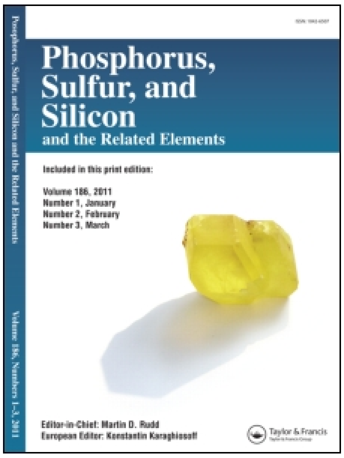

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Synthesis and Characterization of Samarium (III) Tris(O,O' -Dialkyl and Alkylene Dithiophosphates) and Their Adducts with Nitrogen and Phosphorus Donor Bases

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Synthesis and Characterization of Samarium (III) Tris(O,O′-Dialkyl and Alkylene Dithiophosphates) and Their Adducts with Nitrogen and Phosphorus Donor Bases

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Samarium (III) tris(dithiophosphates, $[Sm\{S_2P(OR)_2\}_3.3H_2O]$ *(where* $R = –CH_2CH_2CH_3$ *or* $–C_6H_5$*) and* $[Sm\{S_2PO_2G\}_3.3H_2O]$ *[where* $G = –C(CH_3)_2CH_2\text{-}CH(CH_3)–$, $–CH_2C(CH_3)_2CH_2\text{-}$, $–C(CH_3)_2C(CH_3)_2\text{-}$, $–CH_2CH_2CH(CH_3)$, $–CH_2C(C_2H_5)_2CH_2\text{-}$, *and* $–CH(CH_3)CH(CH_3)\text{-}$*], were prepared by a reaction of* $SmCl_3.6H_2O$ *and ammonium dithiophosphates in distilled water. Adducts of the type* $[Sm\{S_2P(OR)_2\}_3.nL]$ *and* $[Sm\{S_2PO_2G\}_3.nL]$ *[where* $n = 1$, $L = N_2C_{10}H_8$ *and* $n = 2$, $L = P(C_6H_5)_3$*] were prepared by a reaction of samarium (III) tris(dithiophosphates) and nitrogen or phosphorus donor bases in benzene. These newly synthesized compounds have been characterized by elemental analysis, molecular weights measurement, thermogravimetric analysis, UV-visible, IR, and* ^1H *and* ^{31}P *NMR spectral studies. Coordination numbers of eight and nine are suggested for samarium (III) in these derivatives.*

Keywords Dithiophosphate; samarium; triphenylphosphine

INTRODUCTION

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

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chemistry of 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 both phosphorus and sulphur, it was thought worthwhile to study the O,O′-dialkyl and O,O′-alkylene dithiophosphates of samarium (III) and their complexation reaction with nitrogen and phosphorus donor bases.

RESULTS AND DISCUSSION

Samarium (III) tris(dithiophosphate)

All these compounds were prepared by the following metathetical reactions:

$$\mathrm{SmCl_3{\cdot}6H_2O + 3NH_4[S_2P(OR)_2] \xrightarrow[NH_3]{Water} [Sm\{S_2P(OR)_2\}_3{\cdot}3H_2O] + 3NH_4Cl} \qquad (1)$$

$$\mathrm{SmCl_3{\cdot}6H_2O + 3NH_4[S_2PO_2G] \xrightarrow[NH_3]{Water} [Sm\{S_2PO_2G\}_3{\cdot}3H_2O] + 3NH_4Cl}$$

[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 $-CH(CH_3)CH(CH_3)$-; n = 2, 3].

All these compounds are pale yellow-colored solids that are, soluble in common organic (benzene, chloroform, etc.) and coordinating (dimethyl sulphoxide, dimethyl formamide, etc.) solvents. The complexes are quite stable but decompose near their respective melting points. The molecular weight measurement data (Table I) indicate monomeric species in diluted chloroform solution at 45°C. The elemental analysis (C, H, S, and Sm) data (Table I) is in accordance with stoichiometry proposed for the respective compounds.

