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

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

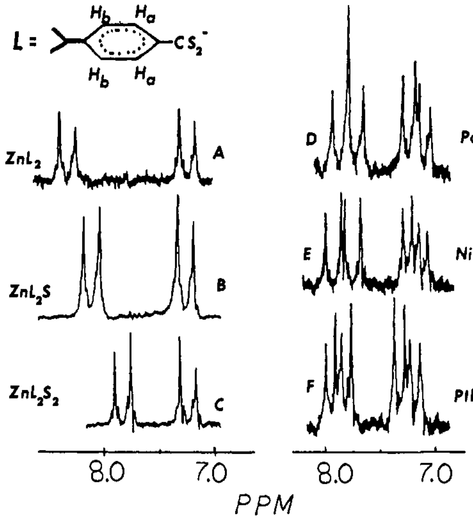


Figure 1. Proton magnetic resonance spectra (in parts per million from TMS at 60 Mc) of dithiocumato complexes of zinc(II), palladium(II), platinum(II), and nickel(II) containing excess sulfur in the phenyl region of the spectrum. The solvent is $\mathrm{CS_2}$.

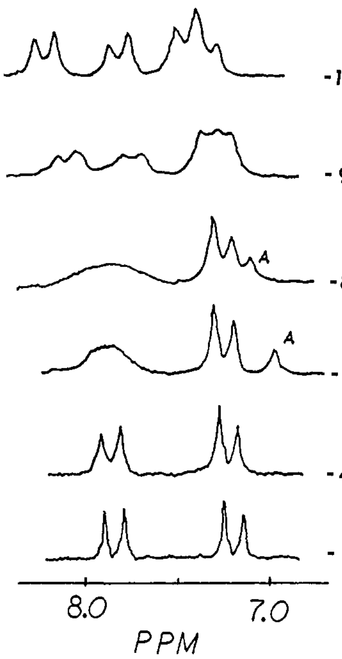
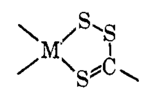


Figure 2. Variable temperature phenyl proton magnetic resonance spectra (in parts per million from TMS at 60 Mc) of $\mathrm{ZnL_2S}$, L = *p*-dithiocumate in 1:1 $\mathrm{CS_2{:}(C_2H_5)_2O}$. A arises from a solvent impurity.

The ability of certain metal dithiolates such as zinc(II) xanthates, $\mathrm{Zn(S_2COR)_2}$, and dithiocarbamates, $\mathrm{Zn(S_2CNR_2)_2}$, to promote the addition of sulfur to olefins has long made these materials useful vulcanization accelerators.[1] However, the mechanism by which these materials cause the sulfur addition process is not established.[1b] Dithiocarbamates and other dithiolates also are known to be effective antifungicidal reagents[2] for certain agricultural diseases. While the biochemical mechanism involved in antifungicidal 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 of these species act as sulfur atom scavengers to form isolable "sulfur-rich" species[4] 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 trithioperoxycarboxylates[4,5] to that of the xanthates and dithiocarbamates[6] 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).



I

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

$$m\mathrm{P(C_6H_5)_3} + \mathrm{ML}_n\mathrm{S}_m\ (m = 1, 2, \ldots, n) \longrightarrow \mathrm{ML}_n + m\mathrm{SP(C_6H_5)_3} \quad (1)$$

spectrophotometrically followed the kinetics in toluene of the reaction of $\mathrm{P(C_6H_5)_3}$ with the $\mathrm{NiL_2S}$ derivative of nickel(II) dithiocumate, which presumably has the planar $\mathrm{NiS_4}$ structure (II), and find that the sulfur atom abstraction follows second order kinetics with

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[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.

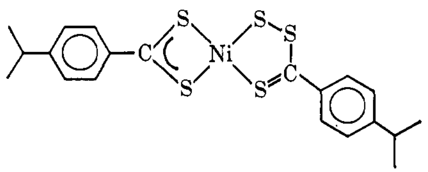
[2] G. D. Thorn and R. A. Ludwig, "The Dithiocarbamates and Related Compounds," Elsevier Publishing Co., New York, N. Y., 1962.

[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 "trithioperoxycarboxylate" 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).

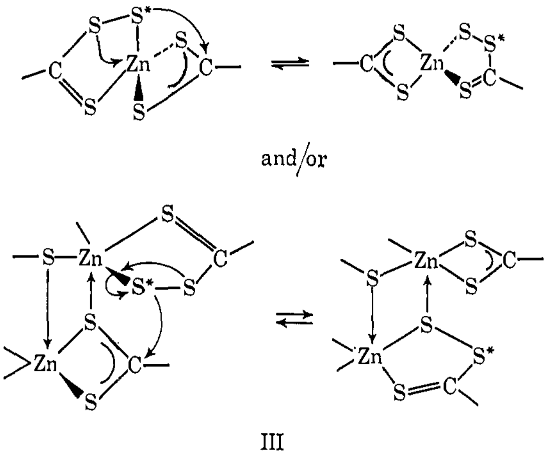


II

$k_2 = 0.91 \pm 0.03\ M^{-1}\ \text{sec}^{-1}$ at 300°K. The activation energy, 7.8 ± 1.0 kcal/mol, and entropy of activation, $\Delta S^{\ddagger} = -37 \pm 2$ eu, are consistent with a mechanism which involves kinetically controlled attack by the phosphine on the sulfur-rich complex, presumably at the sulfur atom of the disulfide linkage which is adjacent to the carbon. It has been established that this sulfur atom is the one removed[7] by triphenylphosphine from the sulfur-rich nickel(II) dithiobenzoate derivative in boiling $CHCl_3$. The sulfur abstraction from the analogous palladium(II) complex with triphenylphosphine is too rapid to be studied by the spectroscopic technique used here to study the nickel(II) derivative. Similarly the abstraction from ZnL_2S_2, where L = *p*-dithiocumate, is also too fast for this technique.

