Synthesis and Characterization of Bis(5,6-dihydro-1,4-dithiin-2,3-dithiolato) nickel(II), nickel(III) and of Related Dialkyl Nickel(II) Dithiolene Complexes

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The reaction between Ni(II) and sodium salt of 5,6-dihydro-1,4-dithiin-2,3-dithiolate (DDDT^2) in the presence of oxygen results in the formation of Ni(III) species, Ni(DDDT)$_2^-$, which is isolated as tetraalkylammonium salt. The same reaction performed in the absence of oxygen yields dianionic Ni(II) species, Ni(DDDT)$_2^{2-}$, which is also isolated as the tetraethylammonium salt. The bis(5,6-dihydro-1,4-dithiin-2,3-dithiolato) nickelate (II) dianion, Ni(DDDT)$_2^2$, reacts with methyl iodide to yield unusually stable bis(methylthio)dithiolene complex, Ni(CH$_3$)$_2$C$_8$H$_8$S$_8$. All the isolated dithiolato-nickel(II) and nickel(III) complexes are characterized by ^{1}H NMR, UV/Vis, IR and mass spectroscopic methods. The internal redox reaction of the nickel(II)- dithiolate has been studied by spectro-electrochemical method and the results were compared with those of other metal-dithiolenes. The alkylated nickel(dithiolene) complex presumably undergoes cis-trans isomerization reaction in solution, judging from the experimental results of variable-temperature ^{1}H NMR measurements.

Introduction

The coordination chemistry of transition-metal dithiolenes has been an area of great interest for a number of years[1] and some molecular superconductors[2,3] based on dithiolene complexes have been reported. The superconductivity observed in BEDT-TTF (BEDT-TTF=bis(ethylenedithiolo) tetrathiafulvalene) compound led to the proposal by Wudl in 1984 that tetrathioethylene unit is the key structural feature that allows for the conduction of electron. BEDT-TTF contains three of these units and bis(dithiolene) complexes of metal ions had been considered as possible candidates for counter ions in molecular solids.[4-7] The ligand, 5,6-dihydro-1,4-dithiin-2,3-dithiolate(DDDT^2-), contains the tetrathioethylene unit and is an ethylene-1,2-dithiolene where the R groups are -CH$_2$CH$_2$- fragments that form a six membered ring. Square planar transition metal complexes of this ligand were suspected to have similar structural characteristics to BEDT-TTF, the only difference being replacement of the C=C bond with a metal atom.
5,6-dihydro-1,4-dithiin-2,3-dithiolate (DDDT^2)
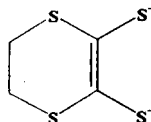
5,6-dihydro-1,4-dithiin-2,3-dithiolate (DDDT^{2-})

With a relevance of the conducting properties for transition metal-dithiolene complexes, we tried to synthesize new Ni(II)-dithiolene complexes. Bereman[7] et al. previously reported that the reaction of Ni(II) and DDDT^2 yielded an oxidized Ni(III)-DDDT complex and they could not obtain Ni(II)-DDDT complex. The oxidant for Ni(II)-DDDT reaction is dioxygen disolved in solvent and we have succeeded in an isolation of Ni(II)- DDDT complex in anaerobic condition and we have investigated the redox properties of Ni

(II)-dithiolate complexes. The electronic and electrochemical property of neutral bis(methylthio)dithiolene Ni(II) complex has been also investigated and compared with those of Schrauzer's results,[11,13] and we also characterized the alkylated neutral Ni(II) species of [Ni(DDDT)$_2$]$^{2-}$ complex by an NMR technique.

Experimental Section

Preparation

2,5,7,9-Tetrathiabicyclo[4,3,0] non-1(6)-en-8-thione (TTBET), was prepared by literature methods[15] and characterized by NMR and mass spectroscopic data. Tetraethylammonium bromide was purchased from Fluka Co., recrystallized from ethanol, and dried in vacuo at 140 °C prior to use. Nickel(II) chloride hexahydrate was purchased from Fisher Scientific Co., and was used without further purification. Methyl iodide was purchased from Fluka Co.. All solvents were dried over Na/benzophenone and was distilled. Methanol was dried over calcium hydride and distilled prior to use. All reactions were carried out under argon with standard Schelenk techniques unless otherwise stated.

Sodium salt of 5,6-dihydro-1,4-dithiin-2,3-dithiolate, Na$_2$(DDDT) was prepared by literature mothods.[5] Yellow-orange precipitates formed immediately was collected, washed with deaerated THF (2 mL), and stored in a Schelenk tube until use. Because it is extremely unstable in air, elemental analysis of Na$_2$DDDT were not made. The Na$_2$ DDDT is, however, fairly stable in alcoholic solution.

[Et$_4$N][Ni(DDDT)$_2$]. This complex was synthesized by literature method.[7] A solution of 2.0 mmol of NiCl$_2\cdot$6H$_2$O in 50 mL of methanol was added dropwise to 0.9 g (4.0 mmol) of Na$_2$DDDT in 100 mL of methanol. The color of the solution changed from amber to dark green as the reaction proceeded. The solution was stirred for 1 hour, after which 1 equivalent of tetraethylammonium bromide was added, and dark green precipitates formed. The dark-green

solid was filtered, and recrystallized from the acetonitrile solution, and obtained as dark-green plated crystals. mp 176 °C ($\pm$1 °C): IR (KBr) 1475(m), 1415(m), 1345(s), 1284(s), 1166(s), 1130(m), 1045(m), 1008(m), 920(m), 885(m), 855(s), 776(m), 475(m), 410(m) cm^{-1}: mass spectrum; parent ion peak at m/e, 418.

