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New 1,3-Dithio Chelates of Nickel(II) from Reactions of Coordinated Ligands. Their Characterization and Oxidation–Reduction Properties

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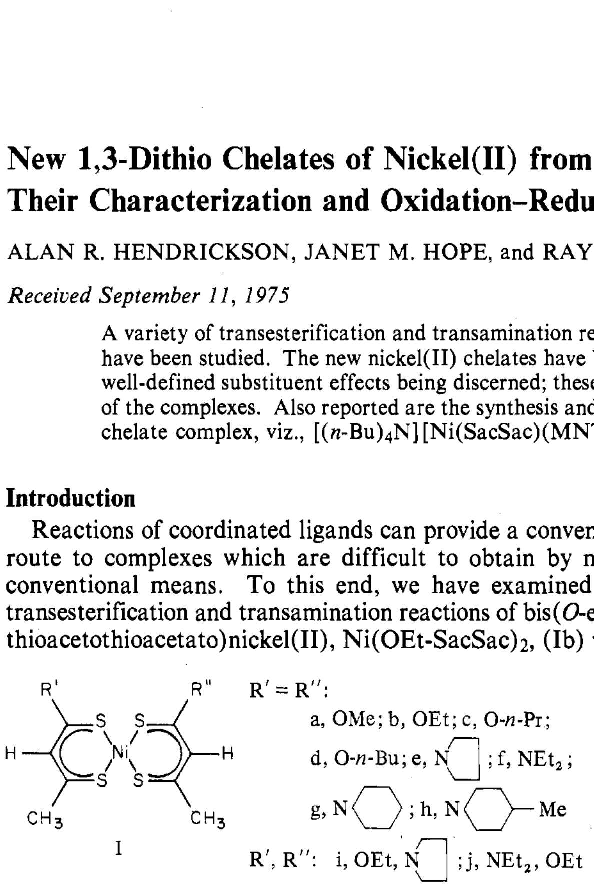
A variety of transesterification and transamination reactions of the coordinated dithio ligand *O*-ethyl thioacetothioacetate have been studied. The new nickel(II) chelates have been characterized by NMR, mass, and electronic spectroscopy, with well-defined substituent effects being discerned; these effects are particularly pronounced in the electrochemical behavior of the complexes. Also reported are the synthesis and unusual redox properties of a new type of mixed 1,2- and 1,3-dithio chelate complex, viz., $[(n\text{-Bu})_4N][Ni(SacSac)(MNT)]$.

Introduction

Reactions of coordinated ligands can provide a convenient route to complexes which are difficult to obtain by more conventional means. To this end, we have examined the transesterification and transamination reactions of bis(*O*-ethyl thioacetothioacetato)nickel(II), Ni(OEt-SacSac)$_2$, (Ib) with alcohols and secondary amines to provide a variety of new 1,3-dithio complexes (Ia–h). Two intermediates in the reactions have also been isolated with one 1,3-dithio ligand possessing an –OR substituent and the other an –NR$_2$ substituent (Ii) and (Ij). Another new type of mixed-ligand complex containing 1,2- and 1,3-dithio ligands has been formed by a ligand-scrambling reaction between Ni(SacSac)$_2$ and $[Ni(MNT)_2]^{2-}$ to afford $[Ni(SacSac)(MNT)]^-$ (II).



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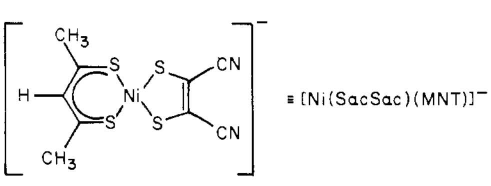


II

The new complexes have been characterized by spectral methods. The redox properties of these and previously known 1,3-dithio chelates of Ni(II) are compared.

Experimental Section

(A) Bis(1-ethoxy-1-thiolobut-1-ene-3-thione)nickel(II), [Ni(OEt-SacSac)$_2$]. This compound was prepared as previously described[1] and used as starting material in the following transesterification and transamination reactions.

(B) Bis(1-alkoxy-1-thiolobut-1-ene-3-thione)nickel(II), [Ni(OR-SacSac)$_2$] (R = Me, *n*-Pr, *n*-Bu). These species were prepared by the general method (B) of refluxing a basic solution of Ni(OEt-SacSac)$_2$ in the appropriate alcohol. Reaction times, solvents, bases, and work-up procedures are given in Table I.

(C) Bis(1-dialkylamino-1-thiolobut-1-ene-3-thione)nickel(II), [Ni(R$_2$N-SacSac)$_2$] (R$_2$N = Et$_2$N, Pyrrolidyl, Piperidyl, 4-Methylpiperidyl). These complexes were prepared by refluxing Ni(OEt-SacSac)$_2$ in acetone with a vast excess of the appropriate secondary amine. With pyrrolidine and piperidine, the products readily precipitated from solution. With the other amines, the disubstituted complexes were separated from mixed-ligand species by chromatography—details are in Table I.

