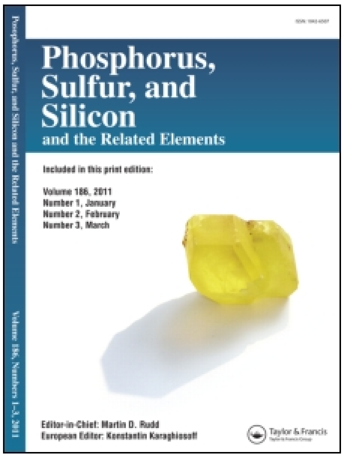

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Spectral Characterization of *O,O'*- Dialkyl and Alkylene Dithiophosphates of Neodymium (III)

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To cite this Article Tripathi, U. N. , Ahmad, Mohd. Safi , Mirza, Rasheda and Siddiqui, Afsham(2007) 'Synthesis and Spectral Characterization of *O,O'*- Dialkyl and Alkylene Dithiophosphates of Neodymium (III)', Phosphorus, Sulfur, and Silicon and the Related Elements, 182: 8, 1779 — 1792

To link to this Article: DOI: 10.1080/10426500701313961

URL: http://dx.doi.org/10.1080/10426500701313961

Phosphorus, Sulfur, and Silicon, 182:1779–1792, 2007

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500701313961

Synthesis and Spectral Characterization of *O,O′*- Dialkyl and Alkylene Dithiophosphates of Neodymium (III)

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Neodymium (III) dithiophosphates of the type; $[Nd\{S_2P(OR)_2\}Cl_2.4H_2O]$, $[Nd\{S_2PO_2G\}Cl_2.4H_2O]$, $[Nd\{S_2P(OR)_2\}_2Cl.3H_2O]$, $[Nd\{S_2PO_2\ G\}_2Cl.3H_2O]$, $[Nd\{S_2P(OR)_2\}_3.3H_2O]$ *and* $[Nd\{S_2PO_2G\}_3.3H_2O]$ *[where* $R = —CH_2CH_2CH_3$ *or* $——C_6H_5$; $G = —C(CH_3)_2CH_2CH(CH_3)—$, $—CH_2C(CH_3)_2CH_2—$, $—C(CH_3)_2C(CH_3)_2—$, $—CH_2CH_2CH(CH_3)$, $—CH_2C(C_2H_5)_2CH_2—$ *and* $—CH(CH_3)CH(CH_3)$*-] were prepared by the reaction of* $NdCl_3.6H_2O$ *and ammonium dithiophosphates in distilled water. These newly synthesized compounds have been characterized by elemental analysis, TGA, UV-visible, IR,* ^{1}H *and* ^{31}P *NMR spectral studies. Coordination numbers of eight and nine are suggested for neodymium (III) in these compounds.*

Keywords Antiferromagnetic; dithiophosphate; electronic spectra; neodymium; TGA

INTRODUCTION

An interesting coordination chemistry of lanthanide elements and important role of their complexes in chemical,[1–3] medical,[4] and industrial[5] processes are enough to recognize them as worthwhile for synthesis of new complexes. Compared to the well-developed chemistry of

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Received November 26, 2006; accepted February 12, 2007.

The authors are thankful to I. I. Sc., Bangalore, A. P. S. University, Reewa and C. D. R. I., Lucknow, for their help in magnetic moment, analytical, and spectral data measurements.

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sulfur-bonded derivatives of transition metals, due to their fascinating modes of bonding[6–8] along with increasing applications in industry[9] and agriculture,[10] much less attention has been paid to lanthanides with such ligands. Dithiocarbamates[11–14] and dithiophosphinates of lanthanide elements along with crystal structures for a few of them have been reported.[15,16] However O,O'-dialkyl dithiophosphates of lanthanide and actinide elements and their adducts have received little attention.[17–19] O,O'-alkylene dithiophosphates are expected to be less labile and have been explored in our laboratory.[20–23] Recently, we have reported O,O'-alkylene dithiophosphates of thorium (IV) and their adducts with nitrogen and phosphorus donor bases.[24] In continuation of our research interest in ligands containing phosphorus and sulphur, we thought it worthwhile to study the O,O'-dialkyl and O,O'-alkylene dithiophosphates of neodymium (III).

RESULTS AND DISCUSSION

All the compounds were prepared by the following metathetical reactions:

$$\mathrm{NdCl_3.6H_2O + NH_4[S_2P(OR)_2]} \xrightarrow[\mathrm{NH_3}]{\mathrm{Water}} \mathrm{[Nd\{S_2P(OR)_2\}Cl_2.4H_2O]}$$
$$+\ \mathrm{NH_4Cl}$$

$$\mathrm{NdCl_3.6H_2O + NH_4[S_2PO_2G]} \xrightarrow[\mathrm{NH_3}]{\mathrm{Water}} \mathrm{[Nd\{S_2PO_2G\}Cl_2.4H_2O]}$$
$$+\ \mathrm{NH_4Cl}$$

$$\mathrm{NdCl_3.6H_2O + nNH_4[S_2P(OR)_2]} \xrightarrow[\mathrm{NH_3}]{\mathrm{Water}} \mathrm{[Nd\{S_2P(OR)_2\}_nCl_{3-n}.3H_2O]}$$
$$+\ \mathrm{nNH_4Cl}$$

$$\mathrm{NdCl_3.6H_2O + nNH_4[S_2PO_2G]} \xrightarrow[\mathrm{NH_3}]{\mathrm{Water}} \mathrm{[Nd\{S_2PO_2G\}_nCl_{3-n}.3H_2O]}$$
$$+\ \mathrm{nNH_4Cl}$$

[where, R = $-\mathrm{CH_2}CH_2CH_3$ or $-\mathrm{C_6}H_5$; G = $-\mathrm{C(CH_3)_2CH_2}CH(CH_3)-$, $-\mathrm{CH_2C(CH_3)_2CH_2}-$, $-\mathrm{C(CH_3)_2C(CH_3)_2}-$, $-\mathrm{CH_2CH_2CH(CH_3)}$, $-\mathrm{CH_2}$ $\mathrm{C}-$ $\mathrm{(C_2H_5)_2CH_2}-$ and $-\mathrm{CH(CH_3)}CH(CH_3)-$; n = 2, 3].

