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Metal Chelates of Biologically Important Compounds. II. Nickel Complexes of Dialkyldithiophosphates and Their Adducts with Nitrogen Heterocycles[1]

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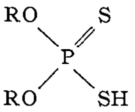
New purple, diamagnetic, square-planar dialkyldithiophosphato complexes of nickel(II), $Ni\{(RO)_2PS_2\}_2$ (R = 2-chloroethyl, cyclohexyl, 1,1-pentafluorophenylethyl) have been prepared. When R = i-C_3H_7, *tert*-C_4H_9, or CH_2CF_3, the products were impure or unstable. It is proposed that the stability of the Ni–S bond in these complexes is sensitive to both steric and electronic effects. The complexes exhibit electronic absorption bands in the regions $(14.65–15.60) \times 10^3$, $(19.05–19.35) \times 10^3$, and *ca.* 25×10^3 cm^{-1}. The NiS_4 chromophore is stabilized by the formation of green, paramagnetic, octahedral species of the type NiS_4N_2 containing pyridine, 4-methylpyridine, 1,10-phenanthroline, or 2,2′-bipyridyl. Adducts were also obtained with 2,2′,2′′-terpyridyl; these contain the chromophore NiS_3N_3. Correlation of the infrared data obtained for the bis-ligand complexes led to the following assignments (cm^{-1}): ν(P–S) 527–575 (w–s), 638–665 (s); ν(P–O) 1005–1065 (m–s), 965–1005 (m); ν(Ni–S) 325–347 (w), 355–361 (s). In the spectra of the adducts ν(P–S) has been assigned at 540–590 (w–s), 658–675 cm^{-1} (s), and ν(Ni–S) has been assigned at 355–387 cm^{-1} (m–s). Some of the complexes have been investigated by means of X-ray structural and thermogravimetric analysis and mass spectrometry. The bis-ligand complexes undergo electron–ion reactions in the mass spectrometer with the stepwise loss of four molecules of alkene. Dta studies show that the species $Ni\{(C_2H_5O)_2PS_2\}_2py$ has transitory existence. Some of the complexes have proved to be active against larvae *Tineola bisselliella* and others display carcinostatic activity in the Walker carcinosarcoma test in mice.

Introduction

In part I[1] of this series chelates of DL-ethionine and *S*-methyl-L-cysteine were reported. We have now investigated the nickel(II) chelates of a number of dialkyldithiophosphates. The diesters of dithiophosphoric acids (I) were first reported in 1908.[2] In 1945 Malatesta and Pizzotti[3] reported the nickel(II), cobalt(III), and iron(II) complexes of dimethyl- and diethyldithiophosphoric acids. Esters of dithiophosphoric acid have been used as insecticides, and dialkyldithiophosphate derivatives are known to possess



I

properties similar to those of nerve gases, inhibiting the hydrolysis of the enzyme acetylcholinesterase to its substrate acetylcholine, thus causing muscular paralysis. The insecticidal, rodenticidal, and fungicidal activity of esters of the type $(RO)_2P(S)SX$ (X = substituted acetylphenyl or alkylurea) are believed to be primarily the result of enzyme inhibition.[4,5] Salts of the type $[PR_4][(RO)_2PS_2]$ have been found to display rather high fungicidal and bacteriological activity; in particular, the compound $[P(C_6H_5)_3C_2H_5][(C_2H_5O)(C_{12}H_{25}O)PS_2]$ is active in $1:8 \times 10^6$ parts in solution toward *Myobact. tuberculosis* human and *Myobact. tuberculosis* avium and in $1:5 \times 10^5$ parts in solution toward *Staphylococcus aureus*, *Bact. anthacoides*, and *Microsporum lanosum*.[6]

In this paper we report (a) the effect of the group R of the dialkyldithiophosphate ligand on the physical properties of the nickel(II) complexes and the ability of the latter to form adducts with nitrogen heterocycles, (b) mass spectral studies of some of the nickel complexes and their adducts, and (c) some tests on the biological activity of metal chelates of dialkyldithiophosphates.

Experimental Section

Analyses.—For nickel analysis it was necessary to decompose the heterocyclic base adducts by fusion with potassium hydrogen sulfate and concentrated sulfuric acid in a silica crucible at red heat. Wet ashing did not give reproducible results, since complete decomposition of the organic matter was not achieved. The bis-ligand complexes were decomposed with a mixture of concentrated sulfuric, nitric, and perchloric acids. Nickel was determined gravimetrically as its dimethylglyoximate.

Analyses for carbon, hydrogen, and nitrogen were carried out by Dr. E. Challen of the Microanalytical Laboratory, School of Chemistry, University of New South Wales. Analysis for carbon on the adducts by the usual combustion technique gave low values. It was necessary to mix vanadium pentoxide with the sample and to use a higher furnace temperature to obtain reliable carbon figures.

Phosphorus and sulfur were determined by the Australian Microanalytical Service, Melbourne, Australia.

Bis(*O,O*′-dialkyldithiophosphato)nickel(II) Complexes.—Phosphorus pentasulfide (22.2 g, 0.10 mol) was placed in a 200-ml, three-necked, round-bottom flask equipped with a nitrogen inlet, a magnetic heater–stirrer, and a Liebig condenser. While the stirrer and nitrogen flow were going, the appropriate alcohol ROH (50 ml) was poured into the flask through the condenser. In the case of $C_6F_5CH_3CHOH$, the alcohol was added in *n*-hexane solution. The mixture was heated until the solution became clear yellow. Nickel chloride hexahydrate (30 g, 0.13 mol) was then added. The resulting purple precipitate was stirred for 10 min; then the mixture was allowed to stand for 30 min

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[1] Part I: S. E. Livingstone and J. D. Nolan, *Inorg. Chem.*, **7**, 1147 (1968).

