Studies on electrochemical and coordination behaviour of phosphiniminocyclotrithiazenes

U. Swarnalatha, A. Sivaramakrishna, C.S. Venkatachalam, M.N. Sudheendra Rao, Tomonori Inoue, Tadaharu Ueda, and Masashi Hojo

Abstract: Electrochemical (polarographic, cyclic voltammetric, and coulometric) and coordination behaviour of several symmetrically and unsymmetrically substituted phosphiniminocyclotrithiazenes have been studied. Polarograms of $R_3PN-S_3N_3$ ($R = C_6H_5$, p-ClC₆H₄, p-H₃CC₆H₄, and (OC₄H₈N)), Ph₂(OC₄H₈N)PN-S₃N₃, and Ph(OC₄H₈N)₂PN-S₃N₃ give two cathodic waves. Cyclic voltammograms of Ph₃PN-S₃N₃ (1) and (OC₄H₈N)₃PN-S₃N₃ (2) reveal nearly the same oxidation peak potential but different reduction potentials. Controlled potential electrolysis of 1 and 2 at +0.6 V indicates exocyclic cleavage and ring degradation. Cathodic reduction behaviour of Ph₃PN-S₃N₃ suggests the possibility for the formation of 1,5-(Ph₃PN)₂S₄N₄ under electrochemical conditions. Reaction of nickel chloride hexahydrate with heterocycle 1 in 1:2 molar ratio in acetonitrile affords the complex, [Ni(S₂N₂H)₂] (A) (90% yield) and [Ph₃PNH₂]Cl salt as products. Analogous reactions with other ligands of this type (two symmetrical (sym.) and three unsymmetrical (unsym.)) except 2 also give A, while ligand 2 reacts with anhyd NiCl₂ in an equimolar ratio to afford a dark green, square-planar complex ((OC₄H₈N)₃PN-S₃N·NiCl₂ (B)) whose ESCA results assist in providing its coordination details. The study reveals a high tendency of these heterocycles to different types of ring cleavage.

Key words: phosphiniminocyclotrithiazenes, polarography and cyclic voltammetry, substituent effect, nickel complexes, ESCA.

Résumé : On a étudié le comportement électrochimique (polarographique, voltampérométrie cyclique et coulométrique) et de coordination de plusieurs phosphiniminocyclotrithiazènes substitués de façon symétrique et asymétrique. Les polarogrammes des R₃PN-S₃N₃ (R = C₆H₅, *p*-ClC₆H₄, *p*-H₃CC₆H₄, OC₄H₈N) Ph₂(OC₄H₈N)PN-S₃N₃ et Ph(OC₄H₈N)₂PN-S₃N₃ présentent deux vagues cathodiques. Les voltampérogrammes cycliques du Ph₃PN-S₃N₃ (1) et (OC₄H₈N)₃PN-S₃N₃ (2) présentent des potentiels d'oxydation maxima qui sont pratiquement les mêmes, mais les potentiels de réduction sont différents. Une électrolyse du composé 1 à potentiel contrôlé, à 0,6 V, indique la présence de clivage exocyclique et de dégradation de cycle. Le comportement du Ph₃PN-S₃N₃ lors de la réduction cathodique suggère la possibilité de formation du 1,5-(Ph₃PN)₂S₄N₄ dans les conditions électrochimiques. La réaction du chlorure de nickel hexahydraté avec l'hétérocycle 1, dans un rapport molaire de 2:1 dans l'acétonitrile, conduit à la formation du complexe [Ni(S₂N₂H)₂] (**A**) (rendement de 90 %) et du [Ph₃PNH₂]Cl. Des réactions analogues (excepté celles avec le produit 2) avec d'autres ligands de ce type (deux symétriques et trois non symétriques) conduisent aussi au produit à **A**. Le composé **2** réagit avec le NiCl₂ anhydre, dans un rapport moléculaire de 1:1, pour fournir un complexe plan carré, vert, (OC₄H₈N)₃PN-S₃N·NiCl₂ (**B**) dont les résultats de spectroscopie d'électrons pour analyse chimique (« ESCA ») fournissent des détails relatifs à sa coordination. Cette étude révèle la grande tendance de ces hétérocycles à donner lieu à des types différents de clivage de cycle.

