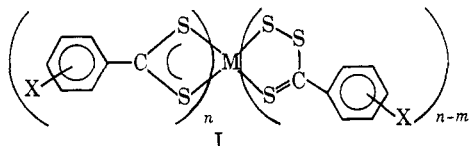


Sulfur Chelates. X. Sulfur Addition and Abstraction in Nickel(II) and Zinc(II) Dithiobenzoates. A Mass Spectroscopic Study Using Sulfur-34

Sir:

The *oxidative addition* of elemental sulfur or anionic polysulfides to transition metal dithioaryl acid complexes has been shown to produce species formulated¹ to contain a chelate ring with a disulfide linkage (I). The X-ray crystallographic structure² of one member of this class of complexes, $\text{Fe}(\text{L-X})_3\text{S}$, $\text{L-X} = p$ -dithio-



toluate, has been completed.

The addition of a sulfur atom to a metal dithiolate and its removal with arylphosphines (to form phosphine sulfides) are reactions likely related to chemistry occurring in rubber vulcanization³ involving species such as the zinc(II) O-alkyl xanthates $[\text{Zn}(\text{S}_2\text{COR})_2]$. Also metal disulfides may be involved in nonheme iron proteins.⁴ These possibilities have stimulated examination of the mechanistic details of the oxidative sulfur addition and abstraction reactions with a variety of metal dithiolates. Here we describe the results of a mass spectroscopic study in which ³⁴S-enriched sulfur was added to the nickel(II) and zinc(II) dithiobenzoates (I, X = H, n = 2) and the "excess" sulfur removed with triphenylphosphine.

Two methods were used to achieve sulfur atom addition to bis(dithiobenzoato)nickel(II). In the *thermal* addition, equimolar amounts of $\text{Ni}(\text{L-H})_2$ and sulfur (37.2% enriched in ³⁴S from the AEC, Oak Ridge, Tenn.) were heated in refluxing dimethylformamide (DMF) for an additional 30 sec after a color change from green-brown to purple occurred. Addition of water precipitated the complex, which was washed with water and air dried. In the *photolytic* addition, a degassed CHCl_3 mixture containing equimolar amounts of enriched sulfur and $\text{Ni}(\text{L-H})_2$ (not completely soluble) was irradiated at 3500 Å with a mercury lamp for ~20 hr. (See footnote 5.) The purple

(1) J. P. Fackler, Jr., D. Coucouvanis, J. A. Fetchin, and W. C. Seidel, *J. Amer. Chem. Soc.*, **90**, 2784 (1968).

(2) D. Coucouvanis and S. J. Lippard, *ibid.*, **90**, 3281 (1968); **91**, 307 (1969).

(3) (a) L. Bateman, Ed., "The Chemistry and Physics of Rubber-like Substances," John Wiley and Sons, Inc., New York, N. Y., 1963; (b) W. Hoffmann, "Vulcanization and Vulcanization Agents," Palmerton Publishing Co., New York, N. Y., 1967.

(4) R. Malkin and J. C. Rabinowitz, *Annu. Rev. Biochem.*, **36**, 113 (1967); T. Kimura, *Struct. Bonding (Berlin)*, **5**, 1 (1968).

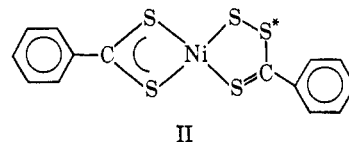
(5) In the photolytic method a blank containing no excess sulfur left essentially unchanged starting materials both with zinc(II) and nickel(II). The addition of $\text{Ni}(\text{L-X})_2$ to solutions containing sulfur just previously subjected to the uv source immediately produces $\text{Ni}(\text{L-X})_2\text{S}$. The 20-hr time period employed in the photolytic addition does not appear critical. Since scrambling of sulfur atoms in the thermal addition procedure in DMF may originate from any of several possible causes, we have not as yet established why it occurs. Any reversible sulfur atom exchange between the sulfur-rich complex and the labeled sulfur in the CHCl_3 solution clearly does not lead to sulfur atom scrambling in the

solution was filtered and evaporated to dryness in the air. Unreacted sulfur was removed by dissolving the $\text{Ni}(\text{L-H})_2\text{S}$ in 1:1 $\text{CHCl}_3:(\text{C}_2\text{H}_5)_2\text{O}$. Solvent removal yielded the desired product.