Anal. Calcd for $NiC_{16}H_{28}NS_8$: C, 34.97; H, 5.14; N, 2.55; S, 46.69. Found: C, 35.15; H, 5.50; N, 2.53; S, 47.50.

[Et$_4$N]$_2$[Ni(DDDT)$_2$]. Under an argon atmosphere and with the use of standard Schlenk techniques, 0.5 g (2.21 mmol) of Na$_2$DDDT and 0.26 g (1.09 mmol) of $NiCl_2 \cdot 6H_2O$ was dissolved in deaerated methanol. The mixture was stirred for 1 hour until the solution turned to dark purple. After the solution was filtered off, 0.464 g (2.21 mmol) of tetraethylammonium bromide in 20 mL of methanol solution was added to the filtrate. The mixture was stirred for 1 hour and then filtered in the Schlenk filtering funnel, and dried with argon gas stream. The purple crude precipitates could not be recrystallized because of extremely oxygen-sensitive property of this compound in solution.

Anal. Calcd. for $NiC_{24}H_{48}N_2S_8$: C, 42.42; H, 7.06; N, 4.12; S, 37.75. Found: C, 43.02; H, 6.21; N, 4.65; S, 34.72.

Ni[(CH$_3$)S$_8$H$_8$C$_8$]. The alkylated nickel(dithiolene) complex was prepared in two different ways:

(a) Reduction of Ni(DDDT)$_2^-$ followed by alkylation; this process was performed by modifying known method. A solution of 0.26 g (1.09 mmol) of $NiCl_2 \cdot 6H_2O$ in 30 mL of methanol was added dropwise to 0.5 g (2.21 mmol) of Na$_2$-DDDT dissolved in 40 mL of methanol. The color of the solution was changed from amber to dark-green as the reaction proceeded.

The solution was stirred for 1 hour, and filtered. The dark green filtrate, $Ni^{III}(DDDT)_2^-$, was reduced by following processes; under an argon atmosphere and with the use of standard Schlenk techniques, the 5 mL of 50%(wt) of NaOH aqueous solution was added to the dark green filtrate, and 0.042 g of NaBH$_4$ was added to the solution with heating to ca. 50 °C for several hours, during which color of the solution was changed from green to brownish-purple. To this solution, methyl iodide (0.15 mL, slight excess over stoichiometric amount) was added. Purple complexes of the methyl derivative were precipitated after standing overnight under argon atmosphere. The reaction mixture was filtered, washed with cold methanol and dried over vacuum. The crude precipitate was recrystallized from methylene chloride solution, affording dark purple complexes.

(b) Direct alkylation of Ni(DDDT)$_2^{2-}$; the preparation was carried out under on argon atmosphere in the Schlenk system. The solvent was sufficiently deaerated before use. The color of the solution was changed from amber to dark purple as the reaction proceeded. The mixture was stirred for 2 hours, and then the purple mixture was filtered under argon atmosphere. The filtrate was bubbled with dry argon gas, and 0.22 mL (3.7 mmol) of methyl iodide was added dropwise with a syringe. After 2 hours, the dark purple products precipitated were filtered, washed with cold methanol, and dried over vacuum. The crude products were recrystallized from methylene chloride solution, affording 0.41 g (49.4%) of dark purple crystals. The product was identified by mass spectroscopy, elemental analysis, and was found to be the same product as it was prepared by method (a); mass

spectrum (FAB method): parent ion at m/e 447, mp 110 °C (dec), Anal. Calcd. for $Ni(CH_3)_2C_8H_8S_8$: C, 26.73; H, 3.12; S, 57.09, Found: C, 26.39; H, 2.98; S, 56.81, ^{1}H NMR (CD$_2$Cl$_2$): at +50 °C (coalescence at 0 °C, 3.13-3.23, 3.02(SCH$_2$CH$_2$S), 2.52 ppm (CH$_3$).

Physical Measurement

IR spectra were obtained from KBr pellets on a Polaris FT-IR spectrophotometer over the range of 4,000-400 cm^{-1}. UV/Vis spectra were recorded on a Shimadzu UV-265 spectrophotometer and near-IR spectra were recorded on a Cary 17D spectrophotometer. The ^{1}H NMR spectra were recorded at various temperature by using a Brucker AM-300 spectrometer (200 MHz). Mass spectra were recorded on a JMS-DX300 mass spectrometer (Jeol Co.). Electrochemical measurements were performed by the use of Potentiostat/Galvanostat Model 273 of EG & G PAR. The voltammograms were recorded with X-Y recorder (Model BD 90 fro Kipp & Zonen). Cyclic voltammetric measurements were made with a three electrode system. The reference electrode was a Ag/AgCl electrode The working electrode used for cyclic voltammetry was a platinum electrode, and auxilary electrode was a small piece of platinum wire. The solutions used for all techniques consisted of 0.1 M tetraethylammonium perchlorate as the supporting electrolyte in N,N-dimethylformamide and/or acetonitrile (spectro-quality grade) with metal complex concentration of 10^{-3}-10^{-4} M. All test solutions were thoroughly degassed with nitrogen saturated with DMF and/or acetonitrile and continuous streams of nitrogen were passed over the solutions while measurements were being taken. The working electrode used for controlled potential electrolysis was a cylindrical platinum-mesh electrode. Coulometric determination of the number of electrons involved in the reaction was undertaken by the use of Potentiostat/Galvanostat Model 273 of EG & G PAR. The electro-reduction reacction is studied by in situ spectro-electrochemistry with rapid spectra scanning in an optically transparent thin-layer cell.

