

measurements.⁹ The water-exchange measurements show a continuous increase in exchange rate as the number of nitrogen donor atoms increases on nickel(II) at 25°. This suggests that factors other than the water-exchange rate are influencing the substitution process. In this context it is interesting that Ni(en)₂²⁺ apparently fails to discriminate between phenanthroline and bipyridine. Jones and Margerum^{20c} in their investigation of the equilibrium between Ni(en)₂²⁺ and Ni(en)₃²⁺ reported the rate of first bond formation for the reaction between Ni(en)₂²⁺ and en is $5.5 \times 10^6 M^{-1} \text{ sec}^{-1}$. The overall rate constant including ring closure to give Ni(en)₃²⁺ is $\sim 1.0 \times 10^6 M^{-1} \text{ sec}^{-1}$. In this case a selectivity factor for chelate formation is more than 10³ times greater in the case of ethylenediamine over that of bipyridine. Thus the structure of the incoming ligand can be important.

On the basis of optical spectra considerations, the two water molecules on Ni(en)₂²⁺ have been assigned^{37,38} a cis configuration in aqueous solution. The presence of appreciable amounts of a trans isomer seems unlikely in that kinetically distinguishable water molecules were not observed in the ¹⁷O nmr water-exchange measurement.⁹ This tends to rule out cis-trans isomerization as a governing factor in differences for the Ni(en)₂²⁺ species.

Acknowledgments.—The authors wish to express their appreciation to the Atomic Energy Commission for financial support under Contract No. AT-(11-1)-1780 and to the Graduate School at the University of Iowa for supporting computational expenses.

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Thioxanthate Complexes. Carbon Disulfide Eliminations to Form Bridged Mercaptide Dimers of Nickel(II) and Palladium(II)

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Received June 30, 1971

Alkyl thioxanthate complexes of nickel(II) undergo a spontaneous solution reaction to eliminate carbon disulfide and form a dimeric mercaptide-bridged complex. Using proton magnetic resonance spectroscopy (pmr) and visible spectroscopy, a kinetic study of this reaction was carried out. The reaction is found to be first order in thioxanthate complex, both in the disappearance of the starting material and in the formation of the mercaptide-bridged species, in chloroform and tetrahydrofuran. Pseudo-first-order kinetics was observed in carbon disulfide. The carbon disulfide dependence is attributed to an equilibrium between the thioxanthate complex and this solvent. The rate of the reaction at a given temperature increased as the alkyl group was varied from ethyl to *tert*-butyl to benzyl, and in the one case studied, the reaction was faster when the metal was nickel than when it was palladium. Rate constants for the reaction were of the order of 10⁻³ to 10⁻¹ min⁻¹ depending on solvent, temperature, alkyl group, and metal. Activation parameters were in the ranges $\Delta H^\ddagger = 22.0\text{--}23.8$ kcal/mol and $\Delta S^\ddagger = +3$ to -7 eu. Radioactive labeling of the mercaptide sulfur of the thioxanthate complex showed that it forms the bridge in the mercaptide-bridged dimeric complex. The syntheses of the thioxanthate-bridged mercaptide complexes of platinum(II), iron(III), and cobalt(III) also are reported in this paper.

Introduction

Transition metal complexes of many monoanionic 1,1-dithiolates have been prepared and studied.^{1,2} Of these probably the most poorly characterized are the complexes of alkyl trithiocarbonates (thioxanthates).^{3,4} In 1961 Schaeffer⁵ reported the preparation of some thioxanthate complexes; however, the chemical properties of these compounds were not discussed. Later, Ewald and Sinn⁶ reported the isolation of several thioxanthate complexes of Ni(II), Cu(II), Co(III), and Fe(III). These authors found the complexes unstable, but the decomposition products were not characterized.

During the past 5 years, we have prepared several metal thioxanthates. With few exceptions these materials decompose when dissolved in organic solvents to

produce mercaptide-bridged dimers, reaction 1. Several of these bridged mercaptide dimers have been characterized.⁷⁻¹⁰ In view of the dearth of information about metal mercaptide complexes generally and the recognition that metal mercaptide species play important roles in biological systems,¹¹ we began a detailed study of the mechanism that leads to the formation of the mercaptide-bridged species from the thioxanthate. We chose nickel(II) and palladium(II) complexes for the study since dimerization rates are particularly suited to investigation by conventional techniques. A preliminary report of these results has appeared.¹²

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Experimental Section

All chemicals were used as purchased unless otherwise specified. Spectral grade solvents (chromatographic grade tetrahydrofuran) were used to obtain the kinetic data, and no precautions were taken to exclude air from the reaction mixtures.

Analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn. Molecular weights were obtained on a Mechrolab vapor pressure osmometer at 37° in chloroform. Melting points were determined on a Laboratory Devices Mel-Temp melting point block and are reported uncorrected in 0°.

Proton magnetic resonance (pmr) spectra of all nickel complexes were recorded on a Varian Instruments A-60 spectrometer. The pmr spectra of all palladium and platinum complexes were recorded on a Varian Instruments HA-100 spectrometer. The temperature of the probe of both instruments was maintained to $\pm 2^\circ$ with a Varian 1040 temperature control unit calibrated with methanol.

The electronic spectra were recorded on a Cary Model 14 spectrophotometer; the temperature was maintained to $\pm 0.5^\circ$ with a thermostated bath.

A Perkin-Elmer 257 grafting infrared spectrometer was used to record infrared spectra.

Sodium Ethyl Trithiocarbonate Solution.—Ethanethiol (4 ml excess) was added to a suspension of sodium hydride (2.3 g, 0.1 mol) in 100 ml of tetrahydrofuran (THF) at 0°. A white suspension of the mercaptide salt formed and carbon disulfide (15 ml) was added dropwise. A yellow solution of the ligand was obtained which was used for the preparation of the complexes.

Sodium Benzyl Trithiocarbonate Solution.—To obtain a solution of this ligand, the procedure for the ethyl derivative was used starting with the benzyl mercaptan. This technique reduced handling of the foul-smelling thiols.

