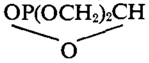
Table VI. Phosphoryl Oxygen Stretching Modes for Trialkyl Phosphates in Solution

Compound	$\nu_{O=P}$, cm^{-1}	Ref
$OP(O\text{-}n\text{-}C_4H_9)_3$	1260	8
$OP(OC_2H_5)_3$	1265	*b*
$OP(OCH_3)_3$	1281	*b*
$OP[OC(CH_3)_2]_2(OCH_3)$	1290	*c*
$OP(OCH_2)_2(OCH_3)$	1300	*d*
$OP(OCH_2)_2C(CH_3)_2(OCH_3)$	1311	*e*
$OP(OCH_2)_3C(CH_2)_4CH_3$[a]	1319	8
 $OP(OCH_2)_2CH$	1340	*f*

[a] Although $OP(OCH_2)_3CCH_3$ is too insoluble for a solution measurement of the O=P frequency, it is expected to be nearly the same as for the more soluble $OP(OCH_2)_3C(CH_2)_4CH_3$. [b] F. S. Mortimer, *Spectrochim. Acta*, 9, 270 (1957). [c] M. G. Newton, private communication. [d] F. Westheimer, private communication. [e] To be published. [f] D. B. Denney and S. L. Varga, *Tetrahedron Letters*, 4935 (1966).

to those found in the adamantane thiophosphate $SP(OCH)_3(CH_2)_3$ (1.58 Å and 105°, respectively).[23]

From Table VI, it can be seen that the center of the band assigned to the O=P stretching mode ranges from 1260 to 1340 cm^{-1} in trialkyl phosphates. Only three O=P bond distances are known for such compounds: $OP(OCH_2)_3CCH_3$ (1.46 Å), $OP(OCH_2)_2(OCH_3)$ (1.44 Å),[21] and $OP[OC(CH_3)_2]_2(OCH_3)$ (1.44 Å).[21] Unfortunately, the uncertainties in these lengths and the O=P frequencies are on the order of the differences, making conclusions concerning a bond-order-bond-length correlation impossible. From a consideration of the gross structures of the phosphates in Table VI, however, it is apparent that there is a general increase in $\nu_{O=P}$ from open-chain (1260–1281 cm^{-1}) to monocyclic (1290–1311 cm^{-1}) to bicyclic (1319–1340 cm^{-1}) systems. That a decrease in the metal extraction properties of the phosphoryl oxygen parallels an increase in $\nu_{O=P}$ has been observed by Burdett and Burger.[24] From these results and the abnormally high $\nu_{O=P}$ value for $OP(OCH_2)_3C(CH_2)_4CH_3$ in Table VI, it is reasonable that this bicyclic phosphate was found to have no observable extraction ability.[8] It is not clear at present what the causes of these trends are, and further studies are in progress in an effort to resolve this question.

(23) P. Anderson and K. E. Hjortaas, *Acta Chem. Scand.*, 14, 829 (1960).

(24) J. L. Burdett and L. L. Burger, *Can. J. Chem.*, 44, 111 (1966).

Sulfur Chelates. VIII.[1] Oxidative Addition of Sulfur to Dithioaryl Acid Complexes of Nickel(II) and Zinc(II)

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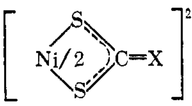
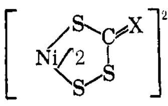
Abstract: Sulfur-rich dithio aromatic acid complexes of nickel(II) and zinc(II) are described. The oxidative addition of sulfur to dithio aromatic acid nickel(II) complexes leads to the addition of one sulfur atom per chelate ring. The bis(perthio acid)nickel(II) species is achieved by metathesis starting with the perthio acid–zinc(II) complex. Evidence is presented that suggests the sulfur addition and abstraction reactions are metal ion influenced and that the perthiodithio mixed-ligand–nickel(II) complex contains both four- and five-membered chelate rings.