All these compounds are purple colored solids. The solubility of these compounds in coordinating solvents (dimethyl sulphoxide, dimethyl formamide, etc.) indicate that these are polymeric in nature. The complexes are quite stable but decompose near their respective melting points. The elemental analysis (C, H, S, Cl, and Nd) data is in accordance with stoichiometry proposed for respective compounds.

The magnetic moment data are summarized in Table I. The effective magnetic moment (μ_{eff}) values for these compounds (1.17 to 1.24 B. M.) are less in comparison with expected values for Nd(III) (i.e., 3.62

TABLE I Electronic Spectral and Magnetic Moment Data for Neodymium (III) Dithiophosphates

Compd. no.	Compound	Electronic spectral bands		Magnetic moment (B. M.) found (Calcd.)
		Assignment	Bands (cm^{-1})	
1	$[Nd\{S_2P(OC_3H_7)_2\}Cl_2.4H_2O]$	$^4I_{9/2} \rightarrow {}^4F_{3/2}$	11468	1.02 (3.62)
		$^4I_{9/2} \rightarrow {}^4S_{3/2}\ {}^4F^b_{7/2}$	13347	
		$^4I_{9/2} \rightarrow {}^4F_{9/2}$	14724	
		$^4I_{9/2} \rightarrow {}^4G_{5/2}\ {}^{b2}G_{7/2}$	16937	
		$^4I_{9/2} \rightarrow {}^4G_{9/2}$	19246	
		$^4I_{9/2} \rightarrow {}^4G_{11/2}$	21595	
5	$[Nd\{S_2PO_2C_6H_{12}\}Cl_2.4H_2O]$	$^4I_{9/2} \rightarrow {}^4F_{3/2}$	11579	1.01 (3.62)
		$^4I_{9/2} \rightarrow {}^4S_{3/2}\ {}^4F^b_{7/2}$	13399	
		$^4I_{9/2} \rightarrow {}^4F_{9/2}$	14778	
		$^4I_{9/2} \rightarrow {}^4G_{5/2}\ {}^{b2}G_{7/2}$	16987	
		$^4I_{9/2} \rightarrow {}^4G_{9/2}$	19292	
		$^4I_{9/2} \rightarrow {}^4G_{11/2}$	21652	
6	$[Nd\{S_2PO_2C_4H_8\}Cl_2.4H_2O]$	$^4I_{9/2} \rightarrow {}^4F_{3/2}$	11518	1.02 (3.62)
		$^4I_{9/2} \rightarrow {}^4S_{3/2}\ {}^4F^b_{7/2}$	13397	
		$^4I_{9/2} \rightarrow {}^4F_{9/2}$	14778	
		$^4I_{9/2} \rightarrow {}^4G_{5/2}\ {}^{b2}G_{7/2}$	16987	
		$^4I_{9/2} \rightarrow {}^4G_{9/2}$	19291	
		$^4I_{9/2} \rightarrow {}^4G_{11/2}$	21650	
12	$[Nd\{S_2PO_2C_5H_{10}\}_2Cl.3H_2O]$	$^4I_{9/2} \rightarrow {}^4F_{3/2}$	11235	1.01 (3.62)
		$^4I_{9/2} \rightarrow {}^4S^4_{3/2}F^b_{7/2}$	13142	
		$^4I_{9/2} \rightarrow {}^4F_{9/2}$	14500	
		$^4I_{9/2} \rightarrow {}^4G_{5/2}\ {}^{b2}G_{7/2}$	16712	
		$^4I_{9/2} \rightarrow {}^4G_{9/2}$	19116	
		$^4I_{9/2} \rightarrow {}^4G_{11/2}$	21405	
13	$[Nd\{S_2PO_2C_6H_{12}\}_2Cl.3H_2O]$	$^4I_{9/2} \rightarrow {}^4F_{3/2}$	11243	1.04 (3.62)
		$^4I_{9/2} \rightarrow {}^4S_{3/2}\ {}^4F^b_{7/2}$	13145	
		$^4I_{9/2} \rightarrow {}^4F_{9/2}$	14500	
		$^4I_{9/2} \rightarrow {}^4G_{5/2}\ {}^{b2}G_{7/2}$	16712	
		$^4I_{9/2} \rightarrow {}^4G_{9/2}$	19118	
		$^4I_{9/2} \rightarrow {}^4G_{11/2}$	21405	
14	$[Nd\{S_2PO_2C_4H_8\}_2Cl.3H_2O]$	$^4I_{9/2} \rightarrow {}^4F_{3/2}$	11233	1.03 (3.62)
		$^4I_{9/2} \rightarrow {}^4S_{3/2}\ {}^4F^b_{7/2}$	13140	
		$^4I_{9/2} \rightarrow {}^4F_{9/2}$	14498	
		$^4I_{9/2} \rightarrow {}^4G_{5/2}\ {}^{b2}G_{7/2}$	16701	
		$^4I_{9/2} \rightarrow {}^4G_{9/2}$	19105	
		$^4I_{9/2} \rightarrow {}^4G_{11/2}$	21395	

(Continued on next page)

TABLE I Electronic Spectral and Magnetic Moment Data for Neodymium (III) Dithiophosphates *(Continued)*