The C, H, N, S elemental analysis was performed at the Korea Research Institute of Standards and Science (Korea Basic Science Center).

Results and Discussion

Under an argon atmospheric condition, [Ni(DDDT)$_2$]$^{2-}$ species was successfully isolated as tetraethylammonium salt. Figure 1-(a) shows the spectral changes by aerial oxidation of isolated [Ni^{II}(DDDT)$_2$]$^{2-}$ species. After being exposed to air, new absorption band appears at 610 nm. This absorption band is coincided with the characteristic absorption band (allowed d-d transition) of [Ni^{III}(DDDT)$_2$] species (see Figure 2). The nickel(III) complexes which we formulated as bis(5-6-dihydro-1,4-dithiin-2,3-dithiolato) nikelate(III), [Ni(DDDT)$_2$]$^-$ is very unstable in solution, and the recrystallization was not possible. The elemental analysis was made on crude product, and the results was poor. Bis(5,6-dihydro-1,4-dithiin-2,3-dithiolato)nickelate(III), [Ni^{III}(DDDT)$_2$] is reduced to the dianion with NaBH$_4$ in methanol solution. After completely being reduced, the characteristic absorption band at 610 nm of [Ni(DDDT)$_2$]$^-$ species disappeared as shown in Figure 1-(b).

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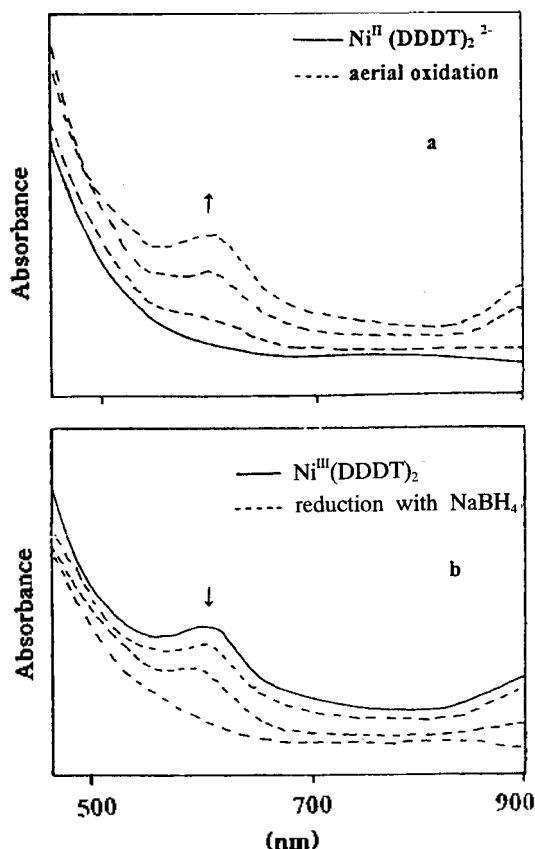

Figure 1. Spectral change observed (a) during aerial oxidation of $Ni(DDDT)_2^{2-}$ (purple transient), and (b) during reduction of $Ni(DDDT)_2$ with $NaBH_4$. The Spectra were obtained in methanolic solution with a time interval of *ca.* 30 minutes.

$$[Ni^{II} (DDDT)_2]^{2-} \xrightleftharpoons[\text{reduction}]{\text{oxidation}} [Ni^{III}(DDDT)_2]$$
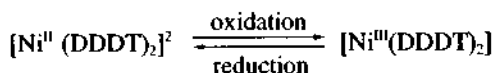
The spectral changes shown in Figures 1-(a) and (b) could be a strong evidence for the presence of redox pair of monoanionic and dianionic complexes in the solution.

The neutral Ni(II)-dithiolene derivative complex was prepared by alkylation of $Ni(DDDT)_2^{2-}$ which displayed IR spectra with all the characteristic ligand and metal dithiolene absorptions present. These characteristic IR bands are summarized in Table 1, along with those of other metal dithiolenes for the comparison. The shifts in IR absorption frequencies of $DDDT^{2-}$ complexes follow the general trends expected as the total charge on the compelx becomes more negative. The C-C frequency increases and the M-S frequencies decrease as the ligand being changed from dithiol-diketonic to dithiolate character.