Bis(ethyl trithiocarbonate)nickel(II).—An aliquot of the ethyl trithiocarbonate solution prepared above was added to an aqueous solution of nickel(II) chloride. The mixture was immediately extracted with several portions of ether and the combined extracts were dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure and shiny black crystals were isolated, mp 99–100°. *Anal.* Calcd for $C_6H_{10}S_3Ni$: C, 21.6; H, 3.0; Ni, 17.0. Found: C, 22.6; H, 3.2; Ni, 17.0.

Bis(benzyl trithiocarbonate)nickel(II).—The complex was obtained in a manner analogous to the one already described for the ethyl compound; however, it was found advantageous to extract the product with chloroform. By adding a large excess of methanol (50% by volume) to the chloroform solution, a crystalline precipitate was formed. The crude precipitate was dissolved in cold chloroform and absolute ethanol (50% by volume) was added. On standing at 0° dark violet crystals were formed and isolated. The compound changes color at 90° and melts at 230°. *Anal.* Calcd for $C_{16}H_{14}S_6Ni$: C, 42.0; H, 3.1. Found: C, 41.6; H, 3.0.

Bis(ethyl trithiocarbonate)-di- μ -ethylthio-dinickel(II).—(a) An aliquot of the ethyl trithiocarbonate solution previously described was added in ≈ 2 -fold excess to a suspension of ethyl mercaptide in THF. The reagent was treated with an aqueous nickel solution in a manner analogous to the one employed in the preparation of the complexes described previously. The chloroform extract was evaporated to dryness and the resulting crystalline material was extracted with cold acetone. The brown-red acetonetic solution was diluted with water (15% by volume). On standing at 0° green crystals were formed, which were recrystallized in the same manner from acetone-water, mp 88–90°. Molecular weight (osmometrically determined): calcd, 513.5; found, 525. *Anal.* Calcd for $C_{10}H_{20}S_8Ni_2$: C, 23.4; H, 3.9. Found: C, 22.9; H, 3.8.

(b) A solution of the bis(ethyl trithiocarbonate)nickel(II) complex described above, in carbon disulfide, was allowed to stand at room temperature for ca. 48 hr. The solvent was removed under reduced pressure and the precipitate was recrystallized from acetone, mp 89–90°. The compound shows nmr and ir spectra identical with those of the compound described in (a).

Bis(benzyl trithiocarbonate)-di- μ -benzylthio-dinickel(II).—A solution of the bis(benzyl trithiocarbonate)nickel(II) complex was allowed to evaporate slowly in the air. The violet solution changed to red-brown and upon total evaporation of the solvent brown-green crystals formed. This product is identical with the material obtained from benzyl mercaptan, carbon disulfide, and nickel chloride.¹⁸ It was recrystallized from CS_2 . Molecular

weight (osmometrically determined): calcd, 760; found, 700. *Anal.* Calcd for $C_{30}H_{28}S_8Ni_2$: C, 47.6; H, 3.7. Found: C, 47.0; H, 3.6.

Bis(tert-butyl trithiocarbonate)nickel(II). An aliquot of a tetrahydrofuran solution of Na_2CS -*tert*-Bu was added to an aqueous solution of nickel chloride yielding a violet-black precipitate. Black-violet crystals were obtained by dissolving the product in cold chloroform and slowly adding ethanol, mp 148–149°. *Anal.* Calcd for $NiS_6C_{10}H_{18}$: C, 30.8; H, 4.6. Found: C, 30.7; H, 4.5.

Bis(tert-butyl trithiocarbonate)-di- μ -(tert-butylthio)nickel(II).—A chloroform solution of $Ni(S_2CS$ -*tert*-Bu)₂ was allowed to stand for about 72 hr at room temperature. The solvent was removed by evaporation in air, leaving green-black crystals. The product was recrystallized from carbon disulfide-pentane, mp 144–145°. *Anal.* Calcd for $Ni_2S_6C_{18}H_{36}$: C, 34.6; H, 5.8. Found: C, 34.1; H, 5.8. Molecular weight: calcd, 624; found, 627.

Bis(tert-butyl trithiocarbonate)palladium(II).—*tert*-Butyl mercaptan (2-methyl-2-propanethiol) (10 ml) and carbon disulfide (6 ml) were added to an aqueous solution of NaOH (4 g). The mixture was stirred at 0° for 2 hr producing a yellow solution of Na_2CS -*tert*-Bu. An aliquot of this solution was added to an aqueous solution of K_2PdCl_4 (2 g). A yellow-orange precipitate formed. The solution was kept at 0° for 0.5 hr and then filtered. The product was recrystallized in the same manner as the corresponding nickel complex, mp 172–174° dec. *Anal.* Calcd for $PdS_6C_{10}H_{18}$: C, 27.5; H, 4.1. Found: C, 26.9; H, 4.3.

Bis(tert-butyl trithiocarbonate)-di- μ -tert-butylthiodipalladium(II).—A solution of $Pd(S_2CS$ -*tert*-Bu)₂ in chloroform was boiled for 2 min. The solvent was evaporated slowly in air. On total evaporation a red-orange solid remained which was recrystallized from carbon disulfide-pentane, mp 168–170° dec. *Anal.* Calcd for $Pd_2S_6C_{18}H_{36}$: C, 30.0; H, 5.0. Found: C, 29.9; H, 5.2. Molecular weight: calcd, 720; found, 742.

Bis(tert-butyl trithiocarbonate)-di- μ -tert-butylthiodiplatinum(II).—An aliquot of aqueous Na_2CS -*tert*-Bu solution was added to a solution of K_2PtCl_4 in water. The solution turned red-orange, but no precipitate formed. After 24 hr a precipitate formed and was filtered. The red-orange powder was recrystallized from carbon disulfide-pentane yielding red crystals, mp 198–199° dec. *Anal.* Calcd for $Pt_2S_6C_{18}H_{36}$: C, 24.1; H, 4.0. Found: C, 23.7; H, 4.1. Molecular weight: calcd, 898; found, 881.

Bis(benzyl trithiocarbonate)- μ -benzylthio-iron(III) Dimer.—The compound was prepared in a manner exactly analogous to the one employed for the preparation of the benzyl trithiocarbonate-nickel complex. (Also see ref 7.) *Anal.* Calcd for $C_{22}H_{21}S_7Fe$: C, 47.83; H, 3.63. Found: C, 47.96; H, 3.91.

