Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Taraszewska, Joanna , Roslonek, Grzegorz and Korybut-daszkiewicz, Bohdan(2000) 'Redox Properties of Novel Dinuclear Ni(II) Bis - Tetraazamacrocyclic Complex', Supramolecular Chemistry, 12: 1, 115 — 121
To link to this Article: DOI: 10.1080/10610270008029811
URL: http://dx.doi.org/10.1080/10610270008029811

SUPRAMOLECULAR CHEMISTRY, Vol. 12, pp. 115-121
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the Harwood Academic Publishers imprint,
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Printed in Malaysia

Redox Properties of Novel Dinuclear Ni(II) Bis - Tetraazamacrocyclic Complex

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Dinuclear Ni(II) bis-tetraazamacrocyclic complex **1** with conjugated double bonds at deprotonated β-diimine linking group was characterized by ^{1}H NMR and cyclic voltammetry. Electrochemical studies indicated high stability of the mixed-valence (Ni^{II}-Ni^{III}) and (Ni^{II}- Ni^{I}) species, respectively. The main factor contributing to the stabilization of the mixed-valence states is the electronic delocalization through the system of the conjugated double bonds at the deprotonated β-diimine linking group. Complex **1** is the first example of dinuclear Ni(II) tetraazamacrocyclic complex exhibiting two one-electron oxidation and two one electron reduction steps.

Keywords: Tetraazamacrocyclic complex, Dinuclear Ni(II) complex, Cyclic voltammetry, Comproportionation constants

INTRODUCTION

Creation of molecules containing spatially separated reactive metal centers is one of the most developing areas of modern inorganic chemistry. Such compounds attract much attention because they allow to study the nature and extent of metal-metal communication,[1] may play a significant role in catalytic processes,[2–4] and serve as models of metalloenzymes.[5] To such compounds belong dinuclear transition metal complexes with macrocyclic polyamines. These complexes possess very high thermodynamic stability, kinetic inertness, and the ability to change easily the oxidation state of the coordinated metal ions.

The redox behavior of Ni(II)/Ni(III) species in dinuclear nickel complexes with amine ligands was studied in complexes consisting of two macrocyclic subunits connected by polymethylene or xylene bridges in which each subunit binds one metal ion[6–9] or by anionic bridging ligand (oxalate) which is able to join two independently coordinating subunits formed by amines.[10,11] Recently such behavior has been studied in $[Ni_2(6,6'\text{-spirobi(cyclam)})]^{4+}$ where (cyclam= 1,4,8,11-tetraazacyclotetradecane).[12] The redox behavior in such complexes is controlled by the ability of the ligand to adopt to the coordination geometry changes, the nature of the bridging ligand, and the distance between metal centers.

Synthesis of a new type of dinuclear nickel bis-tetraazamacrocyclic complex **1** has been recently reported.[13] The schematic structure of the complex, presented in Fig. 1, was established on the basis of the elemental analysis and ^{1}H and ^{13}C NMR spectra in nitromethane. The ^{1}H NMR spectrum of complex **1** indicated the presence of plane of the symmetry in the molecule and consisted of signals characteristic for macrocyclic units as well as the 1H singlet at δ 5.10 and the

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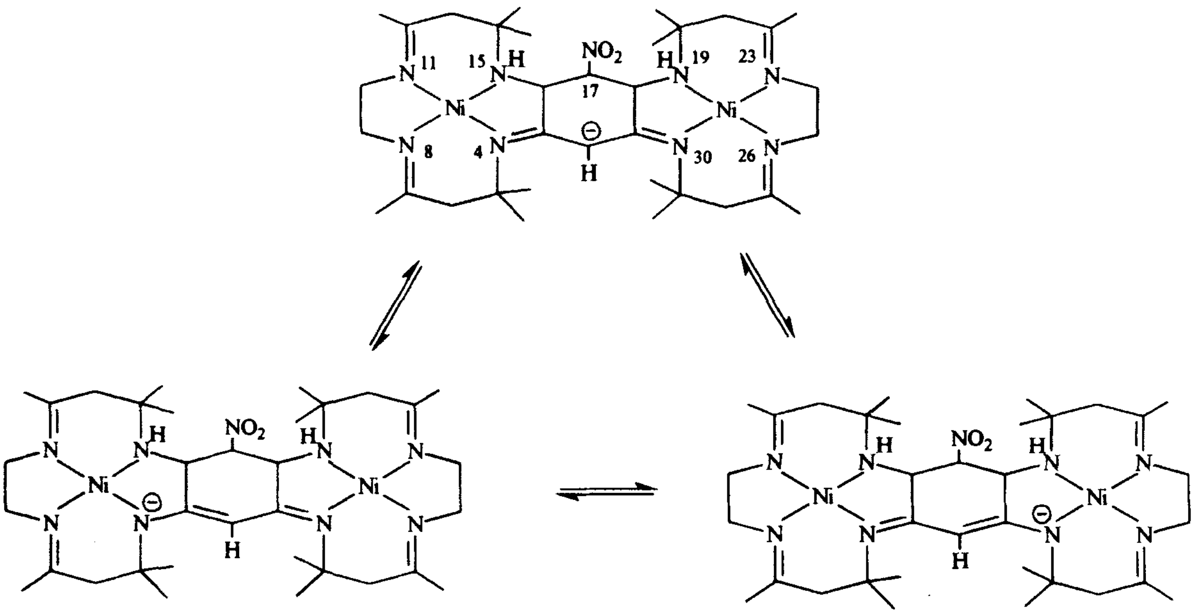