TABLE I Synthetic and Analytical Data for the Complexes

Compd. no.	Compound	Yield (%)	M.P. (°C)	Analysis Found (Calcd.) (in %)					Mol. Wt. Found (Calcd.)
				Sm	S	C	H	N	
1	$[Sm\{S_2P(OC_3H_7)_2\}_3.3H_2O]$	93	410	17.65	22.54	25.36	5.67	—	839.00
				(17.82)	(22.76)	(25.64)	(5.65)	—	(844.24)
2	$[Sm\{S_2P(OC_6H_5)_2\}_3.3H_2O]$	95	435	14.21	18.15	40.83	3.41	—	1041.00
				(14.35)	(18.33)	(41.24)	(3.43)	—	(1048.30)
3	$[Sm\{S_2PO_2C_6H_{12}\}_3.3H_2O]$	94	450	17.78	22.70	25.54	4.99	—	832.00
				(17.95)	(22.92)	(25.79)	(5.01)	—	(838.18)
4	$[Sm\{S_2PO_2C_5H_{10}\}_3.3H_2O]$	98	440	18.72	23.90	22.41	4.50	—	795.00
				(18.90)	(24.14)	(22.63)	(4.52)	—	(796.09)
5	$[Sm\{S_2PO_2C_6H_{12}\}_3.3H_2O]$	91	398	17.97	22.75	25.48	4.99	—	833.00
				(17.95)	(22.92)	(25.79)	(5.01)	—	(838.18)
6	$[Sm\{S_2PO_2C_4H_8\}_3.3H_2O]$	95	425	19.76	24.98	18.92	3.96	—	751.00
				(19.95)	(25.23)	(19.11)	(3.98)	—	(754.00)
7	$[Sm\{S_2PO_2C_7H_{14}\}_3.3H_2O]$	92	395	16.92	21.62	28.37	5.43	—	876.00
				(17.09)	(21.83)	(28.65)	(5.45)	—	(880.27)
8	$[Sm\{S_2PO_2C_4H_8\}_3.3H_2O]$	92	410	19.83	25.12	18.99	3.99	—	750.00
				(19.95)	(25.23)	(19.11)	(3.98)	—	(754.00)
9	$[Sm\{S_2P(OC_3H_7)_2\}_3.N_2C_{10}H_8]$	96	525	15.75	20.10	35.19	5.26	2.94	940.00
				(15.90)	(20.30)	(35.54)	(5.28)	(2.96)	(946.24)
10	$[Sm\{S_2P(OC_6H_5)_2\}_3.N_2C_{10}H_8]$	97	495	12.95	16.54	47.54	3.28	2.41	1146.00
				(13.08)	(16.70)	(48.02)	(3.30)	(2.43)	(1150.30)
11	$[Sm\{S_2PO_2C_6H_{12}\}_3.N_2C_{10}H_8]$	98	465	15.84	20.23	35.41	4.66	3.00	944.00
				(16.00)	(20.43)	(35.76)	(4.68)	(2.98)	(940.18)
12	$[Sm\{S_2PO_2C_5H_{10}\}_3.N_2C_{10}H_8]$	95	490	16.59	21.18	33.10	4.21	3.10	895.00
				(16.75)	(21.39)	(33.43)	(4.23)	(3.12)	(898.09)

(Continued on next page)

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

Compd. no.	Compound	Yield (%)	M.P. (°C)	Analysis Found (Calcd.) (in %)					Mol. Wt. Found (Calcd.)
				Sm	S	C	H	N	
13	$[Sm\{S_2PO_2C_6H_{12}\}_3.N_2C_{10}H_8]$	93	460	15.91 (16.00)	20.29 (20.43)	35.56 (35.76)	4.64 (4.68)	2.96 (2.98)	936.00 (940.18)
14	$[Sm\{S_2PO_2C_4H_8\}_3.N_2C_{10}H_8]$	95	470	17.40 (17.57)	22.25 (22.44)	30.56 (30.86)	3.72 (3.74)	3.25 (3.27)	851.00 (856.09)
15	$[Sm\{S_2PO_2C_7H_{14}\}_3.N_2C_{10}H_8]$	96	480	15.17 (15.32)	19.37 (19.50)	37.53 (37.90)	5.07 (5.09)	2.83 (2.85)	979.00 (982.27)
16	$[Sm\{S_2PO_2C_4H_8\}_3.N_2C_{10}H_8]$	93	460	17.46 (17.57)	22.49 (22.44)	30.62 (30.86)	3.70 (3.74)	3.28 (3.27)	858.00 (856.09)
17	$[Sm\{S_2P(OC_3H_7)_2\}_3.2P(Ph)_3]$	95	540	11.35 (11.44)	14.47 (14.61)	48.84 (49.33)	5.46 (5.48)	— —	1310.00 (1314.24)
18	$[Sm\{S_2P(OC_6H_5)_2\}_3.2P(Ph)_3]$	98	560	9.86 (9.90)	12.53 (12.65)	56.38 (56.94)	3.93 (3.95)	— —	— (1518.30)
19	$[Sm\{S_2PO_2C_6H_{12}\}_3.2P(Ph)_3]$	93	545	11.39 (11.50)	14.54 (14.86)	49.07 (49.56)	5.02 (5.04)	— —	1305.00 (1308.18)
20	$[Sm\{S_2PO_2C_5H_{10}\}_3.2P(Ph)_3]$	96	580	11.79 (11.88)	15.02 (15.17)	47.89 (48.36)	4.72 (4.74)	— —	1261.00 (1266.09)
21	$[Sm\{S_2PO_2C_6H_{12}\}_3.2P(Ph)_3]$	97	560	11.42 (11.50)	14.65 (14.86)	49.41 (49.56)	5.00 (5.04)	— —	1307.00 (1308.18)
22	$[Sm\{S_2PO_2C_4H_8\}_3.2P(Ph)_3]$	98	550	12.16 (12.29)	15.54 (15.69)	46.61 (47.08)	4.39 (4.41)	— —	1226.00 (1224.00)
23	$[Sm\{S_2PO_2C_7H_{14}\}_3.2P(Ph)_3]$	96	580	11.03 (11.14)	14.08 (14.22)	50.38 (50.69)	5.31 (5.33)	— —	— (1350.27)
24	$[Sm\{S_2PO_2C_4H_8\}_3.2P(Ph)_3]$	95	565	12.18 (12.29)	15.59 (15.69)	46.71 (47.08)	4.42 (4.41)	— —	1219.00 (1224.00)