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without heating. The product was filtered off, washed with a little ethanol, and recrystallized from ethanol or *n*-hexane.

The analyses of the nickel complexes and their adducts are given in Table I.

Pyridine and 4-Methylpyridine Adducts.—The nickel complex Ni(dtp)$_2$ (dtpH = dialkyldithiophosphoric acid) was dissolved in the minimum amount of hot ethanol, and pyridine (or 4-methylpyridine) was added dropwise until the solution became green; then a slight excess of base was added. The mixture was cooled to 0° whereupon the green crystalline adduct was filtered off, washed with ether, and dried over phosphorus pentoxide.

Adducts Containing Chelating Nitrogen Heterocycles.—The 2,2′-bipyridyl, 1,10-phenanthroline, and 2,2′,2″-terpyridyl adducts were prepared as follows. The nickel complex Ni(dtp)$_2$ (0.001 mol) was dissolved in the minimum amount of hot ethanol, and a solution of base (0.001 mol) in hot ethanol was added. The mixture was cooled to 0°, and the green crystalline complex was filtered off, washed with ethanol, and dried *in vacuo* over phosphorus pentoxide.

Tris(2,2′-bipyridyl)nickel(II) Dimethyldithiophosphate.—Bis(dimethyldithiophosphato)nickel(II) (0.001 mol) in hot ethanol (15 ml) was treated with a solution of 2,2′-bipyridyl (0.48 g, 0.003 mol) in ethanol (3 ml). The mixture was cooled to 0°, and the crystalline pink complex was filtered off and washed with a small amount of ethanol. *Anal.* Calcd for $C_{34}H_{36}N_6O_4P_2S_4Ni$: C, 48.5; H, 4.3; N, 10.0; Ni, 7.0. Found: C, 48.6; H, 5.1; N, 10.0; Ni, 6.7.

Tris(1,10-phenanthroline)nickel(II) Dimethyldithiophosphate.—In a manner similar to the foregoing, 1,10-phenanthroline monohydrate (0.60 g, 0.003 mol) gave the complex as pink crystals. *Anal.* Calcd for $C_{40}H_{36}N_6O_4P_2S_4Ni$: C, 52.6; H, 4.0; N, 9.2; Ni, 6.4. Found: C, 52.8; H, 4.2; N, 9.1; Ni, 6.3.

Sodium *O,O*′-Diethyldithiophosphate.—A solution of diethyldithiophosphoric acid was prepared by heating a stirred mixture of phosphorus pentasulfide (22.2 g) with ethanol (50 ml) under nitrogen until the solution became clear yellow. The solution was cooled and neutralized with anhydrous sodium carbonate. The excess sodium carbonate was filtered off, and activated charcoal was added to the solution, which was boiled, filtered, and evaporated to dryness. The white residue was recrystallized from alcohol to give the sodium salt, which, being deliquescent, was stored in a desiccator; yield 31.5 g.

Bis(*O,O*′-diethyldithiophosphato)palladium(II) and Bis(*O,O*′-diethyldithiophosphato)platinum(II).—These compounds were prepared by a method similar to that described by Jørgensen.[7] *Anal.* Calcd for $C_8H_{20}O_4P_2S_4Pd$: C, 20.1; H, 4.2. Found: C, 20.2; H, 4.2. Calcd for $C_8H_{20}O_4P_2S_4Pt$: C, 17.3; H, 3.7. Found: C, 17.3; H, 3.7.

Spectra.—The visible and near-infrared spectra were obtained on a Zeiss PMQ II spectrophotometer. The solid-state reflectance spectra were obtained by the use of an RA3 reflectance attachment with magnesium oxide as standard.

The infrared spectra over the range 4000–400 cm^{-1} were obtained in Halocarbon or Nujol mulls with NaCl or KBr plates on a Perkin-Elmer 337 spectrophotometer. The infrared spectra over the range 500–250 cm^{-1} were obtained in Nujol mulls with KBr plates on a Perkin-Elmer 621 spectrophotometer.

The mass spectra were obtained on an MS-902 mass spectrometer.

Magnetic Measurements.—The magnetic susceptibilities were measured at room temperature by the Gouy method.[8] The Gouy tube was calibrated with $CuSO_4 \cdot 5H_2O$ and $HgCo(SCN)_4$. Diamagnetic corrections were calculated from Pascal's constants.

Thermogravimetric and Dta Measurements.—Thermogravimetric data were obtained on a Stanton thermobalance, Model TR-01.

Differential thermal analyses (dta) were carried out on an instrument designed by Mr. P. Brady, Department of Applied Organic Chemistry, University of New South Wales, on the principles outlined by Pakulak and Leonard.[9]

X-Ray Crystallographic Data.—The intensity data were collected on a Siemens automatic diffractometer, coupled to a PDP-8 computer. The data were refined by means of full-matrix least-squares techniques to a final *R* value of 6.6%.

Carcinostatic Activity Tests.—The metal complexes were tested in the Walker carcinosarcoma (intramuscular) test and the L-1210 lymphoid leukemia test in mice at the Cancer Chemotherapy Center, National Institutes of Health, Bethesda, Md.

Larvicidal Activity Tests.—The metal complexes were tested by Dr. R. M. Hoskinson, Wool Research Laboratories, CSIRO Division of Textile Industry, Melbourne, Victoria, Australia, for potential larvicidal activity for the moth proofing of wool. The results of the tests are in the form of feeding damage inflicted on the treated fabric when infested with larvae of *Tineola bisselliella*.