The comparison of electronic spectra and electrochemical behavior of $Ni(DDDT)_2^{2-}$, $Ni(DDDT)_2^-$ and neutral bis (methylthio)dithiolene nickel(II) complex allow us to understand the bonding nature of nickel-dithiolate complexes. Figure 3-(b) shows cyclic voltammogram of [Et₄N][Ni (DDDT)₂] complex. The $Ni(DDDT)_2^-$ species exhibits two reversible reduction processes (peak 1: +0.13 V and peak 2: 0.64 V *vs.* Ag/AgCl electrode) and an irreversible one-electron oxidation process (+0.92 V *vs.* Ag/AgCl electorde). These normal reduction and oxidation peaks are not ob-
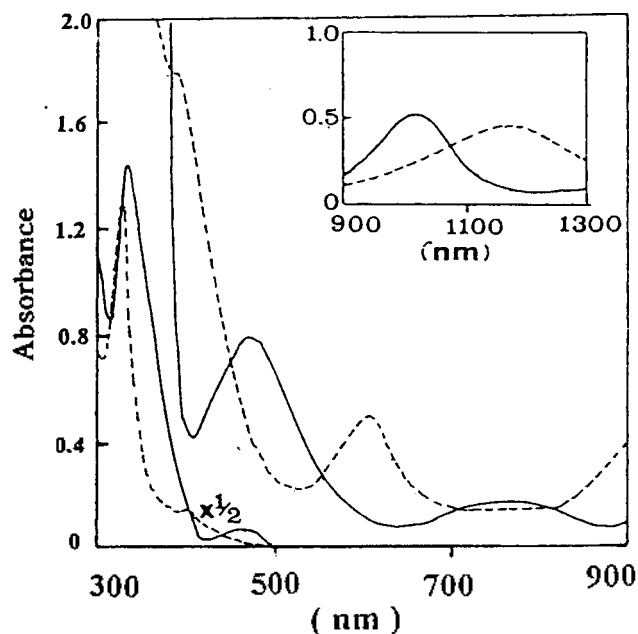
**Figure 2.** Electronic spectra of $(Et_4N)[Ni(DDDT)_2]$ (solid line, 4.62×10^{-4} M in CH_3CN) and $Ni(CH_3)_2C_8H_8S_8$ (dashed line, 6.05×10^{-4} M in CH_2Cl_2).

Table 1. Characteristic infrared bands of nickel dithiolene complexes in cm^{-1}

| Compound	$V_{(C-C)}$	$V_{(C-S)}$	$V_{(R-C\cdot{}^S_C)}$	$V_{(C-C)}$	$V_{(C-C)}$	
$[Et_4N][Ni(DDDT)_2]$	1415	1170	855	410	475	This work
$[Et_4N]_2[Ni(DDDT)_2]$	1498	1167				This work
$Ni(CH_3)_2C_8H_8S_8$	1404	1170	854		450	This work
$[Ni(dmit)_2]^{2-}$	1440	1034	885	311	472	a
		1065	917			
$[Ni(dmit)_2]$	1353	1030	902	317	498	a
		1060				

ᵃ Valade, L.; Legros, J-P; Bousseau, M.; Cassoux, P.; Garbauskas M.; Interrante, L.V. *J. Chem. Soc., Dalton Trans.* **1985**, 783.

served in cyclic voltammogram of free ligand (see Table 2). On the basis of these observations, we propose a redox scheme which involves two step one-electron processes as follow;

$$[Ni(DDDT)_2]^0 \xrightleftharpoons[+0.19V]{+0.13V} [Ni(DDDT)_2]^-$$

$$\xrightleftharpoons[+0.19V]{+0.13V} [Ni(DDDT)_2]^{2-}$$
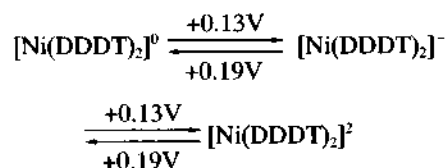
The redox processes occuring at +0.13 V/+0.19 V and - 0.64 V/ - 0.59 V are ascribed to the consecutive and one electron transfer reactions. The number of electorn for these electrode processes was determined by coulommetric measurements. An oxidation peak observed at +0.92V is due to the oxidation of ligand itself. It is plausible to suggest that the electrodic reaction species, $[Ni(DDDT)_2]^0$, would be more easily dissociated as it is scanned to high oxidation potential (up to +1.6 V).

This electrode reaction process was confirmed by adding the free ligand to the test solution: the peak heights at
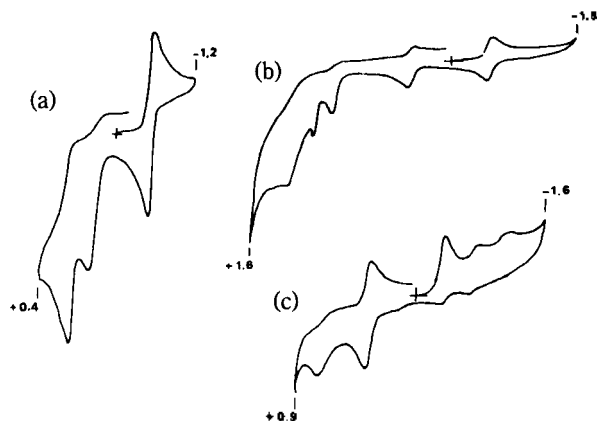
Figure 3. Cyclic voltammograms of (a) Na₂DDDT (5.0×10⁻⁴ M), (b) (Et₄N)[Ni(DDDT)₂] (1.0×10⁻³ M), and (c) Ni(CH₃)₂C₈H₈-Sₓ (1.0×10⁻³ M) in DMF solution at 25 °C. Conditions: scan rate, 100 mV/s; supporting electrolyte, TEAP, 0.1 M; potential expressed with respect to Ag/AgCl reference electrode.

