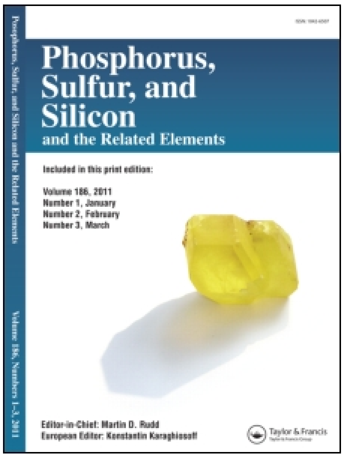

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DIALKYL AND ALKYLENE DITHIOPHOSPHATES OF RUTHENIUM(III)

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Tris-dialkyl dithiophosphates, $Ru[S_2\underline{P(OR)_2}]_3$, R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, i-$C_4H_9$and Ru(III) tris-alkylene dithiophosphate $Ru[S_2\overline{POGO}]_3$, [G= – CMe_2CMe_2-, -$CH_2Me_2CH_2$-,-$CH_2CEt_2CH_2$- and -CMe_2CH_2CHMe- have been synthesized. The complexes are prepared by the reaction of ruthenium trichloride with dialkyl and alkylene dithiophosphoric acids or their ammonium salts in aqueous medium which could be extracted into dichloromethane. These new compounds have been characterized by elemental analysis, molecular weight measurements and spectroscopic [IR., NMR (H^1 and ^{31}P)] studies. On the basis of which plausible structures have been suggested.

INTRODUCTION

Studies on the ruthenium dithiophosphate system have been relatively few[1–3] in comparison to the number of organometallic and classical coordination complexes of ruthenium with dithio acids[4,5] $(RO)_2PS_2^-$, (RCS_2-, $ROCS_2^-$, $RNCS_2^-$) which have been studied over the last two decades. Dialkyl and alkylene dithiophosphates are important because of their use as chelating reagents for the solvent extraction(soft bases)[6,7], as lubricant additives[8,9] and show biocidal activities [10,11].

To the best of our knowledge, there is no other detailed information about the reaction and the structure elucidation of Ru(III) dialkyl and alkylene dithiophosphate except one report which describes an extractive spectrophotometry of ruthenium(III) tris(1,1 diethyldithiophosphate)3. So, it was considered of interest to synthesize and characterize these complexes and elucidate their structural features.

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RESULTS AND DISCUSSION

Ruthenium tris(O,O-dialkyl and alkylene dithiophosphates) have been obtained by the reaction of ruthenium trichloride with the free acids or the ammonium salt of dialkyl and alkylene dithiophosphoric acids in a 1:3 molar ratio in benzene and aqueous medium respectively.

$$RuCl_3 + 3HS_2P(OPr^n)_2 \longrightarrow Ru[S_2P(OPr^n)_2]_3 + 3HCl$$

$$RuCl_3 + 3HS_2\overline{POCH_2CMe_2CH_2O} \longrightarrow Ru[S_2\overline{POCH_2CMe_2CH_2O}] + 3HCl$$

$$RuCl_3 + 3NH_4S_2P(OR)_2 \longrightarrow Ru[S_2P(OR)_2]_3 + 3NH_4Cl$$

$R = Me, Et, Pr^n, Pr^i, Bu^i$ and Ph

$$RuCl_3 + 3NH_4S_2P\overline{OGO} \longrightarrow Ru[S_2P\overline{OGO}]_3 + 3NH_4Cl$$

$G = -CMe_2CMe_2-$, $CH_2CEt_2CH_2-$, $-CMe_2CH_2CHMe-$ and $-CH_2CMe_2CH_2-$

The above complexes of both cyclic and acyclic ligands are dark purple or brown powdery solids (except complexes II and III which is sticky solid), and highly soluble in organic solvents, like benzene, chloroform, dichloromethane and n-hexane. The yields obtained range from 76–89%. The molecular weights determined cryoscopically in benzene, indicated the monomeric nature of these products, (Table I).

IR SPECTRA

The assignments of relevant peaks given in Table IIhave been made on the basis of literature published on various metal dialkyl and alkylene dithiophosphates[12]. The bands due to ν(P)-O-C and ν(P)-O-C are present in the region 1161–917 and 870–760 cm^{-1}. In the cyclic derivatives, broad bands present in the region 955–969 cm^{-1} are due to ring vibrations [13,14]. The bands due to νP=S vibrations are present in the region 663–638 and 650–622 cm^{-1} in cyclic [13] and acyclic derivatives and show a shift ($\delta\nu$=20–10cm^{-1}) to lower frequency from their positions in the corresponding parent acids, thus indicating coordination of the metal atom with the phosphorothionyl sulfur. The bands attributable to νP-S vibrations[16] (symmetric and asymmetric) are present at the region 590–500cm^{-1}. The bands of weak to medium intensity in the region 473–351cm^{-1} may assign to νRu-S vibrations [17].