(D) (1-Alkoxy-1-thiolobut-1-ene-3-thione)(1-dialkylamino-1-thiolobut-1-ene-3-thione)nickel(II) Compounds. (i) Ni(OEt-SacSac)(NEt$_2$-SacSac). Reaction of Ni(OEt-SacSac)$_2$ with diethylamine in acetone was followed by TLC on the reaction mixture. When the optimun yield of mixed-ligand complex was apparent, the reaction mixture was evaporated under vacuum to dryness. The pure mixed-ligand complex was obtained by chromatography and rapid recrystallization from CH$_2$Cl$_2$–petroleum ether.

(ii) Ni(OEt-SacSac)(pyrr-SacSac). The complex prepared as described in (i) was recrystallized from acetone–petroleum ether.

(E) (1-Ethoxy-1-thiolobut-1-ene-3-thione)(1,3-di(phenyl)-1-thioloprop-1-ene-3-thione)nickel(II), [Ni(OEt-SacSac)(Ph-SacPh-Sac)]. Equimolar quantities of Ni(OEt-SacSac)$_2$ and Ni(Ph-SacPh-Sac)$_2$ were refluxed in toluene for 8 h with the product distribution being monitored by TLC. The mixed-ligand complex was obtained after evaporation of solvent under reduced pressure and chromatographic separation on preparative TLC plates (silica) using toluene as solvent. This compound has only been characterized by chromatography and its NMR spectrum.

(F) Tetra-*n*-butylammonium (2-Thiolopent-2-ene-4-thione)(maleonitriledithiolato)nickelate(II), $[(n\text{-Bu})_4N][Ni(SacSac)(MNT)]$. Equimolar quantities of Ni(SacSac)$_2$ and $[(n\text{-Bu})_4N]_2[Ni(MNT)_2]$ were refluxed in acetone for 3 h whereupon the solvent was removed. The residue was dissolved in CH$_2$Cl$_2$ and eluted from a silica column with CH$_2$Cl$_2$ to remove unreacted Ni(SacSac)$_2$. The product was then eluted with acetone. On reduction of the volume of acetone, addition of Et$_2$O, and cooling, crystals of the product were obtained.

Known complexes of the type Ni(R-SacR-Sac)$_2$, used for the redox study, were prepared by literature[2] methods and purified by chromatography.

Instrumentation. Electronic spectra were obtained on a Cary 14 spectrometer. Infrared spectra were obtained in KBr disks on a

Table I. Analytical and Preparative Details for the New Complexes

Compd	% calcd (% found)					Mp, °C	Prep method[a]	Wt of Ib,[e] g	Reaction solvent	Reflux time	Base	Chromatography[b] solvent(s)	Recrystallization solvents
	C	H	N	Ni	S								
Ni(OMe-SacSac)$_2$	34.0 (34.0)	4.0 (3.9)		16.6 (16.9)	36.3 (36.6)	228	B	0.5	MeOH	50 min	KOH (0.1 g)	c	CH_2Cl_2–MeOH
Ni(O-*n*-Pr-SacSac)$_2$	41.1 (41.2)	5.4 (5.4)		14.3 (14.3)	31.3 (31.5)	99	B	1.5	*n*-PrOH (50 ml)	1 hr	NaH (~0.02 g)	20% CH_2Cl_2–pet. ether	CH_2Cl_2–pet. ether
Ni(O-*n*-Bu-SacSac)$_2$	43.9 (43.9)	6.0 (5.8)		13.4 (13.3)	29.3 (29.3)	104	B	0.2	*n*-BuOH (100 ml)	1 hr	NaH (~0.02 g)	20% CH_2Cl_2–pet. ether	CH_2Cl_2–pet. ether
Ni(NEt$_2$-SacSac)$_2$	44.1 (44.0)	6.5 (6.5)	6.4 (6.1)	13.5 (13.3)	29.5 (29.5)	240	C	0.3	Acetone (5 ml)	30 min	Et_2NH (3 ml)	Benzene	CH_2Cl_2–pet. ether
Ni(pyrr-SacSac)$_2$	44.5 (44.5)	5.6 (5.6)	6.5 (6.6)	13.6 (13.5)	29.7 (29.7)	>300	C	0.5	Acetone[d]	2 min	Pyrrolidine (3 ml)	c	CH_2Cl_2–acetone
Ni(pip-SacSac)$_2$	47.1 (47.4)	6.1 (6.2)	6.1 (6.0)	12.8 (13.4)	27.9 (27.6)	275	C	0.4	Acetone (5 ml)	15 min	Piperidine (1 ml)	c	CH_2Cl_2–acetone
Ni(4-Me(pip)-SacSac)$_2$	49.3 (48.9)	6.9 (6.3)	5.7 (5.5)	12.0 (12.3)	26.3 (26.2)	260	C	0.4	Acetone (40 ml)	30 min	4-Methylpiperidine (1 ml)	Benzene	CH_2Cl_2–MeOH
Ni(OEt-SacSac)(NEt$_2$-SacSac)	41.2 (41.2)	5.7 (5.6)	3.4 (3.5)	14.4 (14.4)	31.4 (31.8)	104	D	0.4	Acetone (50 ml)	15 min	Et_2NH (2 ml)	15% CH_2Cl_2–pet. ether	CH_2Cl_2–pet. ether
Ni(OEt-SacSac)(pyrr-SacSac)	41.4 (41.6)	5.2 (5.2)	3.4 (3.4)			~200	D	0.4	Acetone (75 ml)	3 min	Pyrrolidine (1 ml)	Benzene	Acetone–pet. ether
[(*n*-Bu)$_4$N][Ni(SacSac)(MNT)]	52.4 (52.7)	7.6 (7.2)	7.3 (7.4)	10.3 (10.4)	22.4 (21.7)	110	F						