+0.92 V and +1.15 V are increased upon the addition of free ligand to the solution. Above proposed mechanism was quite similar to that of previously suggested by Bowden *et al.*[14] for the redox process of nickel-dithiolate complex in N, N'-dimethylformamide.

Spectroelectrochemical results provide further evidence to confirm the existence of reversible redox process between [Ni(DDDT)₂]⁻ and [Ni(DDDT)₂]²⁻ (see Figure 4). As shown in Figure 4, the reduction of [Ni(DDDT)₂]⁻ is monitored in situ by rapid scan spectrometer. With no potenital applied, the spectrum exhibits maximum absorbances at 610 nm. which are characteristic absorption of [Et₄N][Ni(DDDT)₂].

Changing applied potential by single step from 0.0 V to 0.9 V, the absorbance at 610 nm started to decrease as electrolysis time increased. This indicates that [Niᴵᴵᴵ(DDDT)₂]⁻ has been reduced to [Niᴵᴵ(DDDT)₂]²⁻ species. The vanishing of absorbance at 610 nm as shown in Figure 4 also indicates that the subsequent reduction of the reduced products, Niᴵᴵ(DDDT)₂² has taken place, which is in good accordance with the appearance of reduction peak in the voltammogram as shown in Figure 5. From above results, we can suggest that the redox process of Ni(DDDT)₂ complex

Table 2. The peak potenitial values (E_p) *vs.* Ag/AgCl electrode in cyclic voltammograms of Ni(DDDT)₂ and Ni(CH₃)₂C₈H₈S₈

| Complexes		E_{pc}	E_{pa}	Step reaction
Ni(DDDT)₂	peak 1	+0.13V	+0.19V	Niᴵⱽ ⇌ Niᴵᴵᴵ
	peak 2	0.64V	−0.59V	Niᴵᴵᴵ ⇌ Niᴵᴵ
	peak 3		+0.92V	
	peak 4		+1.08V	
Ni(CH₃)₂C₈H₈S₈	peak 1	+0.14V	+0.19V	Niᴵⱽ ⇌ Niᴵᴵᴵ
	peak 2	−0.61V		Niᴵᴵᴵ ⇌ Niᴵᴵ
	peak 3	−0.93V	(−0.87V)	Niᴵᴵ ⇌ (Niᴵ)
Na₂DDDT	peak 1	−0.78V	−0.69V	
	peak 2		−0.29V	
	peak 3		−0.08V	

*All data were obtained by the use of Pt-inlay electrode in 0.1 M Et₄NClO₄/DMF solution. (at 25 °C)
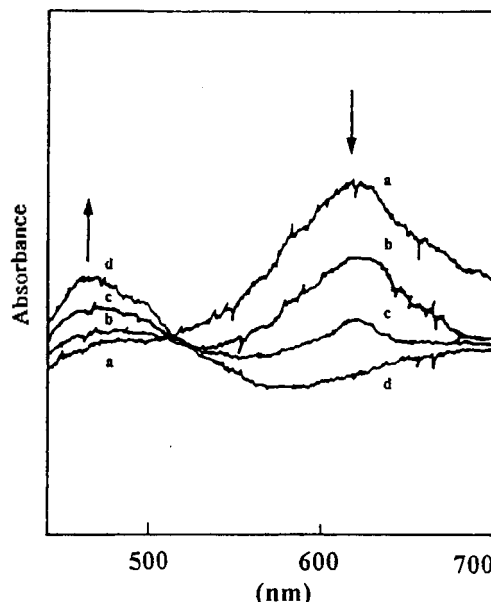
Figure 4. Spectral changes with varied electrolysis time at − 0.90 V of 1.0×10⁻⁴ M (Et₄N)[Ni(DDDT)₂] in DMF/0.1 M TEAP; (a) open circuit, (b) 30 min, (c) 90 min, and (d) 150 min.
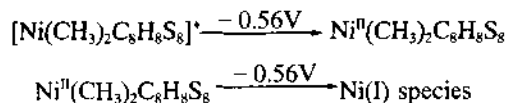
consists of at least two steps.