Results and Discussion

The nickel complexes and their adducts are listed in Table I. The complexes Ni(dtp)$_2$ were obtained as beautifully crystalline purple compounds in yields of *ca.* 65% when R = CH_3, C_2H_5, CH_2CH_2Cl, cyclohexyl, and $CH(CH_3)C_6F_5$. However, when R = isopropyl or *tert*-butyl, the purple crystals were impure, and in the case of *tert*-butyl, the product decomposed rapidly, although adduct formation with pyridine appeared to give a more stable product but this could not be isolated as an analytically pure compound. When R = CH_2CF_3, a purple solution was obtained, but no purple product could be isolated.

From these results it is apparent that steric effects of the alkyl groups can destabilize the Ni–S bond. Branched-chain alkyl groups cause crowding about the phosphorus atom leading to an increase in the phosphorus tetrahedral bond angle; this in turn causes strain in the four-membered P–S–Ni–S ring, thereby destabilizing the Ni–S bond. However, the cyclohexyl group gives a very stable nickel complex. This might be expected, since very little steric strain would be caused by the cyclohexyl group. When R = $CHCH_3C_6F_5$, a complex steric and electronic situation exists, and it appears that the electron-withdrawing effect of the perfluoroaryl group on the α-carbon atom has a predominance over steric effects.

The green paramagnetic pyridine aduct Ni(dtp)$_2$(py)$_2$ (R = C_2H_5) was first reported in 1962.[7] In this investigation we have found that 1:2 adducts of Ni(dtp)$_2$ are readily formed with pyridine and 4-methylpyridine when R = CH_3, C_2H_5, C_6H_{11}, and $CHCH_3C_6F_5$. Some displacement of the dialkyldithiophosphate ligand occurs when R = *i*-C_3H_7 and CH_2CH_2Cl. Adducts with 2,2′-bipyridyl and 1,10-phenanthroline were obtained when R = CH_3, C_2H_5, *i*-C_3H_7, C_6H_{11}, CH_2CH_2Cl, and $CHCH_3C_6F_5$. All the adducts are paramagnetic with magnetic moments within the range 3.14–3.21 BM at room temperature.

The pyridine and 4-methylpyridine adducts are almost certainly trans coordinated. The crystal structure determination of Ni(dtp)$_2$(py)$_2$ (R = CH_3) shows trans coordination of pyridine with the nickel atom in