[a] See Experimental Section. [b] All chromatography run on silica columns. [c] Product did not require chromatography. [d] Saturated solution. [e] Ib = Ni(OEt-SacSac)$_2$.

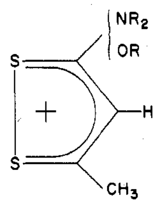
Perkin-Elmer 457 instrument. Mass spectra were obtained on an AEI MS902 spectrometer and NMR spectra were obtained at 100 MHz on a Varian HA100 instrument. Electrochemical data were obtained in actone–0.1 M Et_4NClO_4 solutions and potentials have been measured against an Ag–AgCl–0.1 M LiCl electrode. Electrochemical procedures and instrumentation (PAR 170) were as described previously.[3]

Results and Discussion

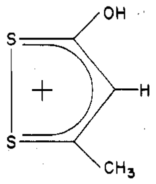
It is with relative ease that Ni(OEt-SacSac)$_2$ is substituted by –OR and some $-NR_2$ groups to afford the complexes Ni(RO-SacSac)$_2$ and Ni(R$_2$N-SacSac)$_2$. Mixed-ligand complexes were frequently observed by TLC in the reaction mixture and in two instances these have been isolated, viz., Ni(OEt-SacSac)(Et$_2$N-SacSac) and Ni(OEt-SacSac)(pyrr-SacSac). This suggests the reaction probably proceeds by a two-step process. A similar two-step reaction is suggested for the conversion of the xanthate Pt(BzXan)$_2$ to the dithiocarbamate Pt(4-Me(pip)dtc)$_2$ although no intermediates were isolated.[4,5] Few reactions of this type have been characterized with Ni(II) complexes,[6] probably because most Ni(II) complexes interact with an attacking base by increasing the coordination number of the Ni(II) ion. Although Ni(OEt-SacOEt-ac)$_2$ forms both five- and six-coordinated adducts with nitrogen bases,[7] Ni(OEt-SacSac)$_2$ does not.[1]

The NMR spectra (Table II) confirm the diamagnetism and constitution of the new complexes with the most notable movement in chemical shift values with substituent changes being apparent in the resonance position of the ring proton. The replacement of two $-CH_3$ groups in Ni(SacSac)$_2$ by two –OR and $-NR_2$ groups progressively moves the ring proton resonance to high fields, i.e., 7.1 → 6.6 → 6.4 ppm (δ values). This trend parallels the expected increase of electron density on the ligand from contributions of canonical forms of the type $>C{=}O^+R$ and $>C{=}N^+R_2$. The ring proton is also slightly shielded in [Ni(SacSac)(MNT)]$^-$ relative to Ni(SacSac)$_2$—a fact that also correlates with the increased charge on the former complex.

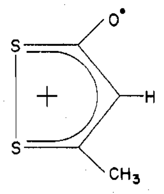
Mass spectral data on the new complexes show a parent ion peak for the monomeric complexes. Ions with one ligand, viz., NiL$^+$, are observed for the –OR substituted ligands although the corresponding peak is weak or absent with the $-NR_2$ substituted complexes. The 1,2-dithiolium ion fragment III is observed in all cases, being a feature of the mass spectra of 1,3-dithio chelates.[8,9]



III



IV



V

For the –OR substituted ions III (R = Et, *n*-Pr, *n*-Bu) loss of an unsaturated fragment leads to ion IV with m/e 133. With –OMe, however, the $\cdot CH_3$ radical is lost homolytically and radical cation V, m/e 132, is formed. These losses are substantiated by the observation of the expected metastable peaks. Similar processes are not apparent with the $-NR_2$ substituted ions. The mass spectrum of the mixed-ligand species Ni(OEt-SacSac)(NEt$_2$-SacSac) exhibits a parent ion peak, together with the peaks observed with Ni(OEt-SacSac)$_2$ and Ni(NEt$_2$-SacSac)$_2$, suggesting that thermal rearrangement on the probe takes place.