$Ph = C_6H_5$.

The magnetic moment data are summarized in Table III. The effective magnetic moment (μ_{eff}) values for these compounds (1.37 to 1.44 BM) are comparable with expected values for Sm(III) (i.e., 1.51 BM).[25,26]

Thermograms have been recorded for these compounds in the range 0°C–600°C. The thermal data are presented in Table III. The compounds show the same kind of decomposition pattern. The weight loss (6.44–7.16%) at 175–180°C corresponds to the loss of three water molecules inside the coordination sphere in these compounds. The presence of a water molecule is also supported by IR spectral data. All these compounds finally gave samarium oxide at ~450°C.

The electronic spectra of these compounds show a number of bands in a visible region due to f-f transitions (Table II). A definite red shift is observed for almost all the transitions compared to aqua ions. The bands observed at 18,789–18,812, 19,880–19,898, 20,650–20,699, 21,401–21,430, 23,264–23,295 and 23,901–23,908 cm^{-1} could be assigned to $^6H_{5/2} \rightarrow {}^4F_{3/2}$, $^6H_{5/2} \rightarrow {}^4G_{7/2}$, $^6H_{5/2} \rightarrow {}^4I_{9/2}$ $^4M_{15/2}$, $^6H_{5/2}$ $^4I_{13/2}$, $^6H_{5/2} \rightarrow {}^4M_{19/2}$, and $^6H_{5/2} \rightarrow ({}^6P\,{}^4P)_{5/2}$ transitions, respectively.

The IR spectra of these compounds have been recorded in the 4000–200 cm^{-1} region, and the important bands are summarized in Table IV. The bands observed in the region 1080–1040 and 828–823 cm^{-1}have been assigned toν[(P)—O—C] and ν[P—O—(C)] stretching vibrations, respectively.[20–24,27–30] The sharp/medium intensity bands present in the region 964–955 cm^{-1} in samarium (III) alkylene dithiophosphates could be due to the ring vibration of dioxaphospholane or dioxaphosphorinane[27–30] rings. The ν[P═S] mode may be characterized by the presence of a band in the 655–650 cm^{-1} region indicating the bidentate nature of dithiophosphate ligands.[20–24,27] The band present in the 590–535 cm^{-1} region may be ascribed to ν[P—S] stretching modes.[25,26] The broad band present in the region 3350–3330 cm^{-1}may be assigned to ν[O—H] stretching indicating the presence of water molecule.

The appearance of a new band (in comparison to a free ligand) in the 370–365 cm^{-1} region indicates the formation of a metal-sulfur bond.[31]

^{1}H NMR spectra of these compounds have been recorded in $CDCl_3$ solution exhibiting the characteristic alkoxy and phenoxy proton signals[23–24,27] (Table V). The observed integration ratio corresponds well with the presence of three dithiophosphate groups suggesting that the ratio of metal to ligand is 1:3.

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 the region 112.54–98.37 ppm is observed. These signals are shifted downward (δ 22–25 ppm) as compared