Compd. no.	Compound	Electronic spectral bands Assignment	Electronic spectral bands Bands (cm^{-1})	Magnetic moment (B. M.) found (Calcd.)
20	$[Nd\{S_2PO_2C_5H_{10}\}_3.3H_2O$	${}^4I_{9/2} \rightarrow {}^4F_{3/2}$	11335	1.01 (3.62)
		${}^4I_{9/2} \rightarrow {}^4S_{3/2}\ {}^4F^b_{7/2}$	13240	
		${}^4I_{9/2} \rightarrow {}^4F_{9/2}$	14585	
		${}^4I_{9/2} \rightarrow {}^4G_{5/2}\ {}^{b2}G_{7/2}$	16800	
		${}^4I_{9/2} \rightarrow {}^4G_{9/2}$	19195	
		${}^4I_{9/2} \rightarrow {}^4G_{11/2}$	21495	
21	$[Nd\{S_2PO_2C_6H_{12}\}_3.3H_2O$	${}^4I_{9/2} \rightarrow {}^4F_{3/2}$	11345	1.04 (3.62)
		${}^4I_{9/2} \rightarrow {}^4S_{3/2}\ {}^4F^b_{7/2}$	13244	
		${}^4I_{9/2} \rightarrow {}^4F_{9/2}$	14580	
		${}^4I_{9/2} \rightarrow {}^4G_{5/2}\ {}^{b2}G_{7/2}$	16795	
		${}^4I_{9/2} \rightarrow {}^4G_{9/2}$	19200	
		${}^4I_{9/2} \rightarrow {}^4G_{11/2}$	21498	
22	$[Nd\{S_2PO_2C_4H_8\}_3.3H_2O]$	${}^4I_{9/2} \rightarrow {}^4F_{3/2}$	11340	1.02 (3.62)
		${}^4I_{9/2} \rightarrow {}^4S_{3/2}\ {}^4F^b_{7/2}$	13248	
		${}^4I_{9/2} \rightarrow {}^4F_{9/2}$	14590	
		${}^4I_{9/2} \rightarrow {}^4G_{5/2}\ {}^{b2}G_{7/2}$	16802	
		${}^4I_{9/2} \rightarrow {}^4G_{9/2}$	19206	
		${}^4I_{9/2} \rightarrow {}^4G_{11/2}$	21500	

B. M.).[25,26] These values suggest that these compounds are antiferromagnetic in nature.

Thermogravimetric Analysis

The thermograms have been recorded for these compounds in the range 0°C to 600°C. The thermal data are presented in Table II. The compounds show same kind of decomposition pattern. In case of $[Nd\{S_2P(OR)_2\}Cl_2.4H_2O]$ and $[Nd\{S_2PO_2G\}Cl_2.4H_2O]$, the weight loss (14–15%) at 180–181°C corresponds to the loss of four water molecules inside the coordination sphere. Similarly in case of $[Nd\{S_2P(OR)_2\}_2Cl.3H_2O]$ and $[Nd\{S_2PO_2G\}_2Cl.3H_2O]$, the weight loss (8.23–9.0%) at 149–168°C and in $Nd\{S_2P(OR)_2\}_3.3H_2O]$ and $[Nd\{S_2PO_2G\}_3.3H_2O]$, the weight loss (6.43–7.22%) at 150–170°C corresponds to the loss of three water molecules inside the coordination sphere. Presence of water molecule is also supported by IR spectral data. All these compounds finally give neodymium oxide at ∼500°C.

TABLE II TGA Data for Neodymium (III) Dithiophosphates

Compd. no.	Compound	Temperature °C	Weight loss (%)	Weight loss between two steps	Activation energy (Cal./mol)
4	$[Nd\{S_2PO_2C_5H_{10}\}Cl_2.4H_2O]$	181	15	15	6.52
		360	25	10	8.16
		555	60	35	5.63
5	$[Nd\{S_2PO_2C_6H_{12}\}Cl_2.4H_2O]$	181	15	15	7.21
		380	32	17	15.16
		558	57	25	9.12
6	$[Nd\{S_2PO_2C_4H_8\}Cl_2.4H_2O]$	180	14	14	5.64
		333	42	28	10.36
		502	72	44	6.76
12	$[Nd\{S_2PO_2C_5H_{10}\}_2Cl.3H_2O]$	168	8.60	8.60	8.01
		285	18.15	9.55	15.02
		390	39.89	21.74	16.82
13	$[Nd\{S_2PO_2C_6H_{12}\}_2Cl.3H_2O]$	149	8.23	8.23	8.23
		310	26.53	18.30	11.16
		410	33.22	7.32	16.12
14	$[Nd\{S_2PO_2C_4H_8\}_2Cl.3H_2O]$	149	9.0	9.0	8.42
		310	27.67	18.67	16.84
		410	48.68	21.01	14.52
17	$[Nd\{S_2P(OC_3H_7)_2\}_3.3H_2O]$	170	6.43	6.43	12.41
		340	37.24	30.81	22.34
		490	59.63	22.39	16.14
21	$[Nd\{S_2PO_2C_6H_{12}\}_3.3H_2O]$	150	6.49	6.49	11.30
		380	28.14	21.65	18.91
		510	59.53	31.39	19.41
22	$[Nd\{S_2PO_2C_4H_8\}_3.3H_2O]$	165	7.22	7.22	11.40
		350	29.70	24.48	21.01
		500	54.99	25.29	15.01

UV-Visible Spectra

The electronic spectra of these compounds show a number of bands in visible region due to f-f transitions (Table I). A definite red shift is observed for almost all the transitions compared to aqua ions. The bands observed at 11,468–11,233, 13,399–13,140, 14,778–14,490, 16,987–16,701, 19,292–19,105 and 21,652–21,395 cm^{-1} could be assigned to $^4I_{9/2} \rightarrow {}^4F_{3/2}$,$^4I_{9/2} \rightarrow {}^4S_{3/2}{}^4F^{b,}_{7/2}$ $^4I_{9/2} \rightarrow {}^4F^4_{9/2,}I_{9/2} \rightarrow {}^4G^b_{5/2}$,$^2G_{7/2}$, $^4I_{9/2} \rightarrow {}^4G_{9/2}$, and $^4I_{9/2} \rightarrow {}^4G_{11/2}$ transitions, respectively.

