $\alpha$ ( $\lambda = 1.54180$ Å)  | CuK $\alpha$ ( $\lambda = 1.54180$ Å)  |
| Scan type                            | $\omega/2\Theta$   | $\omega/2\Theta$   |
| No. of measured refl.                | 7262   | 3366   |
| No. of indep. refl.                  | 5774   | 3083   |
| No. of refl. in ref.                 | 4827   | 2436   |
| No. of variables                     | 426  | 185  |
| Final <i>R</i> value [%]             | 6.93   | 5.74   |
| Final <i>R<sub>w</sub></i> value [%] | 6.63   | 4.69   |
| Weighting scheme                     | <i>Chebyshev</i> <sup>a)</sup>   | <i>Chebyshev</i> <sup>a)</sup>   |

<sup>a)</sup> *Chebyshev* polynomial weighting, see [15].

in the complex with **5** is coordinated by the four N-atoms of the macrocycle and by the S-atom of the thioether in a distorted quadratic pyramidal arrangement. The deviations of the N-atoms from the best plane are  $\pm 0.26$  Å, whereas the central ion is over this plane by 0.32 Å. The structure closely resembles those observed for other tetra-*N*-substituted 1,4,8,11-tetraazacyclotetradecane complexes, the macrocycle being in the *trans-I* configuration [17][18]. Ni–N Bond lengths are in the normal range, and the angles show the amount of distortion (Table 4). Very similar results are obtained from the pentacoordinate structure of the corresponding  $\text{Cu}^{2+}$  complex [Cu(**5**)](ClO<sub>4</sub>)<sub>2</sub>, the two being isomorphous. The deviations of the N-atoms from the best plane are  $\pm 0.27$  Å and again, the metal ion is situated over the plane by 0.27 Å. The only difference between the two complexes is the bond length M(1)–S(1) between the metal ion and the axial ligand: the longer bond in the  $\text{Cu}^{2+}$  complex (2.61 Å) compared to that of the  $\text{Ni}^{2+}$  complex (2.39 Å) is clearly due to the tendency of the  $\text{Cu}^{2+}$  to give *Jahn-Teller* distortions. The weaker axial bond in the  $\text{Cu}^{2+}$  complex is probably responsible for the tendency of solvent molecules to replace the thioether group as discussed above.

The absorption spectrum of [Ni(**6**)](ClO<sub>4</sub>)<sub>2</sub> (Table 3) shows a main band at *ca.* 565 nm, which is solvent-independent in its position but decreases in intensity with increasing solvent polarity, and a second band at 390–410 nm, which moves with the

Table 3. Absorption Spectra ( $\lambda$  in nm and  $\epsilon$  in  $M^{-1}cm^{-1}$ ) of the  $Ni^{2+}$  Complexes with Ligands 4–7 and of the  $Cu^{2+}$  Complexes with Ligands 4, 5, and 7 in Different Solvents

|   | H <sub>2</sub> O                            | MeCN  | DMF   |
|---|---|---|---|
| [Ni(4)](ClO <sub>4</sub> ) <sub>2</sub>               | 344 (1612)<br>390 <sup>a)</sup><br>606 (59) | 344 (900)<br>390 <sup>a)</sup><br>608 (29)  | 344 (755)<br>390 <sup>a)</sup><br>615 (21)  |
| [Cu(4)](ClO <sub>4</sub> ) <sub>2</sub>               | 311 (6787)<br>635 (361)                     | 309 (6260)<br>650 (265)                     | 306 (5923)<br>708 (266)                     |
| [Ni(5)](ClO <sub>4</sub> ) <sub>2</sub>               | 348 (2009)<br>400 <sup>a)</sup><br>614 (73) | 345 (1475)<br>400 <sup>a)</sup><br>613 (54) | 345 (1139)<br>400 <sup>a)</sup><br>616 (37) |
| [Cu(5)](ClO <sub>4</sub> ) <sub>2</sub>               | 314 (6142)<br>645 (454)                     | 307 (2659)<br>670 (132)                     | 307 (5532)<br>708 (249)                     |
| [Ni(6)](ClO <sub>4</sub> ) <sub>2</sub>               | 393 (23)<br>563 (118)                       | 386 (53)<br>568 (83)                        | 411 (66)<br>564 (55)<br>671 <sup>a)</sup>   |
| [Ni(7)](ClO <sub>4</sub> ) <sub>2</sub> <sup>b)</sup> | 351 (852)<br>618 (41)                       | 350 (1593)<br>623 (65)                      | 350 (653)<br>631 (33)                       |
| [Cu(7)](ClO <sub>4</sub> ) <sub>2</sub>               | 314 (5148)<br>645 (381)                     | 312 (5397)<br>379 (3726)<br>655 (488)       | 307 (4160)<br>375 (3938)<br>683 (266)       |