Bis(benzyl trithiocarbonate)- μ -benzylthio-cobalt(III) Dimer.—This compound was prepared in the same manner as the corresponding compound of iron. (Also see ref 9.) *Anal.* Calcd for $C_{22}H_{21}S_7Co$: C, 47.70; H, 3.60. Found: C, 46.65; H, 3.93.

Radiochemical Studies.—Radioactive sulfur-35 (2 mCi, Oak Ridge National Laboratories, 0.77 mg in 0.8 ml of benzene) was diluted approximately 1:10³ with naturally occurring sulfur in toluene and recrystallization from toluene. Benzyl mercaptan was prepared by adding the labeled elemental sulfur (0.1 mol) to a diethyl ether solution of benzyl Grignard and refluxing for 30 min. The mixture was treated with ice (100 g) and concentrated HCl (20 ml). The water layer was extracted several times with diethyl ether. The diethyl ether was evaporated under a stream of nitrogen, and the mercaptan was dissolved in THF. Bis(benzyl thioxanthato)nickel(II) was prepared from the labeled mercaptan as previously described.

Labeled bis(benzyl thioxanthato)nickel(II) (2 g) was dissolved in tetrahydrofuran which had been purified by refluxing with HCl, scrubbed with KOH, and distilled from potassium. The solution was allowed to stand in a closed system for 24 hr. The carbon disulfide formed was distilled directly into a flask containing a petroleum ether solution of piperidine. White crystals of piperidinium cyclopentamethylene dithiocarbamate were formed. The dithiocarbamate was recrystallized from petroleum ether. The THF was evaporated under reduced pressure and the $Ni_2(SCH_2C_6H_5)_2(S_2CSCH_2C_6H_5)_2$ was recrystallized from chloroform-ethanol.

The radioactivity of $Ni(S_2CSCH_2C_6H_5)_2$, $Ni(SCH_2C_6H_5)_2$ - $(S_2CSCH_2C_6H_5)_2$, and the piperidinium cyclopentamethylene dithiocarbamate were obtained on a Technical Measurements Corp. 2G-2A Geiger-Mueller scalar counter.

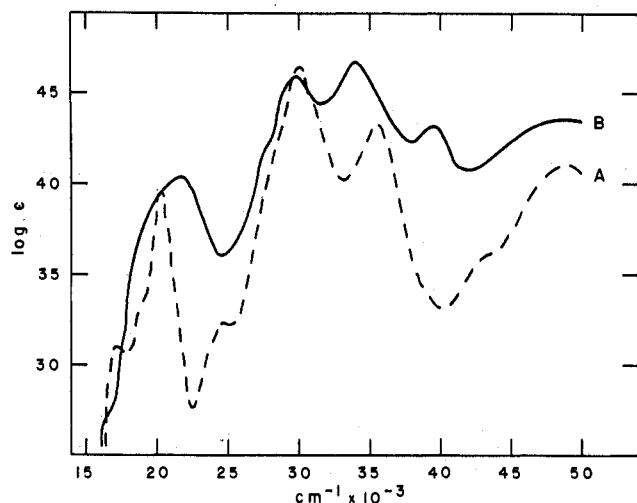


Figure 1.—The electronic spectra of $\text{Ni}(\text{S}_2\text{CSCH}_2\text{C}_6\text{H}_5)_2$, A, and $[\text{Ni}(\text{S}_2\text{CSCH}_2\text{C}_6\text{H}_5)(\text{SCH}_2\text{C}_6\text{H}_5)]_2$, B, in hexane at room temperature. The concentrations of complex are $(5.8 \pm 0.4) \times 10^{-3} M$ and $(3.6 \pm 0.4) \times 10^{-3} M$, respectively.

Results

Gas-liquid chromatography¹⁴ on a 30% Dowtherm on firebrick column established the stoichiometry of reaction 1 for bis(benzyl trithiocarbano)nickel(II) and bis(ethyl trithiocarbano)nickel(II) in chloroform. No other volatile organic products were detected.

Each of the bis(thioxanthato)nickel(II) complexes studied has an absorption band near $20,000 \text{ cm}^{-1}$ with an extinction coefficient of approximately $9 \times 10^3 \text{ l. mol}^{-1} \text{ cm}^{-1}$. As carbon disulfide elimination proceeds, this band is shifted to higher energy, and in the dimeric nickel(II)-thioxanthato complex a band is found at about $22,000 \text{ cm}^{-1}$ with an extinction coefficient of about $1.4 \times 10^4 \text{ l. mol}^{-1} \text{ cm}^{-1}$. Figure 2 shows a series of visible spectra of $\text{Ni}(\text{S}_2\text{CSCH}_2\text{C}_6\text{H}_5)_2$ taken in CS_2 as the carbon disulfide elimination proceeds. Isobestic points are apparent.

In $\text{Pd}(\text{S}_2\text{CS-}i\text{tert-C}_4\text{H}_9)_2$ the low-energy band in the visible spectrum is shifted to about $22,000 \text{ cm}^{-1}$. On dimer formation this band disappears and presumably is under the strong ligand band. Similarly, in the electronic spectrum of $\text{Pt}_2(\text{S}_2\text{CS-}i\text{tert-C}_4\text{H}_9)_2(\text{S-}i\text{tert-C}_4\text{H}_9)_2$ no band is found below $29,000 \text{ cm}^{-1}$.

Spectrophotometric studies of the rate of CS_2 elimination were conducted using wavelengths in the visible region. The concentration of $\text{M}(\text{S}_2\text{CSR})_2$ at any time during the reaction was assumed to be proportional to $(A_t - A_\infty)$, the molar absorbance at time t minus the molar absorbance of the dimer at the chosen wavelength. Since the dimeric species undergo additional slow decomposition, an uncertainty of $\sim 10\%$ is associated with A_∞ .