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TABLE I

METAL CHELATES OF DIALKYLDITHIOPHOSPHATES AND THEIR ADDUCTS

Compound[a]	R	L	Color	Mp, °C	Magnetic moment, μ, BM	ν(P–S), cm^{-1}	ν(Ni–S), cm^{-1}	Analyses, %											
								C		H		N		P		S		Ni	
								Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Ni(dtp)_2$	CH_3	. . .	Purple	122 dec	Diam	648 s, 524 w	355 s, 325 w	12.9	13.1	3.2	3.6			16.4	16.6	34.4	34.6	15.7	15.7
$Ni(dtp)_2L_2$	CH_3	py	Green	117 dec	3.16			31.7	32.1	4.2	4.4	5.3	5.2	11.7	11.4	24.1	24.0	11.1	11.2
$Ni(dtp)_2L$	CH_3	bipy	Green	88 dec	3.17			31.8	31.3	3.8	3.9	5.3	5.4	11.7	11.5	24.2	24.1	11.1	11.3
$Ni(dtp)_2L$	CH_3	phen	Green	139 dec	3.20	658 s, 525 w	355 m	34.7	34.3	3.6	3.6	5.1	4.7	11.2	10.5	23.2	21.4	10.6	10.6
$Ni(dtp)_2$	C_2H_5	. . .	Purple	105	Diam	645 s, 551 w	359 s, 325 w	22.4	22.1	4.7	4.9			14.4	14.4	29.9	30.4	13.7	13.6
$Ni(dtp)_2L_2$	C_2H_5	py	Green	135 dec	3.18			36.8	36.2	5.2	5.1	4.8	5.2	10.6	10.5	21.8	21.6	10.0	10.0
$Ni(dtp)_2L_2$	C_2H_5	γ-pic	Green	123 dec	3.19			37.0	37.6	5.5	5.5	4.6	4.8	10.1	9.9	20.8	20.6	9.5	9.6
$Ni(dtp)_2L$	C_2H_5	bipy	Green	136 dec	3.15	658 s, 540 w	366 s	36.9	37.6	4.8	4.9	4.8	5.0	10.6	10.8	21.9	22.1	10.0	10.0
$Ni(dtp)_2L$	C_2H_5	phen	Green	170 dec	3.22	675 s, 545 w	361 s	39.4	39.0	4.6	4.8	4.6	4.3	10.2	10.0	21.1	20.1	9.6	9.6
$Ni(dtp)_2L$	C_2H_5	terpy	Buff	>300	3.14	670 w, 650 m, 640 w, 548 m	375 w, 349 w, 319 s	41.7	43.7	4.7	4.3	6.3	6.7	9.4	9.0	19.4	17.1	8.9	8.6
$Ni(dtp)_2$	C_6H_{11}	. . .	Purple	180 dec	Diam	640 s, 527 w	359 s, 338 m	44.7	44.4	6.9	6.8			9.6	10.5	19.9	19.8	9.9	10.0
$Ni(dtp)_2L_2$	C_6H_{11}	py	Green	150 dec	3.18			50.8	50.5	6.8	6.7	3.5	3.8	7.7	7.6	15.9	16.1	7.3	7.0
$Ni(dtp)_2L_2$	C_6H_{11}	γ-pic	Green	150 dec	3.19			52.7	51.1	7.1	6.9	3.4	3.7	7.5	7.6	15.4	15.6	7.1	7.0
$Ni(dtp)_2L$	C_6H_{11}	bipy	Green	199	3.20	675 s, 590 m	387 s	51.0	51.0	6.5	6.5	3.5	3.4	7.7	7.8	16.0	15.9	7.3	7.3
$Ni(dtp)_2L$	C_6H_{11}	phen	Buff	214	3.21			52.3	51.0	6.4	6.5	3.4	3.4	7.5	7.8	15.5	15.9	7.1	7.3
$Ni(dtp)_2$	i-C_3H_7	bipy	Green	194 dec	3.18			41.2	41.1	5.7	5.8	4.4	4.7	9.7	9.5	20.0	20.0	9.2	8.9
$Ni(dtp)_2L$	i-C_3H_7	phen	Green	192 dec	3.20			43.3	43.4	5.5	5.4	4.2	4.3	9.3	9.0	19.3	18.3	9.0	9.4
$Ni(dtp)_2L$	i-C_3H_7	terpy	Light brown	>250	3.13	672 w, 655 m, 640 w, 560 w	381 m, 354 w, 318 w	45.1	44.6	5.5	5.7	5.9	5.0	8.6	8.8	17.9	18.3	8.2	7.9
$Ni(dtp)_2$	CH_2CH_2Cl	. . .	Purple	96	Diam	650 s, 549 m	361 s, 325 w	16.9	16.9	2.8	3.2			10.9	11.1	22.6	22.3	10.4	10.5
$Ni(dtp)_2L$	CH_2CH_2Cl	bipy	Green	270 dec	3.18			29.9	29.9	3.3	3.6	3.9	3.9	8.5	8.8	17.8	17.8	8.8	8.8
$Ni(dtp)_2L$	CH_2CH_2Cl	phen	Green	214	3.18			32.1	30.8	3.2	3.4	3.8	3.8	8.2	8.3	17.2	16.3	7.9	7.9
$Ni(dtp)_2$	$CHCH_3C_6F_5$	. . .	Purple	148	Diam	665 w, 575 w		35.0	34.1	1.8	1.9			5.6	5.6	11.6	11.5	5.4	5.4
$Ni(dtp)_2L_2$	$CHCH_3C_6F_5$	py	Green	155	3.19			40.3	40.1	2.1	2.3	2.2	2.7	5.0	4.8	10.3	10.2	4.7	4.7
$Ni(dtp)_2L_2$	$CHCH_3C_6F_5$	γ-pic	Green	154 dec	3.19			41.3	41.2	2.4	2.4	2.2	2.6	4.8	4.8	10.0	10.6	5.2	5.4
$Ni(dtp)_2L$	$CHCH_3C_6F_5$	bipy	Green	179 dec	3.20			40.4	40.0	1.9	2.2	2.3	2.8	5.0	5.0	10.3	10.3	4.7	4.7
$Ni(dtp)_2L$	$CHCH_3C_6F_5$	phen	Green	180 dec	3.21			41.5	41.5	1.9	2.3	2.2	3.2	4.9	4.8	10.1	10.2	4.6	4.8

[a] dtpH = $(RO)_2P(S)SH$.

TABLE II

ELECTRONIC ABSORPTION BANDS FOR $Ni\{(RO)_2PS_2\}_2$

R	Absorption max, $10^{-3}\nu$, cm^{-1}		
CH_3	15.60	19.20	
CH_3CH_2	15.60	19.10	25.0 sh
CH_2CH_2Cl	15.40	19.05	
C_6H_{11}	15.45	19.35	24.8 sh
$CHCH_3C_6F_5$	14.65	19.30	

the plane formed by the four sulfur atoms.[10] The Ni–S distance is 2.49 Å compared with 2.22 Å in the square-planar complex $Ni(dtp)_2$ ($R = CH_3$).[11] On the other hand, adducts containing phenanthroline or bipyridyl must have a cis configuration. A crystal structure determination of $Ni(dtp)_2$phen ($R = C_2H_5$) has established cis coordination.[12] The nickel atom lies on a twofold axis of symmetry which passes through the phenanthroline molecule (see Figure 1). The Ni–S distances are 2.47 and 2.51 Å; the S–P–S bond angle is 81° and the N–Ni–S angle is 94°.[12] The cis configuration of $Ni(dtp)_2$bipy ($R = CH_3$) has also been established; in this compound the Ni–S distances are 2.48 and 2.52 Å.[13]

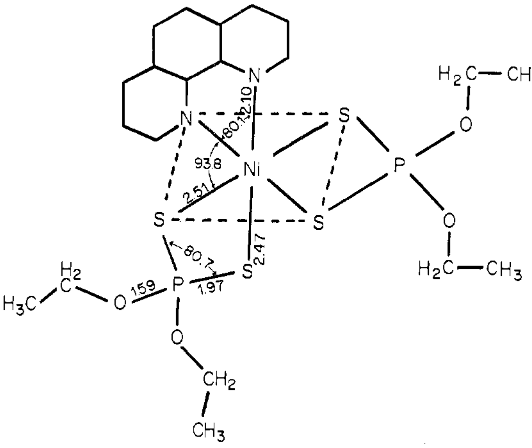

Figure 1.—Structure of $Ni\{(C_2H_5O)_2PS_2\}_2$phen.