TABLE I Synthesis and characterization of dialkyl and alkylene dithiophosphates of ruthenium (III)

S.No	RuCl$_3$	Reactants(g) Ammonium salt of (dtp)	Molar ratio	Products and physical state	M.P°C	Yield%	Analysis% Found/(Calc.) Fou S	P
1		$NH_4S_2P(OMe)_2$	1:3	$Ru[S_2P(OMe)_2]_3$	398	79	33.13	15.72
	0.57	1.44		brown solid			(33.57)	(16.21)
2		$NH_4S_2P(OEt)_2$	1:3	$Ru[S_2P(OEt)_2]_3$		81	28.70	13.83
	0.52	1.55		purple sticky solid			(29.26)	(14.13)
3		$NH_4S_2P(OPr^n)_2$	1:3	$Ru[S_2P(OPr^n)_2]_3$		76	25.72	12.42
	0.65	2.18		brown sticky solid			(25.90)	(12.53)
4		$NH_4S_2P(OPr^i)_2$	1:3	$Ru[S_2P(OPr^1)_2]_3$	163	83	25.63	12.31
	0.56	1.73		purple solid			(25.9)	(12.53)
5		$NH_4S_2P(OBu^i)_2$	1:3	$Ru[S_2P(OBU^i)_2]_3$	125	83	23.14	10.16
	0.43	1.60		purple solid			(23.30)	(11.25)
6		$NH_4S_2P(OPh)_2$	1:3	$Ru[S_2P(OPh)_2]_3$	77	89	20.25	9.81
	0.62	2.71		brown solid			(20.34)	(9,93)
7		$NH_4S_2\overline{POCMe_2CMe_2O}$	1:3	$Ru[S_2\overline{POCMe_2CMe_2O}]_3$	393	78	25.74	12.58
	0.75	2.49		brown solid			(26.16)	(12.63)
8		$NH_4S_2\overline{POCH_2CMe_2CH_2O}$	1 :3	$Ru[S_2\overline{POCH_2CMe_2CH_2O}]_3$	70	86	27.62	13.22
	0.56	1.75		brown solid			(27.73)	(13.39)
9		$NH_4S_2\overline{POCH_2CEt_2CH_2O}$	1 :3	$Ru[S_2\overline{POCH_2CEt_2CH_2O}]_3$	388	85	24.53	11.74
	0.43	1.50		brown solid			(24.75)	(11.95)
10		$NH_4S_2\overline{POCMe_2CH_2CHMeO}$	1:3	$Ru[S_2\overline{POCMe_2CH_2CHMeO}]_3$	98	77	26.31	12, 50
	0.46	1.52		brown solid			(26.15)	(12.62)

TABLE II IR spectral data for rurhenium (III) dialkyl and alkylene dithiophosphate

SNo	*Compound*	*ν(P)-O-C*	*νP-O-(C)*	*Ring vibration*	*νP=S*	*νP-S*	*Ru-S*
1	$Ru[S_2P(OMe)_2]_3$	1005 s	786 m	-	638 m	520 m	311 m
2	$Ru[S_2P(OEt)_2]_3$	1015 m	797 m	-	643 m	500 s	314 s
3	$Ru[S_2P(OPr^n)_2]_3$	986 m	848 m	-	644 m	548 s	428 m
4	$Ru[S_2P(OPr^i)_2]_3$	990 s	862 m	-	622 m	589 m	351 m
5	$Ru[S_2P(OBU^1)_2]_3$	981 m	863 m	-	626 m	589 m	353 w
6	$Ru[S_2P(OPh)_2]_3$	934 s	788 m		650 m	582 m	455 m
7	$Ru[S_2\overline{POCMe_2}\overline{CMe_2}\overline{O}]_1$	1140 s	855 s	955 m	660 s	587 m	428 m
8	$Ru[S_2\overline{POCH_2}\overline{CMe_2}\overline{CH_2}\overline{O}]_3$	1158 m	852 m	969 m	658 m	520 m	454 m
9	$Ru[S_2\overline{POCH_2}\overline{CEt_2}\overline{CH_2}\overline{O}]_3$	1161 m	870 s	968 m	631 m	555 m	473 m
10	$Ru[S_2\overline{POCMe_2}\overline{CH_2}\overline{CHMeO}]_3$	1036 m	860 m	964 m	663 m	551 m	462 w

s = strong, m = medium, w = weak.