FIGURE 1 Schematic structure of complex **1**

1H triplet at δ 5.28 originating from =CH- and >CH-NO_2 linking groups, respectively. In such type of complex one can expect pronounced metal-metal electronic exchange due to the presence of the conjugated double bonds of deprotonated β-diimine linking group.

The aim of the present paper was the confirmation of the structure of complex **1** in acetonitrile (ACN) and dimethylsulfoxide (DMSO) solutions as well as the study of the redox properties of the metal ions.

RESULTS AND DISCUSSION

Structure and spectral characteristics

The preliminary X-ray analysis[14] of complex **1** revealed that the ligand is built of two tetraazamacrocycles joined by two one atom C linkers, thus forming a six membered ring between the macrocyclic unites. The deprotonated carbon atom and two neighboring imine bonds of macrocycle form a conjugated chain between the coordinated nickel(II) ions. The second linking carbon atom is substituted with a nitro group which adopts an axial conformation. The oxygen atoms are pointing towards Ni(II) ions however, the distances between them are about 3.5 Å. Complex **1** has a slightly distorted C_s symmetry with the plane of symmetry perpendicular to the central six membered ring and passing through two central carbon atoms and the nitro group nitrogen atom. Two nickel(II) ions are separated by 7.60 Å, and adopt a square-planar configuration inside of the macrocyclic rings. The macrocyclic unites are bend towards the central nitro group with two NiN_4 planes forming the dihedral angle of 142°.

The NMR spectra (Table I) evidence, that in nitromethane and ACN solutions the main futures of the complex structure are preserved. The number of NMR signals and their relative intensities are consistant with a C_s symmetry of the cation. The ligand is deprotonated since only a single proton is attached to the central (C-2) carbon atom linking the macrocyclic unites. Small vicinal coupling constant (1.6 Hz) of the nitromethine proton (17-H) to protons attached to the neighboring carbon atoms (16-CH and 18-CH) indicates that the dihedral angle between them is close to 90°. In DMSO solution, a substantial broadening of signals oryginating from the central six-membered ring protons occurs. This might be caused by a slow exchange of the activated by the nitro group proton attached to C-17 carbon atom.

TABLE I 125.8 MHz ^{13}C and 500 MHz ^1H NMR data for complex **1** in different solvents (δ in ppm relative to TMS, J in Hz)