TABLE II Electronic Spectral and Magnetic Moment Data for the Complexes

Compd. no.	Compound	Electronic Spectral Bands		Magnetic Moment (BM)
		Assignment	Bands (cm^{-1})	Found (Calcd.)
3	$[Sm\{S_2PO_2C_6H_{12}\}_3 \cdot 3H_2O]$	$^6H_{5/2} \rightarrow {}^4F_{3/2}$	18801	1.37 (1.51)
		$^6H_{5/2} \rightarrow {}^4G_{7/2}$	19898	
		$^6H_{5/2} \rightarrow {}^4I_{9/2}{}^4M_{15/2}$	20699	
		$^6H_{5/2} \rightarrow {}^4I_{13/2}$	21430	
		$^6H_{5/2} \rightarrow {}^4M_{19/2}$	23295	
		$^6H_{5/2} \rightarrow ({}^6P\ {}^4P)_{5/2}$	23900	
4	$[Sm\{S_2PO_2C_5H_{10}\}_3 \cdot 3H_2O]$	$^6H_{5/2} \rightarrow {}^4F_{3/2}$	18789	1.44 (1.51)
		$^6H_{5/2} \rightarrow {}^4G_{7/2}$	19880	
		$^6H_{5/2} \rightarrow {}^4I_{9/2}{}^4M_{15/2}$	20650	
		$^6H_{5/2} \rightarrow {}^4I_{13/2}$	21401	
		$^6H_{5/2} \rightarrow {}^4M_{19/2}$	23284	
		$^6H_{5/2} \rightarrow ({}^6P\ {}^4P)_{5/2}$	23901	
8	$[Sm\{S_2PO_2C_4H_8\}_3 \cdot 3H_2O]$	$^6H_{5/2} \rightarrow {}^4F_{3/2}$	18812	1.39 (1.51)
		$^6H_{5/2} \rightarrow {}^4G_{7/2}$	19892	
		$^6H_{5/2} \rightarrow {}^4I_{9/2}{}^4M_{15/2}$	20660	
		$^6H_{5/2} \rightarrow {}^4I_{13/2}$	21419	
		$^6H_{5/2} \rightarrow {}^4M_{19/2}$	23264	
		$^6H_{5/2} \rightarrow ({}^6P\ {}^4P)_{5/2}$	23908	
11	$[Sm\{S_2PO_2C_6H_{12}\}_3 \cdot N_2C_{10}H_8]$	$^6H_{5/2} \rightarrow {}^4F_{3/2}$	18849	1.36 (1.51)
		$^6H_{5/2} \rightarrow {}^4G_{7/2}$	19957	
		$^6H_{5/2} \rightarrow {}^4I_{9/2}{}^4M_{15/2}$	20729	
		$^6H_{5/2} \rightarrow {}^4I_{13/2}$	21437	
		$^6H_{5/2} \rightarrow {}^4M_{19/2}$	23318	
		$^6H_{5/2} \rightarrow ({}^6P\ {}^4P)_{5/2}$	23980	
12	$[Sm\{S_2PO_2C_5H_{10}\}_3 \cdot N_2C_{10}H_8]$	$^6H_{5/2} \rightarrow {}^4F_{3/2}$	18850	1.39 (1.51)
		$^6H_{5/2} \rightarrow {}^4G_{7/2}$	19957	
		$^6H_{5/2} \rightarrow {}^4I_{9/2}{}^4M_{15/2}$	20725	
		$^6H_{5/2} \rightarrow {}^4I_{13/2}$	21438	

		$^6H_{5/2} \rightarrow {}^4M_{19/2}$	23320	
		$^6H_{5/2} \rightarrow ({}^6P\ {}^4P)_{5/2}$	23978	
16	$[Sm\{S_2PO_2C_4H_8\}_3 \cdot N_2C_{10}H_8]$	$^6H_{5/2} \rightarrow {}^4F_{3/2}$	18850	1.37 (1.51)
		$^6H_{5/2} \rightarrow {}^4G_{7/2}$	19959	
		$^6H_{5/2} \rightarrow {}^4I_{9/2}{}^4M_{15/2}$	20728	
		$^6H_{5/2} \rightarrow {}^4I_{13/2}$	21439	
		$^6H_{5/2} \rightarrow {}^4M_{19/2}$	23319	
		$^6H_{5/2} \rightarrow ({}^6P\ {}^4P)_{5/2}$	23979	
19	$[Sm\{S_2PO_2C_6H_{12}\}_3 \cdot 2P(C_6H_5)_3]$	$^6H_{5/2} \rightarrow {}^4F_{3/2}$	18861	1.34 (1.51)
		$^6H_{5/2} \rightarrow {}^4G_{7/2}$	19968	
		$^6H_{5/2} \rightarrow {}^4I_{9/2}{}^4M_{15/2}$	20736	
		$^6H_{5/2} \rightarrow {}^4I_{13/2}$	21449	
		$^6H_{5/2} \rightarrow {}^4M_{19/2}$	23330	
		$^6H_{5/2} \rightarrow ({}^6P\ {}^4P)_{5/2}$	23986	
20	$[Sm\{S_2PO_2C_5H_{10}\}_3 \cdot 2P(C_6H_5)_3]$	$^6H_{5/2} \rightarrow {}^4F_{3/2}$	18865	1.37 (1.51)
		$^6H_{5/2} \rightarrow {}^4G_{7/2}$	19970	
		$^6H_{5/2} \rightarrow {}^4I_{9/2}{}^4M_{15/2}$	20739	
		$^6H_{5/2} \rightarrow {}^4I_{13/2}$	21450	
		$^6H_{5/2} \rightarrow {}^4M_{19/2}$	23338	
		$^6H_{5/2} \rightarrow ({}^6P\ {}^4P)_{5/2}$	23985	
24	$[Sm\{S_2PO_2C_4H_8\}_3 \cdot 2P(C_6H_5)_3]$	$^6H_{5/2} \rightarrow {}^4F_{3/2}$	18860	1.36 (1.51)
		$^6H_{5/2} \rightarrow {}^4G_{7/2}$	19965	
		$^6H_{5/2} \rightarrow {}^4I_{9/2}{}^4M_{15/2}$	20735	
		$^6H_{5/2} \rightarrow {}^4I_{13/2}$	21448	
		$^6H_{5/2} \rightarrow {}^4M_{19/2}$	23330	
		$^6H_{5/2} \rightarrow ({}^6P\ {}^4P)_{5/2}$	23985	