Infra Red Spectra

The IR spectra of these compounds have been recorded in the 4000–00 cm^{-1} region and the important bands are summarized in

TABLE III IR Spectral Data (cm^{-1})for Complexes

Compd. no.	ν[O—H]	ν[(P)—O—C]	ν[P—O—(C)]	Ring Vib.	ν[P=S]	ν[P–S]	ν[Nd–S]
1	3531 (br)	1035 (s)	865 (m)	—	720 (s)	590 (m)	361 (w)
2	3538 (br)	1083 (s)	910 (m)	—	715 (s)	630 (m)	360 (w)
3	3568 (br)	1025 (s)	880 (m)	920 (m, br)	720 (s)	620 (m)	361 (w)
4	3531 (br)	1160 (s)	890 (m)	970 (m, br)	715 (s)	615 (m)	368 (w)
5	3528 (br)	1055 (s)	860 (m)	930 (m, br)	710 (s)	630 (m)	365 (w)
6	3527 (br)	1075 (s)	855 (m)	925 (m, br)	705 (s)	615 (m)	363 (w)
7	3526 (br)	1060 (s)	900 (m)	995 (m, br)	725 (s)	625 (m)	364 (w)
8	3525 (br)	1050 (s)	890 (m)	980 (m, br)	715 (s)	625 (m)	363 (w)
9	3340 (br)	1060 (s)	890 (m)	—	695 (s)	575 (m)	361 (w)
10	3345 (br)	1175 (s)	885 (m)	—	715 (s)	630 (m)	360 (w)
11	3350 (br)	1165 (s)	880 (m)	990 (m, br)	698 (s)	550 (m)	366 (w)
12	3345 (br)	1170 (s)	885 (m)	985 (m, br)	660 (s)	590 (m)	362 (w)
13	3340 (br)	1175 (s)	865 (m)	989 (m, br)	695 (s)	560 (m)	368 (w)
14	3345 (br)	1149 (s)	875 (m)	990 (m, br)	700 (s)	570 (m)	365 (w)
15	3345 (br)	1159 (s)	870 (m)	1001 (m, br)	695 (s)	560 (m)	362 (w)
16	3340 (br)	1170 (s)	880 (m)	995 (m, br)	690 (s)	600 (m)	366 (w)
17	3350 (br)	1140 (s)	860 (m)	—	695 (s)	570 (m)	361 (w)
18	3355 (br)	1150 (s)	865 (m)	—	690 (s)	540 (m)	360 (w)
19	3345 (br)	1090 (s)	870 (m)	980 (m, br)	650 (s)	580 (m)	362 (w)
20	3340 (br)	1060 (s)	865 (m)	990 (m, br)	698 (s)	560 (m)	361 (w)
21	3352 (br)	1080 (s)	872 (m)	970 (m, br)	700 (s)	570 (m)	366 (w)
22	3354 (br)	1060 (s)	880 (m)	1020 (m, br)	710 (s)	565 (m)	365 (w)
23	3345 (br)	1060 (s)	865 (m)	1010 (m, br)	720 (s)	600 (m)	365 (w)
24	3340 (br)	1080 (s)	870 (m)	1020 (m, br)	710 (s)	610 (m)	362 (w)

br = broad; s = strong; m = medium; w = weak.

Table III. The bands observed in the region 1175–1025 and 910–855 cm^{-1} have been assigned to ν[(P)-O-C] and ν[P-O-(C)] stretching vibrations, respectively.[20–24,27–30] The sharp/medium intensity bands present in region 1020–920 cm^{-1} in neodymium (III) alkylene dithiophosphates could be due to the ring vibration of dioxaphospholane or dioxaphosphorinane[28–30] rings. The ν[P = S] mode may be characterized by the presence of a band in the 725–650 cm^{-1} region indicating the bidentate nature of dithiophosphate ligands.[20–24,27] The band present in the 630–450 cm^{-1} region may be ascribed to ν[P–S] stretching modes.[27,28] The broad band present in the region 3568–5340 cm^{-1}may be assigned to ν[O–H] stretching indicating the presence of water molecule.

Appearance of a new band (in comparison to free ligand) in the 368–360 cm^{-1} region indicates the formation of a metal-sulfur bond.[31]

Multinuclear NMR Spectra

^{1}H NMR spectra of these compounds have been recorded in DMSO-d$_6$ solution exhibiting the characteristic alkoxy and phenoxy proton signals[23–24,27] (Table IV). The signals of complexes are shifted very much downfield as compared to their respective positions in the spectra of free ligands. This is expected because coordinated neodymium(III) has ($\mu_{\text{eff}} = 1.17$ to 1.24 B.M.), therefore it will cause paramagnetic shifting. The observed integration ratio corresponds well with the presence of one dithiophosphate group in compounds 1 to 8.