Solvent Assignment[a]	CD_3NO_2 $\delta^{13}C/\delta^1H^{b\ c}$	CD_3CN $\delta^{13}C/\delta^1H^{b\ c}$	$(CD_3)_2SO$ $\delta^{13}C/\delta^1H^{c}$
7,27- and 12,22-CH_3	23.5, 24.0	23.6, 24.2	22.4, 23.3
	2.15s, 2.31s	2.02s, 2.17s	2.11s, 2.25s
14,20-CH_3 *eq*	25.7	25.4	23.4
	1.38bs	1.26bs	1.17bs
14,20-CH_3 *ax*	25.8	25.9	25.4
	2.36vbs	2.28vbs	2.22vbs
5,29-CH_3	23.7, 26.3	23.8, 26.2	22.6, 25.5
	1.17s, 1.39s	1.06s, 1.29s	1.01s, 1.29s
13,21-CH_2	59.1	58.6	57.0
	2.87d, 3.02d;	2.75d, 2.89d;	2.78d, 2.89d;
	J=14.8	J=14.8	J=14.8
6,28-CH_2	53.4	52.9	51.6
	3.05d, 3.07d;	2.92d, 2.96d;	2.99d, 3.01d;
	J=20.0	J=20.0	J=20.0
9,25-CH_2	54.5	54.2	53.0
	3.72m, 4.04m	3.62m, 3.88m	3.68m, 3.90m
10,24-CH_2	55.6	55.2	53.9
	3.39m, 3.59m	3.22m, 3.45m	3.25m, 3.56m
16, 18-CH	63.9	63.4	61.9
	4.61b	4.45bd, J= 4.5	4.77b
17-CH^d	85.0	84.5	84.6
	5.29t, J=1.6	5.10t, J=1.6	5.07b
2-CH^d	95.0	94.1	91.4
	5.10s	4.92s	4.77s
5,29-C and 14,20-C	56.0, 58.6	55.5, 58.2	54.0, 56.7
1,3-C=N	169.8	169.6	169.2
7,27- and 12,22-C=N	183.9, 184.0	183.2, 183.3	181.7, 182.2
15,19-NH	4.46d, J=6	4.37d, J=4.5	5.26d, J=5.9

a. IUPAC systematic numbering was used: 5,5,7,12,14,14,20,20,22,27,29,29,-dodecamethyl- 17-nitro-4,8,11,15,19,23,26,30-octa-azatricyclo[16,12,0,$0^{3,16}$]tri-aconta-1(30),3,7,11,22,26-hexaen-2-ato-κ^8N] dinickel(II) triperchlorate.

b. assignments were made and confirmed using reported shift data and 2D ^1H – ^{13}C correlation experiments.

c. s-singlet, d – doublet, t – triplet, m – multiplet, vb – very broad, b -broad.

d. C-H groups laying on the plane of symmetry, relative intensity of signals =1/2.

TABLE II Electrochemical parameters (vs. MCE and Fc) and comproportionation constans for complex **1** in ACN, DMF and DMSO containing 0.1 mol dm^{-3} TEAP

Ni$_2$(I,II)/ Ni$_2$(I,I)					*Ni$_2$(II,III)/Ni$_2$(III,III)*			
E_{f1} (V)	E_{f2} (V)	E_{f2}-E_{f1} (V)	K_{com} x10^{-4}		E_{f1} (V)	E_{f2} (V)	E_{f2}-E_{f1} (V)	K_{com} x10^{-4}
-1.465^a	-1.755				1.190^a	1.430		
-1.790^b	-2.080	0.290	8.0	**ACN**	0.865^b	1.105	0.240	1.0
$(100)^c$	(90)				$(60)^c$	(140)		
-1.400^a	-1.690				1.065^a	1.330		
-1.830^b	-2.180	0.290	8.0	**DMF**	0.635^b	900	0.265	3.0
$(90)^c$	(80)				$(150)^c$	(100)		
-1.415^a	-1.680				–	–	–	–
-1.800^b	-2.065	0.310	17.0	**DMSO**				
$(80)^c$	(90)							

a. Potentials measured vs. MCE.
b. Potentials measured vs. Fc.
c. The separations of anodic and cathodic peaks (in mV).

Electrochemical properties of complex 1

The electrochemical properties of complex **1** were studied in ACN containing 0.1 mol dm^{-3} tetraethylammonium perchlorate (TEAP) as supporting electrolyte and 1x10^{-3} mol dm^{-3} of the complex. The cyclic voltammetric (C.V.) curves recorded at scan rate of 0.05V / s are presented in Fig. 2. Two consecutive one – electron redox processes are seen in the positive as well as in negative potential range. In the positive potential range (Fig. 2A) the anodic process, a′, at less positive potential is connected with the oxidation of one of the metal (II) center leading to the mixed-valence (Ni^{II} – Ni^{III}) product. The second anodic process, a″, is ascribed to the one-electron oxidation of the another Ni(II) ion in the mixed-valence complex with formation of the (Ni^{III} – Ni^{III}) species. The first process is reversible and the second one practically irreversible. The formal potentials E_{f1} and E_{f2} calculated as midpoints between anodic and cathodic peaks and the separations between them are collected in Table II.