Mots clés : phosphiniminocyclotrithiazènes, polarographie, voltampérométrie cyclique, effet de substituant, complexes de nickel, ESCA.

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Introduction

A variety of inorganic ring systems (1-2) have been the subject of both coordination and electrochemical studies in

the last couple of decades. Electrochemical studies have helped in providing insight of chemical reactions and served also as a preparative method for both known and new compounds (3–9). Likewise, coordination studies have lead to

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realizing many interesting results and novel complexes of transition metals (10–14).

Phosphiniminocyclotrithiazenes, R₃PN-S₃N₃ are a class of electron-rich inorganic heterocycles (15, 16) having a phosphinimino moiety as the exocyclic substituent and have served as stable derivatives of monosubstituted cyclotrithiazenes $(-S_3N_3)$ (17–18). Ph₃PN-S₃N₃, the first example in this class (8 π system) to be reported in 1961 was subsequently obtained in an improved yield from a detailed reinvestigation study by Chivers and co-workers (19). Some of its reactivity aspects have also been demonstrated (20–22). Oakley and co-workers (20) have shown the usefulness of the redox potential data in rationalizing its electronic absorption and some reactivity features. In an extension of this work, we have prepared a variety of $R_3PN-S_3N_3$ heterocycles and studied their structural and reactivity aspects and have obtained many interesting results (23–26). In addition to the noticeable structural differences (27, 28), we have observed pyrolytic substituent-dependent behaviour of these heterocycles (29). We believe that the presence of a relatively bulky phosphinimino moiety as an exocyclic part of the S₃N₃ ring skeleton and the possibility of substituent variation on phosphorus render them as interesting examples for further studies. Sometime ago, we observed the tendency of these heterocyclic systems to nucleophilic attack by ammonia, amines (30), and phosphines (31, 32) and recently to oxidative cleavage by mild oxidants such as iodine (33).⁴ The results suggested the preferential cleavage of the trithiazene ring skeleton over that of exocyclic substituent. These observations prompted us to undertake this study to probe the coordination and electrochemical behaviour of R₃PN-S₃N₃ ring systems for the first time. In this paper, we report polarographic, cyclic voltammetric, and bulk electrolysis studies as well as coordination behaviour with nickel chloride of many examples of symmetrically and unsymmetrically substituted phosphiniminocyclotrithiazenes.

Experimental

All handling and manipulation of air-sensitive compounds were done in a nitrogen or argon atmosphere. Solvents were purified using standard procedures (34). NiCl₂·6H₂O, NiSO₄·7H₂O, and NiI₂ (s.d. Fine Chemicals), and Ph₃P (Fluka) were used as received. Anhydrous NiCl₂ was prepared by the literature method (35). S_4N_4 (caution: explosion sensitive!) (36), $(OC_4H_8N)_3P$ (37), and different $R_3PN-S_3N_3$ derivatives employed in this study were synthesized by the reported methods (19, 23, 26, 37). Various spectral and analytical facilities used for characterization have been published elsewhere (26). Magnetic measurements were done in a vibrating sample magnetometer (EG & G PARC VSM-155) with 2 mg of the sample. Conductivity measurements were done using a conductometer (Toshniwal CL01/02A) with a glass electrode (cell constant: 1.2708 cm⁻¹) on 1 mM solution of the sample in CH₃CN. ESCA measurements were made using a VG ESCA LAB MK II X-ray photoelectron spectrometer.

Direct-current polarograms were measured on a dropping mercury electrode (DME) using a Yanagimoto polarograph (P-1000) and a Graphtec X-Y recorder (WX-4410-L0). Cyclic voltammograms were recorded at $25 \pm 0.1^{\circ}$ C with a microcomputer-controlled system at a scan rate of 100 mV s⁻¹. Glassy carbon electrode (Tokai Carbon GC-30S), freshly polished with a 0.1 µm diamond slurry was used as the working electrode and a platinum wire served as the counter electrode. Ag/AgNO₃ (0.01 mol dm⁻³ in MeCN) was the reference electrode. Coulometric experiments were performed on a GC fiber electrode using a potentiostat (Hokuto Denko HA-151). Dichloromethane (Wako GR grade) was used as the solvent. The electrolysis was followed by ³¹P NMR spectroscopy using a JEOL JNM-LA400 instrument and (or) electronic spectroscopy using a double-beam spectrophotometer (Hitachi U-2000).

