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Mononuclear nickel(II) thiolates of square-planar geometry: syntheses, spectral and redox properties of $[Ni(SCH_2CH_2S)_2]^{2-}$ and $[Ni(SCH(CH_3)CH(CH_3)S)_2]^{2-}$ and the structure of $(Ph_4P)_2[Ni(SCH_2CH_2S)_2]\cdot 4H_2O$

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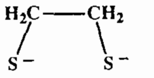
Abstract

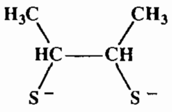
Reaction of $NiCl_2\cdot 6H_2O$ with excess (>10 equiv.) dithiolate ligands ethane-1,2-dithiolate (edt^{2-}) and butane-2,3-dithiolate (bdt^{2-}) in water or ethanol affords the mononuclear thiolato complexes $[Ni(edt)_2]^{2-}$ and $[Ni(bdt)_2]^{2-}$, respectively. These homoleptic thiolates contain square-planar NiS_4 chromophores. The complex $(Ph_4P)_2[Ni(edt)_2]\cdot 4H_2O$ (3) crystallizes in the monoclinic space group $P2_1/c$ with $a=10.590(2)$, $b=16.299(3)$, $c=14.752(3)$ Å, $\beta=100.20(2)°$, $V=2506.0(8)$ Å^3 and $Z=2$. The structure was refined to $R=3.31\%$ by using 2486 unique data ($F_o^2>3\sigma(F_o^2)$). In DMF solution, $[Ni(bdt)_2]^{2-}$ can be oxidized to the nickel(III) complex $[Ni(bdt)_2]^-$ at an extremely low potential of -0.75 V versus SCE. EPR parameters of $[Ni(bdt)_2]^-$ suggest a square-planar structure for this nickel (III) thiolate.

Introduction

The quest for mononuclear thiolato complexes of nickel has gathered momentum following the discovery of a low-potential S-ligated nickel center at the active site of several hydrogenases [1–3]. The propensity of bridge-formation by thiolato sulfur has however resulted in, in most cases, multinuclear complexes of novel structures [4–6]. Monomeric thiolato complexes of bivalent nickel are only known with arenethiolates as ligands and include $(Ph_4P)_2[Ni(SPh)_4]$ [7], $(Et_4N)_2[Ni(SPh)_4]$ [8] and $(Et_4N)_2[Ni(SAr)_4]$ (Ar = C_6H_5,*p*-C_6H_4Cl,*p*-$C_6H_4CH_3$, *m*-C_6H_4Cl) [9]. It is interesting to note that the coordination geometry around nickel in the multinuclear thiolato complexes is predominantly square planar while in $[Ni(SAr)_4]^{2-}$, the four sulfur atoms are arranged in a distorted tetrahedral fashion around the nickel center. As part of our research effort toward syntheses of mononuclear nickel complexes with varying numbers of thiolato S donor centers [9–11], we have been trying to isolate and structurally characterize thiolato complexes with square-planar NiS_4 chromophore. We report in this paper the syntheses and spectral as well as electrochemical properties of two monomeric nickel(II) thiolates that exhibit square-planar stereochemistry. The complexes $(Ph_4P)_2[Ni(edt)_2]\cdot 4H_2O$ (**3**) and $K_2[Ni(bdt)_2]\cdot C_2H_5OH$ (**4**) contain ethane-1,2-dithiolate (edt^{2-}, **1**) and butane-2,3-dithiolate (bdt^{2-}, **2**) as ligands and belong to a new class of homoleptic nickel thiolates. Spectroscopic and redox properties of a complex of composition $(Ph_4P)_2[Ni(edt)_2]$ have appeared previously [12] though no structural features were described**. The structure of **3** is also reported in this paper.



edt^{2-}(**1**)



bdt^{2-}(**2**)

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**That the structure of $K_2[Ni(edt)_2]HCONMe_2\cdot H_2O$ has been determined (but not published) is mentioned in ref. 12.

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Experimental

Preparation of compounds

Ethane-1,2-dithiol (H_2edt) and butane-2,3-dithiol (H_2bdt) were procured from Aldrich Chemical Company and were used without further purification. In the following preparations, degassed solvents were used and all manipulations were performed under an atmosphere of dry and pure dinitrogen.