For neutral bis(dimethyl)dithiolene nickel(II) complex, Ni(CH₃)₂C₈H₈S₈, the redox process seems to be dissimilar to that of monoanionic [Ni(DDDT)₂]⁻ complex(see Figure 3-(c), Table 2). The Ni(CH₃)₂C₈H₈S₈ complex exhibits two reduction process at 0.56 V and 0.88 V *vs.* Ag/AgCl and one oxidation process at +0.19 V *vs.* Ag/AgCl. The peak at 0.56 V is irreversible and the peak at 0.88 V is quasi-reversible. Also the oxidation process at +0.19 V is reversible (i_{pc}/i_{pa} value is one). Thus the electrode process for this neutral Ni(II) complex can be postulated as follow;

$$[Ni(CH_3)_2C_8H_8S_8]^{2+} \underset{+0.14V}{\overset{+0.14V}{\rightleftarrows}} [Ni(CH_3)_2C_8H_8S_8]^{+}$$
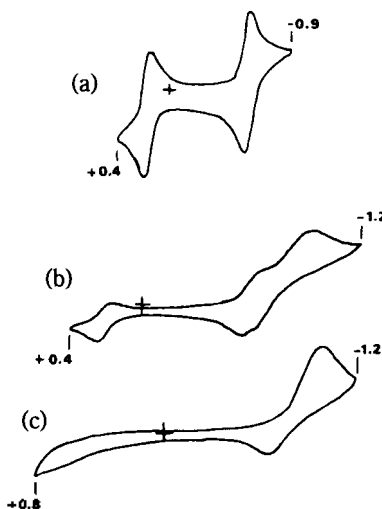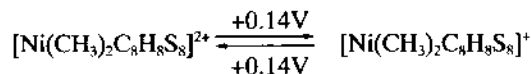
Figure 5. Cyclic voltammogram of Ni(DDDT)₂ complex obtained in DMF at 25 °C after electrolysis at − 0.90 V; (a) open circuit, (b) 90 min, and (c) 150 min.

Table 3. Electronic spectral data of nickel-dithiolene complexes

Compound	Medium	v_{max} ($\varepsilon \times 10^{-3}$ L·mole^{-1} cm^{-1}) kK			
		v_1	v_2	v_3	v_4
Ni(DDDT)$_2^-$	CH$_3$CN	8.55 (2.37)	16.45 (1.06)	25.51 (3.85)	31.65 (30.88)
	DMF		16.35 (1.06)	25.21 (3.45)	
Ni(CH$_3$)$_2$C$_8$H$_8$S$_8$	CH$_2$Cl$_2$	9.80 (1.62)	13.06 (0.16)	21.01 (0.64)	29.59 (14.98)
	DMF		13.23 (0.16)	21.08 (0.64)	30.18 (11.69)

$$[Ni(CH_3)_2C_8H_8S_8]^+ \xrightarrow{-0.56V} Ni^{II}(CH_3)_2C_8H_8S_8$$

$$Ni^{II}(CH_3)_2C_8H_8S_8 \xrightarrow{-0.56V} Ni(I) \text{ species}$$

The electrode processes at -0.56 V and at -0.88 V involve one electron reduction for metal ion: Ni^{III}→Ni^{II} and Ni^{II}→Ni^{I}, respectively. Reversibility of electrochemical process occuring at $+0.14$ V and -0.64 V of [Ni(DDDT)$_2$] complex is presumbly due to the stability of electroactive species in which the stability is due to high electron delocalization in it and high covalency in metal-sulfur bond. And also, electrochemical data indicate that the ability of the ligand to accept electron density increases as the charge on the complex decreases. Comparing the electrochemical results of Ni(DDDT)$_2^-$ with those of Ni(CH$_3$)$_2$C$_8$H$_8$S$_8$ complex, we can suggest that the degree of covalency in M-S bonding of Ni(DDDT)$_2^-$ complex is higher than that of Ni (CH$_3$)$_2$C$_8$H$_8$S$_8$ complex.

The electronic spectra of [Et$_4$N][Ni(DDDT)$_2$] and Ni(CH$_3$)$_2$C$_8$H$_8$S$_8$ complex are shown in Figure 2. There are four maxima in the region between 8,000 and 40,000 cm^{-1}, these bands are quite intense and are very much likely due to the allowed charge-transfer transition (M→L or L→M) or transition localized on the ligands (L→L*)(see Table 3). There are four bands in the [Ni(DDDT)$_2$]$^-$ spectrum, at 8547, 16447, 25510 and 31646 cm^{-1}, respectively. Since the observed one electron separation of 4a$_g$ and 4b$_{2g}$ orbitals in Ni (DDDT)$_2^-$ is *ca.* 8000 cm^{-1}, it is reasonable to assign the band at 8547 cm^{-1} as 4b$_{2g}$→4a$_g$, the first allowed transition, and the band at 16447 cm^{-1} as (3b$_{3g}$→4a$_g$) the in-plane d-d type transition from a molecular orbital energy levels in Ni (dithiolene)$_2^n$ complexes.[15] Thus, we assign the bands at 25510 cm^{-1} as the L→M charge-transfer transitions, which is a transition from in-plane "ligand" π-orbitals to the 3b$_{1g}$ (σ*) "metal" molecular orbital: the 31646 cm^{-1} band is the strongly allowed transition of a L→L* transition.