Sulfur-34 addition to $\text{Zn}(\text{L-H})_2$ was accomplished by the photolytic procedure in CHCl_3 . The orange-colored product, obtained by evaporation of the solvent, was washed with *n*-pentane. The stoichiometry of the material used for this study corresponded to $\text{Zn}(\text{L-H})_2\text{S}_{1.76}$. Since the excess sulfur content in the zinc(II) complexes has been established to be variable by triphenylphosphine titration,^{4,6} we have assumed the solid contains appropriate mixtures of $\text{Zn}(\text{L-H})_2$ and $\text{Zn}(\text{L-H})_2\text{S}_2$ in order to simplify the description of the mass spectral results.⁷

With both zinc(II) and nickel(II), the "sulfur-poor" $\text{M}(\text{L-H})_2$ complex was regenerated from the "sulfur-rich" species by reaction with triphenylphosphine in boiling CHCl_3 . The triphenylphosphine sulfide was removed from the $\text{Ni}(\text{L-H})_2$ with ether. It remained in the zinc sample used for the mass spectral studies, but we have no reason to believe its presence affected the results.

The addition of ³⁵S to $\text{Ni}(\text{CS}_3)_2^{2-}$ in DMF and its quantitative removal with triphenylphosphine⁸ suggested that sulfur addition in this nickel(II) complex is specific. Based on analogy with other phosphine reactions, it further implied that the added sulfur atom resides adjacent to the ligand carbon atom. A similar result for $\text{Ni}(\text{L-H})_2\text{S}$ would produce a material labeled as indicated in II. This could be expected as a direct result of nucleophilic attack by anionic polysulfide



or nucleophilic sulfur chains on the CS_2 carbon atom. Several other 1,1-dithiolate derivatives of CS_2 are already known to show a reaction chemistry describable in terms of nucleophilic substitution at the CS_2 carbon.⁹ While the radioactive ³⁵S study with $\text{Ni}(\text{CS}_3)_2^{2-}$ showed conclusively⁸ that the sulfur atom added to the complex is the same atom subsequently removed by the phosphine, no direct proof determining the position of sulfur atom insertion was obtainable, since degradation studies having chemically specific pathways are un-

photolytic sulfur atom addition to $\text{Ni}(\text{L-H})_2$. With $\text{Zn}(\text{L-H})_2$ the scrambling observed may originate by irreversible exchange of ZnL_2S_2 or ZnL_2S with sulfur in solution or by any of several other intra- or intermolecular processes. Some mechanisms, however, such as *reversible* exchange with the sulfur in solution or transfer of the terminal disulfide sulfur atom among dithiobenzoate ligands do *not* lead to scrambling of the sulfur atoms.

(6) J. P. Fackler, Jr., and J. A. Fetchin, *J. Amer. Chem. Soc.*, **92**, 2912 (1970).

(7) As long as it is recognized that both $-\text{S}_2\text{C}(\text{S})\text{C}_6\text{H}_5$ and $-\text{SC}(\text{S})\text{C}_6\text{H}_5$ are present in the material in the ratio of 1.76:0.24 (88% $\text{Zn}(\text{L-H})_2\text{S}_2$), the formal stoichiometric description we use is unimportant.

(8) D. Coucouvanis and J. P. Fackler, Jr., *ibid.*, **89**, 1346 (1967).

(9) (a) J. P. Fackler, Jr., D. Coucouvanis, W. C. Seidel, R. C. Masek, and W. Holloway, *Chem. Commun.*, 924 (1967); (b) J. P. Fackler, Jr., and W. C. Seidel, *Inorg. Chem.*, **8**, 1631 (1969).

known. However, it was recognized that mass spectrometry might unravel this problem.

The mass spectrum of I ($M = \text{Zn, Ni; } X = \text{H; } n = 2$) shows a strong peak at m/e 121 amu upon inserting the material into a Varian M-66 mass spectrometer by means of a solid sample probe. Temperatures between 150 and 160° were used with an ionization voltage of ~ 60 eV and pressures of $\sim 4\text{--}14 \times 10^{-7}$ Torr. The 121 mass appears to be associated primarily with the SCC_6H_5^+ fragment, at least at high ionization voltages. Corresponding peaks at m/e 122 and 123 are also associated¹⁰ with SCC_6H_5^+ and represent the presence of ^{13}C and ^{34}S (4.22% in naturally occurring sulfur). Qualitative results with $\text{Ni}(\text{L-H})_2$ (Figure 1) clearly establish that the 123 peak is sensitive to the addition of ^{34}S and that added ^{34}S is removed by triphenylphosphine. In fact, unless there is a specific sulfur atom rearrangement in the mass spectrometer (a very unlikely possibility), the sulfur atom insertion in $\text{Ni}(\text{L-H})_2$ by photolysis must be principally adjacent to the carbon and not the metal. With $\text{Zn}(\text{L-H})_2$ sulfur atom scrambling occurs.