(a) Reaction of $Ph_3PN-S_3N_3$ (1) with $NiCl_2 \cdot 6H_2O$ in CH_3CN (2:1)

To a stirred slurry of NiCl₂·6H₂O (0.40 g, 1.67 mmol) in acetonitrile (25 mL), the red heterocyclic ligand **1** (1.39 g, 3.36 mmol) was added in batches over a 15 min interval at room temperature. The colour of the solution changed gradually to dark purple. After 20 h, it was filtered to isolate an off-white precipitate (0.26 g) and a dark purple filtrate. The CH₃CN extract of the precipitate (4 × 3 mL) when cooled gave a small amount of [Ph₃PNH₂]Cl (40 mg), mp 228 to 229°C (lit. (38) value mp 230–232°C). Its IR and ³¹P NMR chemical shift agreed well with an authentic sample (38). The acetonitrile insoluble residue (0.20 g) was metal free (chemical test for Ni was negative) and found to be water soluble.

The purple filtrate upon cooling for 36 h in the refrigerator gave $[Ph_3PNH_2]Cl$ (0.86 g). The residual mother liquor was concentrated and cooled in the deep freezer for a day to isolate purple crystals of $[Ni(S_2N_2H)_2]$ (A) (0.37 g, 90%), mp 155 to 156°C (lit. (39) value mp 156–158°C). Its nickel content, IR, and UV–Vis spectral data (552 nm (2.1 × 10³); 399 nm (4.7 × 10³); 305 nm (11.4 × 10³)) agreed well with the literature data (39).

(b) Reaction of $Ph_3PN-S_3N_3$ (1) with $NiCl_2$ in CH_3CN (2:1)

Anhydrous nickel chloride (0.10 g, 0.77 mmol) was added in small amounts over a 15 min interval to a stirred slurry of ligand 1 (0.64 g, 1.55 mmol) in CH₃CN (25 mL) at room temperature. The observations were same as in reaction (*a*). After 16 h, it was worked up as in reaction (*a*) to isolate an off-white crystalline material ($[Ph_3PNH_2]Cl$ (0.23 g)) followed by the purple crystals of $[Ni(S_2N_2H)_2]$ (80 mg, 42%). An yellowish white insoluble residue (0.13 g) was also obtained from the precipitate part of the reaction.

(c) Reaction of anhyd NiCl₂ with Ph_3P and S_4N_4 in CH_3CN

To a stirred solution of Ph_3P (1.44 g, 5.50 mmol) in CH₃CN (25 mL) at room temperature, S_4N_4 (0.50 g, 2.72 mmol) was added as a solid in small amounts over a 20 min interval. When the reaction mixture had turned dark red in colour (ca. 2 h), anhyd NiCl₂ (0.18 g, 1.39 mmol) was added in aliquots over a 15 min interval and stirred for 20 h. The reaction mixture was filtered to obtain a dark purple

⁴A. Sivaramakrishna, B. Varghese, and M.N.S. Rao. Unpublished results.

	Nickel salt		R ₃ PNS ₃ N ₃ ligands			Product isolated ^b		
	(g)	(mmol)	(g)	(mmol)	Mol ratio		(g)	(%)
NiCl ₂	0.30	2.31	(1) 0.96	2.32	1:1	Α	0.15	27
2						С	0.50	34
NiCl ₂ ·6H ₂ O	0.25	1.05	(1) 0.44	1.06	1:1	Α	0.11	43
						С	0.27	41
NiCl ₂ ·6H ₂ O	0.25	1.05	(1) 0.88	2.13	$1:2^{c}$	Α	0.14	54
						С	0.43	65
NiI ₂	0.22	0.70	(1) 0.30	0.72	1:1	Α	0.06	35
						D	0.22	39
NiSO ₄ ·7H ₂ O	0.20	0.71	(1) 0.60	1.45	1:2	Α	0.15	86
						\mathbf{E}^d	0.36	77
NiCl ₂	0.21	1.62	(5) 0.71	1.63	1:1	Α	0.12	30
						F	0.31	29
NiCl ₂	0.25	1.93	(6) 0.93	1.94	1:1	Α	0.20	42
						\mathbf{G}^d	0.20	27
NiCl ₂	0.18	1.39	(7) 0.59	1.39	1:1	Α	0.15	44
						е	—	
NiCl ₂	0.15	1.16	(8) 0.50	1.16	1:1	Α	0.12	42
						е	—	
NiCl ₂	0.20	1.54	(9) 0.66	1.54	1:1	Α	0.12	32
						е	_	