$(Ph_4P)_2[Ni(edt)_2]\cdot 4H_2O$ (3)

A solution of Na_2edt was prepared by the addition of 1.40 g (25 mmol) of KOH to 1.2 ml (12.6 mmol) of ethane-1,2-dithiol in 30 ml of water. To it was added with stirring a solution of 0.30 g (1.26 mmol) of $NiCl_2\cdot 6H_2O$ in 5 ml of water. The dark greenish-brown solution thus resulted was stirred for 1 h. Next, a batch of 1.13 g (2.7 mmol) of PPh_4Br was added to the reaction mixture and the stirring was continued for an additional 3 h. The red microcrystalline precipitate formed during this period was then collected by filtration, dissolved in 10 ml of acetonitrile and quickly added back to the filtrate. Within minutes, dark red crystals were deposited. The crystals were collected by filtration and dried under vacuum. The filtrate from this step afforded large red blocks, suitable for X-ray studies, on storing at 0 °C for 24 h. The combined yield was 80%. Selected IR bands (KBr pellet, cm^{-1}): 3180(br, s), 2876(m), 2805(w), 1578(m), 1439(s), 1264(m), 1107(s), 996(m), 845(m), 758(m), 724(s), 692(s), 526(s), 462(w). ^1H NMR (300 MHz, $(CD_3)_2SO$, 298 K), δ (ppm from TMS): 1.77 (s, CH_2), 3.36 (s, H_2O), 7.7–8.0 (m, Ph) (integration ratio: 1:1:5).

Anal. Calc. for $C_{52}H_{56}O_4P_2S_4Ni$: C, 62.82; H, 5.64; Ni, 5.91. Found: C, 62.58; H, 5.57; Ni, 5.81%.

$K_2[Ni(bdt)_2]\cdot C_2H_5OH$ (4)

To a solution of 20 mmol of K_2bdt (obtained by mixing 2.5 g of butane-2,3-dithiol and 2.35 g of KOH) in 40 ml of ethanol was added with stirring a solution of 0.49 g (2 mmol) of $NiCl_2\cdot 6H_2O$ in 10 ml of ethanol and the dark greenish-brown solution thus obtained was kept at room temperature for 4 h. The small amount of white precipitate formed during this period was filtered off and the filtrate was stored at 0 °C for 16 h. The dark brown microcrystalline product was isolated by filtration. A second crop of the desired complex was obtained from the mother liquor after cooling (0 °C) for 3 days. The combined yield was 80%. Selected IR bands (KBr pellet, cm^{-1}): 3270(br, s), 2952(s), 1620(br, m), 1442(m), 1360(m), 1235(m), 1186(m), 1050(m), 980(w), 800(w), 685(w), 632(w). ^1H NMR (300 MHz, D_2O, 298 K) δ (ppm from TMS): 2.83 (m, CH), 1.13 (d, CH_3).

TABLE 1. Summary of crystal data, intensity collection and structure refinement parameters for $(Ph_4P)_2[Ni(edt)_2]\cdot 4H_2O$ (3)

Formula	$C_{52}H_{56}O_4P_2S_4Ni$
Crystal color, form	purple, blocks
Crystal system	monoclinic
a (Å)	10.590(2)
b (Å)	16.299(3)
c (Å)	14.752(3)
β (°)	100.20(2)
Space group	$P2_1/c$
V (Å^3)	2506.0(8)
Density calc. (g cm^{-3})	1.317
Z	2
Crystal dimensions (mm)	0.30×0.20×0.20
Absorption coefficient, μ (cm^{-1})	6.52
Radiation, λ (Å)	Mo Kα (0.71069)
Temperature (°C)	24
Scan speed (°/min)	2.0–14.45 (ω scan)
Scan range (°)	1.2 in ω
Background/scan time ratio	0.25
Data collected	3655
No. unique data $[F_o^2 > 3\sigma(F_o^2)]$	2486
Data/variable ratio	8.7:1
R^a (%)	3.31
R_w^b (%)	3.91
Largest Δ/σ in refinement	0.003
Maximum difference Fourier peak (e/Å^3)	0.24

$^a R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b R_w = [\Sigma w(|F_o| - F_c|)^2/w|F_o|^2]^{1/2}$ where $w = 4F_o^2/2\sigma(F_o^2)$.

Anal. Calc. for $C_{10}H_{22}OS_4K_2Ni$: C, 28.37; H, 5.20; Ni, 13.87. Found: C, 28.28; H, 5.11; Ni, 13.35%.