The oxidation of thiols to disulfides[2,3] and the reductive abstraction of sulfur from disulfides by triphenylphosphine[4,5] are well-known reactions in the chemistry of organic sulfur compounds. Recently[6] we have described formally similar reactions involving anionic 1,1-dithiolate complexes of some group VIII metals. Certain of these complexes, I (X = S, NCN, CH(NO$_2$), etc.), are oxidized chemically or with sulfur or polysulfides to sulfur-rich species which appear to be formulated as II. These complexes are reduced[6] by triphenylphosphine to the original dithiolates.



I



II

In an earlier communication we demonstrated[7] that the species originally formulated[8] by Hieber and Brück as tetrakis(dithiobenzoato)-μ-dithio-dinickel(IV) is a ligand-oxidized nickel(II) species.[8a] We have shown that this complex, III (R = H or CH$_3$, M = Ni(II)),

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

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

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

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

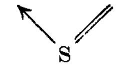
(5) A. A. Watson, *ibid.*, 2100 (1964).

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

(7) J. P. Fackler, Jr. and D. Coucouvanis, *ibid.*, 89, 1745 (1967).

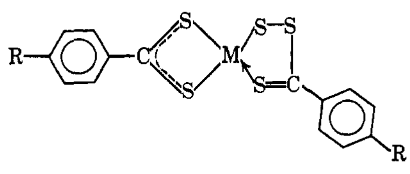
(8) W. Hieber and R. Brück, *Z. Anorg. Allg. Chem.*, 269, 13 (1952).

(8a) Note Added in Proof. D. Coucouvanis and S. Lippard, private communication, have shown conclusively using X-ray crystallography that $Fe(S_2CC_6H_5)_2(S_3CC_6H_5)$ contains a

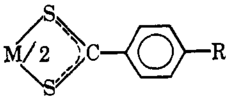


ring.

loses sulfur to triphenylphosphine to form the dithio acid complex IV.



III



IV

In this paper we describe in some detail the preparation and characteristics of the sulfur-rich dithioaryl acid complexes of nickel(II) including a new bis(perthioaryl acid)nickel(II) species and similar complexes with zinc(II). We also demonstrate the utility of the sulfur reductive abstraction reaction with triphenylphosphine to quantitatively determine the oxidized sulfur content in these systems.

Experimental Section

Most chemicals in this research were used as received. Toluene was distilled over sodium, and triphenylphosphine was recrystallized from acetone–water and dried in a stream of nitrogen. Ammonium sulfide was obtained from Fisher Scientific Co. in 20–25% aqueous solution. Products were checked for purity by thin layer chromatography. Analyses were performed by Galbraith and Crobaugh Analytical Laboratories, Knoxville, Tenn. and Cleveland, Ohio, respectively. Recorded melting points are uncorrected.

Physical Measurements. Magnetic susceptibilities were determined at room temperature using a Faraday technique. The calibrant[9] was Hg[Co(SCN)$_4$]. 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 Debye–Scherrer camera utilizing nickel-filtered copper radiation was used to observe the X-ray powder patterns of the complexes. A Varian A-60 nmr spectrometer and a Varian M-66 mass spectrometer were used for nmr and mass spectra, respectively. The major isotope peak of the parent (when observed) has been listed. Solution molecular weights generally were performed using a Mechrolab vapor-phase osmometer calibrated with triphenylphosphine or with benzil.

Preparation of Complexes. The procedure of Bruni and Levi,[10] with some minor modifications, was used to prepare perthioaryl acid complexes of zinc(II). The sulfur-rich nickel(II) complex, perthiobenzoato(dithiobenzoato)nickel(II), was prepared as described previously[7] or by the procedure reported below.

Bis(*p*-perthiotoluato)zinc(II). *p*-Tolualdehyde, 12.0 g (0.1 mol), was added to a mixture of 25 ml of (NH$_4$)$_2$S solution, 3.0 g of sulfur (higher yields were obtained, but unconsistently, with increased amounts of sulfur), and 20 ml of tetrahydrofuran (THF). The mixture was refluxed for 10 min with frequent agitation. The resulting dark red solution was diluted with 100 ml of distilled water and extracted with 200 ml of ether to remove unreacted aldehyde and oxidation products (disulfides). The aqueous solution was filtered to remove a small amount of sulfur and added directly to an aqueous solution of zinc chloride (10 g in 100 ml of water). An insoluble orange precipitate immediately formed which was isolated and washed with methanol. The crude precipitate was dissolved in THF, filtered to separate the zinc hydroxide contaminant, and evaporated to dryness in a hood. Orange-red crystals (~10 g) were isolated in a 44% yield.