Table 1. Reactions of R₃PN-S₃N₃ heterocycles with nickel salts.^a

Note: $\mathbf{A} = \text{Ni}(\text{S}_2\text{N}_2\text{H})_2$; $\mathbf{C} = [\text{Ph}_3\text{PNH}_2]\text{C}$; $\mathbf{D} = [\text{Ph}_3\text{PNH}_2]\text{I}$; (40); $\mathbf{E} = [\text{Ph}_3\text{PNH}_2]_2\text{SO}_4$; $\mathbf{F} = [(\text{C}_5\text{H}_{10}\text{N})_3\text{PNH}_2]\text{C}$ (mp 147–150°C); ³¹P NMR: singlet at 36.0 ppm, gave satisfactory CHN analysis; $\mathbf{G} = [(\text{H}_3\text{C}-\text{NC}_4\text{H}_8\text{N})_3\text{PNH}_2]\text{C}$].

"All reactions were done in CH₃CN at room temperature for ca. 18 h by adding the ligand to a stirred slurry of the nickel salt

^bIn all the reactions, an off-white insoluble residue was obtained in varying amounts. The ionic nature of this water soluble residue was revealed by its broad IR absorptions in the v_{NH} and v_{SO} regions at 3345 and 1095 cm⁻¹, respectively. It is possibly an ammonium salt of the S_xO_y anion.

"This reaction was done by the addition of five drops of water.

^dImpure samples, ³¹P NMR spectra showed strong singlets at 35.1 (E) and 35.6 ppm (G).

"Not isolated, ³¹P NMR spectrum showed a strong singlet at 41.1, 40.6, and 42.0 ppm for the purple coloured reaction mixtures of **7**, **8**, and **9**, respectively.

filtrate and a pale yellow precipitate which when worked up as in reaction (*a*) gave $[Ph_3PNH_2]Cl$ (0.10 g) and a residue (0.11 g). The oily mass left after removal of the solvent from the purple filtrate was chromatographed over a silica gel column using benzene (caution: carcinogen!!) followed by benzene–dichloromethane (1:1) eluants to isolate Ph₃PS (0.40 g), $[Ph_3PNH_2]Cl$ (0.38 g), and $[Ni(S_2N_2H)_2]$ (0.20 g, 61%).

(d) Reaction of $(OC_4H_8N)_3PN-S_3N_3$ (2) with anhyd $NiCl_2$ in CH_3CN (1:1)