Proton Magnetic Resonance Spectra.—The 60-MHz pmr spectrum of $\text{Ni}(\text{S}_2\text{CSCH}_2\text{C}_6\text{H}_5)_2$ in CS_2 shows reso-

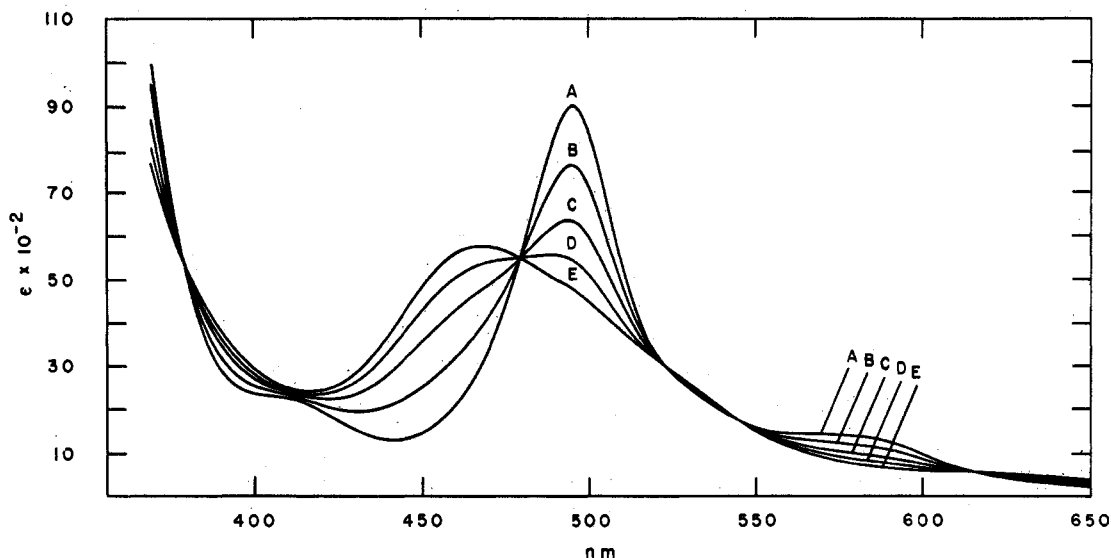


Figure 2.—The electronic spectrum of $\text{Ni}(\text{S}_2\text{CSCH}_2\text{C}_6\text{H}_5)_2$, $(8.7 \pm 0.4) \times 10^{-3} M$, at 35° in CHCl_3 after (A) 1 min, (B) 16 min, (C) 33 min, (D) 70 min, and (E) 240 min.

Electronic Spectra.—The electronic spectra of $\text{Ni}(\text{S}_2\text{CSCH}_2\text{C}_6\text{H}_5)_2$ and $[\text{Ni}(\text{S}_2\text{CSCH}_2\text{C}_6\text{H}_5)(\text{SCH}_2\text{C}_6\text{H}_5)]_2$ are reproduced in Figure 1. The spectra of the corresponding ethyl and *tert*-butyl derivatives are quite similar.

All of the compounds studied, including the Pd(II) and Pt(II) complexes, display two bands in their electronic spectra between $29,000$ and $33,000 \text{ cm}^{-1}$. Two absorption bands have been reported in this region in alkali metal salts of thioxanthates.¹⁵

nances at τ 2.80 and 5.54 with relative intensities of 2:5 which are assigned to the phenyl and methylene protons, respectively. In the corresponding dimer, the bridged benzyl mercaptide ligand appears at τ 2.87 and 7.20. The pmr spectrum of the ethyl dimer derivative is included in the paper by Lewis, *et al.*,⁹ where the partial collapse of the triplet associated with the bridged ethyl group is discussed. The $\text{Ni}(\text{S}_2\text{CS-}i\text{tert-C}_4\text{H}_9)_2$ spectrum shows a single peak at τ 8.01 while the dimer displays a new upfield peak at τ 8.55. The palladium(II) and platinum(II) complexes of *tert*-butyl thioxanthate behave similarly.

Sulfur-35 Labeling.—The benzyl thioxanthate com-

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plex of nickel(II) was prepared from ^{35}S -labeled benzyl mercaptide. After allowing the complex to stand 24 hr at room temperature in tetrahydrofuran, the CS_2 eliminated was recovered as the piperidinium cyclopentadienyl dithiocarbamate and the dimer product was crystallized. No radioactivity was detected above background in the recovered CS_2 product and 80% of the initial count of 5.5×10^7 counts $\text{mol}^{-1} \text{min}^{-1}$ was present in the dimer. The sodium salt of the benzyl trithiocarbonate also shows no evidence for mercaptide sulfur atom interchange.

Kinetic Studies.—The rate of elimination of CS_2 from $\text{M}(\text{S}_2\text{CSR})_2$ to form $[\text{M}(\text{S}_2\text{CSR})-\mu-(\text{SR})]_2$ was studied by both pmr spectroscopy and visible spectroscopy. By both methods the rate of disappearance of $\text{M}(\text{S}_2\text{CSR})_2$ and the formation of product were found to be first order in monomeric complex as indicated by the linearity of the plot of $\ln(A - A_\infty)$ vs. time shown in Figure 3. The results obtained in CS_2 for the benzyl

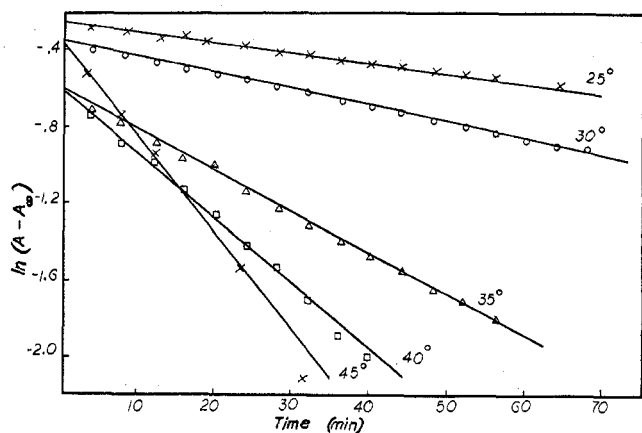


Figure 3.—Plots of $\ln(A - A_\infty)$ vs. time for the reaction of $\text{Ni}(\text{S}_2\text{CSCH}_2\text{C}_6\text{H}_5)_2$ in chloroform at 25, 30, 35, 40, and 45°. A is the absorbance at time t and A_∞ is the absorbance of $[\text{Ni}(\text{S}_2\text{CSCH}_2\text{C}_6\text{H}_5)(\text{SCH}_2\text{C}_6\text{H}_5)]_2$ at 496 nm.

thioxanthate using pmr spectroscopy, with initial concentrations of $(\sim 5-7) \times 10^{-2} M$, and the results obtained spectroscopically for the other complexes at $(2-5) \times 10^{-3} M$ are listed in Table I. The first-order dependence on the concentration of monomer was further established with $\text{Ni}(\text{S}_2\text{CSCH}_2\text{C}_6\text{H}_5)_2$. The $t_{1/2}$ was found to be 56 ± 2 min at an initial concentration of $(3.2 \pm 0.5) \times 10^{-3} M$ and 65 ± 5 min at $(3.2 \pm 0.5) \times 10^{-4} M$. The half-lives of the other monomeric thioxanthates are similarly invariant to monomer concentration in chloroform or tetrahydrofuran.