The product was recrystallized from carbon disulfide by adding absolute ethanol and cooling. Large orange-red needles were produced, mp 192–193°.

Anal. Calcd for $C_{16}H_{14}S_6Zn$: C, 41.50; H, 3.02; Zn, 14.1; mol wt, 464. Found: C, 41.88; H, 3.22; Zn, 14.3; mol wt (in CHCl$_3$), 473.

Anal. Calcd for Bis(perthiobenzoato)zinc(II), $C_{14}H_{10}S_6Zn$: C, 38.9; H, 2.3; Zn, 15.0; mol wt, 436. Found: C, 38.7; H, 2.4; Zn, 14.9; mol wt (in CHCl$_3$), 467.

Bis(dithiofuroato)zinc(II). In a manner similar to the reaction described above for the perthiotoluene derivative, 10 g of furfural (0.1 mol) was treated with ammonium sulfide and sulfur. The reaction mixture was acidified and extracted with ether. The ether layer was extracted with dilute aqueous sodium hydroxide and this solution of the sodium salt of the ligand was used to prepare the zinc complex.[11] The crude zinc complex gave orange-brown crystals from xylene, 12 g, 80% yield, mp 100° dec.

Anal. Calcd for $C_{10}H_6O_2S_4Zn$: C, 34.2; H, 1.7. Found: C, 34.3; H, 2.0.

Bis(*p*-dithiotoluato)zinc(II). Perthiotoluatozinc(II), 2 g, was dissolved in 150 ml of xylene, and 3 g (excess) of triphenylphosphine was added. The solution was brought to reflux and filtered. Upon addition of 50 ml of *n*-pentane and cooling to room temperature, a white oily substance separated (a mixture of Ph$_3$P and Ph$_3$PS). The solution was decanted from the oil and an additional 50 ml of *n*-pentane was added. After removing some of the *n*-pentane under vacuum, yellow needles formed. These were separated from the solution, washed with methanol, and dried in a stream of nitrogen; yield 1.2 g, mp 206–208°.

Anal. Calcd for $C_{16}H_{14}S_4Zn$: C, 48.2; H, 3.5. Found: C, 48.0; H, 3.6.

Bis(dithiobenzoato)nickel(II). Perthiobenzoatodithiobenzoatonickel(II), 1 g, was dissolved in 100 ml of chloroform, and a saturated solution containing excess triphenylphosphine in chloroform was added slowly while stirring and heating to 60°. The violet color of the Hieber–Brück complex[8] disappeared and a deep blue solution was obtained. Upon dilution with 50 ml of ethanol and cooling, blue-violet crystals formed which were washed with ethanol and ether until free of the starting material. The sulfur-rich complex is considerably more soluble in ether than is the dithiobenzoatonickel(II) complex. The yield was 0.8 g, 87% based on the sulfur-rich starting material, mp 221–222° (lit.[8] 219°).

Anal. Calcd for $C_{14}H_{10}S_4Ni$: C, 46.0; H, 2.7; S, 35.1; Ni, 16.1. Found: C, 45.9; H, 2.8; S, 33.9; Ni, 16.0.

Bis(*p*-perthiotoluato)nickel(II). The perthiotoluatozinc complex, 2 g, was dissolved in 30 ml of CS$_2$. To this, a solution of 2 g (excess) of NiCl$_2$·6H$_2$O in 50 ml of absolute ethanol was added with stirring. Upon removing some of the solvent under vacuum, crystals formed which were filtered, washed with absolute ethanol, and dried in a stream of nitrogen. Green crystals, 1.7 g, 85% yield, were obtained. The complex can be recrystallized conveniently from carbon disulfide upon addition of absolute ethanol.

Anal. Calcd for $C_{16}H_{14}S_6Ni$: C, 42.1; H, 3.07; mol wt, 456. Found: C, 42.2; H, 3.61; mol wt (in CHCl$_3$), 446.