Electronic spectral data are collected in Table III and illustrate the bathochromic shift of the first absorption band on replacing the –OR group with $-NR_2$. Interestingly, the

Table II. NMR and Infrared Spectra

Compd	NMR spectra[a] H O	NMR spectra[a] H N	X-CH$_{2\ or\ 3}$	CH$_{2\ or\ 3}$	CH$_{2\ or\ 3}$	CH$_3$	CH$_3$ (ring)	Ir spectra[b] ν(C=C)	ν(C–O)	ν(C–N)
Ni(OMe-SacSac)$_2$	6.58 (s)		4.07 (s)				2.31 (s)	1500	1205	
Ni(OEt-SacSac)$_2$[c]	6.59 (s)		4.46 (q)	1.38 (t)			2.31 (s)	1510	1203	
Ni(O-*n*-Pr-SacSac)$_2$	6.61 (s)		4.36 (t)	1.83 (6)	1.08 (t)		2.32 (s)	1500	1190	
Ni(O-*n*-Bu-SacSac)$_2$	6.59 (s)		4.40 (t)	1.78 (m)	1.46 (m)	0.98 (t)	2.32 (s)	1500	1199	
Ni(NEt$_2$-SacSac)$_2$		6.43 (s)	3.73 (q)	1.29 (t)			2.34 (s)	1530		1430?
Ni(pyrr-SacSac)$_2$[d]		6.34 (s)	(Broad resonances at 1.96, 3.54, 3.76)				2.33 (s)	1526		1441
Ni(pip-SacSac)$_2$		6.53 (s)	(Broad resonances at 1.70, 3.90)				2.33 (s)	1518		1439
Ni(4-Me(pip)-SacSac)$_2$		6.54 (s)	(Broad multiplets at 1.32, 1.80, 3.10, 4.74)				2.32 (s)[e]	1516		1445
Ni(Ph-SacPh-Sac)(OEt-SacSac)	6.64 (s)		4.49 (q)	1.43 (t)			2.36 (s)[f]			
Ni(NEt$_2$-SacSac)(OEt-SacSac)								1522 1499	1200	1430
Ni(pyrr-SacSac)(OEt-SacSac)	6.57	6.37	4.45 (Broad resonances at 2.05, 3.57, 3.80)	1.40			2.29 2.34	1530 1500	1200	1442
[Ni(SacSac)(MNT)][(*n*-Bu)$_4$N]	6.91		2.12 {[(*n*-Bu)$_4$N]$^+$: 3.30, 1.59, 1.05}							
Ni(SacSac)$_2$[g]	7.06						2.31			

[a] δ values with TMS at $\delta = 0.00$ ppm; all spectra obtained in $CDCl_3$. [b] KBr disk; cm^{-1}. [c] A. R. Hendrickson and R. L. Martin, *Inorg. Chem.*, **12**, 2582 (1973). [d] Saturated solution; data obtained by CAT techniques. [e] –CH$_3$ group (0.97 (d)). [f] Aromatic protons (7.2–7.8 (m)). [g] C. G. Barraclough; R. L. Martin, and I. M. Stewart, *Aust. J. Chem.*, **22**, 891 (1969).

Table III. Electronic Absorption Spectra in CH_2Cl_2

Complex	Absorption[a]
Ni(OMe-SacSac)$_2$	681 (1.86), [565] (2.58), 481 (3.08)
Ni(OEt-SacSac)$_2$[b]	677 (1.94), [563] (2.63), 485 (3.52)
Ni(O-*n*-Pr-SacSac)$_2$	[651] (2.18), [564] (2.79), 479 (3.45)
Ni(O-*n*-Bu-SacSac)$_2$	673 (1.90), [560] (2.67), 480 (3.50)
Ni(NEt$_2$-SacSac)$_2$	644 (1.98), [524] (2.94), *c*
Ni(pyrr-SacSac)$_2$[d]	632, [518], [446]
Ni(pip-SacSac)$_2$[e]	646 (1.99), [527] (2.96), [429] (3.68)
Ni(4-Me(pip)-SacSac)$_2$	641 (2.07), [533] (2.96), [429] (3.61)
Ni(OEt-SacSac)(NEt$_2$-SacSac)	657 (1.99), [549] (2.92), *c*
Ni(OEt-SacSac)(pyrr-SacSac)	657 (1.98), [546] (2.93), [509] (3.03), 451 (3.58)
[Ni(SacSac)(MNT)][(*n*-Bu)$_4$N][f]	[751] (2.58), 694 (2.63), 448 (3.63)