TABLE III Thermogravimetric Analysis Data for the Complexes

Compd. no.	Compound	Temperature °C	Weight Loss (%)	Weight Loss Between Two Steps	Activation Energy (Cal./mol)
3	$[Sm\{S_2PO_2C_6H_{12}\}_3.3H_2O]$	178	6.44	6.44	8.21
		380	36.88	30.44	11.91
		450	62.44	25.56	15.50
4	$[Sm\{S_2PO_2C_5H_{10}\}_3.3H_2O]$	180	6.78	6.78	8.31
		280	22.62	15.84	12.91
		440	56.94	34.32	18.30
8	$[Sm\{S_2PO_2C_4H_8\}_3.3H_2O]$	175	7.16	7.16	9.22
		315	29.46	22.30	12.66
		410	54.54	25.08	14.59
9	$[Sm\{S_2P(OC_3H_7)_2\}_3.N_2C_{10}H_8]$	300	26.61	26.61	11.01
		395	42.29	15.68	7.82
		525	61.78	19.49	6.83
11	$[Sm\{S_2PO_2C_6H_{12}\}_3.N_2C_{10}H_8]$	260	14.01	14.01	9.81
		355	26.15	12.14	4.89
		465	41.92	15.77	9.81
12	$[Sm\{S_2PO_2C_5H_{10}\}_3.N_2C_{10}H_8]$	265	13.67	13.67	9.91
		345	22.13	8.46	6.62
		490	38.62	16.49	7.84
17	$[Sm\{S_2P(OC_3H_7)_2\}_3.2P(C_6H_5)_3]$	280	19.64	19.64	12.60
		390	59.53	39.89	25.70
		540	73.92	14.39	23.36
19	$[Sm\{S_2PO_2C_6H_{12}\}_3.2P(C_6H_5)_3]$	250	11.00	11.00	9.62
		310	20.63	9.63	12.68
		545	60.71	40.06	23.36
20	$[Sm\{S_2PO_2C_5H_{10}\}_3.2P(C_6H_5)_3]$	260	11.38	11.36	9.65
		340	18.96	7.58	11.70
		580	60.37	41.41	24.39

TABLE IV 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[Sm–S]	ν[Sm–N]
1	3337 (br)	1045 (s)	823 (m)	—	655 (s)	535 (m)	370 (w)	—
2	3338 (br)	1051 (s)	828 (m)	—	653 (s)	560 (m)	367 (w)	—
3	3330 (br)	1080 (s)	823 (m)	964 (m, br)	650 (s)	540 (m)	369 (w)	—
4	3349 (br)	1063 (s)	825 (m)	955 (m, br)	651 (s)	535 (m)	370 (w)	—
5	3349 (br)	1045 (s)	824 (m)	958 (m, br)	650 (s)	588 (m)	368 (w)	—
6	3350 (br)	1070 (s)	823 (m)	960 (m, br)	653 (s)	570 (m)	370 (w)	—
7	3338 (br)	1080 (s)	823 (m)	964 (m, br)	654 (s)	590 (m)	369 (w)	—
8	3334 (br)	1065 (s)	825 (m)	963 (m, br)	655 (s)	560 (m)	365 (w)	—
9	—	1055 (s)	830 (m)	—	633 (s)	560 (m)	370 (w)	274(w)
10	—	1061 (s)	835 (m)	—	628 (s)	570 (m)	366 (w)	270(w)
11	—	1090 (s)	840 (m)	970 (m, br)	629 (s)	540 (m)	370 (w)	273(w)
12	—	1073 (s)	830 (m)	960 (m, br)	625 (s)	580 (m)	369 (w)	274(w)
13	—	1050 (s)	835 (m)	969 (m, br)	630 (s)	580 (m)	367 (w)	273(w)
14	—	1079 (s)	823 (m)	965 (m, br)	628 (s)	565 (m)	370 (w)	270(w)
15	—	1089 (s)	835 (m)	964 (m, br)	632 (s)	570 (m)	366 (w)	274(w)
16	—	1075 (s)	840 (m)	970 (m, br)	628 (s)	596 (m)	369 (w)	271(w)
17	—	1059 (s)	850 (m)	—	640 (s)	570 (m)	370 (w)	—
18	—	1065 (s)	845 (m)	—	645 (s)	572 (m)	367 (w)	—
19	—	1090 (s)	843 (m)	980 (m, br)	639 (s)	575 (m)	369 (w)	—
20	—	1083 (s)	840 (m)	979 (m, br)	640 (s)	568 (m)	370 (w)	—
21	—	1082 (s)	853 (m)	985 (m, br)	635 (s)	572 (m)	374 (w)	—
22	—	1089 (s)	849 (m)	983 (m, br)	638 (s)	570 (m)	372 (w)	—
23	—	1095 (s)	850 (m)	988 (m, br)	648 (s)	560 (m)	370 (w)	—
24	—	1089 (s)	853 (m)	980 (m, br)	645 (s)	565 (m)	374 (w)	—