<sup>a)</sup> Shoulder. <sup>b)</sup> Shoulder at *ca.* 390 nm cannot be observed.

Table 4. Selected Bond Lengths [ $\text{\AA}$ ] and Angles [deg] in the Structure of the  $Ni^{2+}$  and  $Cu^{2+}$  Complexes with 5 and of the  $Cu^{2+}$  Complex with 7. Arbitrary numbering.

|           | [Ni(5)] <sup>2+</sup> | [Cu(5)] <sup>2+</sup> | [Cu(7)] <sup>2+</sup> |                | [Ni(5)] <sup>2+</sup> | [Cu(5)] <sup>2+</sup> | [Cu(7)] <sup>2+</sup> |
|-----------|-----------------------|-----------------------|-----------------------|----------------|-----------------------|-----------------------|-----------------------|
| M(1)–N(1) | 2.125(3)              | 2.090(3)              | 2.119(3)              | N(1)–M(1)–N(2) | 94.0(1)               | 94.2(1)               | 94.5(1)               |
| M(1)–N(2) | 2.108(3)              | 2.078(3)              | 2.083(3)              | N(1)–M(1)–N(3) | 176.4(1)              | 179.4(1)              | 179.2(1)              |
| M(1)–N(3) | 2.122(3)              | 2.083(3)              | 2.106(3)              | N(1)–M(1)–N(4) | 84.2(1)               | 85.0(1)               | 85.3(1)               |
| M(1)–N(4) | 2.138(3)              | 2.108(3)              | 2.106(4)              | N(2)–M(1)–N(3) | 85.3(1)               | 85.7(1)               | 85.8(1)               |
| M(1)–S(1) | 2.393(1)              | 2.610(1)              | 2.658(1)              | N(2)–M(1)–N(4) | 148.4(1)              | 150.2(1)              | 151.4(1)              |
|           |                       |                       |                       | N(3)–M(1)–N(4) | 94.6(1)               | 94.8(1)               | 94.8(1)               |
|           |                       |                       |                       | N(1)–M(1)–S(1) | 85.75(9)              | 83.6(1)               | 81.4(1)               |
|           |                       |                       |                       | N(2)–M(1)–S(1) | 110.81(8)             | 108.95(9)             | 101.4(1)              |
|           |                       |                       |                       | N(3)–M(1)–S(1) | 97.77(8)              | 96.99(9)              | 97.8(1)               |
|           |                       |                       |                       | N(4)–M(1)–S(1) | 100.53(9)             | 100.6(1)              | 106.8(1)              |

donor properties of the solvent and increases in intensity with increasing polarity of the solvent. This is similar to previous observations that two species are present [1][16]: a square planar one absorbing around 565 nm and a pentacoordinated one which has bands at 390–410 nm and around 670 nm (observed only in DMF solution). The solvent occupies the axial position in the pentacoordinate species. All this indicates that, in contrast to the structures just discussed, the MeO group of [Ni(6)](ClO<sub>4</sub>)<sub>2</sub> is not coordinated to the metal ion. The square planar coordination geometry with two methoxy-substituted pendant chains not bound to the  $Ni^{2+}$  ion is also confirmed by the X-ray structure of [Ni(6)](ClO<sub>4</sub>)<sub>2</sub> (Fig. 3). The unit cell contains two molecules in the ratio 38:62, the first one (Ni(1)) is well ordered (Fig. 3), whereas the second one (Ni(51)), not