Activation parameters obtained from $\ln k$ vs. $1/T$, Figure 4, are presented in Table II. The solvent dependence of the CS_2 elimination from $\text{Ni}(\text{S}_2\text{CSCH}_2\text{C}_6\text{H}_5)_2$ in tetrahydrofuran (THF), CS_2 , and CHCl_3 leads to the data presented in Table I and the activation parameters listed in Table II.

The carbon disulfide dependence of the kinetic parameters is reported in Tables I and II as obtained from the pmr data. It was found that CS_2 solutions prepared for visible spectroscopic investigation of the elimination reaction ($\sim 10^{-3} M$) were stable considerably longer than predicted assuming no CS_2 dependence. Consequently, a series of solutions in tetrahydrofuran was prepared in which the concentration of the complex was held constant and the CS_2 concentration varied.

TABLE I
RATE CONSTANTS FOR THE CARBON DISULFIDE
ELIMINATION REACTION

Compd ^b	Solvent	Temp, ^a °C	$10^{-3}k$, min^{-1}	
$\text{Ni}(\text{S}_2\text{CSEt})_2$	HCCl_3	30	1.4 ± 0.1	
		35	2.3 ± 0.2	
		40	5.1 ± 0.3	
		45	7.1 ± 0.4	
$\text{Ni}(\text{S}_2\text{CS-tert-Bu})_2$	HCCl_3	30	5.1 ± 0.3	
		35	10 ± 1	
		40	17 ± 1	
		45	29 ± 2	
$\text{Ni}(\text{S}_2\text{CSBz})_2$	HCCl_3	25	4.9 ± 0.2	
		30	8.3 ± 0.4	
		35	21 ± 1	
		40	38 ± 2	
		45	49 ± 3	
		THF	25	7.0 ± 0.4
		31	15 ± 1	
		35	27 ± 1	
		42	60 ± 3	
		CS_2	20	1.3 ± 0.1
			25	1.7 ± 0.1
			30	2.6 ± 0.2
$\text{Pd}(\text{S}_2\text{CS-tert-Bu})_2$	HCCl_3	37	14 ± 1	
		30	2.1 ± 0.1	
		35	5.2 ± 0.3	
		40	8.2 ± 0.4	
		45	15 ± 1	

^a Temperature $\pm 0.5^\circ$. ^b Et = C_2H_5 , tert-Bu = $\text{C}(\text{CH}_3)_3$, Bz = $\text{CH}_2\text{C}_6\text{H}_5$.

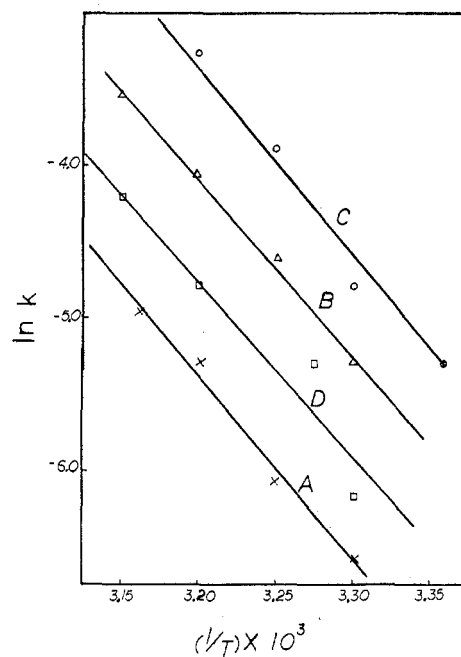


Figure 4.—An Arrhenius plot of $\ln k$ vs. $1/T$ for the CS_2 elimination in CHCl_3 with $\text{Ni}(\text{S}_2\text{CSC}_2\text{H}_5)_2$ (A), $\text{Ni}(\text{S}_2\text{CSC}(\text{CH}_3)_3)_2$ (B), $\text{Ni}(\text{S}_2\text{CSCH}_2\text{C}_6\text{H}_5)_2$ (C), and $\text{Pd}(\text{S}_2\text{CSC}(\text{CH}_3)_3)_2$ (D).

TABLE II
ACTIVATION PARAMETERS OF THE CARBON DISULFIDE
ELIMINATION REACTION

Compd ^a	Solvent	E_a , ^b		
		kcal/mol	ΔH^\ddagger , ^b kcal/mol	ΔS^\ddagger , ^b eu
$\text{Ni}(\text{S}_2\text{CSEt})_2$	HCCl_3	22.6	22.0 ± 0.3	-7
$\text{Ni}(\text{S}_2\text{CS-tert-Bu})_2$	HCCl_3	22.9	22.3 ± 0.3	-4
$\text{Ni}(\text{S}_2\text{CSBz})_2$	HCCl_3	23.5	22.9 ± 0.3	-1
	THF	23.8	23.2 ± 0.4	3
	CS_2	23.1	22.5 ± 0.3	-5
$\text{Pd}(\text{S}_2\text{CS-tert-Bu})_2$	HCCl_3	24.4	23.8 ± 0.4	-1

^a Et = C_2H_5 , tert-Bu = $\text{C}(\text{CH}_3)_3$, Bz = $\text{CH}_2\text{C}_6\text{H}_5$. ^b Uncertainty in E_a and ΔH^\ddagger , ± 0.3 kcal/mol; ΔS^\ddagger , ± 2 eu.