The kinetic lability of sulfur atoms in the zinc(II) sulfur-rich dithiolates is apparent from nuclear magnetic resonance studies comparing sulfur-rich dithiocumates[8] of zinc(II), palladium(II), platinum(II), and nickel(II) with a ML_2S stoichiometry. Figure 1 presents the proton magnetic resonance of these species in the aromatic region. The doubled AB pattern observed for the Ni(II), Pd(II), and Pt(II) species is the anticipated result for complexes containing two distinctly different ligands (II). The chemical shift difference observed in the Zn(II) complex for the H_a and H_b protons as a function of total sulfur content (Figure 1, A, B, and C) and the absence of splitting implicates a *sulfur atom exchange*[9] which makes the aromatic rings magnetically equivalent on the nmr time scale. To test this, solutions of ZnL_2S in 1:1 (v/v) CS_2:$(C_2H_5)_2O$ were cooled to −116° (Figure 2) at which temperature the doubled AB pattern associated with nonequvalent aromatic rings was observed.[9] Preliminary studies of this behavior as a function of temperature and the concentration of ZnL_2S have indicated an activation energy of ~5 kcal/mol for the exchange process. The reaction does not show a simple kinetic dependence on the concentration of complex, however. Extrapolation of the data to room temperature with $\sim 10^{-2}\ M$ concentration of ZnL_2S in the CS_2–ether solvent suggests a lifetime of $\sim 10^{-5}$ sec for a disulfide bond.

Intra- or intermolecular sulfur atom exchange leads directly to the sulfur atom scrambling results observed mass spectrophotometrically with the sulfur-rich zinc(II) dithiobenzoate.[7] The nmr results described here can reflect a sulfur atom exchange and scrambling by path ssimilar to III. Also, exchange between the complex and "free" sulfur may produce the nmr results without causing sulfur atom scrambling.[10] These various possibilities will be considered thoroughly in a full report of this work.[11] However, it is clear from the results reported here that sulfur atom exchange occurs with considerable speed in these zinc(II) dithiolates.



III

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(7) See accompanying communication: Sulfur Chelates. X. J. P. Fackler, Jr., J. A. Fetchin, and J. A. Smith, *J. Amer. Chem. Soc.*, **92**, 2910 (1970).

(8) *Anal.* Calcd for $NiC_{20}H_{22}S_5$: C, 49.90; H, 4.61. Found: C, 49.75; H, 4.60. Calcd for $ZnC_{20}H_{22}S_6$: C, 46.18; H, 4.26. Found: C, 45.41; H, 4.67. Calcd for $ZnC_{20}H_{22}S_4$: C, 52.68; H, 4.86. Found: C, 53.01; H, 5.55. The ZnL_2S solutions are obtained from equimolar amounts of ZnL_2S_2 and ZnL_2. Calcd for $PdC_{20}H_{22}S_5$: C, 45.40; H, 4.19. Found: C, 45.81; H, 4.24. Calcd for $PtC_{20}H_{22}S_5$: C, 38.88; H, 3.59. Found: C, 38.61; H, 3.58.

(9) The chemical shift difference between the two room temperature aromatic ring AB doublets of the ZnL_2S_x is a linear function of x over the complete range from $x = 0$ to $x = 2$. This establishes the fact that the averaging process involves added sulfur. Furthermore, the isopropyl methyl protons show a splitting in the nickel, palladium, and platinum ML_2S species, which is not observed with ZnL_2S. If x is different from 1 for ZnL_2S_x, the intensities of the four peaks centered near 8 ppm at −116° (Figure 2) reflect the unequal concentrations of trithioperoxy and dithiocumate ligands.

(10) The sulfur atom exchange process occurring rapidly in the ZnL_2S system but not detected by nmr at room temperature with nickel, palladium, or platinum is consistent with ^{35}S atom exchange data reported by I. V. Khodzhoeva and Yu. V. Kissen, *Russ. J. Phys. Chem.*, 37, 412 (1963). These authors report an activation energy for the sulfur atom exchange in some metal diethyldithiocarbamates to be lowest with zinc(II). However, their estimated activation energy is larger than we observe for the nmr process by about a factor of 4. The origin of this difference, if real, has not been established but clearly bond rupture must be accompanied by bond formation in any mechanism suggested. Since C–S and S–S bond energies are similar (~60–65 kcal/mol) a mechanism involving concerted S–S bond rupture with C–S bond formation could account for the data provided no net change in metal–sulfur bonding occurs. Such mechanisms may be written, but since detailed molecular geometries are presently unknown with sulfur-rich zinc complexes, we feel such speculation is presently unwarranted. Furthermore, the concentration dependence of the process studied by nmr does not permit a direct interpretation of the activation energy observed. In fact, sulfur atom exchange without position scrambling could lead to the nmr results. A rapid secondary process could produce sulfur atom scrambling.[7]

(11) We acknowledge the support of the National Institutes of Health, Grant No. AM-13558-01, and the NSF, Grant No. GP-11701, for this work.

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Stereospecificity of the Enzymic Synthesis of the *o*-Xylene Ring of Riboflavin

Sir:

The biochemical conversion of two molecules of 6,7-dimethyl-8-(1′-D-ribityl)lumazine (**1**) to riboflavin (**2**) and 4-ribitylamino-5-amino-2,6-dihydroxypyrimidine (**3**) proceeds by the donation of a 4-carbon moiety from one lumazine (**1**, donor) to the 6- and 7-methyl groups of a second substrate molecule (**1**, acceptor) with the accompanying loss of two hydrogens from each of the