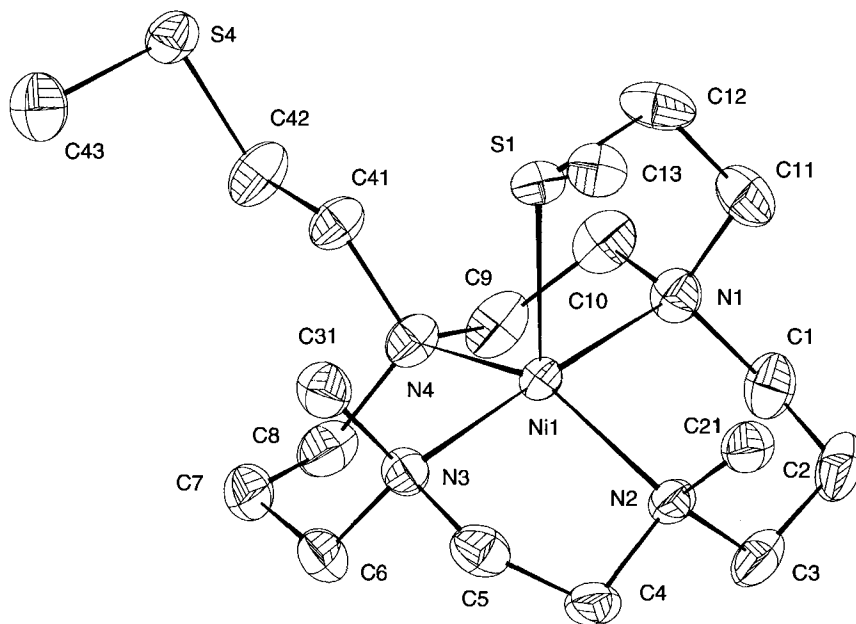


Fig. 1. ORTEP Plot for  $[Ni(5)](ClO_4)_2$ . Arbitrary numbering.

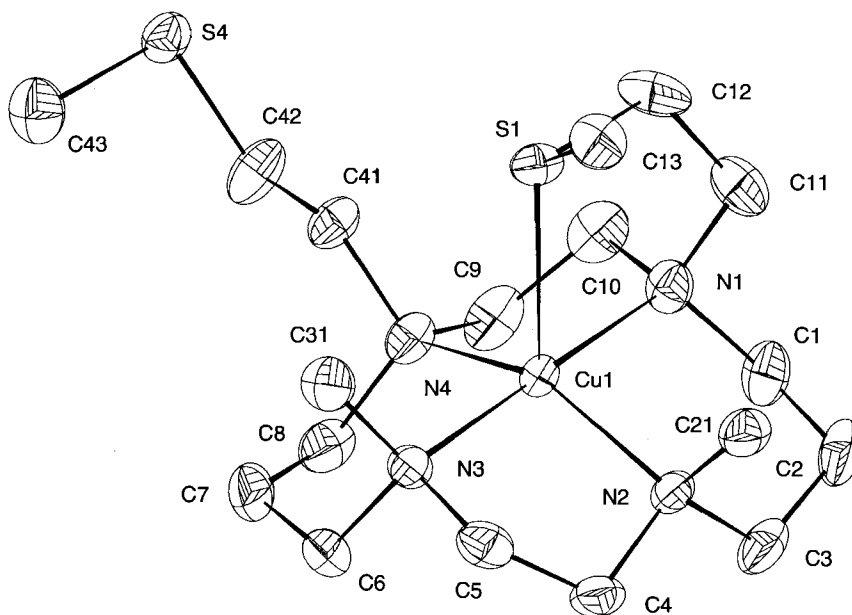


Fig. 2. ORTEP Plot for  $[Cu(5)](ClO_4)_2$ . Arbitrary numbering.