Physical measurements

Electronic absorption spectra were obtained with a Perkin-Elmer Lambda 9 spectrophotometer. Infrared spectra were measured on a Perkin-Elmer 1600 FTIR spectrometer. ^1H spectra were recorded on a General Electric 300 MHz GN-300 instrument. Electrochemical measurements were performed with standard Princeton Applied Research instrumentation using a Pt or glassy carbon (GC) electrode; potentials were measured at ~25 °C versus a saturated calomel electrode (SCE) as reference. EPR spectra were recorded at X-band frequencies by using a Bruker ESP-300 spectrometer. A Johnson Matthey magnetic susceptibility balance was used to monitor the room-temperature susceptibility values in polycrystalline state. Elemental analyses were completed by Atlantic Microlabs, Inc., Atlanta, GA, U.S.A.

X-ray data collection and reduction

Diffraction experiments were performed on a four-circle Siemens R3m/V diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å). The initial orientation matrix was obtained from 15 machine-centered reflections selected from a rotation photograph. Partial rotation photographs around each axis were consistent with a monoclinic crystal system. The final lattice parameters and the orientation matrix were determined from 25 high angle data ($30° < 2\theta < 36°$). Machine parameters, crystal data and data collection parameters are summarized in Table 1. The observed extinctions were consistent with the space group $P2_1/c$. Two standard reflections were recorded after every 98 reflections. Their intensities showed no statistically significant change over the duration of the data collection. The data were processed with the use of SHELXTL program package on a Micro VAX II computer at the Applications Laboratory of Siemens-Nicolet in Madison, WI. An empirical absorption correction was applied to the data based on 9 sets of azimuthal scan data.

Structure solution and refinement

Non-hydrogen atomic scattering factors were taken from the literature tabulations [13]. Positions for the Ni and S atoms were determined by using direct methods. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The structure was refined by the full-matrix least-squares method. The refinement was based on F, the quantity minimized being $w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of refinement, all non-hydrogen atoms were assigned anisotropic temperature factors. Hydrogen atom positions were calculated and allowed to ride on the carbons to which they are attached (d(C–H) = 0.95 Å). Hydrogen atom temperature factors were fixed at 0.060 Å^2. In all cases, contributions of the hydrogen atoms were calculated but not refined. The following data are tabulated: positional parameters (Table 2) and selected bond distances and angles (Table 3). See also 'Supplementary material.'

Results and discussion

Reactions of $NiCl_2 \cdot 6H_2O$ with excess dithiolates (1:10 ratio or higher) afford the mononuclear nickel(II) complexes **3** and **4** in high yields. The present synthesis of **3** is a slightly modified version of the one reported by Holm and coworkers [12]. The reversible equilibrium (1) requires high thiolate concentration in the reaction mixture for the successful isolation of the monomeric species [14].

TABLE 2. Positional parameters[a]

	x	y	z
Ni	0	0	0
S(1)	−1833(1)	408(1)	−821(1)
C(1)	−1445(4)	1397(3)	−1276(3)
C(2)	−109(4)	1415(3)	−1442(3)
S(2)	979(1)	1079(1)	−422(1)
P	7899(1)	5801(1)	1059(1)
C(11)	7809(3)	6115(2)	−119(2)
C(12)	8159(3)	6905(2)	−323(2)
C(13)	8115(3)	7136(3)	−1225(3)
C(14)	7731(4)	6587(3)	−1919(3)
C(15)	7378(4)	5812(3)	−1732(3)
C(16)	7411(3)	5567(2)	−830(2)
C(21)	7580(3)	4721(2)	1060(2)
C(22)	8570(3)	4162(2)	1084(2)
C(23)	8292(4)	3335(2)	966(2)
C(24)	7040(4)	3070(2)	837(2)
C(25)	6067(4)	3618(2)	838(3)
C(26)	6322(3)	4442(2)	946(2)
C(31)	6712(3)	6327(2)	1574(2)
C(32)	6415(3)	6028(2)	2394(3)
C(33)	5521(3)	6439(3)	2810(3)
C(34)	4938(4)	7136(3)	2409(3)
C(35)	5226(3)	7428(2)	1608(3)
C(36)	6110(3)	7036(2)	1189(2)
C(41)	9477(3)	6002(2)	1688(2)
C(42)	9718(3)	5915(2)	2636(2)
C(43)	10934(3)	6035(2)	3122(2)
C(44)	11917(3)	6246(2)	2680(2)
C(45)	11697(3)	6338(2)	1742(2)
C(46)	10477(3)	6210(2)	1236(2)
O(1)	−4030(2)	1084(2)	261(2)
O(2)	−6277(3)	596(2)	−967(2)

[a]Positional parameters are reported ×10^4.

$$2[Ni(SCHRCHRS)_2]^{2-} \rightleftharpoons [Ni_2(SCHRCHRS)_3]^{2-} + SCHRCHRS^{2-} \qquad (1)$$

R = H, CH_3

The dimeric $[Ni_2(edt)_3]^{2-}$ and trimeric $[Ni_3(edt)_4]^{2-}$ complexes have been synthesized previously by using lower Ni:edt^{2-} ratios [5, 8, 12, 15, 16]. Though stable in the solid state, both **3** and **4** are converted into the dimeric species in solution at appreciable rates (*vide infra*). Nevertheless, spectral and redox parameters for these complexes can be obtained with freshly prepared solutions in suitable solvents.