In the negative potential range (Fig. 2B) the cathodic process, c′, at less negative potential is connected with the reduction of one of the metal (II) center leading to the mixed-valence (Ni^{I} – Ni^{II}) product. The second cathodic process, c″, is ascribed to the one-electron reduction of the another Ni(II) ion in the mixed-valence complex with formation of the (Ni^{I} – Ni^{I}) species. Both transformations are quasi-reversible. The formal potentials E_{f1} and E_{f2} and the separations between them are collected in Table II. In the negative potential range is also seen an irreversible cathodic peak at a potential of ca. –1V. It is connected with the one-electron reduction of the -NO_2 group situated at the unit linking the two tetraazamacrocyclic units. This process seems to have no effect on the redox processes of Ni(II) because even after prolonged potential cycling the positions of all redox peaks were unchanged.

The redox behavior of complex **1** was also studied in DMF and DMSO both containing 0.1 mol dm^{-3} TEAP. In DMF the redox behavior was similar to that in ACN however, in the positive

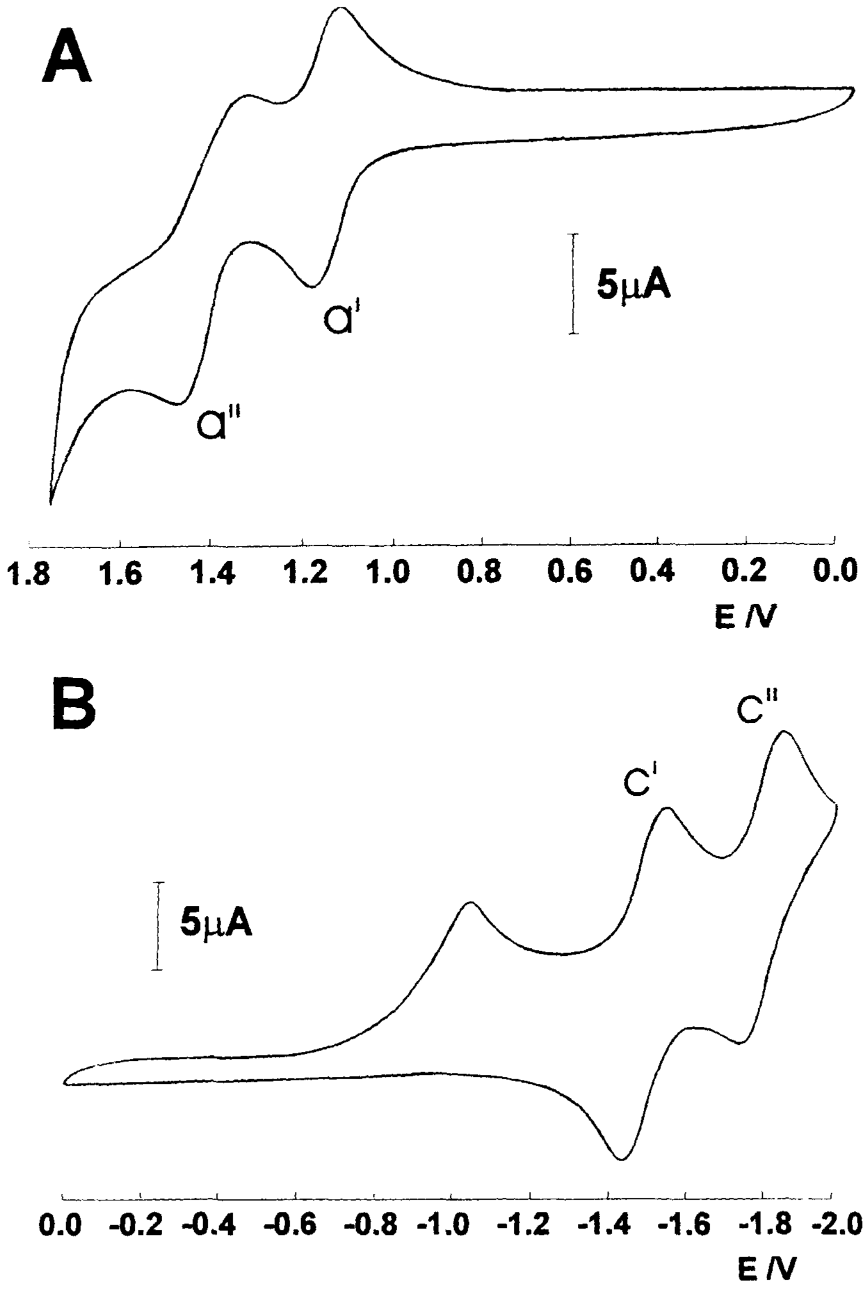

FIGURE 2 Cyclic voltammograms of 1×10^{-3} mol dm^{-3} complex 1 at a GC electrode in ACN containing 0.1 mol dm^{-3} TEAP. Scan rate 0.05Vs^{-1}; (A) anodic potential range, (B) cathodic potential range