[a] Wavelength in nm; brackets, shoulders; parentheses, log ε values. [b] In cyclohexane: 680, [571], 485 nm; ref 1. [c] Not measured in the region. [d] Saturated solution. [e] In benzene: 651, [545], [461], [413] nm. [f] MNT^{2-} = $S_2C_2(CN)_2^{2-}$; run to 900 nm.

mixed-ligand complexes exhibit band positions intermediate between those of the parent compounds suggesting an average ligand field is appropriate for the mixed-ligand complexes.

The earlier assignment of the 1203-cm^{-1} infrared band in Ni(OEt-SacSac)$_2$ to a ν(C–O) mode appears reasonable as this absorption is present in all complexes with the –OR substituent and absent in those with only the –NR$_2$ unit (Table II). The band at ~1440 cm^{-1} in the Ni(NR$_2$-SacSac)$_2$ complexes is suggested to arise from the ν(C–N) mode by analogy with the related band in dithiocarbamate complexes.[10,11]

The redox properties of a series of 1,3-dithio chelates of Ni(II) have been examined in acetone–0.1 M Et_4NClO_4 solution at both Hg and Pt electrodes. All potentials refer to the Ag–AgCl–0.1 M LiCl electrode in acetone. Details of procedures and instrumentation are provided in ref 3.

A few complexes of this type have been examined *polarographically* before although no oxidation waves had been observed at the Hg electrode. In the present series, an irreversible oxidation process is observed at a Pt electrode. Controlled-potential oxidative electrolysis of the deep red-violet Ni(SacSac)$_2$ at +1.3 V gives a pale solution and an *n* value of 4.1 ± 0.1 electrons/mol of Ni(SacSac)$_2$. These facts suggest the formation of 3,5-dimethyl-1,2-dithiolium ions, viz.

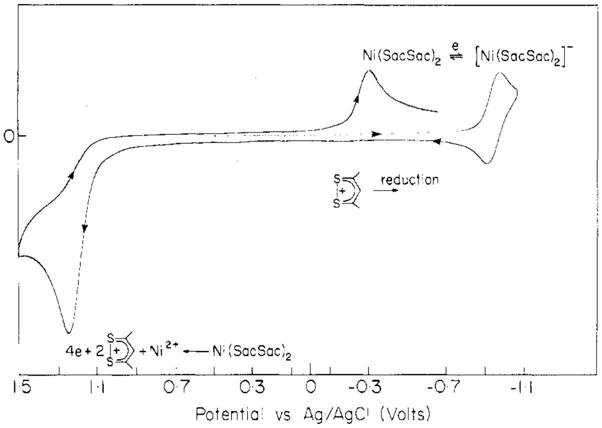
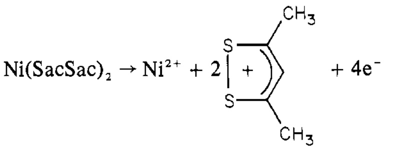


Figure 1. Cyclic voltammogram of Ni(SacSac)$_2$ in acetone–0.1 M Et_4NClO_4 vs. Ag–AgCl–0.1 M LiCl reference electrode.



(1)

A similar process has been observed for the oxidation of Zn(OEt-SacSac)$_2$.[13]

By cyclic voltammetry the oxidation is seen as irreversible (Figure 1). Subsequent cathodic scanning shows the reduction peak due to an uncharacterized, irreversible reduction of the 3,5-dimethyl-1,2-dithiolium ion. The origin of this reduction is confirmed by comparison with the voltammetry of a pure sample of 3,5-dimethyl-1,2-dithiolium iodide.

Spectral characterization during the electrolysis of Ni(SacSac)$_2$ also shows the formation of the 3,5-dimethyl-1,2-dithiolium ion (Figure 2). This study was performed in CH_2Cl_2 saturated with Et_4NClO_4, to extend the spectral range to 270 nm. The *n* value was checked (+1.6 V) in this solvent at 3.8 electrons/mol of Ni(SacSac)$_2$. Chemical oxidation of M(SacSac)$_2$ (M = Co, Ni) with halogens affords the well-characterized 1,2-dithiolium salts $[SacSac]^+{}_2[MX_4]^{2-}$.[14] The oxidative behavior of the 1,3-dithio chelates of Ni(II) under these conditions is markedly different from that of both the 1,2- and 1,1-dithio complexes where the metal chelates remain intact and provide examples of ligand-based[15] and