Bis(perthiobenzoato)nickel(II). This green compound was prepared from the corresponding zinc complex in almost quantitative yields, mp 172–174°.

Anal. Calcd for $C_{14}H_{10}S_6Ni$: C, 39.2; H, 2.3; mol wt, 428. Found: C, 39.7; H, 2.6; mol wt (in CHCl$_3$), 453; mass spectrum, *m/e* 428. The intensities in the regions *m/e* 396 and 364 were considerably larger than the parent peak.

Perthiotoluatodithiotoluatonickel(II). Bis(perthiotoluato)zinc(II), 1 g (0.0022 mol), was dissolved in 120 ml of chloroform, triphenylphosphine, 0.57 g (0.0022 mol), was added, and the solution was refluxed. To the hot solution NiCl$_2$·6H$_2$O in methanol was added with stirring, and a violet precipitate formed at once. The precipitate was recrystallized from carbon disulfide upon the addition of absolute ethanol to give 0.6 g of small violet crystals, mp 219–221°.

The complex also was prepared in a manner similar to the procedure[7] previously described for the benzoic acid derivative.

Anal. Calcd for $C_{16}H_{14}S_5Ni$: C, 45.2; H, 3.3. Found: C, 45.5; H, 3.7.

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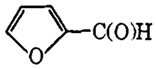
[9] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

[10] G. Bruni and T. G. Levi, *Atti Accad. Lincei*, **32**, 5 (1923); *Chem. Abstr.*, **18**, 2693^9 (1924).

(11) The nomenclature for these complexes is obtained from the fact that the ligand is a derivative of furfural.



A colleague, Lester Friedman, has suggested a nomenclature similar to that used in organic systems but based on a square (quadra) planar chelate ring. Thus bis(dithiofuroato)nickel(II) might be named *quadra*-2,4,5,7-tetrathia-3,6-difuryl-1-nickel(II)-heptane, where "quadra" signifies the square-planar bicyclic structure.

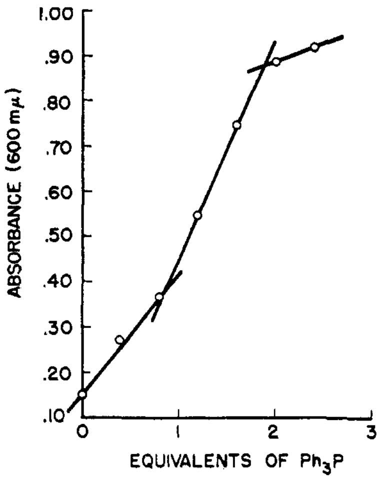


Figure 1. Titration of $Ni(S_3CC_6H_5)_2$ with triphenylphosphine in toluene.

Bis(*p*-dithiotoluato)nickel(II). The triphenylphosphine reduction described above gave blue crystals, mp 240–241°.

Anal. Calcd for $C_{16}H_{14}S_4Ni$: C, 48.9; H, 3.6. Found: C, 47.7, 49.7; H, 3.8, 3.8.

Bis(dithiofuroato)nickel(II). Bis(dithiofuroato)zinc(II) was dissolved in acetone, and an aqueous nickel chloride solution was added with stirring. An insoluble dark blue precipitate formed which was isolated, washed with acetone and ether, and dried. When wet, the compound oxidizes in the air to a violet oxidation product which is very soluble in ether. The blue crystals melt at 212–213°.

Anal. Calcd for $C_{10}H_6O_2S_4Ni$: C, 34.8; H, 1.74. Found: C, 34.5; H, 1.89.

Perthiofuroato(dithiofuroato)nickel(II). Bis(dithiofuroato)zinc(II), 1.0 g, was dissolved in 100 ml of acetone, and 0.38 g of iodine was added. The solution was refluxed for 3 min, and a solution of 0.8 g of $NiCl_2 \cdot 6H_2O$ in 25 ml of 95% ethanol was added. The violet solution which resulted was diluted with 200 ml of water and filtered. Of the product, 0.5 g was isolated, washed with absolute EtOH, and dried, mp 216–217°.