TABLE III
CARBON DISULFIDE DEPENDENCE OF THE CS₂ ELIMINATION REACTION^a

10 ⁴ k, min ⁻¹	[CS ₂], M	10 ⁴ [Ni(S ₂ CSCH ₂ -C ₆ H ₅) ₂], M ^b	10 ⁴ k, min ⁻¹	[CS ₂], M	10 ⁴ [Ni(S ₂ CSCH ₂ -C ₆ H ₅) ₂], M ^b
3.0 ± 0.2		1.2	0.8 ± 0.1	6.8 ± 0.4	1.3
3.1 ± 0.2	0.07 ± 0.005	1.2	0.3 ± 0.05	16.6 ± 1.0	1.5
2.9 ± 0.2	0.23 ± 0.02	1.2	1.1 ± 0.1	16.6 ± 1.0	10.5
2.8 ± 0.2	0.68 ± 0.04	1.2	1.3 ± 0.1	16.6 ± 1.0	87
1.9 ± 0.2	3.4 ± 0.2	1.2			

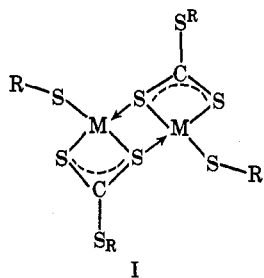
^a In tetrahydrofuran at 35°. ^b Uncertainty in concentration ~10% M.

At low CS₂ concentration the rate changed very little as the concentration of CS₂ was increased. However, as the concentration of CS₂ became larger, small increases in the concentration of this solvent produced large changes in the rate of the elimination reaction. The rate constants obtained for several solutions at different CS₂ concentrations are listed in Table III. This CS₂ dependence at constant nickel concentration can be approximated by two straight lines, one with a slope of zero which governs the reaction at low carbon disulfide concentration and one with a slope of -1 which governs the reaction at high carbon disulfide concentration.

Variations in the concentration of complex in CS₂ solutions also cause a change in the rate of the reaction. The effect of changing the initial concentration of the complex on the rate constant is inversely related to the effect of the CS₂ concentration. At 10⁻² M or higher Ni(S₂CSCH₂C₆H₅)₂ concentration small variations in the initial complex concentration have little effect on the observed rate constant. However, as the concentration of Ni(S₂CSCH₂C₆H₅)₂ becomes smaller, small changes in this concentration produce substantial changes in the rate constant. The rate constants obtained at several concentrations of Ni(S₂CSCH₂C₆H₅)₂ at 35° are listed in Table III.

Discussion

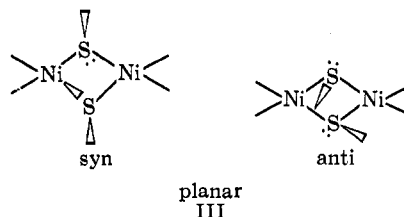
From the physical properties of M(S₂CSR)₂ and the mercaptide dimers formed by CS₂ elimination, it has been assumed² that each metal atom is essentially four-coordinate to sulfur atoms with mercaptide bridges in the dimers. However, as found by Coucouvanis, *et al.*,⁷ in [Fe(S₂CSC₂H₅)₂(SC₂H₅)₂] the thioxanthate ligands as well as the mercaptide ligands may bridge metal atoms. While a bridged dimer structure similar to the iron(III) complex is not likely due to stereochemical constraints of divalent nickel triad metal ions, structures such as I are plausible and not readily



distinguishable from the bridged mercaptide species, II.

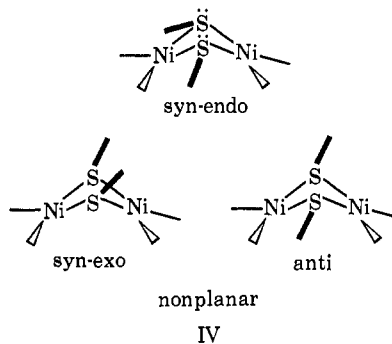


Bridged mercaptide ligands have been found in a variety of complexes.^{7,13,16} In such species, an essentially planar M₂(SR)₂ unit may be either syn or anti, III.



In fact, rapid syn-anti isomerism is also possible and has been reported in a complex containing a coordinated thioether.¹⁷

The X-ray crystal structure of [Ni(S₂CSC₂H₅)(SC₂-H₅)₂]₂ determined by Villa, *et al.*,¹⁰ establishes the presence of bridging mercaptide ligands in a syn-endo M₂(SR)₂ structure, IV, with a short, 2.76 Å, Ni-Ni dis-



tance. A similar type of syn-endo configuration has been observed¹⁸ for [NiS(CH₂CH₂S)₂]₂ and for [Ni₃(SCH₂CH₂NH₂)₄]²⁺.¹⁹ In each of these compounds the S-Ni-S angle is less than 90° (~82°) and the bridging S...S distance about 2.9 Å. This suggests the possibility that a weak S-S interaction may accompany any Ni-Ni interaction (as judged by the Ni-Ni distance).

If we assume that the "folded" mercaptide-bridge dimer structure exists in solution with the nickel(II) species, various isomers might be expected, III and IV. Since the pmr spectrum of Ni(S₂CSCH₂C₆H₅)(SCH₂-C₆H₅) shows only one sharp methylene proton signal for the bridging mercaptide ligand over the temperature range -50 to +50°, we conclude that one or more of the following conditions exist: (1) the barrier to isomerization is very low; (2) chemical shift differences between isomers are too small to detect; (3) only one species dominates in solution. The [Rh(CO)₂SR]₂

(16) (a) P. Woodward, L. F. Dahl, E. W. Abel, and B. C. Crosse, *J. Amer. Chem. Soc.*, **87**, 5251 (1965); (b) N. G. Connelly and L. F. Dahl, *ibid.*, **92**, 7472 (1970), and references therein.

(17) H. A. O. Hill and K. A. Simpson, *J. Chem. Soc. A*, 3266 (1970).

(18) G. A. Barclay, E. M. McPartlin, and N. C. Stephenson, *Acta Crystallogr., Sect. B*, **25**, 1262 (1969).

(19) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **9**, 1878 (1970).