Table IV. Voltammetric Parameters for Redox Processes of Ni(II) Complexes[a]

	Reduction								Oxidation[b]		
	Ac voltammetry[c]				Cyclic voltammetry[d]				Ac voltammetry[c]		
	Pt		Hg		Pt		Hg		Pt		
Compd	E_p, V	$\Delta E_{p/2}$, mV	E_p, V	$\Delta E_{p/2}$, mV	ΔE_p, mV	i_f/i_r	ΔE_p, mV	i_f/i_r	E_p, V	$\Delta E_{p/2}$, mV	i_p/c, μA l. mM^{-1}
$Ni(SacSac)_2$	−0.950	93	−0.955	88	68	1.2	76	1.0	+1.195	187	16
$Ni(OMe\text{-}SacSac)_2$	−0.845	112	−0.844	89	65	1.0	65	1.0	+1.234	142	32
$Ni(OEt\text{-}SacSac)_2$	−0.865	113	−0.862	94	68	1.0	75	1.0	+1.237	133	37
Ni(O-*n*-Pr-SacSac)$_2$	−0.871	100	−0.873	100	72	1.0	66	1.0	+1.243	127	32
Ni(O-*n*-Bu-SacSac)$_2$	−0.873	139	−0.872	107	79	1.0	90	1.0	+1.253	137	38
Ni(pip-SacSac)$_2$	−1.255	102	−1.253	93	105	*e*	*e*		+0.927	179	Satd
Ni(4-Me(pip)-SacSac)$_2$	−1.251	105	*e*		79	1.1	*e*		+0.914	142	Satd
Ni(pyrr-SacSac)$_2$	−1.345	*e*	*e*		74	*e*	*e*		+0.885	*e*	Satd
$Ni(NEt_2\text{-}SacSac)_2$	−1.287	95	*e*		*e*		*e*		+0.865	*e*	Satd
Ni(Ph-SacSac)$_2$	−0.777	93	−0.81[e]	107	67	0.9	80	*e*	+1.162	86	Satd
Ni(Ph-SacPh-Sac)$_2$	−0.606	87	−0.605	*e*	66	*e*	*e*		*e*	*e*	Satd
$Ni(CF_3\text{-}SacSac)_2$	−0.362	92	−0.356	97	72	1.0	72	1.0	>1.5		
$[Ni(MNT)_2]^{2-}$ [f]	−1.546	93	−1.542	94	71	0.9	76	1.0	+0.342	96	62
$[Ni(SacSac)(MNT)]^-$ [f]	−1.178	97	−1.174	90	65	0.9	82	1.0	+0.817	93	42

[a] Acetone–0.1 M Et_4NClO_4 solutions; ~10^{-3} M in Ni(II) complex; potentials vs. Ag–AgCl–0.1 M LiCl electrode. [b] Process irreversible by cyclic voltammetry except for $[Ni(NMT)_2]^{2-}$ where $\Delta E_p = 65$ mV and $i_f/i_r = 1.0$. [c] Scan rate 10 mV s^{-1}. [d] Scan rate 200 mV s^{-1}. [e] Process exhibits poorly defined voltammogram. [f] $[(n\text{-Bu})_4N]^+$ counterion.

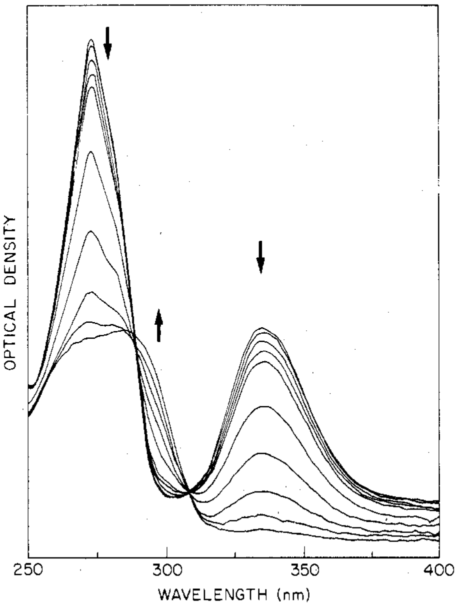
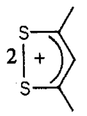


Figure 2. Spectra of a solution of $Ni(SacSac)_2$ during electrolytic oxidation in CH_2Cl_2 saturated with Et_4NClO_4: $Ni(SacSac)_2 \rightarrow Ni^{2+} + 2SacSac^+ + 4e^-$.

metal-based (nickel(III) and -(IV) dithiocarbamates)[16] processes, respectively.

Potentials and related voltammetric data for the other compounds studied are included in Table IV. All of the oxidations are irreversible and are assumed to be related to the process which has been characterized for $Ni(SacSac)_2$.