Following the assignment of the first spin-allowed band in simple square-planar complexes for Ni(CH$_3$)$_2$C$_8$H$_8$S$_8$, we assign the 13055 cm^{-1} band as the in-plane d-d transition, ^1A_g→$^1B_{1g}$(4A$_g$→3b$_{1g}$). Also we assign the band that appear at 35211 cm^{-1} as a L→L* transition, $^1A_{2u}$(3b$_{1u}$→4B$_{3g}$). According to MO diagram previously reported,[15] the highest occupied MO in the d^8 diamagnetic square-planar complexes is the in-plane π* orbital, 4a$_g$.[16,17] Thus, we assign the bands at 21008 and 29586 cm^{-1} as the M→L and L→ M charge-transfer transitions respectively. The 21008 cm^{-1} band is ^1A_g→$^1B_{2u}$(4b$_{2g}$→3a$_u$), and the 29586 cm^{-1} band is ^1A_g→$^1B_{2u}$, $^1B_{3u}$($^1b_{2u}$→$^3b_{1g}$) which is the strongly allowed transition from "ligand" σ-bonding orbitals to the 3b$_{1g}$(σ*) molecular orbital.

Schrauzer *et al.*[18] suggest that metal-dithiolenes show characteristic spectra due to a high degree of electronic delocalization and the presence of low-lying unoccupied orbitals. Therefore, Ni(III) complexes are easily reduced to dimethyl derivative of bis(methylthio)dithiolene nickle(II) complexes. As described in experimental part, neutral Ni (CH$_3$)$_2$C$_8$H$_8$S$_8$ was prepared by reducing Ni^{III}(DDDT)$_2^-$ followed by alkylation with methyl iodide. Product analysis results confirm the prepared compounds as it is formulated.
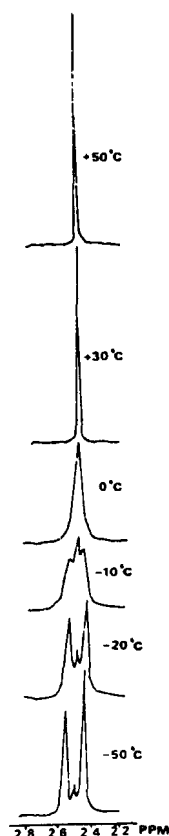
The mass spectrum of the prepared compound exhibits parent ion peak at m/e=447, and further confirms that this compound is alkylated complex in monormeric form. The possible structures for bis(methylthio)dithiolene nickel(II) complex are IA-IC.

IA   IB

IC
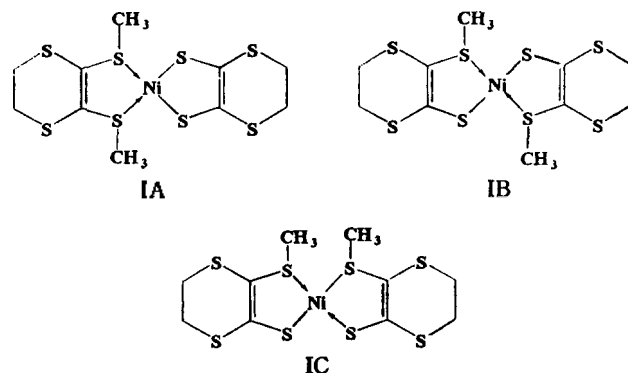
Among three structures, the structure IA seems to be very unstable; during the recrystallization process of neutral Ni^{II} (CH$_3$)$_2$C$_8$H$_8$S$_8$ prepared in methylene chloride, we obtained white polycrystalline compound as a by-product. The mass spectrum of white compound gives parent ion peak at m/e=

Table 4. Characteristic fragmentations and its relative intensities of Ni(CH$_3$)C$_8$H$_8$S$_8$ and C$_6$H$_{10}$S$_4$ (ID)

Ion	m/e	C$_6$H$_{10}$S$_4$ (ID)	Ni(CH$_3$)$_2$C$_8$H$_8$S$_8$
		M.W. 210	449
C$_6$H$_{10}$S$_4$	210	100	
[C$_5$H$_7$S$_4$]$^+$	195	11	
[C$_4$H$_6$S$_4$]$^+$	182	24	
[C$_3$H$_3$S$_4$]$^-$	167	15	
[C$_4$H$_6$S$_2$]$^+$	118	35	
[C$_2$H$_3$S$_2$]$^+$	91	92	
[M-2H]$^+$	447		3
[M-CH$_3$]$^+$	432		1
[M-C$_2$H$_6$S]$^-$	387		6
[M-C$_8$H$_{14}$S$_5$]$^+$	176		19
[M-C$_9$H$_{14}$S$_6$]$^+$	131		100

Figure 6. ^{1}H NMR signals of the methyl group protons of the anti and syn isomers of IB and IC in CD_2Cl_2 at different temperatures.

210, which indicates that this compound is bis(methylthio) dithiolene (ID) (see Table 4). This compound is expected to be produced from the decomposition of unstable IA.

^{1}H NMR measurements show that there are more than one isomer in the solution. According to Scharuzer's report,[19] there is an equilibrium between *trans* and *cis* isomers. In our case, IB and IC isomers seem to be in equilibrium in the solution state.

Figure 6 shows a portion of the variable-temperature ^{1}H NMR spectrum of $Ni(CH_3)_2C_8H_8S_8$ in CD_2Cl_2. In the ^{1}H NMR spectrum of IB at 50 °C, the signal of the methyl group protons appears as a single peak at 2.54 ppm. On cooling, the signal broadens, develops a shoulder, and at 50 °C splits into three signals at 2.57, 2.51, and 2.46 ppm with relative intensities of 4 : 1 : 5. We interpret that there may be the dynamic equilibria involving three isomers (IA, IB and IC). The two major signals at 2.57 and 2.46 ppm coalese at room-temperature (25 °C) and are assigned to the *syn*- and *anti-trans* isomer of IB, which are interconverting by sulfur inversion.