^{1}H NMR SPECTRA

The ^{1}H NMR spectra of these compounds (Table III) show the expected peak patterns. The number of peaks due to the proton on the α --carbon atom of alkoxy or glycoxy group is doubled due to the coupling with phosphorus-31.[18]

^{31}P NMR SPECTRA

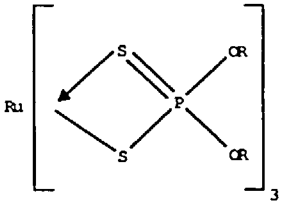
In the proton decoupled ^{31}P NMR spectra (Table III) only one peak for each compound was obtained in the range 68.8–86.1 δ ppm, indicating only one type of phosphorus nucleus in the molecule. However, no noticeable difference was observed in comparison to the parent acids [12,19]It appears that minor difference in the bond angles around phosphorus may not effect the ^{31}P chemical shift. The values of chemical shifts according to Glidewell observations indicates bidentate behavior of the ligand [20]

Molecular weight determination of ruthenium (III) tris-dialkyl and alkylene dithiophosphates showed the monomeric nature of these compounds in benzene. Thus, on the basis of our observation for IR, NMR (^{1}H, ^{31}P) and molecular weight determinations, the following structure (in which ruthenium is six coordinated) is proposed for the tris derivatives.

TABLE III ^1H and ^{31}P spectral data for ruthenium (III) dialkyl and alkylene dithiophosphate

S.No	*Compound*	*^1H Chemical shift - in $CDCl_3$*	*^{31}P Chemical shift in $CDCl_3$*
1	$Ru[S_2P(OMe)_2]_3$	3.7–3.8, d, 18H(OCH_3)	86.02
2	$Ru[S_2P(OEt)_2]_3$	1.3–1.6, t, 18H(CH_3) 4,1–4.3, m, 12H(OCH_2)	86.22
3	$Ru[S_2P(OPr^n)_2]_3$	0,96–1,35, t, 18(CH_3) 1.55–1.8, m, 12H(CH_2) 4.0–4.14, m, 12H(OCH_2)	82.23
4	$Ru[S_2P(OPr^i)_2]_3$	0.96–0.99, d, 36H(CH_3) 3,89–3.97, m, 6H(OCH)	----
5	$Ru[S_2P(OBU^i)_2]_3$	0,96–1,0, d, 36H(CH_3) 1.5–2,0, m, 6H(CH_2) 3,8–4,0, m, 12H(OCH_2)	87.2
6	$Ru[S_2P(OPh)_2]_3$	7.1–7.3, m, 30H(C_6H_5)	86.1
7	$Ru[S_2\overline{POCMe_2}\overline{CMe_2}\overline{O}]_3$	1.15–1.17, d, 36H(CH_3)	76.03
8	$Ru[S_2\overline{POCH_2}\overline{CMe_2}\overline{CH_2}\overline{O}]_3$	0.95–1.23, d, 18H(CH_3) 3,42–4, 17, m, 12H(CH_2O)	72.9
9	$Ru[S_2\overline{POCH_2}\overline{CEt_2}\overline{CH_2}\overline{O}]_3$	0.85–0.90, t, 18H(CH_3) 1.30–1.33, q, 12H(CH_2) 3.96–4.13, m, 12H(CH_2)	96.2
10	$Ru[\ S_2\overline{POCMe_2}\overline{CH_2}\overline{CHMeO}]_3$	1.47–1.67, m, 33H[(CH_3)CH_2C(CH_3) 4.85–5.10, m, 3H(OCH)	

However, it may be worthwhile to mention here that the crystal structure of the corresponding dithiocarbomate complexes, tris(N,N-diethydithiocarbamato) ruthenium(III), Ru[Et Et (dtc)]$_3$have been reported [21] and suggest an octahedral form with bidentate chelating behavior of the ligand.



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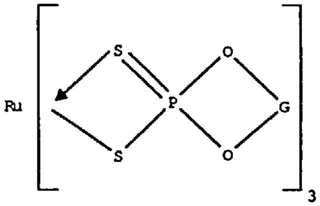

EXPERIMENTAL

Moisture was carefully excluded in the reactions carried out with ruthenium trichloride and dialkyl and alkylene dithiophosphoric acids. Solvents (benzene, chloroform, n-hexane and petroleum ether) were purified and dried before use. Glycols, were purified by distillation. Ru(III) chloride (Alfa) was used as such. Dialkyl and alkylene dithiophosphates were prepared by the method described in literature [22,23]. Sulfur was estimated gravimetrically as barium sulfate [23] and phosphorus estimated as ammonium magnesium phosphate hexahydrate. Molecular weights were determined cryoscopically in benzene. IR spectra were recorded as Nujol mulls on a Perkin-Elmer 2000 FT IR in the range 4000–200 cm^{-1}, using CsI cells. ^1H NMR spectra were recorded in $CDCl_3$ with a Bruker AC250 FT NMR spectrometer using TMS as internal standerd. Phosphorus-31 were also recorded using 85% H_3PO_4 as an external reference.