TABLE IV ^{1}H NMR Data (in δ ppm) for Complexes in DMSO-d$_6$ at Room Temperature

	^{1}H NMR chemical shift (in δ ppm)	
Compd. no.	Neodymium (III) dithiophosphates	Dithiophosphoric acids
1	1.94, t (^{2}J = 7 Hz), 6H (—CH$_3$); 2.76, m, 4H (—CH$_2$); 6.31, m (^{3}J = 16 Hz), 4H (—OCH$_2$)	0.67, t (^{2}J = 7 Hz), 6H (—CH$_3$); 1.13, m, 4H (—CH$_2$); 3.65, m, 4H (—OCH$_2$)
2	8.51, s, 10H (—C$_6$H$_5$)	7.02, s, 10H (—C$_6$H$_5$)
3	2.31, s, 6H (—CH$_3$); 2.53, d (^{2}J = 7 Hz), 3H (—CH$_3$); 3.57, d (^{2}J = 9 Hz), 2H (—CH$_2$); 6.61—5.76, m, 1H (—OCH)	2.51—1.29, m, 11H (—CH$_3$ and —CH$_2$); 5.57—4.71, m, 1H (—OCH)
4	1.99, s, 6H (—CH$_3$); 5.31, d (^{3}J = 18 Hz), 4H (—OCH$_2$)	1.04, s, 6H (—CH$_3$); 4.04, d (^{3}J = 16 Hz), 4H (—OCH$_2$)
5	2.43, s, 12H (—CH$_3$)	1.49, s, 12H (—CH$_3$)
6	2.13, d (^{2}J = 7 Hz), 3H (—CH$_3$); 3.44, m, 2H (—CH$_2$); 4.98, m (^{3}J = 18 Hz), 2H (—OCH$_2$); 5.23, m, 1H (—OCH)	1.42, d (^{2}J = 7 Hz), 3H (—CH$_3$); 1.53, m, 2H (—CH$_2$); 3.58, m (^{3}J = 17 Hz), 2H (—OCH$_2$); 4.68, m, 1H (—OCH)
7	1.96, t (^{2}J = 4 Hz), 3H (—CH$_3$); 2.82, q, 2H (—CH$_2$); 5.28, d (^{3}J = 16 Hz), 4H (—OCH$_2$)	0.81, t (^{2}J = 4 Hz), 3H (—CH$_3$); 1.40, q, 2H (—CH$_2$); 4.18, d (^{3}J = 15 Hz), 4H (—OCH$_2$)
8	2.05, d (^{2}J = 9 Hz), 6H (—CH$_3$); 6.27, m, 2H (—OCH)	1.19, d (^{2}J = 9 Hz), 6H (—CH$_3$); 4.46, m, 2H (—OCH)
9	1.92, t (^{2}J = 7 Hz), 12H (—CH$_3$); 2.73, m, 8H (—CH$_2$); 6.27, m (^{3}J = 17 Hz), 8H (—OCH$_2$)	
10	8.38, s, 20H (—C$_6$H$_5$)	
11	2.29, s, 12H (—CH$_3$); 2.51, d (^{2}J = 7 Hz), 6H (—CH$_3$); 3.51, d (^{2}J = 9 Hz), 4H (—CH$_2$); 6.42—5.29, m, 2H (—OCH)	

(Continued on next page)

TABLE IV ^{1}H NMR Data (in δ ppm) for Complexes in DMSO-d$_6$ at Room Temperature (*Continued*)

	^{1}H NMR chemical shift (in δ ppm)	
Compd. no.	Neodymium (III) dithiophosphates	Dithiophosphoric acids
12	2.02, s, 12H (-CH$_3$); 5.28, d (^{3}J = 16 Hz), 8H (—OCH$_2$)	
13	2.41, s, 24H (—CH$_3$)	
14	2.11, d (^{2}J = 7 Hz), 6H (—CH$_3$); 3.41, m, 4H (—CH$_2$); 4.92, m (^{3}J = 18 Hz), 4H (—OCH$_2$); 5.20, m, 2H (—OCH)	
15	1.92, t (^{2}J = 4 Hz), 6H (—CH$_3$); 3.11, q, 4H (—CH$_2$); 5.25, d (^{3}J = 15 Hz), 8H (—OCH$_2$)	
16	2.01, d (^{2}J = 9 Hz), 12H (—CH$_3$); 6.61, m, 4H (—OCH)	
17	1.95, t (^{2}J = 7 Hz), (—CH$_3$); 2.75, m, (—CH$_2$); 6.38, m (^{3}J = 16 Hz), (—OCH$_2$)	
18	8.45, s, (—C$_6$H$_5$)	
19	2.22, s, (—CH$_3$); 2.54, d (^{2}J = 6 Hz), (—CH$_3$); 3.48, d (^{2}J = 7 Hz), (—CH$_2$); 6.49—5.57, m, 3H (—OCH)	
20	2.01, s, (—CH$_3$); 5.26, d (^{3}J = 18 Hz), (—OCH$_2$)	
21	2.42, s, (—CH$_3$)	
22	2.04, d (^{2}J = 7 Hz), (—CH$_3$); 3.45, m, (—CH$_2$); 4.76, m (^{3}J = 18 Hz), 6H (—OCH$_2$); 5.25, m, 3H (—OCH)	
23	1.97, t (^{2}J = 6 Hz), (—CH$_3$); 3.28, q, (—CH$_2$); 5.36, d (^{3}J = 14 Hz), (—OCH$_2$)	
24	2.03, d (^{2}J = 8 Hz), (—CH$_3$); 6.58, m, (—OCH)	

s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet.