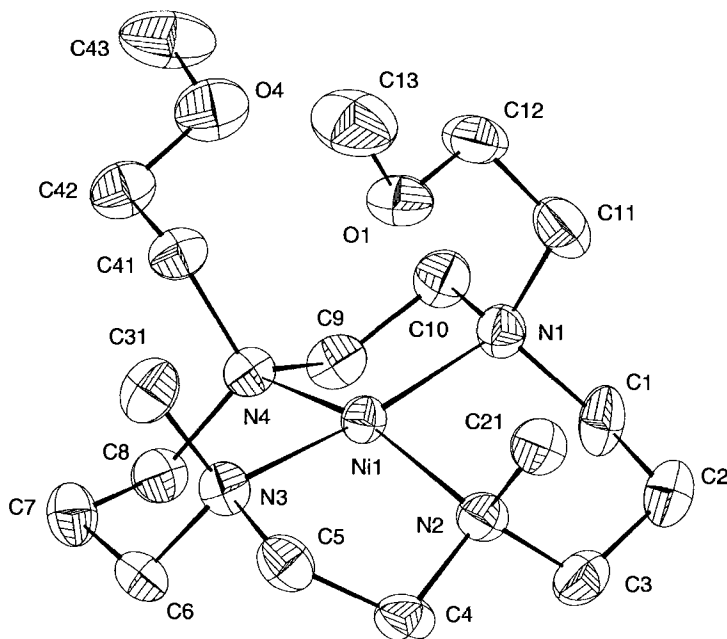


Fig. 3. ORTEP Plot for  $[Ni(6)](ClO_4)_2$ . Arbitrary numbering.

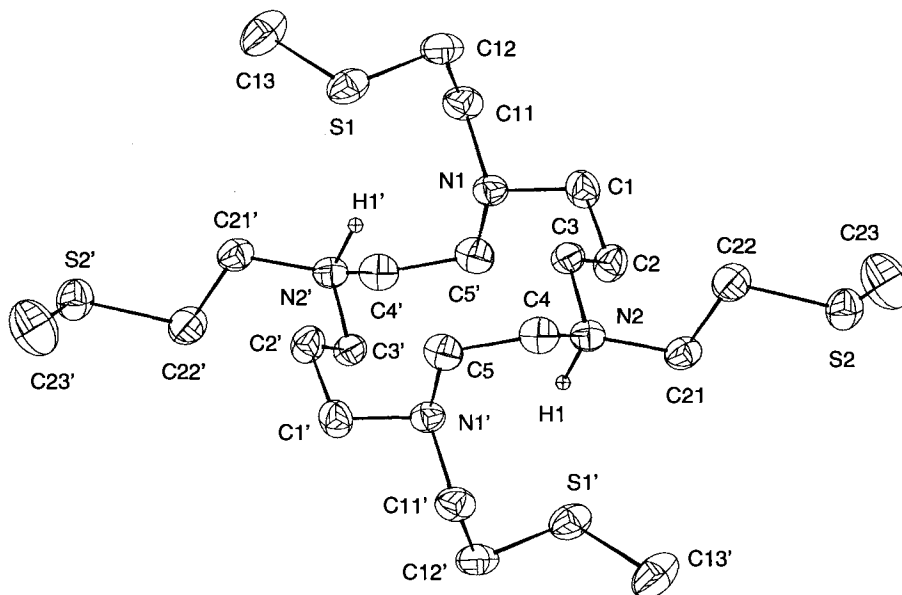
shown) is disordered in one of the side chains. The geometry around the  $Ni^{2+}$  and the configuration of the macrocycle are very similar for both molecules. The  $Ni^{2+}$  ion is coordinated by the four N-atoms of the macrocycle in a tetrahedrally distorted square planar arrangement. The deviations of the N-atoms from the best plane are  $\pm 0.23 \text{ \AA}$ , whereas the central ion is virtually in this plane (0.10 and 0.08  $\text{ \AA}$  for Ni(1) and Ni(51), resp.). The structures of both molecules are similar to those observed for other tetra-*N*-substituted 1,4,8,11-tetraazacyclotetradecane complexes with no axial ligand [17][18]. Ni–N Bond lengths and angles are in the normal range for low-spin square planar  $Ni^{2+}$  complexes (Table 5). The distances between the  $Ni^{2+}$  and the ether O-atoms are all longer than 2.7  $\text{ \AA}$ , which is clearly a nonbonding intramolecular contact.

Table 5. Selected Bond Lengths [ $\text{ \AA}$ ], Nonbonding Intramolecular Contacts [ $\text{ \AA}$ ], and Angles [deg] in the Structure of the  $Ni^{2+}$  Complex with 6. Arbitrary numbering.