Structure of $(Ph_4P)_2[Ni(edt)_2] \cdot 4H_2O$ (3)

The crystal structure of **3** consists of discrete cations, anions and water molecules of crystallization. The water molecules are involved in hydrogen bonding. In addition, one water molecule is hydrogen-bonded to S1 (S1–H12O = 2.405 Å). The geometry

TABLE 3. Selected bond distances and angles in $[Ni(edt)_2]^{2-}$

Distances (Å)					
Ni–S1	2.201(1)	Ni–S2	2.188(1)	S1–C1	1.820(5)
S2–C2	1.810(4)	Cl–C2	1.478(6)		
Angles (°)					
S1–Ni–S2	91.0(1)	S1–Ni–S1′	180.0(1)	S1–Ni–S2′	89.0(1)
S2–Ni–S2′	180.0(1)	Ni–S1–C1	103.6(1)	Ni–S2–C2	102.6(1)
S1–C1–C2	111.4(3)	S2–C2–C1	110.1(3)		

of the cation is as expected [7]. An ORTEP drawing of the anion is shown in Fig. 1. The nickel atom resides on a crystallographically imposed center of symmetry. Two bidentate ethane-1,2-dithiolate ligands comprise the coordination sphere of nickel and the coordination geometry is essentially square planar. The Ni(II)–S distances 2.201(1) and 2.188(1) Å are typical of those found in other thiolato complexes of bivalent nickel [5, 11, 12, 15, 16]. The S–Ni–S angle of 91° is also normal and requires no further comment. Positional parameters are listed in Table 2 while selected bond distances and angles are collected in Table 3.

Properties

Crystals of **3** and **4** are indefinitely stable under dinitrogen atmosphere. However, when the monomeric complexes are dissolved in protic or wet aprotic solvents, rapid conversion to the dimeric $[Ni_2(dithiolate)_3]^{2-}$ species is observed and equilibrium (1) is eventually shifted completely to the right. Conversion to the dimer is slower in aprotic solvents with the slowest rate being monitored in DMF. The process of mononuclear → binuclear conversion has been discussed in detail in a previous report [12].

In aprotic solvents, **3** exhibits quasireversible voltammograms with $i_a/i_c > 1$ and half-wave potentials ($E_{1/2}$) in the range of −0.60 to −0.70 V versus SCE. For example, the $E_{1/2}$ value in DMF is found to be −0.69 V versus SCE while that in acetonitrile has been reported to be −0.68 V versus SCE [12]. The shapes of the voltammograms clearly demonstrate that the oxidized species undergoes degradation and/or some other chemical reaction(s) near the electrode surface. The lifetime of $[Ni(edt)_2]^-$ is drastically reduced in protic solvents like methanol. In such solutions, **3** displays electrochemical characteristics which are typical of irreversible processes. Promising redox behavior is however observed with **4** in DMF. As shown in Fig. 2, the voltammograms approach the reversibility criterion of $i_a/i_c = 1$ even at slow scan speeds. The more negative $E_{1/2}$ value (−0.75 V versus SCE) of **4** illustrates the effect of the electron-donating methyl groups of the ligand on the $[Ni(dithiolate)_2]^{2-}/[Ni(dithiolate)_2]^-$ couple. The shift in the $E_{1/2}$ value also suggests that the observed redox process is associated with the nickel center. Interestingly, the $E_{1/2}$ value of **4** recorded in DMF is very close to that noted for the nickel(II) complex of norbornyldithiolate in the same solvent (−0.76 V versus SCE) [17]. It is, therefore, evident that the

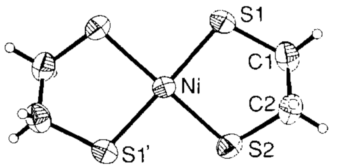

Fig. 1. ORTEP drawing of $[Ni(edt)_2]^{2-}$ showing 50% probability ellipsoids and the atom-labeling scheme.

