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Physico-chemical Studies of Nickel(II) *O,O*-Alkylene Dithiophosphates and their Adducts with Nitrogen Bases

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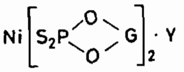
Abstract

Detailed physico-chemical investigations on nickel(II) bis(alkylene dithiophosphates), the preparation and properties of which have been published earlier [1], are described in this paper with a view to throw light on their structural features. These physico-chemical studies include IR, NMR (^{1}H and ^{31}P), electronic spectral and variable temperature magnetic susceptibility studies. The contact shifts for protons of the above adducts in the NMR spectra indicate the involvement of σ- and π-orbitals in spin transfer. Studies of complexation equilibria in solution also indicate the formation of the intermediate mono-adduct species.



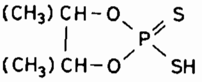
Introduction

Dialkyldithiophosphates of transition metals have received increasing attention in recent years. In addition to their syntheses and various physico-chemical investigations, actual structural determination of a number of these complexes have been made by X-ray diffraction [2]. In these complexes, the dithiophosphate moieties behave generally as bidentate ligands [2–13] with only a few exceptions; the oft-quoted example of the latter is the 2,9-dimethyl-1,10-phenanthroline adduct of bis(dimethyldithiophosphato)-nickel(II) [2], which has been shown to be a five-coordinated square-pyramidal complex, with one of the dithiophosphate groups attached unidentally to nickel. By contrast, examples of unidentally bonded dialkyldithiophosphate complexes of main group elements, are common; for example, the lighter metals of group IV, *i.e.* silicon and germanium. On the other hand, dialkyldithiophosphates were found to bind the dialkyltin moieties uniformly in a bidentate manner. Interestingly, trialkyltin species have been shown to bind these ligands in a unidentate manner, as reported initially from our laboratories [14] and confirmed by X-ray studies by Zuckerman and co-workers [15]. This behaviour is rather unexpected and appears to arise from electronic effects.

In view of the role of steric and electronic factors in the mode of bonding in such derivatives, it was considered of interest to investigate the synthesis and properties of complexes of nickel(II) with less labile alkylene dithiophosphates and their adducts with nitrogen heterocycles.

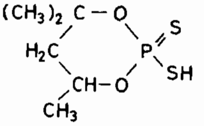
Experimental

Details of syntheses of alkylene dithiophosphoric acids, bis(alkylene dithiophosphates) of nickel(II) and their adducts with nitrogen heterocycles have been reported earlier [1]. The analyses and physico-chemical properties of the nickel derivatives of the following ligands as well as their adducts with pyridine (py) and picolines (β-pic and γ-pic) are given in Table I.



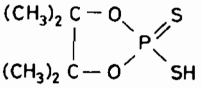
A

(2-mercapto-2-thiono-4,5-dimethyl-1,3,2-dioxaphospholane)



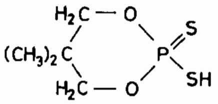
B

(2-mercapto-2-thiono-4,4,6-trimethyl-1,3,2-dioxaphosphorinane)



C

(2-mercapto-2-thiono-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane)



D

(2-mercapto-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinane)

0020-1693/87/$3.50

TABLE I. Analysis and Physico-chemical properties of Nickel(II) Bis(alkylene dithiophosphates) and their Adducts with Nitrogen Bases