With 2,2′,2′′-tetrpyridyl buff to brown 1:1 adducts $Ni(dtp)_2$terpy were isolated where $R = C_2H_5$ and $i\text{-}C_3H_7$. It seems likely that in these complexes the terpyridyl ligand occupies three coordination positions and that one sulfur atom of one dtp ligand is not coordinated. The appearance of additional ν(P–S) and ν(Ni–S) bands in the infrared spectra of the terpyridyl adducts (see Table I) supports this proposed structure in which there are sulfur atoms in two different environments. An analogous situation occurs in the terpyridyl adducts $Ni\{RC(S){=}CHCOCF_3\}_2$terpy ($R = CH_3$, 2-thienyl) reported by Ho, Livingstone, and Lockyer;[14] in these compounds one carbonyl oxygen is not coordinated. A recent structure determination of $Ni(dtp)_2$dimephen ($R = CH_3$; dimephen = 2,9-dimethyl-1,10-phenanthroline) has established that the nickel atom is five-coordinate and that one dithiophosphate ligand is coordinated through one sulfur atom only.[15]

Treatment of $Ni(dtp)_2$ with 3 molar equiv of phenanthroline or bipyridyl results in the displacement of the two dtp ligands. The pink complexes $[Ni(chel)_3](dtp)_2$ (chel = phen, bipy; $R = CH_3$) were isolated. They are paramagnetic (μ = 3.20 BM) and exhibit typical electronic spectra for the octahedral chromophore NiN_6.

Infrared Spectra.—The infrared spectra of the $Ni(dtp)_2$ complexes and of some of the adducts were measured over the range 4000–250 cm^{-1}.

Two bands have been assigned as being essentially ν(Ni–S), as predicted by analogy with the D_{2h} overall symmetry for dithiooxalate complexes discussed by Fujita and Nakamoto.[16] In the spectra of the four-coordinate complexes there are a strong band at 355–361 cm^{-1} and a weak band within the range 325–347 cm^{-1} (see Table I). Adams and Cornell[17] assigned the stronger band at *ca.* 360 cm^{-1} as a combination angle bend δ(C–C–O) + δ(P–O–C). We consider this assignment unlikely, since we do not observe any bands below 440 cm^{-1} in the spectrum of the sodium salt of diethyldithiophosphate. Moreover, the strong band occurs at 355 cm^{-1} when $R = CH_3$ but at 360 cm^{-1} when $R = CHCH_3C_6F_5$; a shift to lower frequency would be expected for an angle bend in the case of the heavier $CHCH_3C_6F_5$ group. Adduct formation causes little shift in the frequency of the strong band which occurs at 355–387 cm^{-1} but the weak band is obscured by absorptions by the aromatic ligands. The appearance of a third band in the spectra of the terpyridyl adducts supports the contention that the Ni–S environment is different in these complexes.

The symmetric and asymmetric stretching frequencies for the P–S bond have been assigned for $Ni(dtp)_2$ as follows: sym, 527–575 cm^{-1} (w–s); asym 638–665 cm^{-1} (s). Assignments for the adducts are as follows: sym, 540–590 cm^{-1} (w–m); asym, 658–675 cm^{-1} (s). These assignments agree well with data for ν(P–S) occurring within the range 568–675 cm^{-1}, obtained for a large number of compounds.[18,19] An increase in the frequency of ν(P–S) in the adducts is to be expected, since there is less demand by the nickel atom for σ electrons from the sulfur atoms. This would tend to increase the bond order and hence the frequency of the P–S bond.

The two bands occurring at 917–1000 cm^{-1} (m–s) and 1005–1065 cm^{-1} (m–s) in the spectra of the four-coordinate nickel complexes have been assigned as ν(P–O) on the basis of published data on P–O frequencies.[20,21]

Electronic Spectra.—The solid-state reflectance spectra of the $Ni(dtp)_2$ complexes and their adducts were measured over the range 25,000–8000 cm^{-1}. The bands are listed in Tables II and III.

The spectra of the purple complexes $Ni(dtp)_2$ show two fairly broad bands, one at 15,600–14,650 cm^{-1} and the other at 19,350–19,050 cm^{-1} with a further absorption which is sometimes discernible as a shoulder at

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TABLE III
ELECTRONIC ABSORPTION BANDS FOR $Ni\{(RO)_2PS_2\}_2L$

R	L	Absorption max, $10^{-3}\nu$, cm^{-1}		
CH_3	bipy	9.00	15.25	23.50 sh
CH_3	phen	9.25	15.45	22.25 sh
CH_3CH_2	bipy	8.90	15.55	>25.0 sh
CH_3CH_2	phen	9.00	15.25	>25.0 sh
CH_3CH_2	terpy	10.20	14.60	21.6 sh
CH_3CH_2	2py	9.00	14.00	
C_6H_{11}	bipy	9.00	15.30	24.6 sh
C_6H_{11}	phen	9.20	15.00	19.90 sh
C_6H_{11}	2py	9.00	15.00	
CH_2CH_2Cl	bipy	8.75	15.25	24.20 sh
CH_2CH_2Cl	phen	9.00	15.30	
$CHCH_3C_6F_5$	phen	9.20	15.25	24.0 sh
$CHCH_3C_6F_5$	bipy	9.30	15.50	24.0 sh
i-C_3H_7	terpy	10.50	14.80	20.0 sh
				24.2 sh

~25,000 cm^{-1} on the strong charge-transfer band in the ultraviolet region. The charge-transfer band has been assigned by Jørgensen as 3p → 4s excitation of sulfur.[7]

The spectra of the spin-free green adducts show typical octahedral spectra with bands in the ranges 9300–8750 cm^{-1} and 15,550–15,000 cm^{-1} and a shoulder at 24,600–19,900 cm^{-1}. These three bands are assigned as shown below

$$^3A_{2g}\,(F) \longrightarrow {}^3T_{2g}\,(F) \qquad \sim 9{,}000 \text{ cm}^{-1}$$
$$\longrightarrow {}^3T_{1g}\,(F) \qquad \sim 15{,}000 \text{ cm}^{-1}$$
$$\longrightarrow {}^3T_{1g}\,(P) \qquad \sim 23{,}000 \text{ cm}^{-1}$$

The terpyridyl adducts, which contain the chromophore NiS_3N_3, show a shift to slightly higher energy for the first band.