Anal. Calcd for $C_{10}H_6O_2S_5Ni$: C, 31.9; H, 1.59. Found: C, 32.5; H, 2.02; mass spectrum, *m/e* 376, 344 (minus one S atom).

Tris(dithiofuroato)iron(III) and -cobalt(III) Complexes. The cobalt and iron complexes could be prepared by treating the cobalt(II) and iron(II) halides with the zinc complex as described above. The cobalt(III) complex was recrystallized from CS_2–hexane, giving dark brown crystals, mp 100° dec.

Anal. Calcd for $C_{15}H_9O_3S_6Co$: C, 37.9; H, 1.84. Found: C, 37.7; H, 2.86.

The iron(III) complex gave dark green crystals, mp 90° dec.

Anal. Calcd for $C_{15}H_9O_3S_6Fe$: C, 37.2; H, 1.85. Found: C, 37.6; H, 2.21.

The tris(dithiofuroato)cobalt(III) complex displays an nmr spectrum similar to that of furfural.

Spectrophotometric Titrations of Complexes with Triphenylphosphine. In a typical experiment, a stock solution of complex (2.5×10^{-4} *M*) in toluene was prepared. Aliquots (10 ml) were placed in 25-ml flasks, and different amounts of triphenylphosphine was added to each flask. The flasks were filled to the mark with toluene and the solutions were permitted to come to equilibrium. The criterion for equilibrium was that the visible spectrum of the solution remain constant over 6 hr. After equilibrium had been reached, the visible spectrum of each of the solutions was measured. Figure 1 is a typical titration curve.

Results

Dithioaryl acid complexes of zinc(II) and nickel(II) containing up to two extra sulfur atoms per metal ion have been prepared. The instability of the alkali metal salts to air oxidation led us to prepare the stable zinc(II) species as starting materials for the metathetical preparation of the nickel(II) and other complexes. The procedure[10] of Bruni and Levi (modified somewhat) utilizing the reaction of aldehydes with ammonium sulfide was used to prepare the ligands. The zinc(II) complex was found by triphenylphosphine titration to have variable sulfur content (1.4–1.7 extra S atoms per metal) unless the acid–base work-up procedure (see Experimental Section) was omitted. Only then could reproducible yields of the perthio derivatives be obtained.

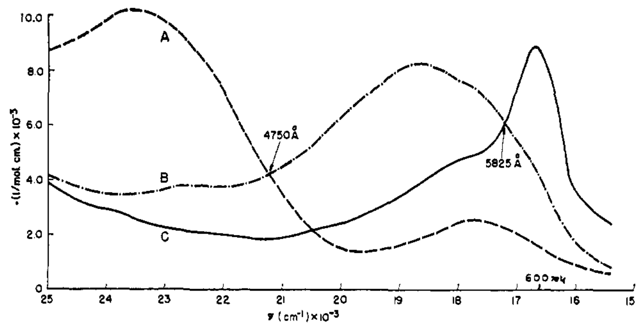


Figure 2. Absorption spectra of (A) $Ni(S_3CC_6H_5)_2$, (B) $Ni(S_2CC_6H_5)(S_3CC_6H_5)$, and (C) $Ni(S_2CC_6H_5)_2$.

Reductive abstraction[12] of sulfur from the perthio derivatives with triphenylphosphine gives the dithioaryl acid zinc(II) complex. For comparison, the zinc(II) complex of dithiobenzoic acid was prepared using dithiobenzoic acid synthesized from the phenyl Grignard.[13]

As reported previously,[9] polysulfide oxidation of nickel(II) dithiobenzoate apparently gives only the mixed-ligand complex. Reaction of the dithiotoluate complex in $CHCl_3$ with aqueous $(NH_4)_2S_x$ produces the violet sulfur-rich (one extra S atom per metal) species. The green bis(perthio) complex does not form under these conditions.