To a stirred slurry of anhyd NiCl₂ (0.15 g, 1.16 mmol) in acetonitrile (25 mL), was added the red ligand 2 (0.53 g, 1.20 mmol) as a solid in small amounts over a 15 min interval at room temperature. The colour of the solution gradually changed to purple along with the formation of a green precipitate. After 20 h, the green precipitate (0.32 g) was separated by a filtration and extracted with CH_3CN (8 × 3 mL). This extract, on cooling in the refrigerator for 10 h, gave a lustrous dark-green solid (0.22 g, 46%) which was identified as (OC₄H₈N)₃PNS₃N·NiCl₂ (**B**), mp 184–186°C. IR (Nujol, cm⁻¹): 1443 (m), 1344 (m), 1293 (w), 1251 (m), 1152 (s), 1126 (s), 1104 (vs), 1018 (s), 1014 (m), 960 (vs), 880 (w), 835 (w), 700 (vs), 662 (w), and 595 (w). UV-vis (nm, L mol⁻¹ cm⁻¹): 580 (9.1 × 10³), 420 (4.1 × 10³), 300 (1.9 \times 10³). ¹H NMR δ (ppm): 3.12 (m, 12H) and 3.60 (m, 12H). ³¹P NMR δ (ppm): 33.7 (s,1P). XPE (B.E. in eV): 141.0 (P_{2p}), 170.5 (S_{2p}), 205.0 (Cl_{2p}), 292.5 (C_{1s}), 405.5 $(N_{1s}),\ 536.5\ (O_{1s}),\ 858.5\ (Ni_{2p}).$ Elemental anal. calcd. for $C_{12}H_{24}N_5O_3PS_3NiCl_2\ (\%):\ C\ 26.54,\ H\ 4.46,\ N\ 12.90,\ Cl\ 13.08,\ Ni\ 10.83;\ found:\ C\ 26.49,\ H\ 4.41,\ N\ 12.51,\ Cl\ 12.93,\ Ni\ 10.73\ (leaving behind a white insoluble residue\ (60\ mg)).$ A further quantity of **B** (0.12 g, 25%) was obtained when the concentrated purple filtrate was cooled in the freezer for a day.

(e) Reaction of $(OC_4H_8N)_3PN-S_3N_3$ (2) with NiCl₂·6H₂O in CH₃CN (1:1)

Nickel chloride hexahydrate (0.20 g, 0.84 mmol) stirred in CH₃CN (25 mL) at room temperature was added the ligand **2** (0.37 g, 0.84 mmol) in small amounts over a 15 min interval. The reaction mixture, which turned gradually to dark purple along with the formation of a green precipitate, was filtered after 18 h. The acetonitrile extract (3×10 mL) of the precipitate when cooled in the freezer for a day yielded a lustrous dark-green solid **B** (0.13 g, 38%). The purple filtrate was concentrated and cooled in the freezer to obtain a further quantity of **B** (50 mg, 14%).

(f) Reaction of anhyd NiCl₂ with $(OC_4H_8N)_3P$ and S_4N_4 in CH₃CN (1:1)

To a stirred solution of $(OC_4H_8N)_3P$ (1.05 g, 3.63 mmol) in CH₃CN (25 mL), S₄N₄ (0.33 g, 1.79 mmol) was added at room temperature over a 20 min interval. When the reaction mixture became dark red (ca. 2 h), anhyd NiCl₂ (0.23 g, 1.77 mmol) was added in aliquots over a 15 min interval and stirred for 15 h. The reaction mixture was then filtered to get

Table 2. The cathodic half-wave potentials $(E_{1/2})$ and the ³¹P NMR chemical shifts of R₃PN-S₃N₃ heterocycles and 1,5- (Ph₃PN)₂S₄N₄.

			³¹ P NMR
Compound	$E_{1/2}$ (V)	vs. Ag/Ag ⁺	chemical shift
Ph ₃ PNS ₃ N ₃	-1.59	-1.97	24.8
(4-ClC ₆ H ₄) ₃ PNS ₃ N ₃	-1.54	-1.90	23.4
(4-MeC ₆ H ₄) ₃ PNS ₃ N ₃	-1.58	-1.94	23.1
Ph ₂ (OC ₄ H ₈ N)PNS ₃ N ₃	-1.57	-1.94	31.2
Ph(OC ₄ H ₈ N) ₂ PNS ₃ N ₃	-0.88	-1.58	30.9
(OC ₄ H ₈ N) ₃ PNS ₃ N ₃	-1.62	-2.07	23.1
$1,5-[Ph_3PN]_2S_4N_4$	-1.56	-1.99	18.1 and 23.6

Fig. 1. Phosphiniminocyclotrithiazenes $((R)(R')(R'')PN-S_3N_3)$ considered in this study.