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

TABLE V ^{1}H NMR and ^{31}P NMR Data (in δ ppm) for Complexes

Compd. no.	^{1}H NMR Chemical Shift in $CDCl_3$ (in δ ppm)	^{31}P NMR Chemical Shift in $CDCl_3$ (in δ ppm)
1	0.93, t, 18H (-CH_3); 1.81, m, 12H (-CH_2); 5.31, m, 12H (-OCH_2)	106.52 (s)
2	7.35, s, 30H (-OC_6H_5)	99.68 (s)
3	2.48–1.22, m, 33H (-$CH_3$and -CH_2); 5.51–4.58, m, 3H (-OCH)	102.46 (s)
4	1.02, s, 18H (-CH_3); 4.31, d (^{3}J = 17 Hz), 12H (-OCH_2)	110.21 (s)
5	1.40, s, 36H (-CH_3)	108.87 (s)
6	2.48–1.08, m, 15H (-$CH_3$and -CH_2); 4.35–3.84, m, 9H (-OCH_2 and -OCH)	98.37 (s)
7	0.95, t, 9H (-CH_3); 2.26, q, 6H (-CH_2); 5.38, d (^{3}J = 15 Hz), 12H (-OCH_2)	105.29 (s)
8	1.07, d, 18H (-CH_3); 5.56, q, 6H (-OCH)	112.54 (s)
9	0.96, t, 18H (-CH_3); 1.85–1.22, m, 12H (-CH_2); 5.38–4.72, m, 12H (-OCH_2) 8.63–7.76, m, 8H (-$N_2C_{10}H_8$)	108.35 (s)
10	7.46, s, 30H (-OC_6H_5) 8.85–7.74, m, 8H (-$N_2C_{10}H_8$)	98.78 (s)
11	2.28–1.25, m, 33H (-$CH_3$and -CH_2); 5.96–4.97, m, 3H (-OCH) 8.65–7.87, m, 8H (-$N_2C_{10}H_8$)	102.74 (s)
12	1.00, s, 18H (-CH_3); 4.13, d (^{3}J = 18 Hz), 12H (-OCH_2) 8.74–7.68, m, 8H (-$N_2C_{10}H_8$)	110.96 (s)
13	1.45, s, 36H (-CH_3) 8.82–7.87, m, 8H (-$N_2C_{10}H_8$)	108.91 (s)
14	2.37–1.06, br, 15H (-$CH_3$and -CH_2); 4.38, m, 9H (-OCH_2 and -OCH) 8.65–8.05, m, 8H (-$N_2C_{10}H_8$)	98.66 (s)
15	0.91, t, 9H (-CH_3); 2.23, q, 6H (-CH_2); 5.42, d (^{3}J = 15 Hz), 12H (-OCH_2) 8.79–7.85, m, 8H (-$N_2C_{10}H_8$)	105.57 (s)
16	1.11, d, 18H (-CH_3); 5.49, q, 6H (-OCH) 8.73–7.68, br, 8H (-$N_2C_{10}H_8$)	113.12 (s)
17	0.94, t, 18H (-CH_3); 1.83, m, 12H (-CH_2); 5.87, m, 12H (-OCH_2); 7.31, m, 30H (-C_6H_5)	106.38 (s) –2.71 (s)
18	7.32, s, 30H (-OC_6H_5) 7.35, m, 30H (-C_6H_5)	99.42 (s) –2.75 (s)
19	2.37–1.01, m, 33H (-$CH_3$and -CH_2); 5.83–4.89, m, 3H (-OCH); 7.95–7.21, m, 30H (-C_6H_5)	102.28 (s) –2.41 (s)
20	1.01, s, 18H (-CH_3); 4.21, d (^{3}J = 17 Hz), 12H (-OCH_2); 7.26, m, 30H (-C_6H_5)	110.16 (s) –2.19 (s)

