Ni(II) O,O-Alylene Dithiophosphates and their Adducts with Nitrogen Bases

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A number of purple, diamagnetic, square-planar dialkyldithiophosphato complexes of nickel(II) Ni-$[S_2P(OR)_2]_2$, have been described in the literature [1–8]. The stability of the Ni–S bond in these complexes is sensitive to both steric and electronic effects. Adducts of $Ni[S_2P(OR)_2]_2$ with pyridine, 4-methylpyridine, 1,10-phenanthroline and 2,2′-bipyridyl are green, paramagentic and octahedral, whereas the sterically crowded ligand 2,9-dimethyl-1,10-phenanthroline forms an adduct having square-pyramidal structure [1].

A survey of the literature revealed that in spite of extensive work on the open chain dialkyldithiophosphate derivatives of metals, no publication has appeared on the synthesis of alkylene dithiophosphates of nickel(II), except a study of the formation constants in solution and isolation of a few complexes [1, 9–11]. It was therefore considered of interest to investigate the synthesis and properties of the complexes of nickel(II) with alkylene dithiophosphates and their adducts with nitrogen heterocycles.

Experimental

Alkylene dithiophosphoric acids were synthesized by the reactions of phosphorus pentasulphide with corresponding glycols in 1:2 molar ratio. Ammonium salts of these alkylene dithiophosphoric acids were prepared by passing dry ammonia through their benzene solutions [12].

IR spectra were measured in nujol-mulls or as KBr pellets in the range of 4000–400 cm^{-1} with a Perkin Elmer model 337 spectrophotometer. ^1H NMR spectra were determined using an EM-360 spectrometer (60 MHz) in $CDCl_3$ solution using TMS as an external indicator. Electronic spectra were recorded in the range 200–780 nm with a S.P. 8–100 U.V./Visible Pye Spectrophotometer.

Sulphur was estimated by Messenger's method and nickel was determined gravimetrically as its dimethylglyoximate.

Bis(2,3-butylenedithiophosphato)nickel(II)

On adding an aqueous solution of nickel(II) chloride (14.17 g) to an alcoholic solution of 2,3-butylenedithiophosphoric acid (9.15 g), a violet precipitate of bis(2,3-butylenedithiophosphato)-nickel(II) (11.06 g, 68%) was obtained, which was recrystallised from dichloromethane and acetone.

Bis(hexylenedithiophosphato)nickel(II)

On adding an aqueous solution of ammonium hexylene dithiophosphate (3.99 g) to an aqueous solution of nickel chloride (2.07 g), bis(hexylene-dithiophosphato) nickel (3.18 g, 76%) was obtained. The compound was recrystallised with a dichloromethane-acetone mixture.

Similarly, bis(tetramethylethylenedithiophosphato)-nickel and bis(neopentylenedithiophosphato)nickel were prepared by employing the above method.

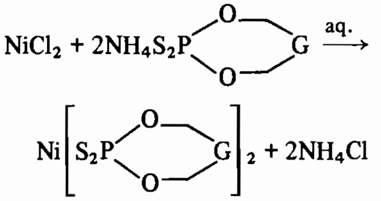
Adducts of Ni(II) Complexes with Nitrogen Bases

To a solution or slurry of the nickel complex in dichloromethane, the base (neat or in acetone solution) was added dropwise till a permanent green colour was obtained (an excess of base was required) and the mixture was kept at room temperature. The green crystals were separated, washed with ether (pyridine and picoline adducts) or ethanol (bipyridyl and phenanthroline adducts) and dried under vacuum.

Adducts of bis(tetramethylethylenedithiophosphato)nickel could be crystallised from the dichloromethane/acetone mixture.

Results and Discussion

The alkylene dithiophosphate derivatives of nickel(II) have been prepared by the reaction of nickel chloride with ammonium alkylene dithiophosphates or the parent alkylene dithiophosphoric acid itself in 1:2 molar ratio at room temperature:



$[G = -(CH_3)_2CC(CH_3)_2-,\ -(CH_3)_2CCH_2CH(CH_3)-,\ -CH_2C(CH_3)_2CH_2-]$

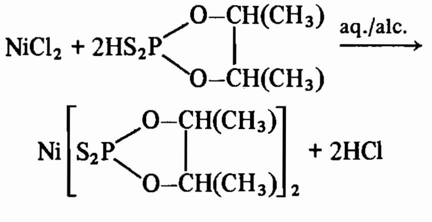


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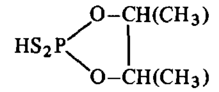
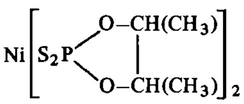
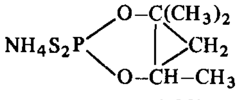
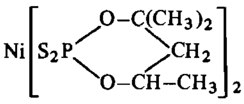
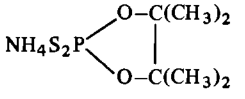
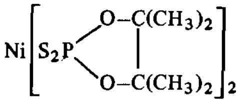
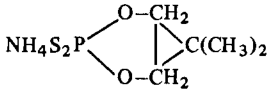
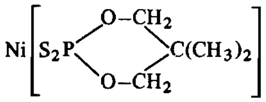
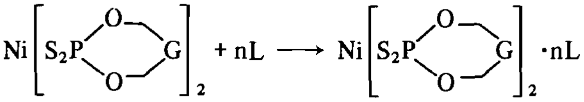
TABLE I. Reactions of Nickel(II) Chloride with Alkylenedithiophosphoric Acid and Ammonium Salts.