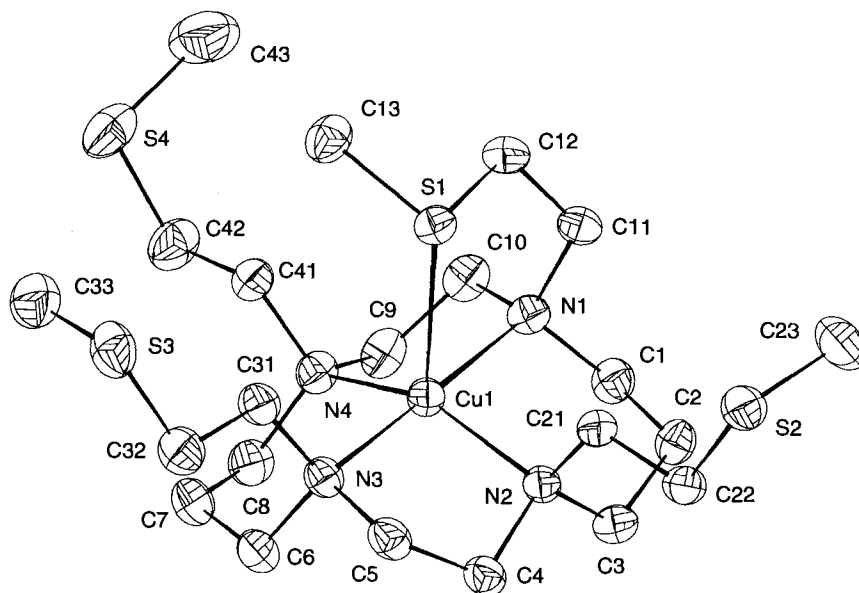
|              |          |                        |          |                    |          |
|--------------|----------|------------------------|----------|--------------------|----------|
| Ni(1)–N(1)   | 2.025(6) | Ni(1) $\cdots$ O(1)    | 2.754(6) | N(1)–Ni(1)–N(2)    | 94.0(3)  |
| Ni(51)–N(51) | 1.989(7) | Ni(1) $\cdots$ O(4)    | 4.775(7) | N(51)–Ni(51)–N(52) | 94.3(4)  |
| Ni(1)–N(2)   | 1.987(6) | Ni(51) $\cdots$ O(51)  | 4.84(2)  | N(1)–Ni(1)–N(3)    | 172.0(3) |
| Ni(51)–N(52) | 2.021(8) | Ni(51) $\cdots$ O(151) | 5.01(1)  | N(51)–Ni(51)–N(53) | 163.3(4) |
| Ni(1)–N(3)   | 2.003(6) | Ni(51) $\cdots$ O(54)  | 2.760(7) | N(1)–Ni(1)–N(4)    | 86.6(2)  |
| Ni(51)–N(53) | 1.962(8) |                        |          | N(51)–Ni(51)–N(54) | 84.6(4)  |
| Ni(1)–N(4)   | 2.001(5) |                        |          | N(2)–Ni(1)–N(3)    | 87.7(3)  |
| Ni(51)–N(54) | 2.004(8) |                        |          | N(52)–Ni(51)–N(53) | 88.1(4)  |
|              |          |                        |          | N(2)–Ni(1)–N(4)    | 162.4(3) |
|              |          |                        |          | N(52)–Ni(51)–N(54) | 171.0(4) |
|              |          |                        |          | N(3)–Ni(1)–N(4)    | 94.1(2)  |
|              |          |                        |          | N(53)–Ni(51)–N(54) | 95.4(4)  |



With ligand **7**, we were able to prepare the Ni<sup>2+</sup> and Cu<sup>2+</sup> complexes in solution. The absorption spectra (*Table 3*) are for both metal ions very similar to those of the corresponding complexes with **4** and **5** so that the same coordination geometries can be expected. In addition to the structural results in solution, the X-ray structure for the doubly protonated ligand **7** · 2H<sup>+</sup> (*Fig. 4*) and for [Cu(**7**)](ClO<sub>4</sub>)<sub>2</sub> were solved (*Fig. 5*).