(Continued on next page)

TABLE V ^{1}H NMR and ^{31}P NMR Data (in δ ppm) for Complexes *(Continued)*

Compd. no.	^{1}H NMR Chemical Shift in $CDCl_3$ (in δ ppm)	^{31}P NMR Chemical Shift in $CDCl_3$ (in δ ppm)
21	1.47, s, 36H (-CH_3) 8.36–7.74, m, 30H (-C_6H_5)	108.57 (s) –2.30 (s)
22	2.42–1.05, m, 15H (-$CH_3$and -CH_2); 4.18–3.89, m, 9H (-OCH_2 and -OCH) 8.21–7.76, m, 30H (-C_6H_5)	98.41 (s) –2.89 (s)
23	0.91, t, 9H (-CH_3); 2.23, q, 6H (-CH_2); 5.41, d ($^3J = 16$ Hz), 12H (-OCH_2) 7.88, m, 30H (-C_6H_5)	105.33 (s) –2.52 (s)
24	1.06, d, 18H (-CH_3); 5.58, q, 6H (-OCH); 7.91, m, 30H (-C_6H_5)	112.36 (s) –2.68 (s)

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

to their respective positions in the free ligand spectra, indicating the bidentate nature of the dithiophosphate ligand.[23–25,30–31]

Adducts of Samarium (III) tris(dithiophosphate)

All these adducts were prepared by the following metathetical reactions:

$$[Sm\{S_2P(OR)_2\}_3.3H_2O] + N_2C_{10}H_8 \xrightarrow{\text{Benzene}} [Sm\{S_2P(OR)_2\}_3.N_2C_{10}H_8] + 3H_2O \quad (2)$$

$$[Sm\{S_2PO_2G\}_3.3H_2O]+N_2C_{10}H_8 \xrightarrow{\text{Benzene}} [Sm\{S_2PO_2G\}_3.N_2C_{10}H_8] + 3H_2O \quad (3)$$

$$[Sm\{S_2P(OR)_2\}_3.3H_2O]+2P(C_6H_5)_3 \xrightarrow{\text{Benzene}} [Sm\{S_2P(OR)_2\}_3.2P(C_6H_5)_3] + 3H_2O \quad (4)$$

$$[Sm\{S_2PO_2G\}_3.3H_2O]+2P(C_6H_5)_3 \xrightarrow{\text{Benzene}} [Sm\{S_2PO_2G\}_3.2P(C_6H_5)_{38}] + 3H_2O \quad (5)$$

Adducts of samarium (III) tris(dithiophosphates) with 2,2′-bipyridyl are pink-colored solids, while adducts with triphenyl phosphine are yellow-colored-solids. All these adducts are soluble in common organic (benzene, chloroform, etc.) and coordinating (dimethyl sulphoxide, dimethyl formamide, etc.) solvents. The adducts are quite stable in air at r.t. but decompose near their respective melting points, which are higher than that of the parent samarium (III) tris(dithiophosphate).

The molecular weight measurement data indicate monomeric species also for these compounds.

The magnetic moment data are summarized in Table II. The effective magnetic moment (μ_{eff}) values for these adducts (1.34 to 1.39 BM) are comparable with expected values for Sm(III) (i.e., 1.51 BM).[25,26]

The thermal data (recorded in the range 0°C–600°C) are presented in Table II. The adducts show the same kind of decomposition pattern. The weight loss (11.00–26.61%) at 250–300°C corresponds to the loss of O-alkyl and O-alkylene moieties in the adducts. All these compounds finally give samarium oxide at ~510°C.

The electronic spectral data of the adducts are summarized in Table II.

The IR spectral data recorded in the 4000–200 cm^{-1} region are summarized in Table IV. These data are quite similar to those obtained from the original parent samarium (III)-tris(dithiophosphate) with only slight shifting of the bands, suggesting again the bidentate nature of the dithiophosphate ligand.[20–24,27] The appearance of two new bands in adducts of samarium (III) tris(dithiophosphates) with 2,2′-bipyridyl (in comparison to a free ligand) in the regions 274–270 and 370–366 cm^{-1} indicate the formation of a metal-nitrogen bond, and metal-sulfur bondrespectively.[31]

^{1}H NMR spectra (Table V) of these derivatives have been recorded in $CDCl_3$exhibiting the characteristic alkoxy and phenoxy proton signals along with aromatic proton signals from the additional base ligands. The observed integration ratios correspond well with the presence of one nitrogen donor and two phosphorus donor bases in these compounds.