1 - Reaction of ruthenium trichloride with di-n-propyl dithophosphoric acid in a 1:3 molar ratio

A mixture of ruthenium trichloride ($RuCl_3$ 0.48g) and di-n-propyl dithiophosphoric acid (1.51g) in a 1:3 molar ratio in benzene was refluxed and stirred for (~6h), till the liberation of HCl ceased. The color of the mixture changed to brown. The solvent was removed under reduced pressure and the desired compound was washed several times by petroleum ether.

2 - Reaction of ruthenium trichloride with ammonium dialkyl and alkylene dithiophosphate in a 1:3 molar ratio

Ruthenium trichloride dissolved in dilute hydrochloric acid solution was added to a solution of the ammonium salt of dialkyl and alkylene dithiophosphate (in excess). The mixture was stirred at room temperature (21°C) for ~ 6h and refluxed for 1/2 h with constant stirring. A 20 cm^3 volume of dichloromethane was added and the mixture transferred to a separation funnel, then was shaken vigorously for 2 minutes and washed many times by distilled water. The organic phase was dried and washed several times with petroleum ether and again liquid dried in vacuum.

Pertinent experimental and analytical data for these experiments are summarized in (Table I).

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References

[1] V. K. Jain, V. S. Jakkal; J1. Organomet 515, 81 (1996).
[2] V. K. Jain, Transition Met. Chem., **18**, 312 (1993).
[3] Kenjiro Hayshi, Yoshiaki Sasaki, Shoji Tagashira; Analytical Sciences **3**, 55 (1987).
[4] M. A. Bennet, M. J. Bruce and T. W. Matheson in G. Wilkinson, F. G. A. Stone and E. W. Abel (eds), Comprehensive Organometallic Chemistry Vol. **4**, Pergamon Press, Oxford, 1982
[5] M. Schorder and T. A. Stephesen, G. Wilkinson, R. D. Gillard and J. A. Mc Cleverty (eds). Comprehensive Coordination Chemistry,Vol. **4**, Pergamon Press, Oxford –1987
[6] H. Bode and W. A rnswald, Fresenius, Z. Anal. Chem., **185**, 179 (1962).
[7] R. C. Peurson, J. Am. Chem. Soc., **85**, 3533 (1963).
[8] H. H. Farmer, B. W. Malone and H. F. Tompkins, Lubr. Eng. **23**, 57 (1967).
[9] L. S. Kharchenko, G. G. Kupko, G. M. Rykhlevskjj and Yu. t. t. Tordash, Khim, Tekhnol. Topl. Masel, 1,46; Chem. Abstr, **81**,123954(1974).
[10] D. R. Baker, US Paten, 3919418, (1974); Chem. Abstr., **84**, 85644 (1976).
[11] US Patent, 3947481; Chem. Abstr, 46856; US Patent, 4012421; Chem. Abstr. Kubo H. Agr Biol, **29**, 42 (1965).
[12] J. S. Yadav, R. K. Mehrotra and G. Srivastava, Polyhedron, **6**, 1687 (1987).
[13] J. Cason, W. N. Baxter and De Acetis, J. Org. Chem., **74**, 247 (1959).
[14] R. A.Y. Jones and A.R. Katritzky, J. Chem. Soc. A, 4376 (1960).
[15] H. P. S. Chauhan, C. P. Bhasin, G. Srivastava and R. C. Mehrotra, Phosphorus and Sulfur, **15**, 99 (1983).
[16] C. P. Basin, G. Srivastava and R. C. Mehrotra, Inorg. Chim. Acta., **77**, L131 (1983).
[17] S. Kumar and N. K. Kaushik, Synth. React. Inorg. Met-Org. Chem., **12**, 159 (1982)
[18] R. Ratanani, G. Srivastava and R. C. Mehrotra, Inorg. Chim. Acta., **161**, 253 (1989).
[19] J. S. Yadav, R. K. Mehrotra and G. Srivastava, Inorg. Chim. Acta., **162**, 227 (1989).
[20] C. Glidewell, Inorg. Chim. Acta., **25**,159 (1987).
[21] L.H.Pignolet, Inorg. Chem. **13**, 2051 (1974).
[22] R. J. Rao, G. Srivastava and R. C. Mehrotra, Inorg. Chim. Acta., **111**, 163 (1986).
[23] B. P. Singh, G. Srivastava and R. C. Mehrotra, J. Organomet. Chem., **171**, 35 (1979).