*Fig. 4. ORTEP Plot for Ligand 7 · 2H<sup>+</sup>. Arbitrary numbering.*



*Fig. 5. ORTEP Plot for [Cu(**7**)](ClO<sub>4</sub>)<sub>2</sub>. Arbitrary numbering.*

The ligand is in the [3434] conformation [17], and the two protons are *trans* to each other at N(2) and N(2)'. A selection of bond lengths and angles for the structure of  $7 \cdot 2H^+$  is given in Table 6. Interesting is the observation that the ammonium protons form internal H-bonds to N(1) and S(1) with bond lengths of 2.215 and 2.463 Å, respectively. The angles N(2)–H(1)–N(1) and N(2)–H(1)–S(1) are 116.3 and 153.7°, respectively. In the  $Cu^{2+}$  complex of 7, the ligand adopts the *trans-I* configuration, and the  $Cu^{2+}$  is pentacoordinated by the four N-atoms of the ring and the S-atom of one side chain. The deviations of the N-atoms from the best plane are  $\pm 0.27$  Å, and the central ion is situated over the plane by 0.25 Å. A selection of bond lengths and bond angles for  $[Cu(7)](ClO_4)_2$  is given in Table 4.

The cyclic voltammetry of the  $Ni^{2+}$  complexes with a methyl-thioether pendant chain (ligands 4, 5, and 7) exhibit a metal ion centered electrode process at potentials between – 0.64 and – 0.77 V, corresponding to the  $Ni^{II}/Ni^I$  redox couple. The characteristics of the voltammetric peaks  $c_1$  and  $a_1$  recorded on GCE and HMDE are given in Table 7. It is interesting to note that increasing the number of methylthio-substituted pendant chains affects the  $Ni^{II}/Ni^I$  electrode process shifting the potential to more positive values. The  $Ni^{II}/Ni^I$  electrode processes fit well to a reversible one-electron transfer scheme similar to that observed for  $[Ni(cyclam)]^{2+}$  (cyclam = 3) [19] or its tetramethylated derivative  $[Ni(tmc)]^{2+}$  (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) [9]. Similarly reversible is the  $Ni^{II}/Ni^I$  process for the tetraazamacrocyclic complex with the methoxy-substituted pendant chain  $[Ni(6)](ClO_4)_2$  (Table 7).

Using a hanging Hg drop electrode (HMDE), and extending the potential to more negative values, two additional peaks  $c_2$  and  $c_3$  (– 1.60 and – 2.35 V vs. SCE) can be observed for the complexes with 4, 5, and 7 (Fig. 6), representing ligand-centered reduc-

Table 6. Selected Bond Lengths [Å] and Angles [deg] in the Structure of Ligand  $7 \cdot 2H^+$ . Arbitrary numbering.

|            |          |                  |          |
|------------|----------|------------------|----------|
| N(1)–C(1)  | 1.462(4) | C(1)–N(1)–C(5')  | 110.3(3) |
| N(1)–C(11) | 1.471(4) | C(1)–N(1)–C(11)  | 109.4(3) |
| N(1)–C(5') | 1.472(4) | C(5')–N(1)–C(11) | 112.6(3) |
| N(2)–C(3)  | 1.499(4) | C(3)–N(2)–C(4)   | 112.3(2) |
| N(2)–C(21) | 1.506(4) | C(3)–N(2)–C(21)  | 114.5(2) |
| N(2)–C(4)  | 1.495(4) | C(4)–N(2)–C(21)  | 112.0(3) |
|            |          | C(3)–N(2)–H(1)   | 104.6(3) |
|            |          | C(21)–N(2)–H(1)  | 108.8(1) |
|            |          | C(4)–N(2)–H(1)   | 103.7(1) |

Table 7. Characteristics of the Voltammetric Studies for the  $Ni^{II}/Ni^I$  Redox Couple in the  $Ni^{2+}$  Complexes with 4–7 (1 mM; 0.1M  $Pr_4N(BF_4)$  in MeCN at 25°)