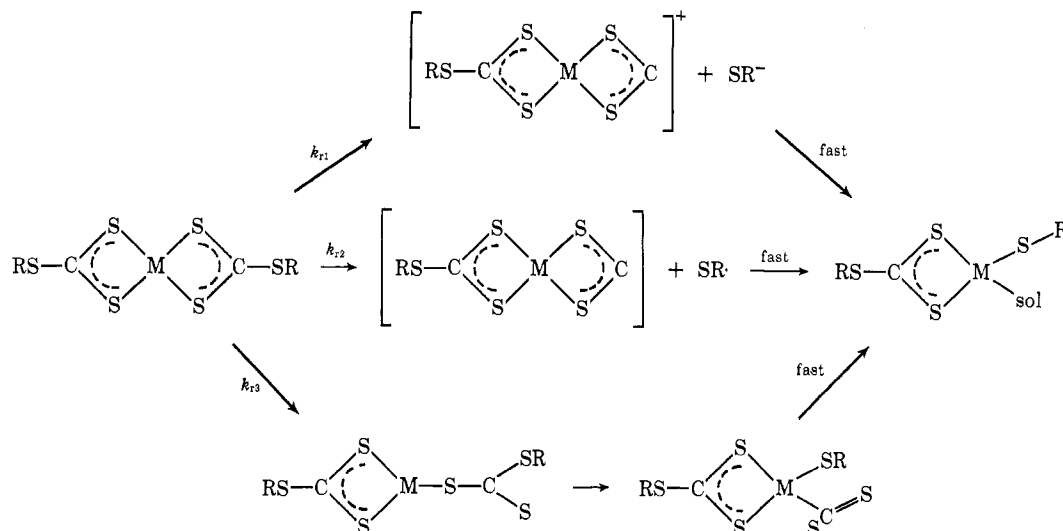
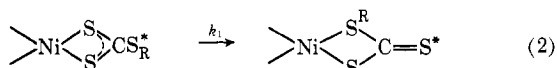


Figure 5.—Possible pathways for the unimolecular decomposition of $M(S_2CSR)_2$ to a solvated intermediate.

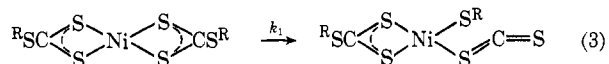
complex also appears static on the nuclear magnetic resonance time scale.²⁰

Because inversion barriers about coordinated sulfur are of the order of 5–17 kcal/mol^{21,22} and since there is no reason to believe that the chemical shifts for bridging mercaptide ligand protons will be totally insensitive to stereochemistry, we are inclined to assume that predominantly one stereoisomer exists in solution although syn-endo to syn-exo interconversion (no inversion at sulfur is required) may be too fast to detect by the procedure used.

The kinetic data presented for the CS_2 elimination and dimer formation indicate that the rate-determining step at low CS_2 concentration is first order in the monomer complex. One process that fits this requirement is an intramolecular rearrangement of the monomer, reaction 2, involving either alkyl cation transfer²³ or



stereochemical rearrangement. The former possibility is eliminated by the results of the labeling studies using ³⁵S. However, a $-SR$ shift to the metal ion with concomitant CS_2 coordination, reaction 3, cannot be



ruled out from our data. Carbon disulfide coordination to transition metals is well established.²⁴

The carbon disulfide dependence observed for the elimination reaction with $Ni(S_2CSCH_2C_6H_5)_2$ indicates a pseudo-first-order rate law and an inverse dependence on the CS_2 concentration. A reaction of a mercaptide

(20) M. Dekkar, G. R. Knox, and C. G. Robertson, *J. Organometal. Chem.*, **18**, 161 (1969).

(21) E. W. Abel, R. P. Bush, J. F. Hopton, and C. R. Jenkins, *Chem. Commun.*, 58 (1966).

(22) P. Haake and P. C. Turley, *J. Amer. Chem. Soc.*, **89**, 4611 (1967).

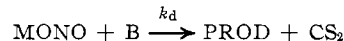
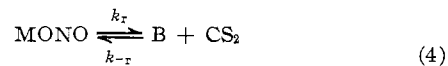
(23) Alkylation of coordinated thiols is well known: D. H. Busch, *Science*, **171**, 241 (1971). Furthermore, alkyl group transfer occurs¹³ in the rearrangement and decomposition of metal xanthates (J. P. Fackler, Jr., W. C. Seidel, M. Myron, *Chem. Commun.*, 1133 (1969)) and dithiophosphates (J. J. Dickert and C. N. Rowe, *J. Org. Chem.*, **32**, 647 (1967)).

(24) (a) L. Marko, G. Bor, and E. Klumpp, *Angew. Chem.*, **75**, 244 (1963); (b) M. C. Baird and G. Wilkinson, *Chem. Commun.*, 514 (1966); (c) M. C. Baird, G. Hartwell, Jr., R. Mason, A. I. M. Rae, and G. Wilkinson, *ibid.*, 92 (1967).

species with CS_2 to regenerate the monomer would lead to such behavior. As reported by Blandon, Bruce, and Knox⁸ and confirmed by us, the dimer does not reversibly react with CS_2 . However, CS_2 is known to insert into metal-sulfur bonds of nonbridging mercaptide species^{25–27} and recently McCormick²⁸ showed that metal amines react directly with CS_2 to form dithiocarbamate complexes.

The general rate expression described by the CS_2 dependence, Table III, must contain a two-term denominator which is linear in $[CS_2]$. Also, the data indicate a dependence on $[M(S_2CSR)_2]$ which is greater than first order but reduces to first order at low CS_2 concentration and high complex concentration.

Assuming steady-state conditions, the reaction sequence of (4) is consistent with these observations,



where MONO is the monomer, PROD is the dimer, and B is an intermediate yet to be specified. The rate expression obtained is given in (I). It is seen that this

$$\frac{d[PROD]}{dt} = \frac{k_r[MONO]^2}{[MONO] + (k_{-r}/k_d)[CS_2]} \quad (I)$$

expression leads to the required first-order behavior with respect to monomer concentration when $[CS_2]$ is very small.

The ratio of k_d/k_{-r} for $Ni(S_2CSCH_2C_6H_5)_2$ can be estimated from Table III since $k_{-r}[CS_2] \cong k_d[MONO]$ when $[CS_2] \cong 1 M$ and $[MONO] \cong 10^{-3} M$. Thus $k_d/k_{-r} \cong 10^3$ and (I) becomes (II), at least at 35°.