potential range the first process showed poorer reversibility, and the second one better reversibility than in ACN. In DMSO we observed the formation of the mixed-valence complexes in the negative potential range however, in the positive potential range it was difficult to record two separeted pairs of peaks. In this case the axial coordination of the metal center by DMSO may be difficult due to the steric reasons, therefore Ni(III) can not be formed.

Under our experimental conditions potentials of ferrocene (Fc) redox system vs. 1MCE were 0.326V, 0.430V and 0.387V in ACN, DMF and DMSO, respectively. Expression of the formal potentials vs. this internal reference system (Table II) indicates that the kind of solvent has small influence on the redox processes connected with formation of Ni(I), and essential influence on the redox processes connected with formation of Ni(III). A significant shift of the first and second redox process toward less positive values with increasing solvent donor number is connected with stronger solvation of highly charged cations.

According to our knowledge complex **1** is the first example of the dinuclear tetraazamacrocyclic Ni(II) complex exhibiting two consecutive one-electron redox processes in the positive as well as in the negative potential range with formation of the mixed-valevce Ni^{II}- Ni^{III} and Ni^{I}-Ni^{II} species, respectively.

Such behavior has been reported by Mandal et al.[15] for dicopper (II) complexes with fully saturated macrocycles in which two copper (II) centers were bridged by two phenolic oxygens with two secondary amine nitrogen donors completing the distorted CuN_2O_4 planes. However, in these complexes two one-electron oxidation steps were recorded in ACN and two one-electron reduction steps in DMSO, respectively.

Comproportionation equilibria

The equilibrium constants K_{com}. associated with the comproportionation processes

$$[Ni^{II}-Ni^{II}]^{3+} + [Ni^{III}-Ni^{III}]^{5+} \Longleftrightarrow 2[Ni^{II}-Ni^{III}]^{4+} \tag{1}$$

and

$$[Ni^{II}-Ni^{II}]^{3+} + [Ni^{I}-Ni^{I}]^{+} \Longleftrightarrow 2[Ni^{I}-Ni^{II}]^{2+} \tag{2}$$

were estimated from the equation

$$K_{com.} = \exp[(E_{f2}-E_{f1})F/RT] \tag{3}$$

where E_{f1} and E_{f2} are the potentials related to the first and the second redox steps in each process (Table II).

The values of K_{com}. for both processes are included in Table II. The presented data reveal high stability of the mixed-valence states $[Ni^{II}-Ni^{III}]$ and $[Ni^{II}-Ni^{I}]$ relative to the isovalent ones.

Due to the large distance between the two metal centers (more than 7 Å) the contribution to the K_{com}. of the electrostatic factor arising from repulsion of the similarly charged metal centers may be neglected. We assume that the main factor contributing to the stabilization of the mixed valence states is the electronic delocalisation through the system of the conjugated double bonds at the deprotonated β-diimine linking group. Stability of the $[Ni^{I}-Ni^{II}]$ and $[Ni^{I}-Ni^{I}]$ species can be additionally enhanced by the C=N groups present in the macrocycle. An enhancement of the stability of copper(I) and the destabilization of copper(III) mixed-valence species with stepwise increase of the ligand unsaturation has been observed by Mandal et al.[15]. Also Okawa et al.[16] for similar dinuclear nickel complexes with full unsaturation of the azomethine centers observed successive reversible reduction of Ni(II) but no redox waves connected with oxidation to Ni(III). The reason of this behavior[16,17] is that the unsaturated macrocycle can accept electrons from Cu(I) or Ni(I) through the antibonding orbital of the C=N linkages wheras the saturated macrocycle acts solely as electron donor. This can explain the higher values of K_{com}. obtained by us for mixed-valence $[Ni^{I}-Ni^{II}]$ species than for $[Ni^{II}-Ni^{III}]$ ones.

Lack of unsaturation in up to now studied dinuclear tetraazamacrocyclic Ni(II) complexes may be the reason that they stabilized only higher oxidation states of Ni(II) and lower oxidation states could not be reached.