Product	Colour (melting point °C)	Analysis (%) Found (Calc.)		Magnetic moment μ (BM)	Electronic spectra λ_{max} (nm)
		Ni	S		
(i) Bis(alkylene dithiophosphato) nickel(II)					
NiA_2	violet (214,d)	13.89 (13.82)	30.4 (30.1)	diamagnetic	688, 520, 394, 320
NiB_2	violet (215,d)	12.21 (12.21)	27.4 (26.6)	diamagnetic	692, 528, 394, 320
NiC_2	light violet (240,d)	12.36 (12.21)	26.7 (26.6)	diamagnetic	685, 518, 392, –
NiD_2	grey (210,d)	12.89 (12.96)	28.2 (28.3)	diamagnetic	– – – –
(ii) Adducts of bis(alkylene dithiophosphates) of nickel(II) with nitrogen bases					
$NiA_2 \cdot 2py$	green (140)	9.87 (10.07)	22.0 (22.0)	2.87	1082, 625
$NiA_2 \cdot 2\gamma pic$	green (180)	9.68 (9.61)	21.4 (21.0)	3.10	1080, 620
$NiA_2 \cdot 2\beta pic$	green (170)	9.64 (9.61)	21.8 (21.0)	3.21	– –
$NiB_2 \cdot 2py$	green (158)	9.07 (9.19)	19.9 (20.0)	3.20	1050, 608
$NiB_2 \cdot 2\gamma pic$	green (150)	8.82 (8.80)	19.3 (19.2)	3.11	1090, –
$NiB_2 \cdot 2\beta pic$	green (156)	8.72 (8.80)	19.3 (19.2)	3.11	1115, 655
$NiC_2 \cdot 2py$	green (135)	9.10 (9.19)	20.4 (20.0)	3.04	1095, 640
$NiC_2 \cdot 2\gamma pic$	green (154)	8.19 (8.80)	19.4 (19.2)	3.09	1095, 660
$NiC_2 \cdot 2\beta pic$	green (149)	8.30 (8.80)	19.2 (19.2)	3.12	1090, 665
$NiD_2 \cdot 2py$	dirty green (180)	9.48 (9.61)	–	3.05	– –
$NiD_2 \cdot 2\gamma pic$	dirty green (145)	9.00 (9.19)	19.9 (20.0)	3.02	– –
$NiD_2 \cdot 2\beta pic$	dirty green (174)	9.20 (9.19)	20.0 (20.0)	2.96	– –
$Ni[S_2P(OC_2H_5)_2] \cdot 2py$	shining green (178)	9.85 (10.0)	21.6 (21.8)	3.10	1105, 655

IR spectra were measured in nujol mulls or as KBr disks in the range of 4000–200 cm^{-1} on a Perkin-Elmer Model 337 spectrophotometer. ^1H and ^{31}P NMR spectra were recorded using TMS and 85% H_3PO_4 as internal and external standard respectively. The experiment for the determination of contact shift was carried out on XL-100 A spectrometer using $CDCl_3$ as a solvent and TMS as the internal reference. Electronic spectra of diamagnetic complexes were recorded in the range 200–780 nm with a S.P.8–100 UV–Vis spectrophotometer in dichloromethane, whereas the spectra of octahedral complexes were determined on a Cary-17-D model in respective bases. Magnetic susceptibility was measured by the Faraday method.

A brief account of the elucidation of the structural features of these derivatives on the basis of spectroscopic and magnetic properties is presented below.

Results and Discussion

Infrared Spectra

Two bands present in the regions 1160–1030 cm^{-1} and 890–830 cm^{-1} may be assigned to (P)–O–C and P–O–(C) stretching vibrations respectively

[17]. The bands present between 1000–900 cm^{-1} may be attributed to the ring vibrations of the dioxaphospholanes and dioxaphosphorinanes [18, 19], which are probably coupled with C–C stretching vibrations. A strong band due to $\nu(P=S)$ observed in the region 710–670 cm^{-1} in the spectra of alkylene dithiophosphoric acids and their ammonium salts is shifted to lower frequency by ~35 cm^{-1} in the corresponding nickel derivatives. This probably indicates a bidentate chelation of the ligand with nickel. The bands present in the region 630–500 cm^{-1} are attributed to P–S symmetric and asymmetric vibrations.

Magnetic Resonance Spectra

The ^1H NMR spectra of diamagnetic complexes show characteristic resonances of the corresponding alkylene protons (Table II).

TABLE II. ^1H NMR Spectral Data

Compound	Chemical shift (ppm)
NiA_2	1.2–1.7, d(CH_3) 12 H 4.3, bs (CH) 8 H
NiB_2	1.3–2.1, m (CH_3) 4.7, bs (CH) 2 H
$NiC_2 \cdot 2py$	1.64, s (CH_3) *ortho-*, s 53.12 *meta-*, s 23.44 *para,* s 11.23
$NiC_2 \cdot 2\gamma pic$	1.61, s (CH_3) *ortho-* – *meta-* 26.80 *para-* –5.37
$Ni[S_2P(OC_2H_5)_2]_2$	1.38, t (CH_3) 12 H 4.33, q (CH_2) 8H
$Ni[S_2P(OC_2H_5)_2]_2 \cdot 2py$	1.25, s(CH_3) 12 H 1.6, s(CH_3) 8 H *ortho-*25.2 *meta-*11.5 *para-*4.16

bs = broad singlet; d = doublet; q = quartet; s = singlet; t = triplet.