When the CS_2 concentration is small, the pseudo-first-

$$\frac{d[PROD]}{dt} = \frac{k_r[MONO]^2}{[MONO] + 10^{-3}[CS_2]} \quad (II)$$

order rate constant becomes k_r and for the nickel(II) complex we have (III), at 35°. Thus only with $[MO-$

$$\frac{d[PROD]}{dt} = \frac{27 \times 10^{-3}[MONO]^2}{[MONO] + 10^{-3}[CS_2]} \quad (III)$$

(25) H. Hasegawa, *Nippon Kagaku Zasshi*, **73**, 728 (1952).

(26) W. E. Duncan, E. O. Ott, and E. E. Reid, *Ind. Eng. Chem.*, **23**, 381 (1931).

(27) G. Chancel, *C. R. Acad. Sci.*, **31**, 521 (1850).

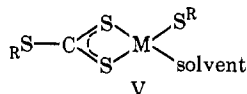
(28) B. J. McCormick and R. J. Kaplan, *Can. J. Chem.*, **48**, 1876 (1970).

$NO] \leq 10^{-3}[CS_2]$ will deviations from first-order kinetics appear.

The stoichiometry for the overall reaction suggests that the rate of loss of monomer is the same as the rate of appearance of dimer product. The pmr and visible spectra establish this to within the limits of sensitivity of the techniques. From reaction 4, assuming steady-state conditions for [B], we see that the kinetic expressions reduce to (IV), as required by the stoichiometry of the system.

$$-\frac{d[MONO]}{dt} = \frac{2k_1[MONO]^2}{[MONO] + \frac{k_{-1}}{k_d}[CS_2]} \quad (IV)$$

It is reasonable to assume that B in reaction 4 is a partially or completely solvated monomeric mercaptide species such as indicated in V. As such, it would be



expected to react with CS_2 to form the starting material or with another molecule of starting material to form the dimeric product. The rate increase observed for the reaction of $Ni(S_2CSC_6H_5)_2$ in THF compared with the reaction in $CHCl_3$ or CS_2 is consistent with the formation of such a species. However, no attempt has been made to isolate such a complex with more strongly coordinating solvents such as amines or phosphines.

The formation of a solvated intermediate such as V requires the breaking of a C-S bond and the formation of a metal-sulfur atom bond to the mercaptide ligand. While several possibilities exist, the rather low activation energy of ~ 25 kcal/mol must be consistent with the process. Three reasonable pathways are sketched in Figure 5.

Heterolytic C-S bond cleavage, k_{r1} in Figure 5, leads to the formation of a positively charged complex frag-

ment and the mercaptide ion. The solvent dependence indicated in Tables I and II is consistent with the formation of a solvated charged species.²⁹ Also the relative insensitivity of the activation energy to solvent charges and the negative ΔS^\ddagger , which becomes more negative with low solvent polarity, are trends consistent³⁰ with this reaction pathway.

A homolytic scission of the C-S bond, k_{r2} in Figure 5, is not as likely as the previous pathway for several reasons. No electron spin resonance signal is detected nor is disulfide product observed, two expected consequences of radical SR formation. Furthermore, the activation parameters are not typical of radical formation. Mislow and coworkers^{31,32} have suggested that homolytic carbon-sulfur atom bond cleavage generally requires $\Delta H^\ddagger \approx 40$ kcal/mol and $\Delta S^\ddagger \approx 25$ eu. In a situation wherein ΔH^\ddagger and ΔS^\ddagger more closely approximated the present data,³² a readily detectable epr signal was obtained.

The third reaction pathway suggested by Figure 5, the concerted pathway k_{r3} , seems about equally reasonable with the heterolytic cleavage, k_{r1} . It is perhaps only a modification of the postulate that a rearrangement to a CS_2 -coordinated species may occur with the CS_2 rapidly displaced by solvent. The activation parameters and solvent relationships observed are of little help in commenting on this pathway.

Acknowledgment.—The support of the National Science Foundation, GP-11701, and the National Institutes of Health, AM-1358, is recognized in this study. We also thank Professor S. J. Lippard for numerous discussions of data obtained at Columbia University.

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(31) P. Bichart, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, **88**, 3138 (1966).

(32) E. G. Miller, D. R. Rayner, and K. Mislow, *ibid.*, **88**, 3139 (1966).

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Kinetics of the Reactions of 2,2'-Bipyridyl with Potassium Tetrachloropalladate(II) and Potassium Tetrachloroplatinate(II)

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Received June 1, 1971

The reaction between bipyridyl (bipy) and K_2MCl_4 ($M = Pd, Pt$) produces $M(bipy)Cl_2$ by a second-order process. Reactions are carried out in water with $10^{-3} M$ concentrations of ligand and metal complex at 5° for Pd and at 55° for Pt. In acidic solutions, bipyridyl reacts with MCl_4^{2-} ($k_2 = 1.2 M^{-1} sec^{-1}$ for Pd; $k_2 = 0.0027 M^{-1} sec^{-1}$ for Pt) and also with $M(H_2O)Cl_3^-$ ($k_2 = 37 M^{-1} sec^{-1}$ for Pd; $k_2 = 0.029 M^{-1} sec^{-1}$ for Pt). The reaction of bipyridyl is so much slower than aquation under the conditions employed that the equilibrium between the tetrachloro and the trichloroquo complexes is maintained. As the pH is increased, the two metal complexes behave differently. Platinum reacts with bipy and $bipyH^+$ at different rates, preferring the protonated ligand. Palladium does not discriminate between bipy and $bipyH^+$, and the rate is pH independent until the aquo ligands begin to be deprotonated; then there is a marked increase in rate. Although bipyridyl reacts very slowly, some nucleophiles (notably ammonia) are almost as slow, and one, *trans*-crotylammonium ion, is even slower. No evidence seems to exist that any reaction of MCl_4^{2-} complexes follows the usual two-term rate law (eq 1).

Although the tetrachlorometalate(II) ions of palladium and platinum have been known for a long time

and used extensively as synthetic starting materials, only recently have their kinetics begun to be widely studied. Early work on $PtCl_4^{2-}$ aquation and chloride exchange reactions was done by Martin and cowork-

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