MATERIALS AND METHODS

Materials

All chemicals were Merck p.a. grade reagents. The solvents used were drided and purified according to literature procedures[18].

Electrochemistry

The CV experiments were carried out in three-electrode system at 20±0.5°C. A glassy carbon (GC-30) electrode (Tokai Carbon Co., Japan) sealed in a Teflon tube was used as the working electrode. The counter electrode was a platinum plate. A 1M aqueous NaCl calomel electrode was used as the reference electrode. It was connected to the electrolytic cell via an intermediate vessel, filled with the solution under investigation. The GC electrode prior to use was polished with 0.3μm. alumina slurry on Buehler (Chicago, Il., USA) polishing cloth to a mirror-like surface. Solutions were deaerated by pure and dry argon. During the measurements, the gas was passed over the solution.

The CV curves were recorded using a measuring system consisting of an EP-20A potentiostat, an EG-20 function generator (both produced by ELPAN, Poland) and an x-y recorder.

NMR spectra

The 500 MHz ^{1}H NMR and 125.8 MHz ^{13}C NMR spectra were recorded on a Bruker AM 500 spectrometer at room temperature. Spectra were acquired using 90^0 flip angle pulses and 32K data points to achieve a digital resolution of 0.3Hz (or 0.0006 ppm) per point. An internal standard TMS was used.

Acknowledgements

We thank prof. J. Lipkowski for preliminary X-ray data of complex **1**.

References

1. Vigato, P.A., Tamburini, S. and Fenton, D.E. (1990). Coord. Chem. Rev., **106**, 25.
2. Collin, J.-P., Jouaiti, A. and Sauvage, J.-P. (1988). Inorg. Chem., **27**, 1986.
3. Mochizuki, K, Goto, H., Suwabe, M. and Sakakibara, T. (1991). Bull. Chem. Soc. Jpn., **64**, 1750.
4. Mochizuki, K., Manaka, S., Takeda, J. and Kondo, T. (1996). Inorg. Chem., **35**, 5132.
5. Fenton, D.H. and Okawa, H. (1993). In Perspectives on Bioinorganic Chemistry, Hay, R.W., Dilworth, J.R. and Nolan, K.B. (Eds.), JAI Press, London, **2**, p. 81.
6. Ciampolini, M., Fabbrizzi, L., Perotti, A., Poggi, A., Seghi, B. and Zanobini, F. (1987). Inorg. Chem., **26**. 3527.
7. De Santis, G., Fabbrizzi, L., Licchelli, M. and Pallavicini, P. (1992). Coord. Chem. Rev., **120**, 237.
8. Kaden, Th. A. (1994). In Transition Metals in Supramolecular Chemistry., Fabbrizzi, L. and Poggi, A. (Eds.), Kluver Academic Publishers, NATO ASI Series, p. 211.
9. Rosokha, S.V., Lampeka, Y.D. and Maloshtan, I.M. (1993). J. Chem. Soc. Dalton Trans., 631.
10. Battaglia, L.P., Bianchi, A., Bonamartini Corradi, A., Garcia-Espana, E., Micheloni, M. and Julve, M. (1988). Inorg. Chem., **27**, 4174.
11. Taraszewska, J., Rostonek, G., Lampeka, Y.D. and Maloshtan, I.M., J. (1998). J. Electroanal. Chem., **452**, 49.
12. Mc Auley, A. and Subramanian, S. (1997). Inorg. Chem., **36**, 5376.
13. Korybut-Daszkiewicz, B. (1992). J. Coord. Chem., **27**, 219.
14. Lipkowski, J. private communication.
15. Mandal, S.K., Thomson, L.K., Nag, K,, Charland, J-P. and Gabe, E.J., (1987). Inorg. Chem., **26**, 1391.
16. Okawa, H., Aratake, Y., Motoda, K-I., Ohba, M., Sakiyama, H. and Matsumoto, N. (1996). Supramol. Chem., **6**, 293.
17. Okawa, H., Tadokoro, M., Aratake, Y., Ohba, M., Shindo, K, Mitsumi, M., Koikawa, M., Tomono, M. and Fenton, D.E. (1993). J. Chem. Soc. Dalton Trans., 253.
18. Mann, C.K. (1969). in Electroanalytical Chemistry, Bard, A.J. (Ed.), Marcel Dekker, New York, p. 57.