The perthio derivatives of nickel(II) can be formed from the zinc(II) complexes, however. Orange-brown solutions of the nickel(II) perthio species in toluene can be titrated with triphenylphosphine to the mixed-ligand or parent dithio acid complex (Figure 1). The violet nickel(II) dithiobenzoate complex containing one extra sulfur atom per metal, as prepared by sulfur abstraction, was identical with the material described by Hieber and Brück.[7,8]

The visible spectra of the nickel(II) dithioaryl acid, mixed-ligand, and perthioaryl acid complexes are sufficiently different (Figure 2) to use these data for identification purposes. When stoichiometric quantities of bis(dithiotoluato)nickel(II) and bis(perthiotoluato)-nickel(II) are dissolved in $CHCl_3$ and allowed to stand overnight, the mixed-ligand complex, as shown by its visible spectrum and analytical separation, is obtained in 100% yield.

The infrared spectra of the nickel(II) and zinc(II) complexes have been recorded. The low-energy (300–

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[12] Throughout this paper we refer to "oxidative addition" and "reductive abstraction" to specify that sulfur is added or abstracted by a reaction analogous to oxidation or reduction of the ligand. However, the formal oxidation state of the sulfur atom may not change in the process. The abstraction of a sulfur atom by triphenylphosphine is generally referred to as an "oxidation" of the phosphine; hence the term "reductive abstraction" of sulfur atoms by the phosphine appears appropriate. As we have indicated previously,[6] chemical or electrochemical oxidation of certain 1,1-dithiolates results in sulfur-rich species (along with decomposition). "Reduction" with borohydride also appears to remove sulfur from the sulfur-rich species.

[13] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. IV, Chemical Publishing Co., New York, N. Y., 1962.

Table I. X-Ray Powder Patterns for Nickel(II) and Zinc(II) Dithiotoluates

$Ni(S_2CC_7H_7)_2$	$Ni(S_2CC_7H_7)_2S$	$Ni(S_2CC_7H_7)_2S_2$	$Zn(S_2CC_7H_7)_2$	$Zn(S_2CC_7H_7)_2S$	$Zn(S_2CC_7H_7)S_2$
	11.163 (s)				9.858 (vw)
9.226 (vs)	9.265 (vw)	9.665 (vs)	9.458 (s)	9.458 (s)	
	8.497 (m)				9.907 (s)
		7.437 (w)		8.465 (s)	8.457 (m)
	6.172 (w)			6.335 (s)	
	5.840 (m)	5.733 (w)	6.079 (s)		
5.455 (w)	5.573 (m)	5.498 (w)	5.772 (w)	5.783 (vw)	5.761 (w)
5.205 (s)		5.286 (w)		5.612 (w)	
	4.924 (vw)		5.340 (w)		
		4.545 (vw)	4.972 (w)		4.775 (w)
4.011 (vw)		4.111 (m)		4.656 (s)	4.611 (w)
	3.957 (vw)		4.415 (s)	4.420 (s)	4.422 (vw)
3.595 (s)	3.574 (s)	3.686 (s)	4.260 (w)		4.228 (vw)
		3.443 (m)	3.905 (w)	3.926 (vw)	
3.335 (vw)	3.366 (vw)	2.283 (vw)		3.800 (m)	3.811 (m)
3.197 (vw)		3.179 (w)	3.734 (w)	3.687 (w)	
3.082 (m)		3.039 (vw)	3.500 (w)	3.505 (w)	
		2.756 (w)		3.432 (vw)	3.418 (vw)
2.581 (w)				3.224 (vw)	3.265 (vw)
		2.266 (w)	3.190 (w)		
		2.177 (w)	3.152 (m)	3.160 (m)	
		1.911 (vw)	3.001 (w)		
			2.885 (w)	2.880 (w)	2.886 (vw)
			2.655 (w)	2.653 (w)	

900 cm^{-1}) region for the nickel(II) dithiotoluate series is presented in Figure 3 as it shows the S–S vibration near 530 cm^{-1} for the sulfur-rich species.

A green material, not yet completely identified but probably a Ph_3P adduct of $Ni(S_2CC_6H_5)_2$, was observed when the perthio derivative was treated with more than 2 mol of triphenylphosphine in toluene. The continuing change in absorbance at 600 mμ (Figure 1) with addition of Ph_3P beyond the second inflection point is indicative of this reaction.