The mixed-ligand complex $[Ni(SacSac)(MNT)]^-$ exhibits both oxidation and reduction steps with the latter process being at a potential (−1.18 V) intermediate between those of the two parent complexes, $Ni(SacSac)_2$ (−0.95 V) and $[Ni(MNT)_2]^{2-}$ (−1.55 V). The reduction of $[Ni(MNT)_2]^{2-}$ to $[Ni(MNT)_2]^{3-}$ appears to involve a metal-based reduction to the d^9 Ni(I) complex[17] although the metal ion oxidation state in $[Ni(SacSac)(MNT)]^{2-}$ is unknown. The oxidation potential of the mixed-ligand complex also lies between those of the two parent complexes although the oxidation processes of the three complexes are completely different. As shown above, $Ni(SacSac)_2$ undergoes a ligand-based oxidation resulting in decomposition of the complex and formation of 3,5-dimethyl-1,2-dithiolium ions. $[Ni(MNT)_2]^{2-}$ has been shown to undergo a ligand-based oxidation with the retention of the NiS_4 core in $[Ni(MNT)_2]^-$.[15] However, $[Ni(SacSac)(MNT)]^-$ undergoes an irreversible oxidation represented by

$2[Ni(SacSac)(MNT)]^- \rightarrow [Ni(MNT)_2]^- + 2$  $+ Ni^{2+} + 5e^-$ (2)

Coulometric oxidation affords n = 2.5 electrons/mol of $[Ni(SacSac)(MNT)]^-$. The electronic spectrum of the oxidized solution is that of $[Ni(MNT)_2]^-$; subsequent reduction affords $[Ni(MNT)_2]^{2-}$.

The products of oxidation, $[Ni(MNT)_2]^-$ and the dithiolium ions, are readily detected and confirmed by voltammetry. It is worth noting further that, although the products of oxidation are the same as would be obtained from an equimolar mixture of $Ni(SacSac)_2$ and $[Ni(MNT)_2]^{2-}$, the potential of the oxidation (+0.817 V) is not sufficiently large to oxidize the $Ni(SacSac)_2$ component (+1.195 V) of such a mixture.

Reduction of $Ni(SacSac)_2$ has been examined *polarographically* at a dropping mercury electrode (DME) where the process was shown to be eq 3 and 4.

$$\begin{tikzcd}
\mathrm{Ni(SacSac)_2} \arrow[r, "e^-", shift left] & \mathrm{[Ni(SacSac)_2]^-} \arrow[l, shift left] \arrow[r, "e^-", shift left] \arrow[d] & \mathrm{[Ni(SacSac)_2]^{2-}} \arrow[l, shift left] & (3) \\
 & \text{“}\mathrm{[Ni(SacSac)_2]^{-}}\text{”} \arrow[r, "e^-", shift left] & \text{“}\mathrm{[Ni(SacSac)_2]^{2-}}\text{”} \arrow[l, shift left] & (4)
\end{tikzcd}$$

The nature of the complexes in quotes was not explored.[12] In the present study the reduction of the series of Ni(II) complexes has been examined by voltammetry at both Hg and Pt electrodes and the data are collected in Table IV. The instability of $[Ni(SacSac)_2]^-$ is also confirmed by voltammetry. The electronic configuration of the reduced complexes is not known.

The effect of substituents on the reduction potential of the Ni(II) complexes is quite dramatic. For the complexes examined in this work, the reduction potentials cover a range of 1.0 V, progressing from −0.362 V for $Ni(CF_3\text{-}SacSac)_2$ to −1.345 V for $Ni(pyrr\text{-}SacSac)_2$. The potential trend follows the usual progression of substituent effects as embodied in the Taft parameters. A plot of $\sum\sigma_m$ per ligand vs. redox potential

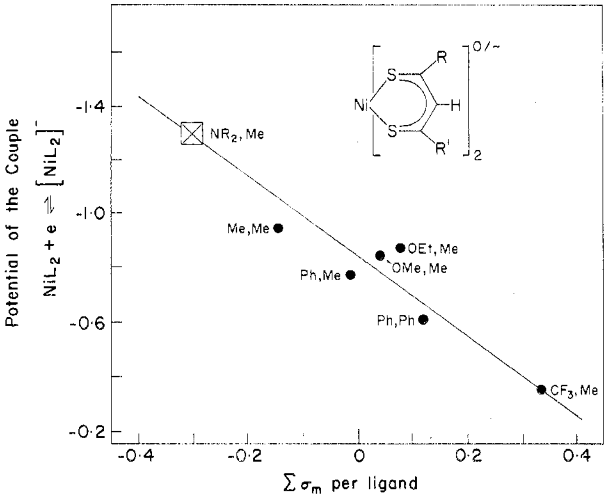


Figure 3. Correlation between substituent effects on Ni(R-SacR'-Sac)$_2$ (approximated by $\Sigma\sigma_m$) and the reduction potentials of the complexes.