|                | Hanging Hg drop electrode (HMDE) |           |              |                         | Glassy C electrode (GCE) |           |              |                         |
|----------------|----------------------------------|-----------|--------------|-------------------------|--------------------------|-----------|--------------|-------------------------|
|                | $c_1$ [V]                        | $a_1$ [V] | $E^{o'}$ [V] | $E_{c_1} - E_{a_1}$ [V] | $c_1$ [V]                | $a_1$ [V] | $E^{o'}$ [V] | $E_{c_1} - E_{a_1}$ [V] |
| $[Ni(4)]^{2+}$ | – 0.803                          | – 0.719   | – 0.761      | 0.084                   | – 0.803                  | – 0.711   | – 0.757      | 0.092                   |
| $[Ni(5)]^{2+}$ | –                                | –         | –            | –                       | – 0.762                  | – 0.668   | – 0.715      | 0.094                   |
| $[Ni(6)]^{2+}$ | – 0.799                          | – 0.719   | – 0.759      | 0.080                   | – 0.819                  | – 0.714   | – 0.767      | 0.105                   |
| $[Ni(7)]^{2+}$ | –                                | –         | –            | –                       | – 0.687                  | – 0.593   | – 0.640      | 0.094                   |

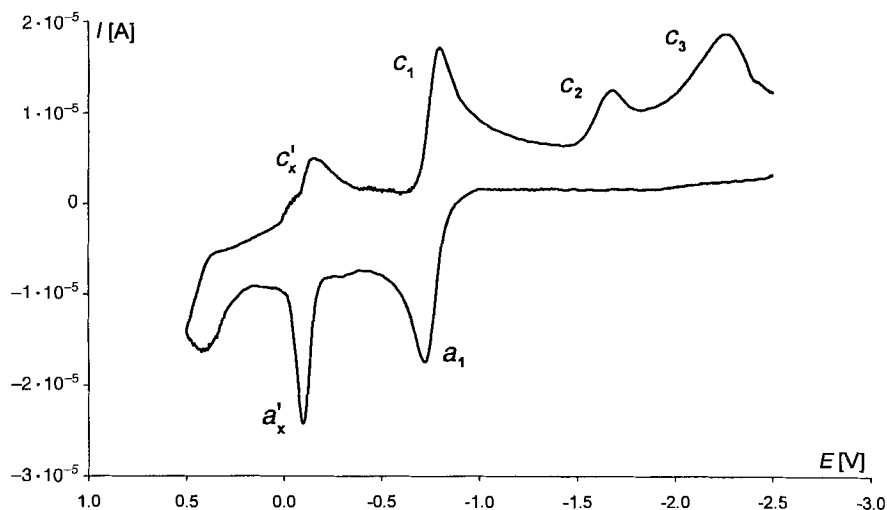


Fig. 6. Cyclic Voltammograms on HMDE for the  $\text{Ni}^{2+}$  complex with **4** (81 mM)

tions. No corresponding anodic signals appear indicating that the products of the reduction undergo further chemical reactions. Both the reduction peak  $c_3$  and the oxidation peak  $a_x'$  are not present when the MeS is replaced by the MeO group. Since reductive cleavage of a MeS can more easily take place than that of a MeO group, this could be responsible for the appearance of peak  $c_3$  at *ca.*  $-2.3$  V vs. SCE. The anodic half-cycle peak  $a_x'$  (which may be ascribed to Hg oxidation in presence of thiolate) appears at *ca.* 0 V, together with the corresponding cathodic peak  $c_x'$  at *ca.*  $-0.2$  V vs. SCE.

In conclusion, we have here a series of tetraazamacrocyclic complexes of which the  $\text{Ni}^{2+}$  ones can be used as models to mimic the properties of F430. In the oxidized  $\text{Ni}^{2+}$  form, the metal ion binds the pendant MeS group so that the two reactive centers are in close contact. In addition, the  $\text{Ni}^{2+}$  can be reduced to  $\text{Ni}^+$  at *ca.*  $-0.8$  V vs. SCE, a value close to that of F430 ( $-0.89$  V [20]), and at more negative potentials, the MeS group is reductively cleaved to give a thiol, which can be detected electrochemically. Although these systems cannot be catalytic, since the substrate is covalently attached to the macrocycle in form of a side chain, they show several aspects and properties of the native system F430.

This work was supported by the *Bundesamt für Bildung und Wissenschaft* through a *COST-D1* grant, and this is gratefully acknowledged. We also thank the *University of Warsaw* for supporting the electrochemical work through grant BST 502.