The X-ray powder patterns (Table I) clearly show the lack of isomorphism between the diamagnetic nickel(II) and zinc(II) dithiotoluate derivatives. They also show that three distinct species are produced in the nickel(II) series of complexes. A crystalline zinc mixed-ligand complex is suggested by the presence of some lines not attributable to either the dithio or perthio derivatives, but the data are not conclusive on this point. The correspondence of several lines with the sulfur-free and perthio species and the variable content of sulfur obtained for different preparations suggests a lack of stoichiometry for the zinc "sulfur-rich" species, even though it appears crystalline.

Parent ion peaks are observed in the mass spectra of bis(perthiobenzoate)nickel(II) and the "sulfur-rich" mixed-ligand complexes of nickel(II) with dithiobenzoic and dithiofuroic acids. The mass spectrum of $Ni(S_3CC_6H_4CH_3)_2$ shows only weak lines near *m/e* 456 but strong lines at *m/e* 424 and 426 and *m/e* 392 and 394, indicative of the loss of one and two sulfur atoms, respectively, from the complex.

Discussion

The diamagnetic complex described[8] by Hieber and Brück as a nickel(IV) derivative of dithiobenzoic acid has been shown by nmr studies[7] of the toluene derivative and by data reported here to be a nickel(II) complex of the mixed-ligand perthio–dithio aromatic acid. Chemical oxidation of the dithio acid complex leads invariably to this species. The bis(perthio) derivative cannot be obtained by oxidation of the dithio species, but it can be obtained by a metathetical synthesis starting with the zinc(II) complexes.

While a complete understanding of the structures of these sulfur-rich species must await a detailed X-ray crystallographic investigation,[8a] some stereochemical features seem fairly certain from several lines of available evidence. First, the diamagnetism of the nickel(II) species and their visible spectra (no low-energy band near 10,000 cm^{-1}) show that the bisdithio, the bisperthio, and the dithio–perthio (mixed-ligand) aromatic acid species all contain an essentially square-planar arrangement of four sulfur atoms about the metal ion. Weak intermolecular sulfur–metal interactions may be present in the solid state. The dithio acid species are known to form adducts with organic bases quite readily.[1,14]

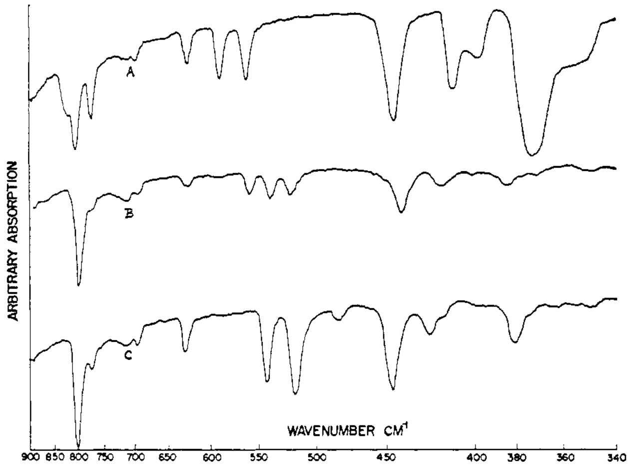

Figure 3. Far-infrared spectra (300–500 cm^{-1}) of (A) $Ni(S_2CC_6H_5)_2$, (B) $Ni(S_2CC_6H_5)(S_3CC_6H_5)$, and (C) $Ni(S_3CC_6H_5)_2$.

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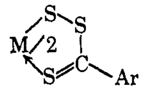
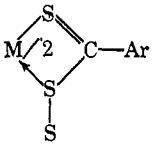
(14) H. Krebs, E. F. Weber, and H. Fassbender, *Z. Anorg. Allg. Chem.*, 276, 128 (1954).

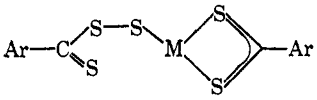
The stereochemical arrangement about the zinc(II) atom in any of these compounds is not known. Because of the wide variety of structures now known[15-17] for zinc–sulfur complexes, it would be presumptuous to suggest geometries for these species.[18] However, the charge-separation arguments we used previously to suggest a five-membered chelate ring (II, V) for the $M(S_3CX)_2^{2-}$ complexes[6] are valid[19] for both the nickel(II) and zinc(II) perthio acid chelates reported here.