Mass Spectra.—The mass spectra of the complexes $Ni(dtp)_2$ and some of their adducts were obtained. The former gave good mass spectra but the mass spectra of the adducts were more difficult to obtain, due to their much lower vapor pressure. In the case of the adducts, the molecular ion peak was not well defined. The presence of nickel, sulfur, and chlorine in the metal complexes, with their readily distinguishable isotopic abundances, facilitated the elucidation of the fragmentation patterns.

The complex $Ni\{(C_2H_5O)_2PS_2\}_2$ gives as its base peak the molecular ion (Figure 2). The presence of metastable peaks indicates the occurrence of electron–ion reactions involving the elimination of ethylene and the free radical $\cdot OC_2H_5$. Table IV lists the relative abundance and mass number data.

TABLE IV
MASS SPECTRAL DATA FOR $Ni\{(C_2H_5O)_2PS_2\}_2$

m/e	Rel abund, %	Reaction	Metastable peak $m^* = m_2^2/m_1$
428	100	$M\cdot^+$	
383	36	Loss of $\cdot OC_2H_5$	$342.7 = 383^2/428$
400	18	Loss of C_2H_4	$373.8 = 400^2/428$
372	19	Loss of $2C_2H_4$	$346.0 = 372^2/400$
344	20	Loss of $3C_2H_4$	$318.1 = 344^2/372$
316	21	Loss of $4C_2H_4$	$290.3 = 316^2/344$

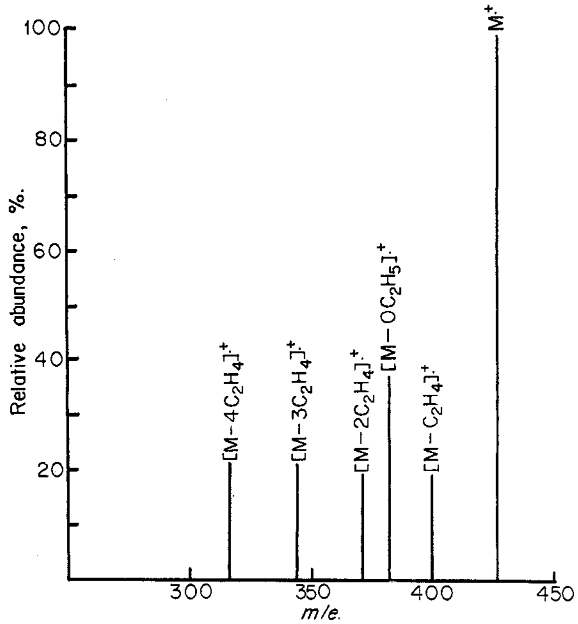
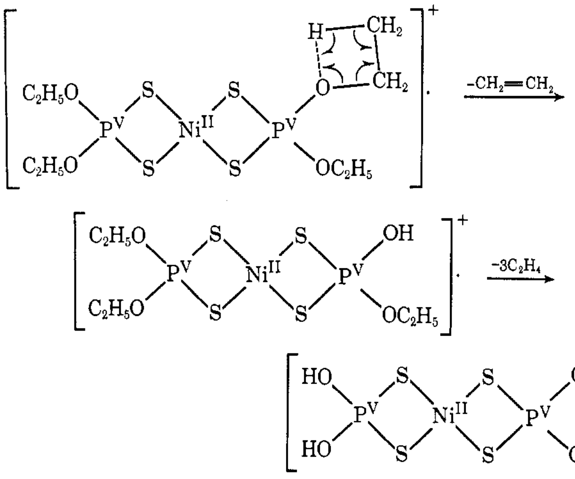


Figure 2.—Mass spectrum of $Ni\{(C_2H_5O)_2PS_2\}_2$.

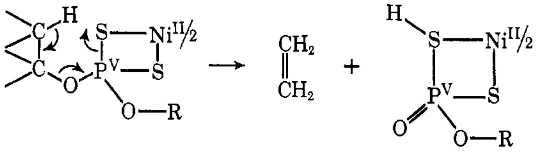
The loss of a neutral species, C_2H_4, from $Ni\{(C_2H_5O)_2PS_2\}_2$ probably occurs *via* a McLafferty type of rearrangement as shown in Scheme I. Transfer of a hydrogen atom to oxygen occurs in a four-membered cyclic mechanism. When all four ethoxy groups have undergone this reaction, the final product has the nickel atom still in an S_4 environment.