The ^{31}P NMR spectral data for these compounds are summarized in Table V. In the proton decoupled ^{31}P NMR spectra of these compounds, only one peak for each compound in 5 the region 115.27–97.64 ppm is observed. These signals are shifted very much downfield (δ 54–56 ppm) as compared to their respective positions in the spectra of free ligands,

TABLE V ^{31}P NMR Data (in δ ppm) for Complexes in DMSO-d_6 at Room Temperature

	^{31}P NMR chemical shift (in δ ppm)	
Compd. no.	Neodymium (III) dithiophosphates	Dithiophosphoric acids
1	148.68 (s)	84.20 (s)
2	149.36 (s)	80.13 (s)
3	132.55 (s)	77.20 (s)
4	138.07 (s)	77.07 (s)
5	149.95 (s)	92.39 (s)
6	137.64 (s)	78.50 (s)
7	147.02 (s)	94.20 (s)
8	142.25 (s)	79.00 (s)
9	149.17 (s)	
10	131.47 (s)	
11	136.79 (s)	
12	143.21 (s)	
13	141.69 (s)	
14	132.84 (s)	
15	139.53 (s)	
16	145.27 (s)	
17	128.19 (s)	
18	138.86 (s)	
19	134.78 (s)	
20	142.85 (s)	
21	141.28 (s)	
22	139.57 (s)	
23	147.82 (s)	
24	144.96 (s)	

indicating the paramagnetic shifting by coordinating neodymium(III) and bidentate nature of the dithiophosphate ligand.[23–24,27,32,33]

On the basis of these studies octacoordinated geometry for neodymium (III) dithiophosphate; $[Nd\{S_2P(OR)_2\}Cl_2.4H_2O]$, $[Nd\{S_2PO_2G\}Cl_2.4H_2O]$, $[Nd\{S_2P(OR)_2\}_2Cl.3H_2O]$, and $[Nd\{S_2PO_2G\}_2Cl.3H_2O]$ may be proposed, while for $[Nd\{S_2P(OR)_2\}_3.3H_2O]$ and $[Nd\{S_2PO_2G\}_3.3H_2O]$, nonacoordinated geometry may be proposed.

EXPERIMENTAL

Ammonium salts of O,O′-dialkyl and alkylene dithiophosphoric acids were prepared by the reaction of the desired dry alcohol or glycol with phosphorus pentasulfide in 4:1 or 2:1 molar ratio, respectively, in dry benzene followed by passing dry ammonia gas in the reaction solution.[27]

All other chemicals were of A.R. grade and were used without further purification. The complexes described in the present article were synthesized by the following general routes.

Preparation of $[Nd\{S_2P(OR)_2\}Cl_2.4H_2O]$ ($R = C_6H_5$)

An aqueous solution of $NdCl_3.6H_2O$ (0.9650 g; 2.69 mmol) was added dropwise to the aqueous solution of $NH_4[S_2P(OC_6H_5)_2\}$ (0.7989 g; 2.69 mmol) with constant stirring. The reaction mixture was refluxed for 20 hours to ensure the completion of reaction. The resulting solution was cooled and made basic by adding dilute ammonia solution. The precipitate thus obtained was filtered and washed several times with distilled water and dried in electric oven at 120°C (1.4527 g; 95%). All the compounds of the type $[Nd\{S_2P(OR)_2\}Cl_2.4H_2O]$, $[Nd\{S_2P(OR)_2\}_2Cl.3H_2O]$ and $[Nd\{S_2P(OR)_2\}_3.3H_2O]$ were prepared by this route. The analytical details are listed in Table VI.

Preparation of $[Nd\{S_2PO_2\}Cl_2.4H_2O]$ ($R = C_5H_{10}$)

An aqueous solution of $NdCl_3.6H_2O$ (0.9650 g; 2.69 mmol) was added dropwise to the aqueous solution of $NH_4[S_2P(OC_6H_5)_2\}$ (0.5729 g; 2.69 mmol) with constant stirring. The reaction mixture was refluxed for ~18 hours to ensure the completion of reaction. The resulting solution was cooled and made basic by adding dilute ammonia solution. The precipitate thus obtained was filtered and washed several times with distilled water and dried in electric oven at 110°C (1.1857 g; 91%). All the compounds of the type $[Nd\{S_2PO_2G\}Cl_2.4H_2O]$, $[Nd\{S_2PO_2G\}_2Cl.3H_2O]$ and $[Nd\{S_2PO_2G\}_3.3H_2O]$ were prepared by this route. The analytical details are listed in Table VI.

MEASUREMENTS

Electronic spectra were recorded in THF solution on Hitachi-U-2000 spectrophotometer. IR spectra were recorded as nujol mulls using CsI cells on Perkin-Elmer Model 577 FT-IR spectrophotometer in the range 4000–200 cm^{-1}. ^1H NMR and ^{31}P NMR were recorded at room temperature in DMSO-d_6 solutions on a Bruker DRX-300 spectrometer, operated at 300 and 90 MHz for ^1H and ^{31}P using TMS (tetramethyl silane) and H_3PO_4 as internal standards respectively. Magnetic moment studies were carried out on a Gouy balance at room temperature. Thermo gravimetric analysis (TGA) was carried out at a heating rate of 5° per minute