Experimentally, qualitative and semiquantitative observations of some reaction rates for the nickel(II) species point directly toward the formation of a five-membered chelate ring of the type indicated in III or V. We find that the chemical oxidation of the dithio acid nickel(II) species stops with the addition of only one sulfur atom. If a chelate ring of type VI were being formed, there would be no apparent reason for the reaction to stop with the addition of only one sulfur atom. As the bis(perthio)nickel(II) complex can be prepared by ligand exchange, there is little evidence to believe that a chelate ring of type VI is present. The observation of the parent ion peak in the mass spectrometer for the bis(perthiobenzoato)nickel(II) complex, *m/e* 428, also argues against a "dangling" sulfur atom since such groups normally are removed in the ionization process of the M-66 spectrometer. The rapid reaction (minutes) of triphenylphosphine with the zinc(II) perthio complex to remove two sulfur atoms, and with the nickel(II) perthio species to remove one sulfur atom while the second sulfur atom is lost much more slowly (several hours at room temperature), requires further study to be thoroughly understood. For example, these differences may be consistent with the varying effect of the metal ions in promotions of the type we outlined[6] for sulfur addition and abstraction with $M(CS_3)_2^{2-}$. However, since zinc(II) complexes are known to be relatively more labile than nickel(II) complexes, the differing rates of sulfur abstraction may imply that metal–sulfur atom bond breaking occurs prior to, or along with, the sulfur abstraction. While it is unlikely that both metal–sulfur bonds of a ligand break to free the ligand before reaction with phosphine in nonpolar media, one metal–sulfur atom bond might break. In fact, rupture of the thiocarbonyl–metal atom bond leads to VII, a structure similar to the structure of dithio acid disulfides, species known to react rapidly[5,20] with phosphines to lose a sulfur atom.





VI



VII

The sulfur atom adjacent to the thiocarbonyl is likely to be the sulfur atom abstracted. (Conceivably a weakening of the metal–thiocarbonyl bond could accomplish the same result.) If the rate-determining step involves the breaking of the metal–sulfur bond or if a preequilibrium dissociation to VII occurs prior to phosphine attack, the rate Zn(II) > Ni(II) would be expected. Furthermore, this type of mechanism could explain the rapid reaction of the bis(perthio)nickel(II) species if the second perthio chelate ring weakens a metal–sulfur bond of the perthio chelate ring to a greater degree than does a dithio chelate ring. In the case of the mixed-ligand nickel(II) complex, the thiocarbonyl is *trans* to a dithio acid sulfur atom, but in the bis(perthio) complex it could be *trans* to a disulfide sulfur atom, an atom likely to produce a greater *trans* effect than the less anionic thioacid sulfur atom.

The mixed-ligand nickel(II) complexes may owe their seemingly anomalous stability to effects of the type indicated above or as we suggested previously[7] to the achievement of a good balance between the opposing effects of chelate ring size and resonance stabilization. An energy gain due to formation of a less sterically strained five-membered ring may be offset by energy loss due to a reduced electron delocalization over the chelate rings. Thus, only one chelate ring of the nickel(II) dithio aromatic acid complex, where inter-ring interactions must be large, can be expanded by sulfur addition.

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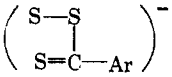
(15) M. Bonamico, G. Mazzone, A. Vaciago, and L. Zambonelli, *Acta Crystallogr.*, **19**, 898 (1965).

(16) H. P. Klug, *ibid.*, **21**, 536 (1966).

(17) H. B. Gray, *Progr. Transition Metal Chem.*, **1**, 239 (1965).

(18) In solution the geometry is probably tetrahedral since the complexes are monomeric.

(19) The anion



Ar = aromatic moiety, would be expected to coordinate through the sulfide and thiocarbonyl sulfur atom and not the –S– sulfur atom which would be relatively electron "poor."

(20) A. A. Watson, *J. Chem. Soc.*, 892 (1949).