If the assumption is made that the ratio of the 123-amu peak to the total intensity of 121, 122, and 123 reflects the ^{34}S content of the SCC_6H_5^+ fragment,¹⁰ quantitative information about the sulfur atom insertion and sulfur atom scrambling is obtained. As indicated in Tables I and II, I_{123}/I_{TOT} varies with the experimental conditions of sulfur addition⁵ and is also metal ion dependent.

While space does not permit a detailed analysis of the quantitative mass spectral results in this communication, some specific points are to be made in connection with the information contained in Tables I and II. "C addition statistical" assumes that the

Table I. Mass Spectroscopic Data for $\text{Ni}(\text{S}_2\text{CC}_6\text{H}_5)_2\text{S}$ from ^{34}S -Enriched^a Sulfur

Substance	Condition	I_{123}/I_{TOT}^b
	Calculated	
$\text{Ni}(\text{L-H})_2\text{S}$	C addition statistical	0.127
	S-S cleavage	0.372
	Sulfur scrambling	0.112
	S addition	0.0456
$\text{Ni}(\text{L-H})_2$	Specific C removal	0.0456
	Random disulfide or S scrambling	0.112
	Found	
$\text{Ni}(\text{L-H})_2\text{S}$	Photolytic in CHCl_3	0.151
	Thermal in DMF	0.113
$\text{Ni}(\text{L-H})_2$	Photolytic addition	0.054
	Thermal addition	0.099

^a Sulfur 37.2% enriched in ^{34}S . ^b $I_{\text{TOT}} = I_{121} + I_{122} + I_{123}$. Data obtained with a Varian M-66 spectrometer with heated probe temperatures of $\sim 150^\circ$.

sulfur adds adjacent to the carbon atom and that the SCC_6H_5^+ fragment is statistically produced by both M-S and C-S cleavage. Specific "S-S cleavage" means that sulfur in each SCC_6H_5^+ comes from the

(10) Below ~ 17 eV the 122-amu intensity increases abnormally. This peak corresponds to m/e for $^{58}\text{Ni}^{32}\text{S}_2^+$ which may be produced. The $^{60}\text{Ni}^{32}\text{S}_2^+$ peak at m/e 124 can monitor the formation of this species. There is a gradual change in the intensity of the 122-amu peak with time as the sample remains in the heated sample probe. The origin of this effect is not yet understood. The I_{123}/I_{TOT} ratio does not appear to be sensitive to the probe temperature.

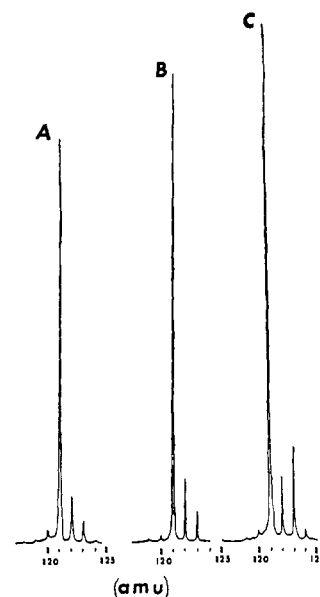


Figure 1. Mass spectra in the $\text{C}_6\text{H}_5\text{CS}^+$ fragment region of A, $\text{Ni}(\text{L-H})_2$; B, $\text{Ni}(\text{L-H})_2$ from which excess sulfur is removed with triphenylphosphine; and C, $\text{Ni}(\text{L-H})_2\text{S}$ from sulfur 37.2% enriched in ^{34}S .

disulfide linkage with the sulfur atom addition adjacent to carbon. "Sulfur scrambling" implies a statistical decomposition with a statistical sulfur distribution throughout the complex. "S addition" implies sulfur atom addition adjacent to the metal. "Specific C removal" implies that the sulfur atom entering the complex adjacent to the carbon atom is removed by the phosphine. The intensity ratios expected in the final $\text{Ni}(\text{L-H})_2$ after sulfur atom removal under conditions of complete or partial S atom scrambling are also given.