Sl. No.	Reactants (g)		Product (g)	Yield %	Colour
	A	B			
1	 (14.17)	$NiCl_2$ (9.15)	 (11.06)	68	Violet
2	 (3.99)	$NiCl_2$ (2.07)	 (3.18)	76	Violet
3	 (7.63)	$NiCl_2$ (3.95)	 (5.91)	74	Light violet
4	 (11.11)	$NiCl_2$ (6.14)	 (6.56)	56	Grey

The products obtained are violet coloured, except bis(neopentylenedithiophosphato)nickel, which is grey. The bis(tetramethylethylenedithiophosphato)-nickel and bis(neopentylenedithiophosphato)nickel are insoluble in common organic solvents but bis-(2,3-butylenedithiophosphato)nickel and bis(hexylenedithiophosphato)nickel are soluble in halocarbon solvents.

The adducts of the above complexes with nitrogen bases have been prepared by mxing the reactants in dichloromethane:



[n = 2, L = pyridine or 4-picoline; n = 1, L = 2,2'-bipyridyl or 1,10-pehnanthroline]

The 2,2'-bipyridyl adducts depict a shining green colour.

The formulae of the compounds shown above have been based on elemental analyses, including those of nickel and sulphur.

Infrared Spectra

The bands present in the region 1050–1000 cm^{-1} and 895–805 cm^{-1} may be assigned to (P)–O–C and P–O–(C) stretching vibrations respectively [13]. The bands between 990–900 cm^{-1} may be attributed to the ring vibrations of the dioxaphospholanes and dioxaphosphorinanes [14, 15], which are probably coupled with C–C stretching vibrations. A sharp peak in the region 700–620 cm^{-1} has been assigned to (P=S) vibrations. The bands present in the region 630–490 cm^{-1} are attributed to P–S symmetric and asymmetric vibrations.

Electronic Spectra

The spectra of $Ni(dtp)_2$ complexes [dtp = alkylene dithiophosphates] were measured over the range of 50,000–12820 cm^{-1} (200–780 n.m.). The spectra of the purple complexes show three bands at 14.70–14.45 × 10^3 cm^{-1}, 19.30–19.23 × 10^3 cm^{-1} and 25.38 × 10^3 cm^{-1} in visible region with a single band at 31.25 × 10^3 cm^{-1} in the near ultraviolet region.

Almost identical electronic transitions indicate a square-planar geometry for these new alkylene dithiophosphate complexes, similar to these observed for the open chain dialkyldithiophosphates of nickel(II).

Acknowledgement

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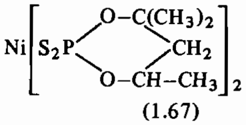
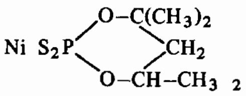
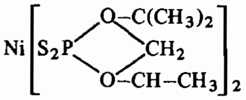
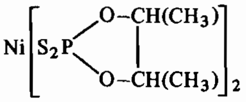
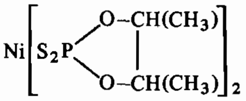
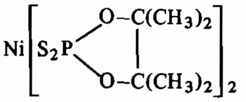
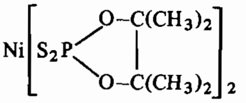
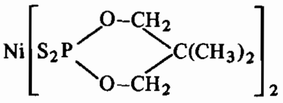
TABLE II. Adducts of Ni(II) Complexes with Nitrogen Bases.

Sl. No.	Reactants A (g)	Reactants B (excess)	Adduct formed molar ratio (yield g)	Yield %	Colour
1	 (1.67)	Pyridine	1.2 (1.97)	89	Green
2	 (0.89)	4-picoline	1:2 (0.90)	73	Green
3	 (1.97)	Bipyridyl	1:1 (2.35)	90	Green
4	 (1.51)	Pyridine	1:2 (1.68)	81	Green
5	 (1.03)	Bipyridyl	1:1 (1.13)	81	Shining green
6	 (1.75)	Pyridine	1:2 (1.91)	83	Green
7	 (1.29)	Bipyridyl	1:1 (1.24)	73	Shining green
8	 (1.41)	Pyridine	1:2 (1.49)	79	Green

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