	<u>R</u>	<u>R'</u>	<u>R"</u>
_R R' R'	C_6H_5	C_6H_5	C ₆ H ₅ (1)
	OC4H8N	OC ₄ H ₈ N	OC4H8N (2)
P	p-ClC ₆ H ₄	p-CIC ₆ H ₄	p-CIC ₆ H ₄ (3)
Ń	$p-H_3CC_6H_4$	p-H ₃ CC ₆ H ₄	<i>р</i> -Н ₃ СС ₆ Н ₄ (4)
Ì	$C_5H_{10}N$	$C_5H_{10}N$	C₅H ₁₀ N (5)
∠Ś <u>,</u>	CH3NC4H8N	CH3NC4H8N	CH3NC4H8N (6)
Ņ Ņ Ņ	C_6H_5	C_6H_5	OC ₄ H ₈ N (7)
Î 🦳 Î	C ₆ H₅	OC4H8N	OC4H8N (8)
³ Ν ³	C_6H_5	$C_5H_{10}N$	C₅H ₁₀ N (9)

a green precipitate and dark purple filtrate. The CH₃CN extract (6 × 5 mL) of the precipitate when cooled in the freezer for a day gave the lustrous dark-green solid **B** (0.23 g, 31%). A further quantity of **B** (0.12 g, 17%) was recovered from the purple filtrate from which a slightly impure $(OC_4H_8N)_3PS$ (0.38 g) was also isolated in two subsequent crops.

All other reactions performed in this study are summarized in Table 1.

Results and discussion

The reported reactions of phosphiniminocyclotrithiazenes include: (*i*) adduct formation (20, 37); (*ii*) thermolysis (21, 23); (*iii*) substituent exchange (22); (*iv*) ring conversions (23); and (*v*) chemical and hydrolytic degradation (41). We have now studied the first electrochemical and coordination behaviour of several such heterocyclic systems carrying different substituents on phosphorus (Fig. 1) and the results are described here.

Electrochemical behaviour

A polarographic investigation was carried out on $R_3PN-S_3N_3$ (R = phenyl (1), morpholino (2), p-chlorophenyl (3), and *p*-tolyl (4)) (symmetrically substituted) and $Ph_2(OC_4H_8N)PN-S_3N_3$ (7) and $Ph(OC_4H_8N)_2PN-S_3N_3$ (8) (unsymmetrically substituted) to evaluate substituent effects on redox potentials, if any, in this class of heterocycles. All of them were found to give two cathodic waves (Fig. 2) with significantly differing $E_{1/2}$ values. A comparison (Table 2) reveals that among the symmetrical ones, $E_{1/2}$ for first and second waves vary over a 80 to 170 mV range, respectively.

Fig. 2. The polarograms of: (*a*) 0.5 mmol dm⁻³ Ph₃PN-S₃N₃, and (*b*) 0.5 mmol dm⁻³ 1,5-(Ph₃PN)₂S₄N₄ in dichloromethane containing 0.1 mol dm⁻³ n-Bu₄NClO₄.



The *p*-chlorophenyl derivative had the lowest value while the morpholino derivative had the greatest. Unsymmetrical ones showed very different $E_{1/2}$ values to each other. Also, no smooth trend in the $E_{1/2}$ values was observed in the series $(C_6H_5)_x(OC_4H_8N)_{3-x}PN-S_3N_3$ (x = 0, 1, 2, 3). Similar irregularities have been observed in ³¹P NMR chemical shifts of several unsymmetrically substituted tri-coordinate phosphorus(III) and tetra-coordinate phosphorus(V) compounds containing amino substituents (42), which seem to suggest that the unsymmetrical environment around phosphorus has a more pronounced effect than the additive effects of the substituents attached (Table 2).

An interesting observation made in this study is that the polarographic reduction of 1 at -1.6 V produced a reduction wave at ca. -2.0 V that corresponded with the reduction wave of $1,5-(Ph_3PN)_2S_4N_4$ (-1.99 V) thereby suggesting the possibility of the conversion of 1 to $1,5-(Ph_3PN)_2S_4N_4$ under electrochemical reduction. Such a ring conversion occurring under the influence of a nucleophile has been previously observed (23, 30, 32). Conceivably, the dimerization of "Ph_3PN-S_2N_2" arising from the cleavage of Ph_3PN-S_3N_3 leads to the formation of this eight-membered heterocycle (eqs. [1] and [2]).