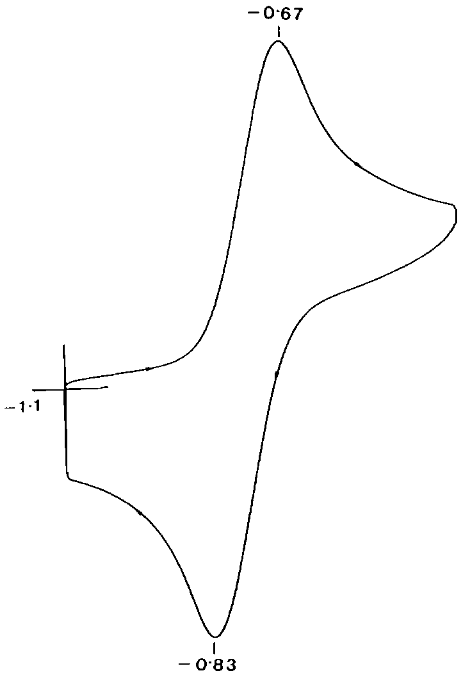

Fig. 2. Cyclic voltammogram of **4** in DMF (GC electrode, 50 mV/s scan speed, 0.1 M tetrabutylammonium perchlorate as supporting electrolyte). Potentials are indicated against an aqueous SCE.

anionic tetrathiolate environment drastically lowers the oxidation potentials of classical nickel(II) complexes and in certain cases brings the Ni(II)/Ni(III) redox potential down in the range of the nickel-containing active site(s) of hydrogenases (-0.39 to -0.64 V versus SCE [1]).

The propensity of nickel(II) thiolates to undergo irreversible oxidation [8, 18] seldom allows detection and characterization of the nickel(III) product. Nevertheless, in recent years, several groups have been able to characterize the Ni(III) species by spectroscopic techniques [11, 19, 20]. In the present study, the nickel(III) complex $[Ni(bdt)_2]^-$ has been studied by EPR spectroscopy. Oxidation of **4** in DMF by $IrCl_4$ affords $[Ni(bdt)_2]^-$ which exhibits an axial EPR spectrum (Fig. 3) with $g_{\parallel}=2.187$ and $g_{\perp}=2.042$. Since low-spin Ni(III) centers in square-planar geometry give rise to EPR spectra with $g_{\parallel}>g_{\perp}$ [21, 22], it appears that $[Ni(bdt)_2]^-$ retains a square-planar geometry in DMF solution. Further support to this assignment comes from the facts that addition of ligands like imidazole to solution of **4** in DMF neither alters the $E_{1/2}$ value of the $[Ni(bdt)_2]^{2-}/[Ni(bdt)_2]^-$ couple nor brings about a change in the EPR spectrum of the oxidized species [19, 23]. In contrast, the nickel-containing active site(s) of hydrogenase and several peptido complexes of trivalent nickel [19, 20] display rhombic EPR spectra with $g_{\perp}>g_{\parallel}$, consistent with low-spin Ni(III) in a tetragonal geometry [21, 22]. It is, therefore, quite unlikely that the nickel center(s) in the enzyme is present in a regular square-planar array of cysteinyl sulfurs.

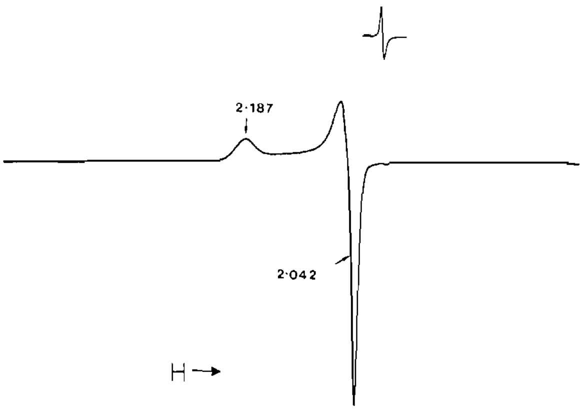

Fig. 3. X-band EPR spectrum of $[Ni(bdt)_2]^-$ in DMF glass (120 K). Instrument settings: microwave frequency, 9.475 GHz; modulation amplitude, 2 G; modulation frequency, 100 KHz; receiver gain, 5×10^4; time constant, 0.3 s. Apparent g values are indicated.

Supplementary material

Thermal parameters (Table S1), positional parameters for hydrogen atoms (Table S2), bond distances and angles associated with the PPh_4^+ cation (Table S3) and the structure factor table (Table S4) (total 15 pages) are available from the authors on request.

Acknowledgment

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