In ^{31}P NMR spectra (Table V) of these derivatives, the phosphorus atom of the dithiophosphato moiety shows one signal in the 113.12–98.41 ppm region for each compound, and an additional phosphorus signal in the −2.19–2.89 ppm region was recorded in the complexes with the triphenyl phosphine base. The downfield (δ 22–25 ppm) shifting of the signal due to the dithiophosphato phosphorus atom also confirms the bidentate nature of dithiophosphato moieties in these derivatives.[23,24,27,32,33]

On the basis of these studies, nonacoordinated and octacoordinated geometries for samarium (III) tris(dithiophosphates) and their adducts, respectively, 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 a 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 analytical grade reagent and were used without further purification. The complexes described in this article were synthesized by the following general routes.

Preparation of $[Sm\{S_2PO_2C_5H_{10}\}_3.3H_2O]$

An aqueous solution of $SmCl_3.6H_2O$ (0.4853 g; 1.33 mmol) was added dropwise to the aqueous solution of $NH_4[S_2PO_2C_5H_{10}]$ (0.8499 g; 3.99 mmol) with constant stirring. The reaction mixture was refluxed for 20 h to ensure the completion of reaction. The resulting solution was cooled and made basic by adding diluted ammonia solution. The precipitate thus obtained was filtered and washed several times with distilled water and dried in an electric oven at 120°C (1.0376 g; 98%). Compounds **1–8** were prepared by this same procedure. The analytical details are listed in Table I.

Preparation of $[Sm\{S_2PO_2C_5H_{10}\}_3.N_2C_{10}H_8]$

$[Sm\{S_2PO_2C_5H_{10}\}_3.3H_2O]$ (0.8040 g; 1.01 mmol) dissolved in 15 mL benzene was mixed and stirred with (0.1575 g; 1.01 mmol) $N_2C_{10}H_8$in 20 mL benzene for 4 h. The solvent was reduced to 10 mL under reduced pressure and left overnight. Pink crystals thus deposited were removed and washed with n-hexane (0.8617 g; 95.0%). The analytical results are presented in Table I. Compounds **9–16** were prepared by this method.

Preparation of $[Sm\{S_2PO_2C_5H_{10}\}_3.2P(C_6H_5)_3]$

Benzene (15 mL) solution of $[Sm\{S_2PO_2C_5H_{10}\}_3.3H_2O]$ (0.7483 g; 0.94 mmol) was mixed with benzene (20 mL) solution of $P(C_6H_5)_3$(0.4931 g ; 1.88 mmol) and stirred for 4 h. The solvent was reduced to 10 ml under reduced pressure and left overnight. Yellow precipitates thus deposited were removed and washed with n-hexane (1.1425 g; 96.0%). The analytical results are presented in Table I. Compounds **17–24** were prepared by this method.

Measurements

Electronic spectra were recorded in chloroform solution on a Hitachi-U-2000 spectrophotometer. IR spectra were recorded as nujol mulls using caesium iodide (CsI) cells on a Perkin-Elmer Model 577 FT-IR spectrophotometer in the range 4000–200 cm^{-1}. ^1H NMR and ^{31}P NMR were recorded at r.t. in $CDCl_3$ solutions on a Bruker DRX-300 spectrometer, operated at 300 and 90 MHz for ^{1}H and ^{31}P using TMS (tetramethyl silane) and H_3PO_4 as internal standards, respectively. Molecular weights were measured on a Knauer Vapor Pressure Osmometer in $CHCl_3$ at 45°C. Magnetic moment studies were carried out on a Gouy balance at r.t. Thermogravimetric analysis was carried out at a heating rate of 5°C per minute using an instrument with a Rigaku Thermoflex PTC-10A processor supplied by University Science Instrument Centre, Delhi University, New Delhi, (India). Carbon, hydrogen, and nitrogen were estimated by Coleman carbon-hydrogen-nitrogen analyzers.

Sulphur was estimated by standard method.[34] Samarium was estimated by decomposing the compound by boiling with HNO_3 until dryness. This process was repeated 4 to 5 times, then the solid was treated with water followed by oxalic acid solution. The precipitate was filtered, washed, and then ignited in a platinum crucible and weighed as Sm_2O_3.[35]

CONCLUSIONS

The present study describes the series of samarium (III) tris(dithiophosphates) and their adducts with nitrogen and phosphorus donor bases. Although it is quite difficult to comment on the molecular structure of these compounds in a solid state without actual X-ray crystal structure analysis of at least one of the products. However, the bidentate behavior of the dithiophosphato moieties in these compounds has been confirmed by IR and ^{31}P NMR data. On the basis of these studies, nonacoordinated and octacoordinated geometries for samarium (III) tris(dithiophosphates) and their adducts, respectively, may be proposed.

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