SCHEME I



Alternatively, olefin elimination may occur by transfer of a proton to the sulfur atom in a six-membered cyclic mechanism as shown in Scheme II. This mechanism is believed to operate during the thermal decomposition of metal dialkyldithiophosphates.[22,23]

SCHEME II



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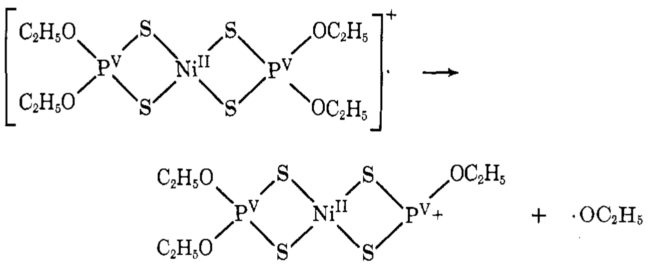
The mechanism for the loss of the ethoxy radical may be written as homolytic fission of the P–O bond to yield an even-electron ion (Scheme III). The mass spectrum also shows the presence of the ethoxy ion $OC_2H_5^+$ which may be formed by a homolytic fission process with the odd electron remaining on the NiS_4 species.

SCHEME III



The complex $Ni\{(C_6H_{11}O)_2PS_2\}_2$ and its bipyridyl adduct $Ni\{(C_6H_{11}O)_2PS_2\}_2$bipy behave in a similar manner to $Ni\{(C_2H_5O)_2PS_2\}_2$ with the stepwise loss of four cyclohexene molecules. The data for the bipyridyl adduct are given in Table V.

TABLE V

MASS SPECTRAL DATA FOR $Ni\{(C_6H_{11}O)_2PS_2\}_2$bipy

m/e	Rel abund, %	Reaction	Metastable peak
644	27	$[M - \text{bipy}]^+ = M'$	
562	78	$M' - C_6H_{10}$	$490.4 = 562^2/644$
480	18	$M' - 2C_6H_{10}$	$410.0 = 480^2/562$
398	33	$M' - 3C_6H_{10}$	$330.0 = 398^2/480$
316	100	$M' - 4C_6H_{10}$	$250.9 = 316^2/398$
156	47	bipy$^+$	. . .

The complex $Ni\{(ClCH_2CH_2O)_2PS\}_2$ behaves in a different manner. There is evidence for the loss of one and two molecules of hydrogen sulfide, accompanied by complex decomposition. From the intensities and isotope patterns observed in the high- and low-voltage spectra this decomposition appears to be thermal rather than electron–ion.

The mass spectra of $Ni\{(C_2H_5O)_2PS_2\}_2$phen and $Ni\{(C_6H_{11}O)_2PS_2\}_2$bipy show no molecular ion peak but rather fragmentation occurs as with $Ni\{(RO)_2PS_2\}_2$ with ions at *m/e* 156 and 180, resulting from 2,2′-bipyridyl and 1,10-phenanthroline, respectively, in moderately high abundance. Fragmentation of phenanthroline and bipyridyl at the inlet temperature (170°) is probably accompanied by thermal decomposition. However, a metastable peak at *m/e* 107 in the mass spectrum of $Ni\{(C_6H_{11}O)_2PS_2\}_2$bipy appears to be due to the loss of a molecule of HCN from bipyridyl. The data for $Ni\{(C_2H_5O)_2PS_2\}_2$phen are given in Table VI.

TABLE VI

MASS SPECTRAL DATA FOR $Ni\{(C_2H_5O)_2PS_2\}_2$phen

m/e	Rel abund, %	Reaction	Metastable peak
428	41	$[M - \text{phen}]^{\cdot+} = M'$	
383	2	$M' - C_2H_5O\cdot$	342.7
400	4	$M' - C_2H_4$	373.8
372	6	$M' - 2C_2H_4$	346.0
344	6	$M' - 3C_2H_4$	318.1
316	7	$M' - 4C_2H_4$	290.3
187	100	$[(HO)_2PS_2Ni]^+$ (?)	. . .
180	30	phen$^+$	. . .

There is no evidence of metastable peaks in the lower *m/e* region. It seems probable that decomposition is thermal rather than electron–ion in this region, since low-voltage spectra show isotope patterns which are not reproduced at higher voltages. This region was not investigated further. Decomposition may also be catalyzed by phosphoric acids formed in the chamber; this behavior has been observed with phosphates.[24]

Thermogravimetric and Dta Studies.—Thermogravimetric determinations of the pyridine adducts $Ni\{(RO)_2PS_2\}_2(py)_2$ ($R = CH_3, C_2H_5, C_6H_{11}$) indicate that there is a stepwise loss of pyridine with considerable overlap of peaks (see Figure 3). The results confirm the existence of the species $Ni\{(C_2H_5O)_2PS_2\}_2$py which is unstable and loses pyridine rapidly. This is consistent with a positive entropy effect for this species, previously studied in solution by Carlin, *et al.*[25] On the other hand, thermogravimetric studies on $Ni\{(C_6H_{11}O)_2PS_2\}_2$bipy and $[Ni\{(C_6F_5CH_3CHO)_2PS_2\}_2(py)_2]$ show decomposition with no definite stepwise loss in weight.

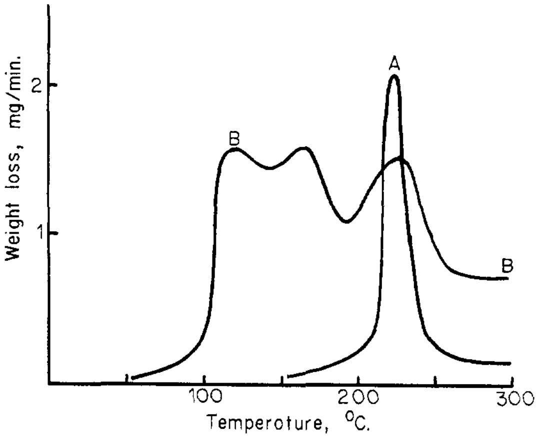


Figure 3.—Thermogravimetric curves: A, $Ni\{(C_2H_5O)_2PS_2\}_2$; B, $Ni\{(C_2H_5O)_2PS_2\}_2(py)_2$.