The ^1H NMR spectra of paramagnetic adducts, on the other hand, show large downfield isotropic shift for the protons of pyridine and substituted pyridine as has been reported earlier for other paramagnetic pyridine complexes of nickel [20–23]. These shifts may be ascribed to Fermi contact interactions. For pyridine octahedrally coordinated to NiC_2, all the base protons are shifted downfield from their diamagnetic positions; this can be explained on the basis of unpaired spin delocalizing from the metal ion to the σ-orbital of the pyridine. In the γ-picoline adduct of NiC_2 the downfield shift of the α- and β-protons and the upfield shift of the γ-methyl protons indicate that in addition to σ delocalization, π delocalization is also present to some extent, which becomes apparent only at the γ-position [21]. The methyl protons of the alkylene dithiophosphate moieties of NiC_2 show upfield shift in both the complexes (with pyridine and γ-picoline). As the signal due to the *ortho* protons for the pyridine adduct of NiC_2 could not be observed, its position was calculated by the method used by Dhingra [24].

The variation in the values of chemical shifts of protons in 1 M deuterochloroform solution of pyridine with increasing concentration of NiC_2 is shown in Fig. 1. The values of contact shifts increase in the order: α>β>γ protons. This result also showed that the unpaired spin on the nickel(II) delocalizes on to the pyridine ring, probably due to the back bonding from metal ion to pyridine.

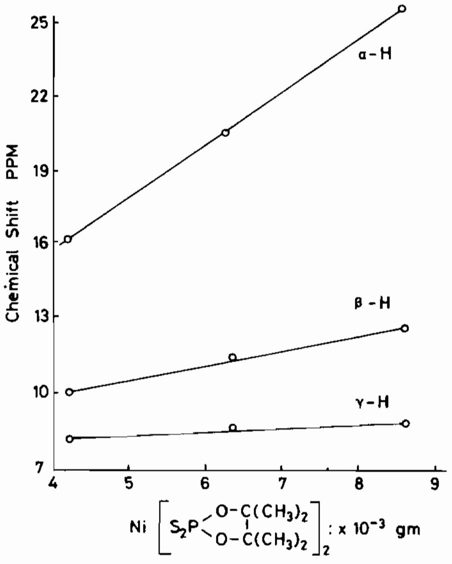
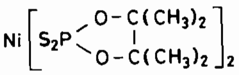


Fig. 1. Variation of chemical shifts of protons in 1 M $CDCl_3$ solution of pyridine with increasing amount of



$$Ni\left[S_2P\begin{matrix}O-C(CH_3)_2\\|\\O-C(CH_3)_2\end{matrix}\right]_2$$

The ^{31}P chemical shift values in the spectra of a few representative compounds, are higher than those of the parent acids and the data are given in Table III.

Magnetic Measurements (Tables IV and V)

The magnetic susceptibility values of nickel(II) bis(alkylenedithiophosphates) point to the square-planar geometry of these complexes [3]. Except for $NiA_2 \cdot 2py$ the value of magnetic moments for all the base adducts fall in the range 2.96–3.20 BM, which corresponds to two unpaired spins anticipated for octahedral geometry of nickel(II) complexes [3].

TABLE III. ^{31}P NMR Spectral Data

Compound	Chemical shift (ppm)
A	95.49
NiA_2	110.00
C	93.07
$NiC_2 \cdot 2\gamma pic$	113.00
NiB_2	84.73

TABLE IV. Magnetic Susceptibility of $NiC_2 \cdot 2\gamma pic$ at Different Temperatures

Temperature (K)	$\chi_M \times 10^{-6}$ (c.g.s.)	$\chi'_M \times 10^{-6}$ (c.g.s.)	μ_{eff} (BM)
14.4	46001	46397	2.31
16.2	43615	44011	2.38
20.6	37649	38045	2.50
24.2	33407	33803	2.55
27.8	30358	30754	2.61
31.7	27176	27572	2.64
40.4	19938	20334	2.56
58.2	16703	17099	2.82
83.0	10738	11134	2.71
105.5	8749	9145	2.77
130.0	7158	7554	2.80
154.10	6283	6679	2.86
295.3	3632	4028	3.08

χ_M and χ'_M are uncorrected and corrected molar susceptibility respectively.