#### REFERENCES

- [1] C. L. Schmid, C. Kempf, A. Taubert, M. Neuburger, M. Zehnder, Th. A. Kaden, K. Bujno, R. Bilewicz, *Helv. Chim. Acta* **1996**, *79*, 1011.
- [2] Th. A. Kaden, *Topics Curr. Chem.* **1984**, *121*, 157; P. Bernhardt, G. A. Lawrence, *Coord. Chem. Rev.* **1990**, *104*, 297; Th. A. Kaden, in 'Crown Compounds towards Future Application', Ed. S. R. Cooper, VCH Publishers, New York, 1992, p. 135; Th. A. Kaden, in 'Advances in Supramolecular Chemistry', Ed. G. W. Gokel, JAI Press Inc., Greenwich, 1993, Vol. 3, p. 65.

- [3] D. Tschudin, A. Riesen, Th. A. Kaden, *Helv. Chim. Acta* **1989**, 72, 131.
- [4] W. Schibler, Th. A. Kaden, *J. Chem. Soc., Chem. Commun.* **1981**, 603; Th. A. Kaden, D. Tschudin, U. Studer, U. Brunner, *Pure Appl. Chem.* **1989**, 61, 879.
- [5] See, e.g., S. J. Lippard, J. M. Berg, 'Principles of Bioinorganic Chemistry', University Science Books, Mill Valley, 1994; J. Bertini, H. B. Gray, S. J. Lippard, J. S. Valentine, 'Bioinorganic Chemistry', University Science Books, Mill Valley, 1994.
- [6] B. Jaun, *Metal Ions Biol. Syst.* **1993**, 29, 287.
- [7] A. Pfaltz, B. Jaun, A. Fässler, A. Eschenmoser, R. Jeanchen, H. H. Gilles, G. Diekert, R. K. Thauer, *Helv. Chim. Acta* **1982**, 65, 828; A. Fässler, A. Kobelt, A. Pfaltz, A. Eschenmoser, C. Bladen, A. R. Battersby, R. K. Thauer, *ibid.* **1985**, 68, 2287; G. Färber, W. Keller, C. Kratky, B. Jaun, A. Pfaltz, C. Spinner, A. Kobelt, A. Eschenmoser, *ibid.* **1991**, 74, 697.
- [8] B. Jaun, A. Pfaltz, *J. Chem. Soc., Chem. Commun.* **1986**, 1327.
- [9] E. K. Barefield, G. M. Freemann, D. G. Van Derveer, *Inorg. Chem.* **1986**, 25, 552; M. S. Ram, S. Riordan, *J. Am. Chem. Soc.* **1995**, 117, 2365.
- [10] E. K. Barefield, F. Wagner, U. D. Hodges, *Inorg. Chem.* **1976**, 15, 1370; F. Wagner, E. K. Barefield, *ibid.* **1976**, 15, 408.
- [11] E. K. Barefield, F. Wagner, A. W. Herlinger, A. R. Dahl, *Inorg. Synth.* **1976**, 16, 220.
- [12] A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, 27, 435.
- [13] D. Watkin, R. Carruthers, P. Betteridge, 'CRYSTALS', Chemical Crystallography Laboratory, Oxford, 1990.
- [14] 'International Tables for Crystallography', Vol. IV, Table 2.2B, Kynoch Press, Birmingham, 1974.
- [15] J. R. Carruthers, D. J. Watkin, *Acta Crystallogr., Sect. A* **1979**, 35, 698.
- [16] M. Micheloni, P. Paoletti, S. Bürki, Th. A. Kaden, *Helv. Chim. Acta* **1982**, 65, 587.
- [17] J. C. Boyens, S. M. Dobson, in 'Stereochemical and Stereophysical Behaviour of Macrocycles', Ed. I. Bernal, Elsevier, Amsterdam, 1987, Vol. 2, p. 1.
- [18] M. Oberholzer, M. Neuburger, M. Zehner, Th. A. Kaden, *Helv. Chim. Acta* **1995**, 78, 505; T. Hiroshi, *J. Chem. Soc., Chem. Commun.* **1983**, 970; N. W. Alcock, A. Benniston, S. J. Grant, H. A. A. Omar, P. Moore, *ibid.* **1991**, 1573.
- [19] F. Lovecchio, E. S. Gore, D. H. Busch, *J. Am. Chem. Soc.* **1974**, 96, 3109.
- [20] B. Jaun, *Chimia* **1994**, 48, 50.