exhibits a reasonable correlation although the nonavailability of some parameters and the inadequacy of σ_m values in the present context detracts from the correlation (Figure 3). The observed trend is obviously related to the electron density at the ligating sulfur groups which is at a maximum with $-NR_2$ groups and a minimum with the electron-withdrawing $-CF_3$ substituent. The electron-rich sulfur ligands stabilize the Ni(II) complex with respect to the reduced form, while the opposite pertains for the electron-withdrawing substituents. These phenomena are discussed more fully in a forthcoming review article.[18]

Registry No. Ni(OEt-SacSac)$_2$, 41523-92-6; Ni(OMe-SacSac)$_2$, 19998-79-9; Ni(O-*n*-Pr-SacSac)$_2$, 58298-11-6; Ni(O-*n*-Bu-SacSac)$_2$, 58298-12-7; Ni(Et$_2$N-SacSac)$_2$, 58298-13-8; Ni(pyrr-SacSac)$_2$, 58298-14-9; Ni(pip-SacSac)$_2$, 58298-15-0; Ni(4-Me(pip)-SacSac)$_2$, 58298-16-1; Ni(OEt-SacSac)(NEt$_2$-SacSac), 58298-17-2; Ni-(OEt-SacSac)(pyrr-SacSac), 58298-18-3; Ni(OEt-SacSac)(Ph-SacPh-Sac), 58312-82-6; [(*n*-Bu)$_4$N][Ni(SacSac)(MNT)], 58312-81-5; Ni(SacSac)$_2$, 10170-79-3; [(*n*-Bu)$_4$N]$_2$[Ni(MNT)$_2$], 18958-57-1; Ni(Ph-SacPh-Sac)$_2$, 21609-14-3; MeOH, 67-56-1; *n*-PrOH, 71-23-8; *n*-BuOH, 71-36-3; Et$_2$NH, 109-89-7; pyrrolidine, 123-75-1; piperidine, 110-89-4; 4-methylpiperidine, 626-58-4.

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Electron Distribution in μ-Acetylene-bis(cyclopentadienylnickel) by Low-Temperature X-Ray Diffraction

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The crystal and molecular structure of μ-acetylene-bis(cyclopentadienylnickel), $(\eta^5\text{-}C_5H_5Ni)_2CH{\equiv}CH$, has been determined by single-crystal x-ray diffraction at room and liquid nitrogen temperature. The compound crystallizes in an orthorhombic space group *Fm*2*m*, with four molecules in the unit cell. Cell dimensons are $a = 17.209$ (8), $b = 6.606$ (3), and $c = 9.311$ (5) Å, at room temperature and $a = 17.195$ (14), $b = 6.489$ (14), and $c = 9.162$ (8) Å at 77 K. The dinuclear molecule has *mm* symmetry. A short Ni–Ni distance of 2.345 (3) Å is found. The cyclopentadienyl ring shows a static disorder around the axis that passes through the nickel and the center of the ring. The acetylene ligand is cis bent with a CC distance of 1.341 (6) Å. The electron density maps support a straight metal–metal bond with a double maximum along its axis and a predominance of bonding between the nickel atoms and a slightly antibonding acetylene b_1 orbital in the metal–acetylene interaction.

Introduction

Metal clusters have been of major interest for the recent quarter of the century. Because of the normally found short metal–metal distance and diamagnetic behavior, a metal–metal interaction is firmly established. However, the nature of this bond is still controversial. $Co_2(CO)_8$ is an example. The structure[1] was found to be surprisingly close to that of $Fe_2(CO)_9$[2] with one bridge carbonyl missing. In both cases, there are 17 valence electrons around Co and Fe atoms. By introducing a metal–metal bond between the two metal atoms, the 18-electron rule would be satisfied and the short intermetallic distance could be explained. Early studies on dinuclear Rh,[3] Co,[4a] Fe,[4b] and Ni[4a] complexes led to a proposal of a "bent" metal–metal bond shared by one electron of d^2sp^3 hybridization from each metal atom and a completely filled t_{2g} orbital ($t_{2g}{}^6$). The molecular orbital scheme described by Sumner et al. corresponds to a "straight" metal–metal bond, with the sixth octahedral vertex occupied by a lone pair of electrons and five electrons in the t_{2g} orbital around each atom ($t_{2g}{}^5$), which forms an a_1 σ type "straight" metal–metal bond and e π, π^* molecular orbitals. The purpose of the present work is to investigate the nature of this metal–metal bond with density maps based on accurate x-ray diffraction data. This technique has been applied successfully on a number of