TABLE V. Magnetic Susceptibility of $NiA_2 \cdot 2\gamma pic$ at Different Temperatures

Temperature (K)	$\chi_M \times 10^{-6}$ (c.g.s.)	$\chi'_M \times 10^{-6}$ (c.g.s.)	μ_{eff} (BM)
13.8	25066	25415	1.67
14.4	24439	24788	1.68
20.4	24001	24349	1.99
24.0	22747	23096	2.10
27.8	22058	22407	2.23
31.6	20366	20715	2.28
40.9	16418	16767	2.34
56.0	12846	13195	2.43
85.0	9368	9717	2.57
107.5	7852	8200	2.65
130.0	6705	7053	2.70
289.0	4085	4434	3.20

χ_M and χ'_M are uncorrected and corrected molar susceptibilities respectively.

The low temperature magnetic susceptibility measurements in the range 14 to 295 K have been made for four paramagnetic base adducts of nickel(II) bis(*O,O*-alkylene dithiophosphates) as well as for pyridine adduct of diethyldithiophosphate.

The magnetic moments of $Ni[S_2P(OC_2H_5)_2]_2 \cdot 2py$, $NiC_2 \cdot 2py$ and $NiB_2 \cdot 2py$ show temperature independent paramagnetism. In all the three cases $1/\chi_M^{Corr}$ *versus* T plot gives a straight line with value of θ as 0 K.

The magnetic moments of $NiA_2 \cdot 2\gamma pic$ and $NiC_2 \cdot 2\gamma pic$ are found to be temperature dependent. This is suggestive of antiferromagnetic exchange coupling [25]. $1/\chi_M^{Corr}$ *versus* T plot gives the Weiss constant, $\theta = -22$ K and -12 K respectively. The low value of θ in the latter complex indicates weak antiferromagnetic interaction. The variable temperature magnetic data for the above two complexes are illustrated in Fig. 2.

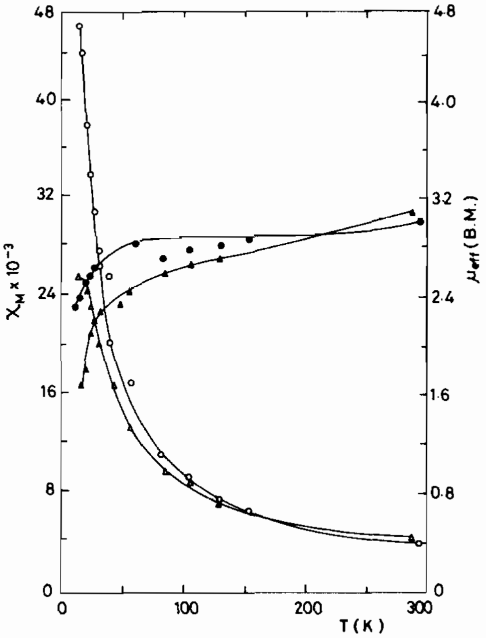
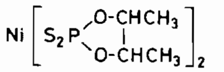
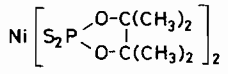


Fig. 2. Corrected molar susceptibility (△:○) and effective magnetic moment (▲:●) as a function of temperature, for

(a) 
$Ni[S_2P(O\text{-}CHCH_3)(O\text{-}CHCH_3)]_2$ 2·γpic (triangles)

(b) 
$Ni[S_2P(O\text{-}C(CH_3)_2)(O\text{-}C(CH_3)_2)]_2$ 2·γpic (circles).

Electronic Spectra (Table VI)

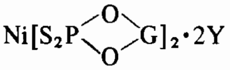
The spectra of the purple alkylene dithiophosphates show three bands at 686–692, 518–528 and 392–394 nm in the visible region with a band at 320 nm in the near ultraviolet region. These transitions are very close to the transitions observed in nickel(II) bis(diethyldithiophosphate). Assuming effective D_{2h} symmetry for these complexes, the first three bands can be assigned to $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_{2g}$ and $^1A_{1g} \rightarrow {}^1E_g$ transitions respectively.