Table II. Mass Spectroscopic Data for $\text{Zn}(\text{S}_2\text{CC}_6\text{H}_5)_2\text{S}_2$ from ^{34}S Enriched^a Sulfur

Substance ^b	Condition	I_{123}/I_{TOT}^c
	Calculated	
$\text{Zn}(\text{L-H})_2\text{S}_{1.76}$	C addition statistical	0.190
	S-S cleavage	0.372
	Sulfur scrambling	0.146
	S addition	0.0454
$\text{Zn}(\text{L-H})_2$	Specific C removal	0.0454
	Random disulfide	0.118
	Sulfur scrambling	0.146
	Found	
$\text{Zn}(\text{L-H})_2\text{S}_{1.76}$	Photolytic addition	0.170
$\text{Zn}(\text{L-H})_2$	Photolytic addition	0.165

^a Sulfur 37.2% enriched in ^{34}S . ^b $\text{Zn}(\text{L-H})_2\text{S}_{1.76}$ assumed to be 88% $\text{Zn}(\text{L-H})_2\text{S}_2$ and 12% $\text{Zn}(\text{L-H})_2$. ^c $I_{\text{TOT}} = I_{121} + I_{122} + I_{123}$. Data obtained with a Varian M-66 spectrometer using a heated probe, 150–160°.

The large I_{123}/I_{TOT} ratios found for the $\text{Zn}(\text{L-H})_2$, 0.165, and for the $\text{Ni}(\text{L-H})_2$ obtained from the thermal addition, 0.099, show conclusively that some sulfur atom scrambling occurs. With no scrambling, the ratio expected is ~ 0.045 . With the zinc(II) complex, this scrambling occurs at room temperature, but with nickel(II) we are led to believe that it was caused in part by the elevated temperatures used in the thermal

addition. Little sulfur atom scrambling is apparent from the photolytic addition to $\text{Ni}(\text{L}-\text{H})_2$, $I_{123}/I_{\text{TOT}} = 0.054$. Based on nucleophilic attack by $^+\text{SS}_2\text{S}^-$ on the CS_2 carbon atom this result would be expected.

Two important conclusions are to be drawn from this work. Upon sulfur addition to $\text{Zn}(\text{L}-\text{H})_2$, sulfur scrambling occurs to distribute "added" sulfur into all sulfur atom positions in the molecule. With $\text{Ni}(\text{L}-\text{H})_2$, sulfur atom addition and removal may be highly specific. In the photolytic addition the added sulfur appears adjacent to the CS_2 carbon atom.¹¹

(11) We are grateful to the Public Health Service, AM-13558-01, and the NSF, GP-7889 and GP-11701, for generous support of this work.

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Sulfur Chelates. XI. Sulfur Atom Lability in Sulfur-Rich Metal Dithiolates

Sir:

The ability of certain metal dithiolates such as zinc(II) xanthates, $\text{Zn}(\text{S}_2\text{COR})_2$, and dithiocarbamates, $\text{Zn}(\text{S}_2\text{CNR}_2)_2$, to promote the addition of sulfur to olefins has long made these materials useful vulcanization accelerators.¹ However, the mechanism by which these

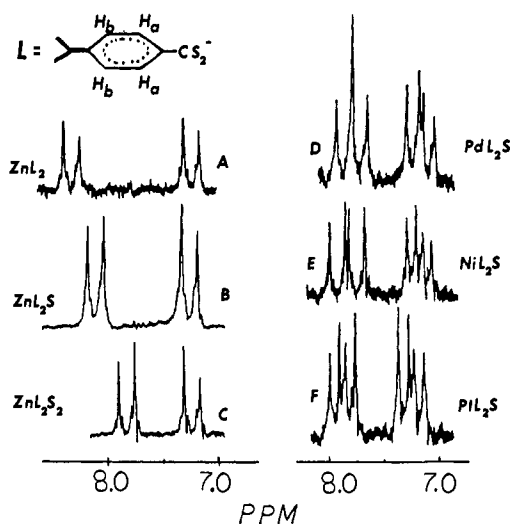


Figure 1. Proton magnetic resonance spectra (in parts per million from TMS at 60 Mc) of dithiocumato complexes of zinc(II), palladium(II), platinum(II), and nickel(II) containing excess sulfur in the phenyl region of the spectrum. The solvent is CS_2 .