[1]
$$Ph_3PN-S_3N_3 + e^- \rightarrow Ph_3PN-S_3N_3^{-\bullet}$$

 $\rightarrow Ph_3PN-S_2N_2 + NS^{\bullet}$

$$[2] \qquad 2Ph_3PN-S_2N_2 \rightarrow 1,5-(Ph_3PN)_2S_4N_2$$

The fragment NS' possibly gets converted to S_4N_4 . Chivers and Hojo (4) have observed a similar dimerization of "Ph₂CNSNSO" under electrochemical reduction. The polarograms of $R_3PNS_3N_3$ in acetonitrile containing **Fig. 3.** The cyclic voltammograms of: (*a*) 0.5 mmol dm⁻³ Ph₃PN-S₃N₃, and (*b*) 0.5 mmol dm⁻³ ($OC_4H_8N_3PN$ -S₃N₃ in dichloromethane containing 0.1 mol dm⁻³ *n*-Bu₄NClO₄.

0.1 mol dm⁻³ Et_4NClO_4 were rather complicated; e.g., $\text{Ph}_3\text{PNS}_3\text{N}_3$ gave successively five cathodic waves at -1.25, -1.59, -1.98, -2.47, and -2.73 V vs. Ag/0.01 mol dm⁻³ AgNO₃-MeCN. The second and the third waves correspond to the two waves observed in dichloromethane.

Figure 3 shows the cyclic voltammograms on the GC electrode of **1** and **2**. Both gave a sharp anodic peak nearly at the same potential (+0.6 V) but their cathodic peak potentials are found to be different. Other examples considered in the study also gave a similar anodic peak in the range +0.60 to +0.65 V. In an earlier study, Swarnalatha (33) observed the anodic peak potential values ($E_{a,p}$ vs. SCE) for **5**, Ph[(C₆H₁₁)₂N](C₅H₁₀N)PN-S₃N₃, and Ph[(C₆H₁₁)₂N](Me₂N)-PN-S₃N₃ in acetonitrile at 0.51, 0.56, and 0.61 V, respectively.

Controlled potential electrolysis of $Ph_3PNS_3N_3$ and $(OC_4H_8N)_3PNS_3N_3$ were carried out on a GC fiber electrode at +0.60 V. The initial red colour of the solution disappeared within a few minutes and the ³¹P NMR spectra recorded for the solutions after electrolysis gave only one signal at 37.5 and 34.6 ppm, respectively, which may be due to the formation of the corresponding phosphinimines. The absence of characteristic UV–Vis absorptions of the heterocycle (15, 16) after electrolysis suggests the disruption of the S₃N₃ ring skeleton during electrolysis.

Coordination behaviour

A detailed study of the reactions of nickel chloride with $Ph_3PN-S_3N_3$ (1) was first carried out and only selected reactions were done in other cases which include 2, 5, and 6 (symmetrical variety) and 7, 8, and 9 (unsymmetrical variety). Ligand 1 reacts with nickel chloride at room temperature to afford the previously known nickel complex





 $([Ni(S_2N_2H)_2]$ (A)) (43) and the phosphiniminium salt $([Ph_3PNH_2]Cl$ (C)) (38) as major products. Both the products were isolated in ca. 90% yield when the ligand (1) to hydrated NiCl₂ ratio was 2:1 which suggests that the reaction conceivably proceeds as in the eq. [3].

[3] $2Ph_3PN-S_3N_3 + [Ni(H_2O)_6]Cl_2$ $\rightarrow [Ni(S_2N_2H)_2] + 2[Ph_3PNH_2]Cl + \cdots$

The coordinated water molecules of nickel chloride are found to participate in the reaction but those performed with deliberate addition of water or with anhyd NiCl₂ afforded relatively low yields of **A** and **C** implying that: (*i*) H₂O only in small amounts is necessary for the reaction; and (*ii*) NiCl₂ and (or) CH₃CN employed in the study are presumably slightly wet. Depending on the conditions, varying yields of **A** and **C** were isolated from several of these reactions. This reaction, which occurs for different anions of nickel (Cl⁻, Γ , SO⁴₄⁻) was also favoured when the precursor reaction (that of S₄N₄ and Ph₃P) was performed in the presence of NiCl₂ (*Experimental*).