TABLE VI Synthetic and Analytical Data for the Complexes

Compd. no.	Compound	Yield (%)	M.P. (°C)	Analysis Found (Calcd.) (in %) Nd	S	C	H	Cl
1	$[Nd\{S_2P(OC_3H_7)_2\}Cl_2.4H_2O]$	92	320	28.54 (28.82)	12.67 (12.79)	14.25 (14.39)	4.37 (4.39)	14.05 (14.19)
2	$[Nd\{S_2P(OC_6H_5)_2\}Cl_2.4H_2O]$	95	328	25.12 (25.37)	11.15 (11.26)	25.09 (25.34)	3.14 (3.16)	12.37 (12.49)
3	$[Nd\{S_2PO_2C_6H_{12}\}Cl_2.4H_2O]$	90	380	28.66 (28.94)	12.72 (12.84)	14.28 (14.45)	3.99 (4.01)	14.11 (14.25)
4	$[Nd\{S_2PO_2C_5H_{10}\}Cl_2.4H_2O]$	91	360	29.49 (29.78)	13.08 (13.21)	12.27 (12.39)	3.59 (3.71)	14.52 (14.66)
5	$[Nd\{S_2PO_2C_6H_{12}\}Cl_2.4H_2O]$	91	380	28.74 (28.94)	12.79 (12.84)	14.37 (14.45)	3.98 (4.01)	14.18 (14.25)
6	$[Nd\{S_2PO_2C_4H_8\}Cl_2.4H_2O]$	88	333	30.36 (30.66)	13.48 (13.61)	10.10 (10.20)	3.38 (3.40)	14.94 (15.09)
7	$[Nd\{S_2PO_2C_7H_{14}\}Cl_2.4H_2O]$	91	350	28.00 (28.15)	12.37 (12.49)	16.23 (16.39)	3.53 (3.51)	13.73 (13.86)
8	$[Nd\{S_2PO_2C_4H_8\}Cl_2.4H_2O]$	96	398	30.39 (30.66)	13.74 (13.61)	10.14 (10.20)	3.36 (3.40)	14.96 (15.09)
9	$[Nd\{S_2P(OC_3H_7)_2\}_2Cl.3H_2O]$	89	390	22.06 (21.85)	18.57 (18.39)	21.59 (21.80)	4.22 (4.24)	5.36 (5.38)
10	$[Nd\{S_2P(OC_6H_5)_2\}_2Cl.3H_2O]$	87	395	17.94 (18.12)	15.92 (16.08)	36.55 (36.19)	3.24 (3.26)	4.44 (4.46)
11	$[Nd\{S_2PO_2C_6H_{12}\}_2Cl.3H_2O]$	92	400	21.94 (21.96)	19.33 (19.52)	21.75 (21.96)	4.59 (4.57)	5.43 (5.41)
12	$[Nd\{S_2PO_2C_5H_{10}\}_2Cl.3H_2O]$	96	390	23.19 (22.97)	20.19 (20.39)	18.92 (19.11)	4.12 (4.14)	5.67 (5.65)
13	$[Nd\{S_2PO_2C_6H_{12}\}_2Cl.3H_2O]$	91	410	21.01 (21.96)	19.38 (19.52)	21.79 (21.96)	4.55 (4.57)	5.46 (5.41)
14	$[Nd\{S_2PO_2C_4H_8\}_2Cl.3H_2O]$	92	420	24.06 (24.04)	21.55 (21.34)	16.10 (16.08)	3.64 (3.66)	5.21 (5.91)

(Continued on next page)

TABLE VI Synthetic and Analytical Data for the Complexes *(Continued)*

Compd. no.	Compound	Yield (%)	M.P. (°C)	Analysis Found (Calcd.) (in %) Nd	S	C	H	Cl
15	$[Nd\{S_2PO_2C_7H_{14}\}_2Cl.3H_2O]$	91	410	21.30	18.54	24.33	4.99	5.88
				(21.09)	(19.72)	(21.57)	(4.97)	(5.91)
16	$[Nd\{S_2PO_2C_4H_8\}_2Cl.3H_2O]$	92	420	23.80	21.13	16.05	3.68	5.88
				(24.04)	(21.34)	(16.08)	(3.66)	(5.91)
17	$[Nd\{S_2P(OC_3H_7)_2\}_3.3H_2O]$	94	340	17.05	22.71	25.55	5.71	—
				(17.22)	(22.93)	(25.80)	(5.73)	—
18	$[Nd\{S_2P(OC_6H_5)_2\}_3.3H_2O]$	92	340	17.17	22.86	51.46	4.28	—
				(17.34)	(23.09)	(51.97)	(4.30)	—
19	$[Nd\{S_2PO_2C_6H_{12}\}_3.3H_2O]$	96	345	17.19	23.07	25.73	5.03	—
				(17.34)	(23.09)	(25.98)	(5.05)	—
20	$[Nd\{S_2PO_2C_5H_{10}\}_3.3H_2O]$	90	380	18.09	24.08	22.58	4.54	—
				(18.27)	(24.32)	(22.80)	(4.56)	—
21	$[Nd\{S_2PO_2C_6H_{12}\}_3.3H_2O]$	95	380	17.18	22.86	25.76	5.07	—
				(17.34)	(23.09)	(25.98)	(5.05)	—
22	$[Nd\{S_2PO_2C_4H_8\}_3.3H_2O]$	95	350	19.48	25.44	19.08	4.03	—
				(19.29)	(25.69)	(19.27)	(4.01)	—
23	$[Nd\{S_2PO_2C_7H_{14}\}_3.3H_2O]$	93	345	16.49	22.19	28.57	5.47	—
				(16.51)	(21.98)	(28.85)	(5.49)	—
24	$[Nd\{S_2PO_2C_4H_8\}_3.3H_2O]$	93	350	19.10	25.49	19.15	4.00	—
				(19.29)	(25.69)	(19.27)	(4.01)	—

using an instrument with Rigaku Thermoflex PTC-10A processor supplied by USIC, Delhi University, New Delhi (INDIA). Carbon, hydrogen and nitrogen were estimated by Coleman C.H.N. analyzers.

Sulphur and chlorine were estimated by standard method.[34] Neodymium was estimated by decomposing the compound by boiling with HNO_3 till dryness. This process was repeated 4 to 5 times then solid was treated with water followed by oxalic acid solution. The precipitate was filtered, washed and then ignited in platinum crucible and weighed as Nd_2O_3.[35]

CONCLUSIONS

Present study describes the series of neodymium(III) dithiophosphates. Although it is quite difficult to comment on the molecular structure of these compounds in solid state without actual X-ray crystal structure analysis of at least one of the products. However, the bidentate behaviour of the dithiophosphato moieties in these compounds has been confirmed by IR, and ^{31}P NMR data. On the basis of these studies octacoordinated geometry for neodymium (III) dithiophosphate; $[Nd\{S_2P(OR)_2\}Cl_2.4H_2O]$, $[Nd\{S_2PO_2G\}Cl_2.4H_2O]$, $[Nd\{S_2P(OR)_2\}_2Cl.3H_2O]$, and $[Nd\{S_2PO_2G\}_2Cl.3H_2O]$ may be proposed, while for $[Nd\{S_2P(OR)_2\}_3.3H_2O]$ and $[Nd\{S_2PO_2G\}_3.3H_2O]$, nonacoordinated geometry may be proposed.