materials cause the sulfur addition process is not established.^{1b} Dithiocarbamates and other dithiolates also are known to be effective antifungal reagents² for certain agricultural diseases. While the biochemical mechanism involved in antifungal action is not known, it is apparent from studies carried out in our laboratories that most metal dithiolate derivatives of carbon disulfide are readily oxidized,³ and that certain

(1) (a) For a general review of the chemistry of 1,1-dithiolates see D. Coucouvanis, *Progr. Inorg. Chem.*, in press; (b) W. Hoffmann, "Vulcanization and Vulcanization Agents," Palmerton Publishing Co., New York, N. Y., 1967.

(2) G. D. Thorn and R. A. Ludwig, "The Dithiocarbamates and Related Compounds," Elsevier Publishing Co., New York, N. Y., 1962.

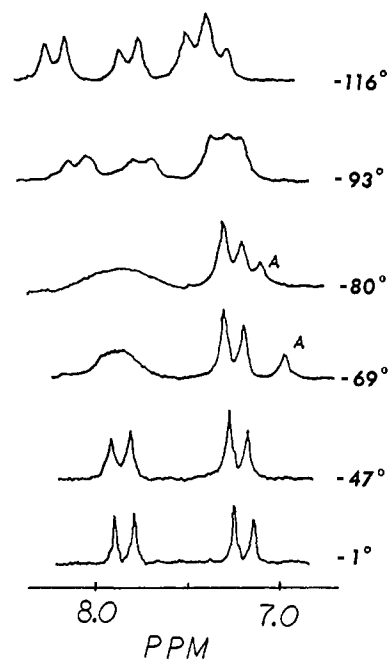
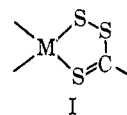


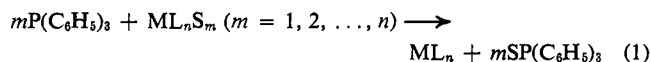
Figure 2. Variable temperature phenyl proton magnetic resonance spectra (in parts per million from TMS at 60 Mc) of ZnL_2S , $\text{L} = p$ -dithiocumate in 1:1 $\text{CS}_2:(\text{C}_2\text{H}_5)_2\text{O}$. A arises from a solvent impurity.

of these species act as sulfur atom scavengers to form isolable "sulfur-rich" species⁴ containing one or more disulfide chelate rings (I). While no sulfur-rich derivatives of dithiocarbamates or xanthates have been



isolated to date, the similarity of the known chemistry of the metal derivatives of trithioperoxy-carboxylates^{4,5} to that of the xanthates and dithiocarbamates⁶ suggests that sulfur-rich derivatives of these latter materials are very likely intermediates in systems containing added sulfur. In this communication we wish to report the preliminary results of spectrophotometric and nmr kinetic studies with sulfur-rich dithioarylates of nickel(II), palladium(II), platinum(II), and zinc(II).

Triphenylphosphine extracts a sulfur atom from sulfur-rich dithiolates to produce triphenylphosphine sulfide and the metal dithiolate (reaction 1). We have



spectrophotometrically followed the kinetics in toluene of the reaction of $\text{P}(\text{C}_6\text{H}_5)_3$ with the NiL_2S derivative of nickel(II) dithiocumate, which presumably has the planar NiS_4 structure (II), and find that the sulfur atom abstraction follows second order kinetics with

(3) D. Coucouvanis and J. P. Fackler, Jr., *J. Amer. Chem. Soc.*, **89**, 1346, 1745 (1967).

(4) While "sulfur-rich" is a useful descriptive term for these species, the names "perthiocarboxylate," "thioacyldisulfide," and "trithioperoxy-carboxylate" also have been used. The latter name, suggested by *Chemical Abstracts*, is preferred in formal usage.

(5) J. P. Fackler, Jr., D. Coucouvanis, J. A. Fetchin, and W. C. Seidel, *J. Amer. Chem. Soc.*, **90**, 2784 (1968).

(6) D. Coucouvanis and J. P. Fackler, Jr., *Inorg. Chem.*, **6**, 2047 (1967).