The purple complex **A** has attracted in the past, several studies. Scheme 1 shows the different reaction routes from which **A** has been isolated previously. It is noteworthy that methanol is used in all the methods which is presumably the source of protons. A notable feature of the present work is that **A** is isolated in near quantitative yield and by a simple work-up procedure without involving chromatography. Interestingly, ligands **5–9** also afforded the same complex (**A**) but its recovery from the reaction mixtures posed considerable difficulty. The corresponding phosphiniminium chloride by-product was either isolated in small amounts or identified by ³¹P NMR spectroscopy.

Contrary to the ligands 1 and 5–9, $(OC_4H_8N)_3PN-S_3N_3$ (2) reacts in an equimolar ratio with NiCl₂ (in both hydrated and anhydrous forms) under similar conditions to afford a dark green lustrous complex (B) in moderate to good yield (Fig. 4). The use of anhydrous salt and dry solvent were found to be more favourable for the formation of **B**, which could also be isolated from the analogous reaction of $(OC_4H_8N)_3P$ with S_4N_4 in presence of NiCl₂ in ca. 50% yield. Neither **A** nor the corresponding phosphiniminium chloride ($[(OC_4H_8N)_3PNH_2]$ Cl) was isolated from any of the reactions tried. Though reasons for this unique behaviour are not clear, the differences in the stabilities of the (amino) phosphinimines and their possible derivatives may well be a contributing factor for this difference.

The complex **B** is air stable and less soluble in CH_3CN , CH_2Cl_2 and THF compared to **A**. Its solution though appears



Scheme 1. Reported methods for the preparation of the $Ni(S_2N_2H)_2$ complex.



Fig. 5. Sulfur region of the XPE spectrum of complex **B** showing deconvolution and curve fitting (the dotted line represents the experimental curve).





purple. affords upon cooling shining dark green microcrystalline solid which is very different to A. On the basis of its elemental analysis, diamagnetic nature ($\mu_{\rm B}$ = 0.13), negligible electrical conductivity ($\lambda = 0.0021 \text{ ohm}^{-1} \text{ cm}^2$), ¹H and ³¹P NMR data and the fact that its IR spectrum resembles that of (OC₄H₈N)₃PN-S₃N (31), we propose its structure as shown in Fig. 4. Complex B is a tetracoordinate, neutral, square-planar complex that has $(OC_4H_8N)_3PN-S_3N$ as the new ligand. Though many metal complexes of the bidentate ligand S₃N⁻ have been reported in the literature (45, 48-50), to the best of our knowledge this is the first time that a neutral S₃N ligand and its bidentate mode of ligation are observed. Unfortunately, all the efforts to obtain single crystals of **B** proved futile. However, its X-ray photoelectron spectral results (ESCA) were found to be in accordance with the structure proposed. The spectrum reveals the presence of all the constituent elements (Experimental) as well as the divalent and low-spin nature of nickel (51). The broad and unsymmetrical nature of the peak observed in the sulfur region (ca. 170 eV) was suggestive of the nonequivalent nature of sulfur atoms present in the ligand. This peak, upon repetitive deconvolution steps, gave features supportive of three kinds of sulfurs (Fig. 5) as in the structure proposed. In contrast, the nitrogen peak was found to be symmetrical and unresolved (FWHM = 2.52 V). A similar symmetrical and unresolved nitrogen peak was observed by Bossa et al. (52) for the nitrogens of [Ni(S₂N₂H)₂].

Conclusion

New and interesting results as well as substituentdependent behaviour were observed in the electrochemical and coordination studies of several phosphinimino cyclotrithiazenes (symmetrical and unsymmetrical ones). The synthetic advantage of the use of such heterocycles has been demonstrated. $Ph_3PN-S_3N_3$ serves as a source of the "S₂N₂H⁻⁻" ligand and affords [Ni(S₂N₂H)₂] in near quantitative yield while (OC₄H₈N)₃PN-S₃N₃ offers a new and neutral S-N ligand. Its complex with nickel chloride was isolated and characterized. More coordination studies especially of the neutral ligand, R_3PN-S_3N with different metal substrates merit consideration. Such studies are underway.

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