The differential thermal analysis (dta) curve for $Ni\{(C_2H_5O)_2PS_2\}_2(py)_2$ (Figure 4) confirms previous evidence for the existence of the unstable species $Ni\{(C_2H_5O)_2PS_2\}_2$py. The curve shows two well-defined maxima: the one at 135° involves the loss of one pyridine molecule, while the second at 143° involves the decomposition of the intermediate species by the loss of the second pyridine molecule.

The complex $Ni\{(C_6F_5CH_3CHO)_2PS_2\}_2(py)_2$ gives a complicated dta curve with a broad maximum at 153–166°; the melting point is 155°. No attempt has been made to interpret these energy changes. The data for this compound are given in Table VII.

Thermal decomposition of metal dithiophosphates

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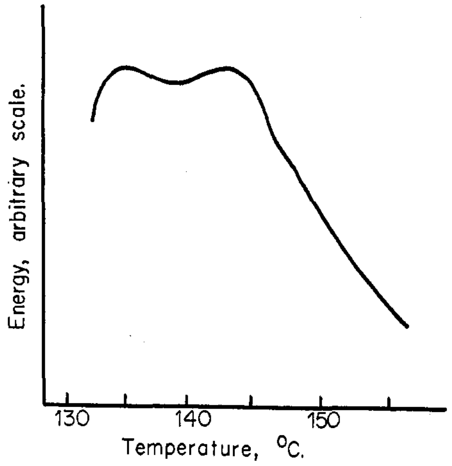

Figure 4.—Dta curve for $Ni\{(C_2H_5O)_2PS_2\}_2(py)_2$.

TABLE VII

DTA DATA FOR $Ni\{(C_6F_5CH_3CHO)_2PS_2\}_2(py)_2$

Maxima, °C	Minima, °C
140	151
153–166	172
174	177
181	

leads to olefin formation. Dickert and Rowe[22] suggested that the dependence of thermal stability of metal dialkyldithiophosphates on variation of both the alkyl group structure and the size of the metal ion is related to an initial isomerization reaction, followed by an intramolecular (cis) elimination of olefin. The mass spectral data also show a ready elimination of olefin. It seems likely that isomerization and olefin elimination are responsible for the complex nature of the dta curves. This postulate is consistent with the NiS_4 chromophore being extremely stable.

Carcinostatic Activity.—Some of the metal chelates have been tested in the L-1210 lymphoid leukemia and the Walker carcinosarcoma 256 (intramuscular) tumor systems in mice. The complexes $M(dtp)_2$ ($M = Ni$, Pd, Pt; $R = CH_3$) are active in the Walker 256 tumor system; the palladium complex reduces the cancer to 6% relative to the control specimen under optimum conditions.

Larvicidal Activity.—Several of the metal chelates were tested for larvicidal activity against *Tineola bisselliella* with the objective of their being useful as agents for the mothproofing of wool. Of those tested only $Ni\{(ClCH_2CH_2O)_2PS_2\}_2$ has significant larvicidal activity.

CONTRIBUTION FROM THE INSTITUTE FOR SOLID STATE PHYSICS, THE UNIVERSITY OF TOKYO, ROPPONGI, MINATO-KU, TOKYO, JAPAN, AND THE INSTITUTE OF PHYSICAL AND CHEMICAL RESEARCH, YAMATO MACHI, SAITAMA, JAPAN

Spectroscopic Study of the Interaction between the Central Metal Ions in the Crystals of Bis(dimethylglyoximato)nickel(II) and Related Complexes

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In the region of 160–700 nm, polarized absorption spectra were measured for single crystals of nickel and palladium dimethylglyoximes and of α- and β-nickel ethylmethylglyoximes, in addition to the visible and ultraviolet absorption spectra of the solutions. By comparing the observed transition energies and oscillator strengths in solution with the theoretical values, the 26.5- and 30.5-kK bands were ascribed to the metal-to-ligand charge-transfer transition and the 38.3-kK band was ascribed to the locally excited transition of the ligand. The crystal spectra polarized perpendicular to the *c* axis exhibit no remarkable change compared with those in solution. In the spectra polarized parallel to the *c* axis, however, two additional bands appear at 18.6 and 52.5 kK and at 20.5 and 53.6 kK for nickel dimethylglyoxime and β-nickel ethylmethylglyoxime, respectively. On the basis of the observed polarization and also of the theoretical consideration of the peak positions and oscillator strengths, the bands at ~53 and ~20 kK were interpreted to be the charge-transfer band between the neighboring nickel atoms and the $3d_{z^2} \rightarrow 4p_z$ transition band, respectively.

Introduction

According to the X-ray diffraction study,[2] the bisdimethylglyoximato complexes of nickel, palladium, and platinum (hereafter, abbreviated to $Ni(dmg)_2$, $Pd(dmg)_2$, and $Pt(dmg)_2$, respectively) have an isomorphous crystal structure in which the planar complex molecules are stacked face to face forming a column parallel to the *c* axis. In the crystalline state, they show sharp absorption bands polarized parallel to the column at 18.6, 21.5, and 15.1 kK for $Ni(dmg)_2$, $Pd(dmg)_2$, and $Pt(dmg)_2$, respectively. The appearance of these characteristic bands has been studied by several authors in connection with the intermolecular interactions in the crystal.[3–7]

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[1] (a) The Institute for Solid State Physics, The University of Tokyo. (b) The Institute of Physical and Chemical Research.

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