The third signal at 2.51 ppm, which remains observable
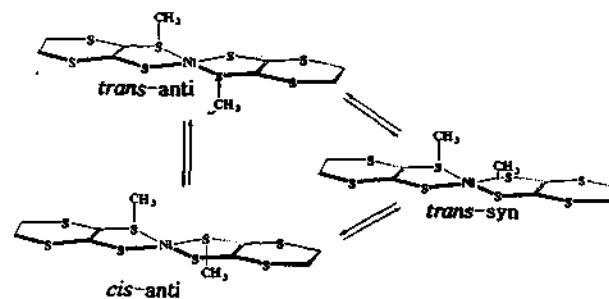
up to -10 °C is assigned to the *cis-anti* isomer, generated by a backbone isomerization process. The *cis-anti* isomer could not be isolated in the solid state. Furthermore, no signal attributable to the *cis-syn* isomer was observed. Its formation either by sulfur inversion or backbone isomerization is apparently sterically unfavorable.

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Influence of Amphoteric Behaviour of Oxide Materials on the Selectivity of Micro and Mesoporous Ceramic Membranes

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Electrostatic interaction is a very important parameter for the membrane selectivity. In this work, the electrical double layer establisment on the surface of metal oxide material from the Stern-Grahame model has been described. Then, some examples of rejection using micro and mesoporous ceramic membranes have been given. A correlation between the charges of the membrane material and the species to be filtered has been precised. Two rejection mechanisms have to be taken into account the size of the solutes and the electrostatic interactions.

Introduction

Nanofiltration (NF) can be defined by the pore diameter size, in the range 0.5 to 2 nm or by the membrane cut-off from 300 to 1 000 D. The interest of nanofiltration is due to the salt rejection particularly for multivalent ions, to the higher permeability and lower working pressure than those of reverse osmosis. The lowest range of UF (pore diameters less than about 10 nm) can be associated to NF for the mechanisms of ion rejection.

In case of neutral species, the criteriom of solute size related to pore diameters is preponderant. For ionic species as salts, the rejection cannot be explained by the size exclusion. Electrostatic interaction has to be considered. The model of Levine *et al.*[1] can be used to predict the rejection rate. Ion rejection increases when membrane charge and co-ion charge increase too and ion rejection decreases when ionic strength increases. it is clear that electric interactions are dominant for the selectivity of the membranes.

In the literature, it can be found many examples on the influence of membrane charge on the performances of organic membranes.[2,3] These studies have been also applied for instance to avoid the fouling of organic membranes by proteins[4]; electrostatic repulsion acts to decrease adsorption and flux reduction.

If we are looking at the earliest definition of nanofiltration, which was also named hyperfiltration, only was mentionned the anion rejection due to a negative residual charge of organic membranes.[5] This model is now applied to inorganic ones[6] to explain the rejection of anions and cations due to the amphoteric behaviour of the oxide material by using the triple layer model.[7]

## Electrical double layer

In case of ceramic membranes, the oxide material has am-

photeric properties and it can be positively or negatively charged depending of the pH value:

$$M\text{-}OH + H^+ \Leftrightarrow M\text{-}OH_2^+$$
$$M\text{-}OH + OH^- \Leftrightarrow M\text{-}O^- + H_2O$$
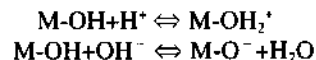
In an electrolyte solution the total charge of ceramic particles is also due to the redistribution of the counter-ions according to the complexation reactions:

$$M\text{-}OH_2^+ + A^- \quad - \quad M\text{-}OH_2^+ \dots A^-$$
$$M\text{-}O^- + C^+ \quad - \quad M\text{-}O^- \dots C^+$$
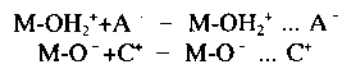
The distribution of the ions in the solution is modified: the co-ions are rejected and the counter-ions are attracted by the membrane surface. Different models were developed for explaining these phenomena and answer to the question: what is the origin of the electrical double layer? The Stern-Grahame model can be used and described as follows: a particle, immersed in a solution, acquires a surface charge and accumulates a counter-charge in order to preserve global electroneutrality; this counter-charge layer or compact layer is surrounded by a diffuse layer. Surface, compact, and diffuse layer charges make up the electrical double layer (Figure 1).

Amphoteric reactions take place on the O plane. Complexation reactions occur on the β plane. The d plane is the limit between compact and diffuse layers. The compact layer is moving with particles when they are put in an electric field.

The potential decreases linearly between charge planes in the compact layer and presents an analogy with parallel plate capacitors in series. The potential on the d plane φ_d is called zeta-potential (ζ potential). In the diffuse layer, excess number of counter-ions decreases exponentially until the concentrations of positive and negative ions are equal like in the bulk solution. The potential varies according to the reduced Poisson-Boltzmann equation: