Sulfur Chelates. IV.[1] Sulfur Addition to Dithiolato Complexes of Nickel(II)

D. Coucouvanis and John P. Fackler, Jr.

Contribution from the Department of Chemistry, Case Institute of Technology, Cleveland, Ohio 44106. *Received October 12, 1966*

Abstract: Certain 1,1-dithiolate metal complexes have been found to react with elemental sulfur to form new complexes containing one additional sulfur atom per ligand. Studies of the oxidation of $Ni(CS_3)_2^{2-}$ were of special interest since oxidation by iodine as well as with elemental sulfur produced the anion $Ni(CS_4)_2^{2-}$. The reaction of these sulfur-rich species with triphenylphosphine results in the loss of one sulfur atom per ligand from the complex. Radioactive sulfur-35 tracer studies showed that the sulfur atom added is the same one abstracted by the triphenylphosphine. Physical and chemical properties of these new complexes suggest that the addition of sulfur expands the size of the chelate ring. Cyclic polarograms show the sulfur-rich species are reversibly oxidized while the 1,1-dithiolates themselves are not. The spectral properties of the sulfur-rich species are reported. The nickel(II) complexes are diamagnetic and presumably planar.

The oxidation of thiols to disulfides[2,3] and the reduction of the disulfides to monosulfides[4,5] are reactions well known to the chemistry of organic sulfur compounds. For example, the abstraction of sulfur from disulfides[4,5] or sulfur[6] with $P(C_6H_5)_3$ has been studied extensively. Similar sulfur addition and abstraction reactions with metal complexes containing sulfur-coordinated ligands have not been reported previously in spite of the considerable interest displayed recently in sulfur-containing metal complexes.[7,8]

During the investigation of 1,1-dithiolate complexes of transition metal ions,[9] we have noted that complexes of nickel(II) of the type $Ni(S_2CX)_2^{2-}$ with X = $CHNO_2$,[9] S,[1] $C(CN)COC_6H_5$, NCN,[1] $C(CN)CONH_2$,[10] or $C(CN)COOC_2H_5$[10] react with iodine in DMSO (dimethyl sulfoxide), or with elemental sulfur in DMF (dimethylformamide), to give the new anionic complexes of type $Ni(S_3CX)_2^{2-}$. These sulfur-rich species react with triphenylphosphine to produce in high yield the original 1,1-dithiolate complex (reaction 1) and triphenylphosphine sulfide.

$$Ni(S_3CX)_2^{2-} + P(C_6H_5)_3 \longrightarrow SP(C_6H_5)_3 + Ni(S_2CX)_2^{2-} \quad (1)$$

In this paper we describe the formation and properties of these new sulfur-rich species. Also studies of the addition and abstraction of radioactive sulfur-35 to $Ni(S_2CS)_2^{2-}$ are described and discussed.

Experimental Section

Chemicals. All of the chemicals in this research were used as received. Benzoylacetonitrile was purchased from Eastman Organic Chemicals. Radioactive sulfur-35 in a toluene solution with ~50-μcurie activity was purchased from Nuclear Chicago Corp., Chicago, Ill. Analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Melting points recorded are uncorrected. The complexes have been checked for purity by thin layer chromatography whenever feasible.

Physical Measurements. Magnetic susceptibilities were determined at room temperature using a Faraday technique. The calibrant was $Hg[Co(SCN)_4]$.[11]

Infrared spectra were obtained with a Beckman IR-8 recording spectrophotometer, frequency calibrated with polystyrene. Ultraviolet, visible, and near-infrared spectra were obtained with a Cary Model 14 recording spectrophotometer. A Beckman IR-5A recording spectrophotometer was used to examine the compounds from 600 to 200 cm^{-1}. Conductance measurements at room temperature were made with a Leeds and Northrup conductivity bridge.

The X-ray powder patterns of the complexes were observed with a Debye-Scherrer camera utilizing nickel-filtered copper radiation.

Oxidation–reduction studies in spectroquality DMSO (Matheson) were made using a stationary platinum wire electrode in a three-electrode cell with a cyclic potential scanner. A saturated calomel electrode was used as the reference electrode and a 0.1 *M* solution of $(C_3H_7)_4NPF_6$ in DMSO was used as the supporting electrolyte.

Radioactive reactants and products were measured for activity with a thin window Geiger–Mueller counter on an R.I.D.L. scanner. Recrystallized sulfur was used to produce a sulfur mixture having the activity indicated in Table VI.

Trithiocarbonato Complexes. The tetraphenylarsonium and benzyltriphenylphosphonium bis(trithiocarbonato)nickel(II) salts were prepared as reported previously.[1]

Perthiocarbonato Complexes. Potassium perthiocarbonate, K_2CS_4, was prepared as described by Yeoman.[12]

Bis(benzyltriphenylphosphonium)bis(perthiocarbonato)nickel(II), $(BzPh_3P)_2Ni(CS_4)_2$. To a solution of 1.4 g of nickel(II) acetate, $Ni(OAc)_2 \cdot 4H_2O$, in 75 ml of water, a solution of 2.18 g of K_2SC_4 in 25 ml of H_2O was added with stirring. The solution was filtered. To the clear brown-red filtrate a solution of 4.0 g of $BzPh_3PCl$ in 100 ml of a 1:1 acetone–water mixture was added with stirring. A red-brown precipitate formed at once which was filtered, air-dried, and dissolved in hot nitromethane. Upon addition of ether to first cloudiness and cooling to 0°, 3.5 g of brown-red crystals were isolated. 60% yield, mp 209–210°.

Anal. Calcd for $C_{52}H_{44}P_2S_8Ni$: C, 59.7; H, 4.2. Found: C, 60.1; H, 4.3.

Bis(tetraphenylarsonium)bis(perthiocarbonato)nickel(II). The tetraphenylarsonium salt of the complex was prepared in a manner similar to that for the benzyltriphenylphosphonium salt with a 50% yield.

Anal. Calcd for $C_{50}H_{40}As_2S_8Ni$: C, 54.3; H, 3.62. Found: C, 54.7; H, 3.47.

Bis(triphenylmethylarsonium)bis(1-nitroethylene-2,2-dithiolato)nickel(II), $(MePh_3As)_2Ni(NED)_2$. This complex was prepared as indicated previously.[9] To a solution of 0.43 g of K_2NED[13] in 50 ml of an ethanol–water (2:1) mixture, a solution of 0.25 g of Ni-

---

(1) Part III: J. P. Fackler, Jr., and D. Coucouvanis, *J. Am. Chem. Soc.*, **88**, 3913 (1966).

(2) F. H. McMillan and J. A. King, *ibid.*, **70**, 4143 (1948).

(3) M. Schmidt and W. Siebert, *Angew. Chem.*, **78**, 607 (1966).

(4) A. Schönberg and M. Z. Barakat, *J. Chem. Soc.*, 892 (1949).

(5) A. A. Watson, *ibid.*, 2100 (1964).

(6) P. D. Bartlett and G. Meguerian, *J. Am. Chem. Soc.*, **78**, 3710 (1956).

(7) A. H. Maki, T. E. Berry, A. Davison, R. H. Holm, and A. L. Balch, *ibid.*, **88**, 1080 (1966), and references therein.

(8) H. B. Gray, *Progr. Transition Metal Chem.*, **1**, 239 (1966); G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **88**, 3235 (1966).

(9) J. P. Fackler, Jr., and D. Coucouvanis, *Chem. Commun.*, 566 (1965).

(10) D. Coucouvanis and J. P. Fackler, Jr., to be published.

(11) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

(12) E. W. Yeoman, *ibid.*, **119**, 38 (1921).

(13) E. Freund, *Ber.*, **52B**, 542 (1919).

$(OAc)_2 \cdot 4H_2O$ and 1 g of $(MePh_3As)I$ in 30 ml of 95% ethanol was added with stirring. The resulting deep blue solution was boiled for 2 min and filtered. On cooling, 0.8 g of blue-violet needles was isolated in ~82% yield. The precipitate was washed with water and ether and was air-dried, mp 195–196°.

Anal. Calcd for $C_{42}H_{36}As_2N_2O_4S_4Ni$: C, 51.92; H, 3.95; N, 2.88; S, 13.24. Found: C, 51.08; H, 3.83; N, 2.80; S, 12.99.

Bis(benzyltriphenylphosphonium)bis(1-nitroethylene-2,2-dithiolato)nickel(II). This salt, mp 221–221.5°, was prepared as above in an 80% yield.

Anal. Calcd for $C_{54}H_{46}P_2N_2O_4S_4Ni$: C, 62.6; H, 4.45; N, 2.70. Found: C, 62.5; H, 4.50; N, 2.50.

Bis(triphenylbenzylphosphonium)bis(nitroethylene-2,2-dithiolato)-platinum(II). Potassium tetrachloroplatinum(II), 0.42 g, was dissolved into 50 ml of water, and the solution was filtered into a solution of 0.45 g of K_2NED and 0.8 g of $BzPh_3PCl$ in 50 ml of water. The bright red precipitate which formed was filtered off and dissolved into a minimum amount of hot nitromethane, and ether was added until the first cloudiness appeared. On cooling 1 g, 79% yield, of dark red needles was isolated.

Anal. Calcd for $C_{54}H_{46}P_2N_2O_4S_4Pt$: C, 55.3; H, 3.93; N, 2.92. Found: C, 54.4; H, 3.97; N, 2.21.

Bis(triphenylbenzylphosphonium)bis(1-nitroethylene-2,2-dithiolato)palladium(II). Palladium(II) chloride, 0.15 g, was refluxed for 15 min in 150 ml of ethanol. The ethanolic solution was filtered into an aqueous solution of 0.77 g of $BzPh_3PCl$ and 0.43 g of K_2NED. A golden brown precipitate was recovered which on recrystallization from nitromethane–ether gave 0.8 g of product, mp 209–210°, 89% yield.

Anal. Calcd for $C_{54}H_{46}P_2N_2O_4S_4Pd$: C, 59.8; H, 4.25; N, 2.63. Found: C, 58.48; H, 4.41; N, 2.49.

Sodium Benzoylacetonitrile. The sodium salt of benzoylacetonitrile was prepared in almost quantitative yields by treating a solution of benzoylacetonitrile in ethanol with a stoichiometric amount of sodium hydroxide in absolute ethanol.

Bis(tetrabutylammonium)bis(1-benzoyl-1-cyanoethylene-2,2-dithiolato)nickel(II), $[(C_4H_9)_4N]_2Ni(BCD)_2$. Sodium benzoylacetonitrile, 2 g, was dissolved into 50 ml of DMSO. To the solution, 8 ml of carbon disulfide was added with stirring. The solution immediately turned color from pale yellow to red. After 10 min of stirring, a hot solution of 2.4 g of $Ni(OAc)_2 \cdot 4H_2O$ and 6 g of tetrabutylammonium bromide in 80 ml of ethanol–water (1:1) was added with stirring. A red-violet solution developed instantly which, upon addition of 50 ml of water, deposited a red-violet precipitate. The precipitate was recovered, air-dried, and dissolved into 350 ml of hot acetone. The solution was filtered and water added to first cloudiness. On cooling, ~5 g of crystalline product was recovered, mp 170–171°. A 78% yield based on sodium benzoylacetonitrile was obtained.

Anal. Calcd for $C_{52}H_{82}N_4O_2S_4Ni$: C, 63.6; H, 8.36; N, 5.71. Found: C, 63.4; H, 8.37; N, 6.00.

Preparation of $(BzPh_3P)_2Ni(CS_4)_2$ from $(BzPh_3P)_2Ni(CS_3)_2$. (a) Reaction of $(BzPh_3P)_2Ni(CS_3)_2$ with Iodine in DMSO. Iodine, 0.3 g, was dissolved in 20 ml of DMSO, and the solution was added to a solution of $(BzPh_3P)_2Ni(CS_3)_2$ in 30 ml of DMSO. The resulting red solution turned brown after it was agitated for 5 min. Addition of 150 ml of water produced a brown-yellow precipitate. The solution was filtered, and the filtrate upon addition of aqueous $AgNO_3$ gave 0.45 g of silver iodide. The above precipitate was isolated from the aqueous DMSO and dissolved into hot nitromethane. Ether was added in excess, and upon cooling 0.45 g of crystals was isolated, mp 207–208°. The yield based on nickel(II) was ~44%. A mixture with $(BzPH_3P)_2Ni(CS_4)_2$ prepared from K_2CS_4 melted at 206–207°.

(b) Reaction of $(BzPh_3P)_2Ni(CS_3)_2$ with Sulfur in DMSO. The $(BzPh_3P)_2Ni(CS_3)_2$, 1.0 g, was dissolved into 55 ml of DMSO and 0.065 g of sulfur was added. The red solution was heated to 80° with frequent agitation. After 15 min the color changed to brown. (Similar treatment of a sulfur-free red solution of $Ni(CS_3)^{2-}$ resulted in no change.) Upon addition of 150 ml of water a brown precipitate was formed which after recrystallization from nitromethane gave 0.93 g of brown crystals, mp 207–208°, yield 90%. The infrared spectrum of the compound was identical with those of the products prepared by the other procedures.

Reaction of $(BzPh_3P)_2Ni(CS_4)_2$ with Ph_3P in DMSO. Triphenylphosphine, 0.7 g, and $(BzPh_3P)_2Ni(CS_4)_2$, 1.6 g, were dissolved into 50 ml of DMSO, and the brown-to-red solution was warmed to 75° for 20 min. The solution was allowed to cool and 150 ml of water was added. A red precipitate formed which was removed by filtration, leaving a colorless filtrate. The crude product was extracted with 80 ml of boiling benzene for 5 min and filtered. On evaporation of the filtrate, 0.8 g of white crystals of Ph_3PS was obtained, identified by its melting point and infrared spectrum. The red precipitate that remained was dissolved into 100 ml of DMSO, and 100 ml of water added. On standing 1.2 g of red crystals, $(BzPh_3P)_2Ni(CS_3)_2$, was isolated (92% yield).

Chemical Oxidation of Bis(1-nitroethylene-2,2-dithiolato)nickel-(II), $[BzPh_3P]_2Ni(NED)_2$. To $[BzPh_3P]_2Ni(NED)_2$, 1 g, dissolved in 50 ml of DMSO, 0.13 g of I_2 was added with stirring. The violet color almost immediately changed to deep red. Upon addition of 100 ml of water, a black precipitate formed which was filtered, washed with two 10-ml portions of methanol and ether, and dried. On recrystallization from nitromethane–ether, 0.45 g of very dark red crystals was isolated in ~40% yield, mp 183–186°.

Anal. Calcd for $C_{54}H_{46}P_2N_2O_4S_6Ni$: C, 58.9; H, 4.18; N, 2.54. Found: C, 57.7; H, 4.19; N, 2.50.

Reaction of Sulfur with $[BzPh_3P]_2Ni(NED)_2$. To $[BzPh_3P]_2Ni(NED)_2$, 1 g, dissolved into 50 ml of DMF, a solution of 0.07 g of sulfur in 10 ml of benzene was added. The mixture was heated to ~80° for 2 min. It was allowed to cool, and diethyl ether was added until the first appearance of cloudiness. Upon refrigeration to 0°, 0.95 g (~90% yield) of dark red crystals was isolated, mp 184–185°. The product was shown by its infrared spectrum, melting point, and thin layer chromatography (in CH_3NO_2) to be identical with the product from the iodine oxidation.

Reaction of $[BzPh_3P]_2Ni(NED)_2S_2$ with Ph_3P. To $[BzPh_3P]_2Ni(NED)_2S_2$, 1 g, dissolved into 50 ml of DMSO 0.7 g of Ph_3P was added and the solution was heated to 50° for 5 min, during which time a color change from red to violet occurred. Upon addition of water and cooling, 0.75 g (~80% yield) of blue-violet crystals was isolated, mp 220–221°. The product was found by its infrared spectrum and melting point to be identical with the original dithiolate prepared previously (see above).

The Reaction of $[Bu_4N]_2Ni[BCD]_2$ with Sulfur. The $[Bu_4N]_2Ni[BCD]_2$ was treated with elemental sulfur in DMSO in a manner similar to the one presented above. The product, orange-brown crystals, melted at 169–170°. This product reacts with Ph_3P in DMF to regenerate the parent dithiolate in 80% yield.

Anal. Calcd for $C_{52}H_{82}N_4O_2S_6Ni$: C, 59.8; H, 7.84; N, 5.36. Found: C, 61.18; H, 8.00; N, 6.21.

Results

Certain square-planar 1,1-dithiolate nickel(II) complexes[14] react with oxidants or elemental sulfur to form new sulfur-rich complexes. In Table I the physical properties of the sulfur-rich complexes $(Ph_4As)_2Ni(CS_4)_2$, $(BzPh_3P)_2Ni(NED)_2S_2$, and $(Bu_4N)_2Ni(BCD)_2S_2$ are compared with their 1,1-dithiolate progenitors.

Table I. Physical Properties of CS_4, NED,[a] $NEDS_2$, BCD,[a] and $BCDS_2$ Complexes

Complex	Color	$\Lambda(10^{-3}\ M)^b$	Mp, °C
$(Ph_4As)_2Ni(CS_3)_2$	Bright red	171	217–218
$(Ph_4As)_2Ni(CS_4)_2$	Brown	176	208–209
$(Ph_4As)_2Pt(CS_4)_2$	Red	160	259–262
$(Ph_3MeAs)_2Ni(NED)_2$	Blue-violet	...	195–196
$(BzPh_3P)_2Ni(NED)_2$	Blue-violet	154	221–222
$(BzPh_3P)_2Pd(NED)_2$	Golden brown	...	209–210
$(BzPh_3P)_2Pt(NED)_2$	Deep red	164.5	235 dec
$(BzPh_3P)_2Ni(NED)_2S_2$	Dark red	141	183–186
$(Bu_4N)_2Ni(BCD)_2$	Red-violet	144	170–171
$(Bu_4N)_2Pt(BCD)_2$	Orange-red	...	...
$(Bu_4N)_2Ni(BCD)_2S_2$	Orange-brown	156	169–170

[a] NED = $S_2CCH(NO_2)^{2-}$ and BCD = $S_2CC(CN)COC_6H_5$. [b] Nitromethane solvent at ~24°; 1:1 electrolyte $\Lambda(10^{-3}\ M)$ ~70–90 $ohm^{-1}\ cm^{-1}$; 2:1 electrolyte $\Lambda(10^{-3}\ M)$ ~160–180 $ohm^{-1}\ cm^{-1}$, $\Lambda(10^{-3}\ M)$ ~210–230 $ohm^{-1}\ cm^{-1}$. These complexes are all diamagnetic.

---

[14] Preliminary data suggest palladium(II) and platinum(II) complexes behave similarly. In addition to those ligands reported in detail here, qualitative evidence for this type of oxidation with sulfur exists for nickel(II) complexes with the ligands S_2CNCN^{2-}, $S_2C(CN)CONH_2^{2-}$, and $S_2C(CN)COOC_2H_5^{2-}$.

Table II. Far-infrared Spectra of Complexes[a]

$(BzPh_3P)_2Ni(CS_4)_2$	$(BzPh_3P)_2Ni(CS_3)_2$	$(BzPh_3P)_2Ni(NED)_2S_2$	$(BzPh_3P)_2Ni(NED)_2$	$(Bu_4N)_2Ni(BCD)_2S_2$	$(Bu_4N)_2Ni(BCD)_2$
620 (w)	620 (w)	615 (m)	615 (m)	590 (w)	590 (w)
572 (m)	572 (m)	578 (m)	578 (m)	565 (m)	565 (m)
					550 (sh)
546 (w)	546 (w)	546 (w)	546 (w)		
			525 (w)		
505 (vs)	507 (vs)	507 (vs)	507 (vs)	513 (m)	
	495 (vs)	495 (vs)	495 (vs)		497 (m)
488 (vs)		476 (m)		478 (s)	477 (w)
467 (w)	467 (w)	465 (w)	465 (w)		
447 (m)	447 (m)	444 (m)	444 (m)		
432 (w)		427 (w)	427 (w)	433 (w)	
379 (m)	383 (s)	389 (m)	392 (s)	386 (m)	382 (s)
		376 (m)	376 (m)	376 (m)	
349 (w)					353 (w)
333 (w)				324 (w)	
320 (w)				300 (w)	

[a] Nujol mulls on polyethylene plates were used.

Each are diamagnetic, 2:1 electrolytes. Their infrared spectra (Figures 1a and b and Table II) show many similarities to the 1,1-dithiolate species but also some very important differences, especially in the S–S vibration region[15] 430–490 cm^{-1}. The strong band near 1035 cm^{-1} in the $(Ph_4As)_2Ni(CS_4)_2$ spectrum is particularly significant since a band at slightly lower frequency, 1010 cm^{-1}, has been assigned to the C=S stretch[1] in $(Ph_4As)_2Ni(CS_3)_2$.

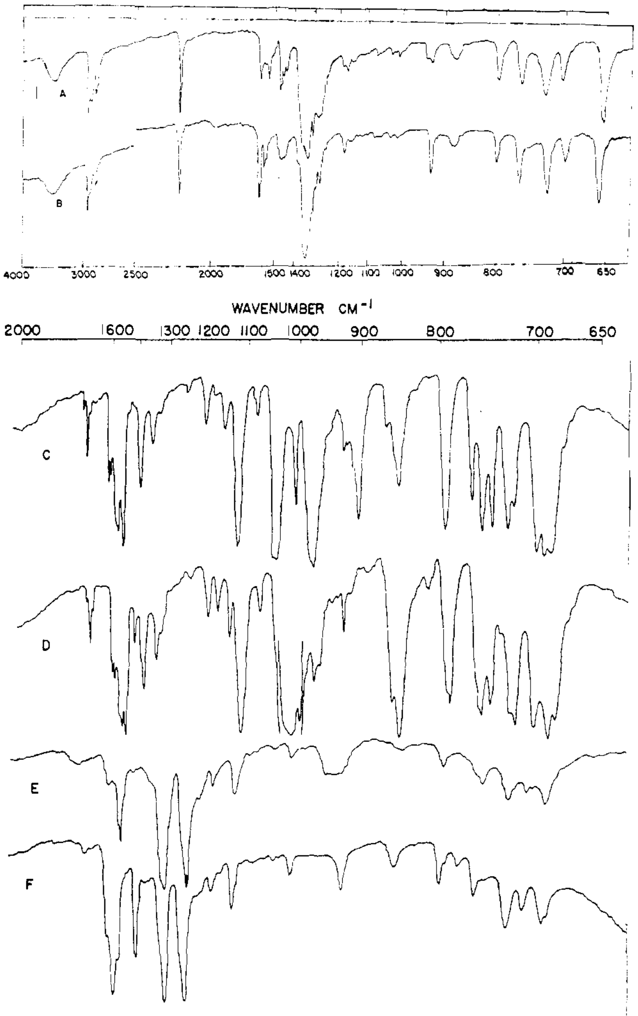


Figure 1. Infrared spectra of complexes: (A) $[(n\text{-}C_4H_9)_4N]Ni[BCD]_2S_2$, (B) $[(n\text{-}C_4H_9)_4N]Ni[BCD]_2$, (C) $[(C_6H_5CH_2)(C_6H_5)_3P]_2Ni[CS_3]_2S_2$, (D) $[(C_6H_5CH_2)(C_6H_5)_3P]_2Ni[CS_3]_2$, (E) $[(C_6H_5CH_2)(C_6H_5)_3P]Ni[NED]_2S_2$, (F) $[(C_6H_5CH_2)(C_6H_5)_3P]_2Ni[NED]_2$ (A, B, and E, KBr disk; C, D, and F, Nujol mull).

The X-ray diffraction powder patterns (Table III) indicate convincingly that these sulfur-rich species are new crystalline complexes.

The visible and ultraviolet spectra of both the 1,1-dithiolates and their sulfur addition products are recorded and presented in Figure 2 and Table IV. A characteristic change in the spectrum accompanies the sulfur addition. The high-intensity band near 19,000 cm^{-1} is shifted to higher energies while the band at 27,000 cm^{-1} is split and loses some intensity. This behavior also has been observed upon sulfur addition to other 1,1-dithiolate species. No bands of the d–d type could be observed since they are obscured by the high-intensity near-ultraviolet absorption.

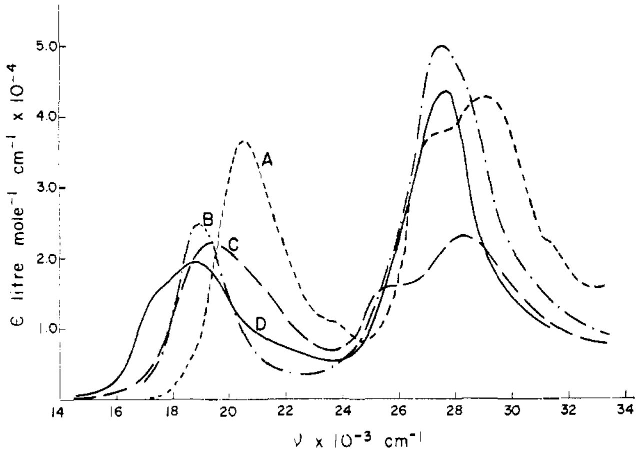


Figure 2. Ultraviolet-visible spectra of (A) $[(n\text{-}C_4H_9)_4N]Ni[BCD]_2S_2$, (B) $[(n\text{-}C_4H_9)_4N]Ni[BCD]_2$, (C) $[(C_6H_5CH_2)(C_6H_5)_3P]_2Ni[NED]_2S_2$, and (D) $[(C_6H_5CH_2)(C_6H_5)_3P]_2Ni[NED]_2$.

The electrochemical oxidation–reduction properties of the 1,1-dithiolates studied here, and their sulfur addition products, in DMSO are summarized in Table V. Using 0.1 *M* $[(n\text{-}C_3H_7)_4N]_2PF_6$ as the electrolyte and the well-studied[6,7,8,16] $Ni(MNT)_2{}^{2-}$ for a standard, cyclic

---

(15) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 352.

(16) E. J. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *J. Am. Chem. Soc.*, 87, 3016 (1965).

Table III. X-Ray Diffraction Data. *d* Spacings of Some Strong Lines

Metal complex[b]	*d* spacings, A						
$(Ph_4As)_2Ni(CS_4)_2$[c]	4.16	3.47		2.94	2.70	2.40	2.30
$(BzPh_3P)_2Ni(CS_4)_2$[c]	11.62	7.35	6.35	5.86	4.22	4.05	3.98
$(BzPh_3P)_2Pd(CS_4)_2$	11.73	7.35	6.37	5.82	4.25	4.12	3.99
$(BzPh_3P)_2Ni(NED)_2$	14.57	9.04	7.31	6.46	5.47	4.52	4.17
$(BzPh_3P)_2Pd(NED)_2$	14.45	9.13	7.37	...[a]	...[a]	4.52	4.16
$(BzPh_3P)_2Pt(NED)_2$	14.45	9.13	7.28	6.48	...[a]	4.50	4.17
$(BzPh_3P)_2Ni(NED)_2S_2$	4.43		3.89	2.62		2.09	
$(Bu_4N)_2Ni(BCD)_2$	8.47	4.68		3.23	2.43	2.26	2.01
$(Bu_4N)_2Pt(BCD)_2$	...[a]	4.72		3.29	...[a]	2.19	2.01
$(Bu_4N)_2Ni(BCD)_2S_2$	5.17	4.17		3.72	2.80	2.61	2.04

[a] Weak; could not be read. [b] Ph = C_6H_5, Bz = C_7H_7, Bu = C_4H_9. [c] Chromium Kα radiation was used.

Table IV. Electronic Spectra of CS_4,[a] NEDS, BCDS, NED, and BCD in DMSO

$\bar{\nu}_{max}$, cm^{-1}	ε, l. mole^{-1} cm^{-1}	$\bar{\nu}_{max}$, cm^{-1}	ε, l. mole^{-1} cm^{-1}
$Ni(CS_4)_2^{2-}$		$Ni(BCD)_2^{2-}$	
21,600	5.2×10^3	18,900	2.4×10^4
25,700	1.6×10^4	27,500	5.0×10^4
27,800 (sh)	1.3×10^4		
31,800	1.6×10^4	$Ni(BCD)_2S_2^{2-}$	
		20,600	3.6×10^4
$Ni(NED)_2^{2-}$		23,800 (sh)	1.1×10^4
17,300 (sh)	1.5×10^4	27,200	3.7×10^4
18,000	1.9×10^4	29,200	4.2×10^4
27,700	4.4×10^4	31,500	2.2×10^4
$Ni(NED)_2S_2^{2-}$			
19,300	2.2×10^4		
21,000 (sh)	1.9×10^4		
25,500	1.6×10^4		
28,300	2.3×10^4		

[a] The spectrum of the CS_3 nickel complex is reported in ref 1.

Table V. Oxidation-Reduction Properties of Complexes

Metal complex[a]	V_{oxid}, v	Comments
$(Ph_4As)_2Ni(CS_4)_2$	+0.265	Reversible oxidation, irreversible reduction
$(Ph_4As)_2Ni(CS_3)_2$	+0.16	Irreversible oxidation and reduction
$(BzPh_3P)_2Ni(NED)_2S_2$	+0.29	Reversible oxidation but no reduction wave observed
$(BzPh_3P)_2Ni(NED)_2$	+0.30	Poorly defined oxidation and reduction
$(Bu_4N)_2Ni(BCD)_2S_2$	+0.30	Reversible oxidation wave but reduction wave not observable
$(Pr_4N)_2Ni(MNT)_2$	+0.255	Completely reversible
$(Pr_4N)_2Cu(MNT)_2$	+0.28	Reversible oxidation but no reduction observed on cycling
$(Pr_4N)_2Ni(i\text{-}MNT)_2$	+0.42	Irreversible oxidation and reduction
$(Pr_4N)_2Ni(CDC)_2$	+0.38	Irreversible oxidation and reduction

[a] *i*-MNT = $S_2CC(CN)_2^{2-}$ and CDC = S_2CNCN^{2-}.

polarograms were obtained (Figure 3) which show the oxidation of the sulfur-rich species to be reversible at a stationary platinum electrode. This is in contrast to the 1,1-dithiolates which are irreversibly oxidized.[1] Reduction waves for both the 1,1-dithiolates and their sulfur addition products are ill-defined. As reported by others[16] the $Ni(MNT)_2^{2-}$ shows reversible one-electron oxidation and reduction waves in the same solvent system; however, the $Cu(MNT)_2^{2-}$ complex does not give a well-defined reduction wave at scanning speeds of ~1-20 cps. The potentials for the oxidation of the 1,1-dithiolates which show sulfur addition and their sulfur addition products are not drastically different from the potentials observed with the MNT^{2-} complexes.

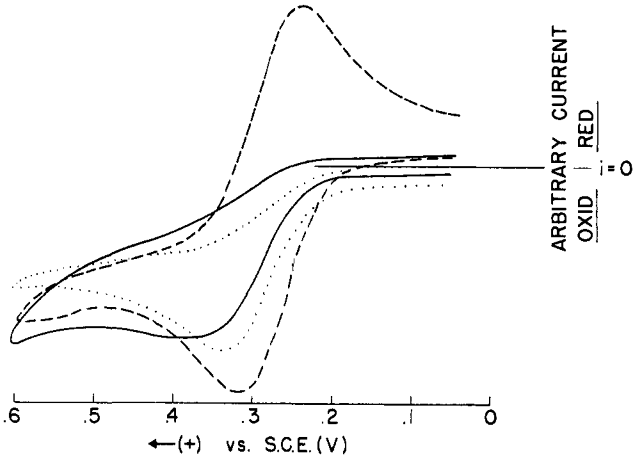


Figure 3. Cyclic polarograms: --------, $Ni(MNT)_2^{2-}$, ———, $Ni(NED)_2S_2^{2-}$, and ·····, $Ni(CS_3)_2S_2^{2-}$.

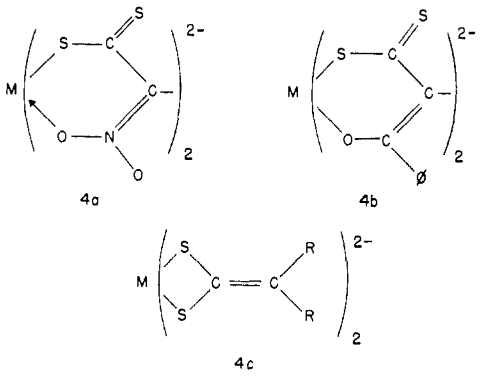
In order to determine unequivocally that one sulfur atom is oxidatively added per ligand in the complex and also with some hope that the position of addition might be determined, $Ni(CS_3)_2^{2-}$ was oxidized with radioactive sulfur-35 and subsequently reduced with Ph_3P. Using DMF as a solvent, the resulting $(Ph_4As)_2Ni(CS_4)_2$ complex isolated showed the activity expected for addition of one sulfur atom per ligand (Table VI).

Table VI. Isotopic S^{35} Addition Data[a]

Expt	S	$(Ph_4As)_2Ni(CS_4)_2$	$(Ph_4As)_2Ni(CS_3)_2$	Ph_3PS
1	2.5×10^5	6.0×10^5	0.8×10^5	2.0×10^5
2	2.5×10^5	7.1×10^5	0.4×10^5	2.1×10^5

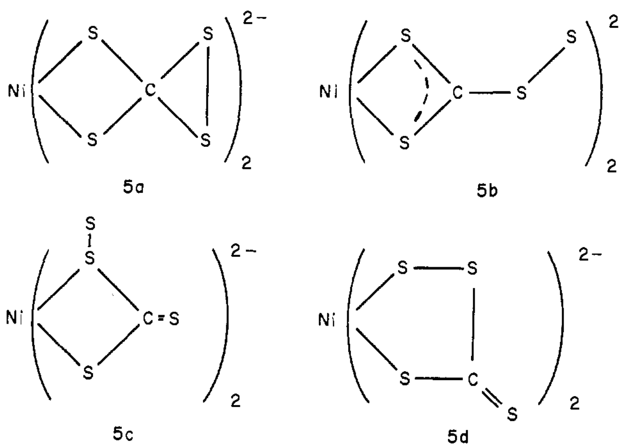
[a] Counts/mmole 10 min. Counts reported above the background count; 190 counts/10 min for expt 1 and 220 counts/10 min for expt 2.

Ph_3PS and $(Ph_4As)_2Ni(CS_3)_2$ recovered from the Ph_3P reduction of the radioactive perthiocarbonate complex each showed some activity. However, the data (Table VI) clearly show that the active sulfur is preferentially removed by the Ph_3P. In fact, the residual activity (5-10%) in $(Ph_4As)_2Ni(CS_3)_2$ may be



4a 4b 4c

Figure 4.



5a 5b 5c 5d

Figure 5.

attributed to the difficulty in separating the two products.

It is important to reiterate the fact that the anionic Ni(CS$_4$)$_2^{2-}$ complexes can be prepared by oxidation with iodine, oxidative addition of sulfur, or from the alkali metal salt of the perthiocarbonate (see Experimental Section). The iodine oxidation leads to a $\sim$50% conversion of the Ni(CS$_3$)$_2^{2-}$ to Ni(CS$_4$)$_2^{2-}$ while the sulfur addition accomplishes this conversion nearly quantitatively. Preliminary studies indicate Ni(*i*-MNT)$_2^{2-}$ does not readily add sulfur.

Discussion

The complexes of S$_2$CCHNO$_2^{2-}$ (NED) and S$_2$CC(CN)COC$_6$H$_5^{2-}$ (BCD) are two more examples in the new series of anionic complexes described previously.[1,9] These species, like the complexes of CS$_3^{2-}$, are oxidized chemically by elemental iodine and have irreversible oxidation potentials close to the potential observed for the 1,2-dithiolate complex[8] Ni(MNT)$_2^{2-}$. The oxidation of this latter compound, however, is reversible. The isomer of MNT^{2-}, namely 1,1-dicyanoethylene-2,2-dithiolate,[1,17] *i*-MNT^{2-}, is oxidized chemically with some difficulty compared with Ni(MNT)$_2^{2-}$ and displays an electrochemically irreversible oxidation potential in DMF (Table V) at a $\sim$0.15-v higher potential than Ni(MNT)$_2^{2-}$. It is significant that Ni(*i*-MNT)$_2^{2-}$, unlike the other 1,1-dithiolate complexes reported in this study, does not oxidatively add sulfur. We attribute this difference in behavior to the relatively high potential necessary to oxidize this species.

The oxidative addition of sulfur to a metal 1,1-dithiolate complex to our knowledge has not been described previously. Presumably such reactions can occur, however, with metal dithiocarbamate scavengers used in vulcanization processes.[18] The product of this sulfur addition is a relatively stable species containing one additional sulfur per ligand. This has been shown conclusively by elemental analysis and radioactive sulfur-35 addition and abstraction studies. In addition the CS$_4^{2-}$ complex prepared from K$_2$CS$_4$ is identical with the species resulting from sulfur addition to Ni(S$_2$CS)$_2^{2-}$.

The complexes in this study presumably all have a square-planar coordination of sulfur atoms about the metal ion. This is confirmed by the diamagnetism of the nickel(II) complexes and, where studied, their isomorphism with the palladium(II) and platinum(II) species. Preliminary X-ray structural studies[19] show Ni(S$_2$CS)$_2^{2-}$ to be nearly planar.

A reasonable structure can be written (Figure 4) in which only one sulfur atom per ligand in the Ni(NED)$_2^{2-}$ and Ni(BCD)$_2^{2-}$ complexes is coordinated to the metal. Six-membered sulfur-oxygen chelate rings would be formed. However, we have rejected this possibility in favor of coordination through the sulfurs (Figure 4c). In addition to the similarities in properties between these complexes and the previously characterized 1,1-dithiolates,[1] Ni(CS$_3$)$_2^{2-}$ and Ni(S$_2$CNCN)$_2^{2-}$, and the general preference of nickel(II), palladium(II), and platinum(II) for sulfur rather than oxygen ligands, the infrared evidence establishes beyond doubt the absence of metal-oxygen bonding in Ni(BCD)$_2^{2-}$. With this complex there are clearly at least two bands in the 1560–1610 cm^{-1} spectral region (Figure 1), and at least one of them must be a carbonyl stretch. No band characteristic of coordinated carbonyl is found in the 1450–1550-cm^{-1} region.[20] The monothiodibenzoylmethane complex of nickel(II) which contains a six-membered ring similar to that in Figure 4b shows bands[21] at 1490 and 1510 cm^{-1}.

With Ni(NED)$_2^{2-}$, the infrared data are not conclusive owing to the complexity in the region in which NO$_2$ absorptions are usually found. However, the nearly identical behavior of Ni(NED)$_2^{2-}$, Ni(CS$_3$)$_2^{2-}$, and Ni(BCD)$_2^{2-}$ to oxidation and sulfur addition and the strikingly similar ultraviolet spectra of these complexes (Figure 2) indicates that a coordination to the nitrate oxygen atom in Ni(NED)$_2^{2-}$ is very unlikely.

The chemical oxidation of 1,1-dithiolates to disulfides is hardly surprising in view of the products obtained by oxidation of (CH$_2$SH)$_2$,[22] dithiocarbamates, xanthates, and thiophosphates.[23] In these cases coupling occurs to form dimers which contain the disulfide linkage. Since the sulfur-rich products Ni(NED)$_2$S$_2^{2-}$ and Ni(BCD)$_2$S$_2^{2-}$ have very similar spectral, chemical, and electrochemical properties to Ni(CS$_4$)$_2^{2-}$ and

---

(17) B. G. Werden, E. Billig, and H. B. Gray, *Inorg. Chem.*, **5**, 78 (1966).

(18) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Chemical Publishing Co., New York, N. Y., 1962, p 231; H. Krebs, E. F. Weber, and H. Fassbender, *Z. Anorg. Allgem. Chem.*, **276**, 128 (1954).

(19) I. C. Paul, University of Illinois, private communication.

(20) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 217.

(21) D. Coucouvanis, unpublished results; see also S. E. Livingstone, Proceedings of the Eighth International Conference on Coordination Chemistry, Vienna, 1964, p 376.

(22) H. Fassbender, *Ber.*, **20**, 400 (1887).

(23) O. Foss, *Acta Chem. Scand.*, **1**, 8 (1947).

thus very likely an identical arrangement of chelate rings, the remainder of the discussion will be restricted to a consideration of the oxidative addition (and subsequent abstraction) of sulfur to the complex anion $Ni(S_2CS)_2^{2-}$.

The addition of one sulfur atom per ligand to $Ni(S_2CS)_2^{2-}$ results in a species which could conceivably have any one of the structures given in Figure 5. The infrared spectrum of the complex immediately rules out 5a and 5b since the presence of a $>C{=}S$ stretch (see Results) is clearly indicated at 1035 cm^{-1}. This band is shifted to slightly higher energy than it appears in $Ni(CS_3)_2^{2-}$.

We are left with the possibility that $Ni(CS_4)_2^{2-}$ contains the structural arrangement of either 5c or 5d. Either structure is sterically acceptable. However, there are several observations that lead us to believe the correct formulation is that given in 5d, namely the five-membered chelate ring structure.

First, charge distribution alone favors 5d over 5c. In 5c, one of the coordinated sulfurs is three-coordinate, hence somewhat positive, while the dangling sulfur must be nearly uninegative. While structure 5c is not without analogy, since species such as Ph_3PS and pyridine N-oxide exist, no disulfide has been proved to contain such an arrangement. Structure 5d does not suffer from this type of charge separation.

The far-infrared spectrum tends to favor 5d over 5c. Sulfur–sulfur stretches in disulfides are notably weak in the infrared but are strong in the Raman effect.[15] The presence of a strong new band (Table II) near 480 cm^{-1} in the sulfur-rich complexes, the S–S stretching region,[15] seems in keeping with the large dipole moment change expected for S–S vibrations in the cyclic structure (other atoms must also move).

The fact that $Ni(CS_4)_2^{2-}$ prepared from K_2CS_4 is identical with the species formed from sulfur addition also tends to favor 5d for the structure of the perthiocarbonato complex. There is little reason to believe coordination to an uncharged sulfur should occur in preference to coordination with a charged sulfur atom. In fact, considerably less charge presumably resides on each sulfur attached to the carbon atom, owing to resonance delocalization, than resides on the disulfide sulfur atom in question.[24]

Finally, in contrast to the lack of well-defined oxidation waves for the four-membered ring 1,1-dithiolate complexes (Table V), the sulfur-rich species show reversible oxidation[25] and hence the existence of at least a short-lived[25] $Ni(CS_4)_2^-$. Structure 5d is expected to show increased resonance delocalization of electronic charge over 5c and hence is favored by these data.[26]

While a definitive determination of the structure of $Ni(CS_4)_2^{2-}$ must await a complete X-ray structural study, the present data suggest the formation of the five-membered chelate ring. Hence the sulfur addition reaction likely involves an insertion of a sulfur atom into the chelate ring of the complex.

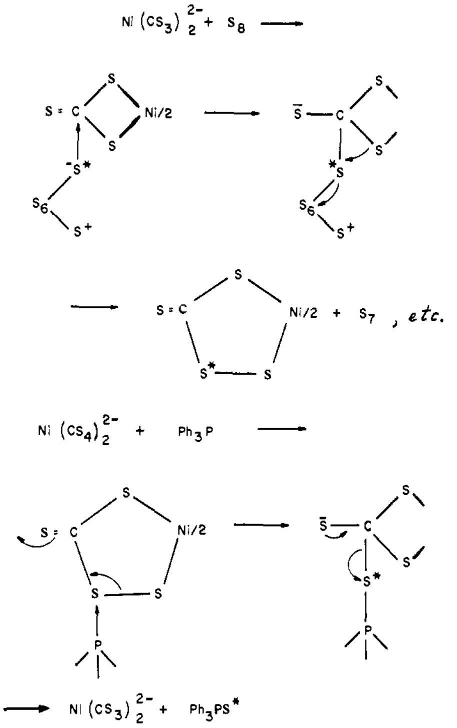


Figure 6.

The sulfur addition to $Ni(CS_3)_2^{2-}$ and the subsequent extraction by Ph_3P of the same sulfur atom that is added might be thought to favor structure 5c over 5d for the sulfur-rich species since a dangling sulfur would be held relatively weakly. However, Ph_3P is a nucleophile and as such should abstract the least negative sulfur atom. This must be one adjacent to the carbon since some negative charge will be delocalized through the carbon to the thiocarbonyl sulfur atom. Hence, the dangling sulfur atom in 5c is likely not to be the one removed by Ph_3P.

While a detailed mechanism is not warranted at this time, a series of steps consistent with the nucleophilic character of Ph_3P and in keeping with the five-membered ring formulation can be presented to explain the addition and subsequent removal of the same sulfur atom in the radioactive sulfur-35 study. The scheme given in Figure 6 also is consistent with the studies of Bartlett and Meguerian[6] on the reaction of sulfur with Ph_3P and the work of Watson[5] with Ph_3P abstraction of sulfur from disulfides. The activated complexes for both the sulfur addition and the abstraction reaction may have similarly structured chelate rings.[27]

Acknowledgment. This study was supported, in part, by a grant (GP-4253) from the National Science Foundation and a grant from the donors of the Petroleum Research Fund, as administered by the American Chemical Society. We wish also to acknowledge the help of Professor T. Kuwana with the electrochemical measurements.

---

(24) This argument differs from the first one in that the addition of sulfur to the complex need not require dissociation. It should be pointed out that ammonium polysulfide also can be used to form the sulfur-rich species.

(25) No esr signal could be observed on chemical oxidation of $Ni(CS_4)_2^{2-}$ in DMSO.

(26) The similarity of the structure (5d) we suggest for $Ni(CS_4)_2^{2-}$ to that of $cis\text{-Pd}\left(\begin{smallmatrix}S-S\\S\end{smallmatrix}{>}NH\right)_2$ [J. Weiss, *Fortschr. Chem. Forsch.*, 5, 635 (1966)] has been pointed out by a referee.

(27) Since $Pd(CS_4)_2^{2-}$ and $Pt(CS_4)_2^{2-}$ lose sulfur to Ph_3P as readily as does $Ni(CS_4)_2^{2-}$ while changes in the X for the $Ni(S_2CX)_2^{2-}$ species strongly influence the ease of sulfur addition, it is reasonable to conclude that the sulfur added and subsequently removed by Ph_3P is adjacent to the carbon rather than the metal.