TABLE VI. Spectrophotometric Titration of NiA_2 with β-Picoline and of NiB_2 with Pyridine

Molar ratio		λ_{max} (nm)	Coordination number
NiA_2	β-picoline		
1	0	688, 520, 394	4
1	2	688, 512, 340	4
1	4	728, 450, 340	5
1	8	728, 450, 356	5
1	16	728, 450, 356	5
1	32	728, 450, 344	5
NiA_2 in 17.98% β-pic		660, 334	6
NiB_2	Pyridine		
1	0	692, 528, 394	4
2	1	698, 520, 390	4
1	2	690, 520, 390	4
1	4	700, 520(w), 450(w), 388(w)	4 + 5
1	14	720(s), 540(v.w.), 452(s)	4 + 5
1	21	720(s), 452(s)	5
NiB_2 in 12.07% py		680	6

w = weak, s = strong, v.w. = very weak.

In contrast to the earlier report [6] about the instability of nickel(II) bis(diethyldithiophosphate), no decomposition was observed when the spectra of $Ni[S_2P(OC_2H_5)_2]_2$ and NiA_2 were rescanned after keeping them in solution for four weeks. The spectra of green paramagnetic adducts show much variation in the number and position of absorption bands. According to Livingstone and Mihkelson [3] and Nanjo and Yamasaki [4], two bands are observed at 1111, 714 and 1125 and 676 nm respectively in the spectra of the pyridine adducts of nickel(II) bis(diethyldithiophosphate). Francis *et al.* [5] on the other hand, have reported three bands at 1169, 1109 and 669 nm for pyridine and substituted pyridine adducts of nickel(II) bis(diisopropyldithiophosphate). In the present investigations we have observed two bands in the electronic spectra of base adducts, $Ni[S_2P(OC_2H_5)_2]_2 \cdot 2Y$ and



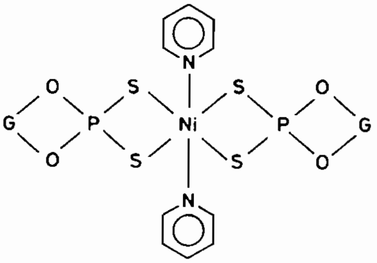
$$Ni[S_2P\overset{O}{\underset{O}{<>}}G]_2 \cdot 2Y$$

(y = pyridine, β- and γ-picolines). The formation of pyridine adducts of bis(*O,O*-hexylenedithiophosphato)–nickel(II) was studied spectrophotometrically in varying ratio of pyridine to complex. The initial spectrum of nickel bis(*O,O*-hexylenedithiophosphate) is characteristic of a square-planar complex showing three bands at 692, 528 and 394 nm. On adding pyridine gradually, the band at 692 nm is shifted towards a higher wave length, the band at 528 nm disappears and a new band at 452 nm appears. On further addition of pyridine, two bands at 720 and 452 nm are observed which point to the formation of five-coordinated intermediate species. On further addition of pyridine, the spectra do not indicate the presence of five-coordinated species and only one broad band at 680 nm confirms the presence of six-coordinated species.

The spectrophotometric titration of nickel(II) bis(2,3-butylenedithiophosphate) with β-picoline was similarly conducted. The above titration also confirms the formation of six-coordinated biadducts, $NiA_2 \cdot 2\beta pic$ through the formation of the intermediate monoadduct species, $NiA_2 \cdot \beta pic$. The band observed at 340 nm could not be assigned with confidence.

As expected for a sterically hindered base like 2-picoline only the five-coordinate complex exists in solution.

The above spectral and magnetic sutdies indicate the following structure for six-coordinated pyridine adducts of nickel(II) bis(*O,O*-alkylene dithiophosphates)



Although the above plausible structure also requires confirmation by X-ray crystallography, the structure of the analogous γ-picoline adducts can be predicted to be more complicated involving associated molecules in view of the temperature dependent paramagnetism of the latter derivatives which is indicative of antiferromagnetic exchange.

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