REFERENCES

[1] G. R. Willey, T. J. Woodman, and M. G. B. Drew, *Polyhedron*, **16,** 3385 (1997).

[2] K. Binnemens, R. Van Deun, D. W. Bruce, and Y. G. Galyametadinov, *Chemical Physics Letters*, **300,** 509 (1994).

[3] E. Aminaka, T. Tsutsui, and Sh. Saito, *Jpn. J. Appl. Phys.*, **33,** 1061 (1994).

[4] O. N. Riebroa, W. N. Biyushkin, and T. I. Malinowski, *Dokl. A. N. USSR*, **266,** 1391 (1991).

[5] E. M. Larson, A. J. G. Ellison, F. W. Lytle, A. Navrotsky, R. B. Greegor, and J. Wong, *J. Non-Crystalline solids*, **130,** 260 (1991).

[6] R. C. Mehrotra, G. Srivastava, and B. P. S. Chauhan, *Coord. Chem. Rev.*, **55,** 207 (1984).

[7] U. N. Tripathi, R. Bohra, G. Srivastava, and R. C. Mehrotra, *Polyhedron*, **11,** 1187 (1992).

[8] U. N. Tripathi, G. Srivastava, and R. C. Mehrotra, *Trans. Met. Chem.*, **19,** 564 (1994).

[9] T. A. Guiton and C. G. Pantano. *Sol-gel Processing of Sulfide*, Plenary Lecture at 5th International Workshop on Glasses, Ceramics and Gels, Rio-de-Janerio. Abstract A-2 (1989).

[10] M. Umemura, M. Konishi, A. Fukushimali, J. Hisaneo, and T. Okeimoto, Eur. Pat., EP, 205, 165; *Chem. Abstr.*, **106,** 87468n (1987).

[11] T. H. Siddall III and W. E. Stewart, *J. Inorg. Nucl. Chem.*, **32,** 1147 (1970).

[12] C. Y. Su, N. Tang, M. Y. Tan, W. S. Liu, and X. M. Gan, *Polyhedron,* **15,** 73 (1996).

[13] C. Y. Su, M. Y. Tan, N. Tang, X. M. Gan, Z. F. Zhang, O. J. Xue, and K. B. Yu, *Polyhedron*, **16,** 1643 (1997).

[14] C. Y. Su, M. Y. Tan, N. Tang, X. M. Gan, and L. P. Cai, *Synth. React. Inorg. Met.-Org. Chem.*, **27,** 291 (1997).

[15] A. A. Pinkerton and D. Schwarzenbach, *J. Chem. Soc. Dalton Trans.*, 1300 (1979).

[16] P. N. M. Das, W. Kuchen, H. Keck, and G. Hagele, *J. Inorg. Nucl. Chem.*, **39,** 833 (1997).

[17] T. Imai, M. Nakamura, K. Nagai, Y. Okhi, Y. Suzuki, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc. Jpn.,* **59,** 2115 (1968).

[18] M. Ciampolini and N. Nardi, *Chem. Soc. Dalton Trans.,* 2121 (1977).

[19] D. Patlee, C. Musikas, A. Faure, and C. Chachaty, *J. Less-Common Met.,* **122,** 295 (1986); *Chem. Abstr.*, **106,** 23942 (1987).

[20] U. N. Tripathi, A. Chaturvedi, M. S. Singh, and R. J. Rao, *Phosphorus and Sulphur*, **122,** 167 (1997).

[21] U. N. Tripathi and M. S. Singh, *J. Ind. Chem. Soc.*, **760,** 360 (1999).

[22] U. N. Tripathi, P. P. Bipin, R. Mirza, and A. Chaturvedi, *Pol. J. Chem.*, **73,** 1751 (1999).

[23] U. N. Tripathi, P. P. Bipin, R. Mirza, and S. Shukla, *J. Coord. Chem.*, **55(10)**, 1111 (2002).

[24] U. N. Tripathi and M. S. Ahmad, *J. Coord. Chem.*, **59(14),** 1583 (2006).

[25] A. F. Trotman-Dickinson, *Comprehensive Inorganic Chemistry* (Pergamon Press, London, 1973), Vol. 1.

[26] A. A. Khan and K. Iftikhar, *Polyhedron*, **16(23)**, 4153 (1997); *Chem. Abstr.*, **128,** 28153 (1997).

[27] H. P. S. Chauhan, C. P. Bhasin, G. Srivastava, and R. C. Mehrotra, *Phosphorus and Sulphur*, **15,** 49 (1983).

[28] D. E. C. Corbridge, Topics in Phosphorus Chemistry. In *Interscience*: M. Grayson and E. J. Griffith, Eds., (Wiley-Interscience, New York, 1969), Vol. 6.

[29] L. C. Thomas, *Interpretation of the Infra-red Spectra of Organophosphorus Compounds* (Heyden, London, 1974).

[30] L. D. Quin, *The Heterocyclic Chemistry of Phosphorus* (Wiley-Interscience, New York, 1981).

[31] K. Nakamoto, *Infra-red Spectra of Inorganic and Coordination Compounds* (Wiley-Interscience, New York, 1970).

[32] C. Glidewell, *Inorg. Chem. Acta*, **25,** 159 (1977).

[33] B. P. S. Chauhan, G. Srivastava, and R. C. Mehrotra, *Synth. React. Inorg. Met.-Org. Chem.*, **13,** 1050 (1982).

[34] A. I. Vogel, *A Textbook of Quantitative Organic Analysis* (E L B S and Longman, London, 1973).

[35] A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis* (E L B S and Longman, London, 1985).