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Platinum(II) *O,O*-Alkylene Dithiophosphates and their Adducts

C. P. BHASIN, G. SRIVASTAVA and R. C. MEHROTRA

Department of Chemistry, University of Rajasthan, Jaipur-302004, India

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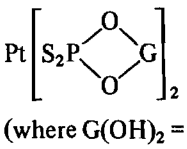
Abstract

O,O-Alkylene dithiophosphate derivatives of the general formula



(where $G(OH)_2$ = 2,3-dimethylbutane-2,3-diol; butane-2,3-diol; 2-methylpentane-2,4-diol) have been synthesized by treatment of potassium chloroplatinate(II) with ammonium alkylene dithiophosphates in 1:2 molar ratios. IR, NMR (^1H and ^{31}P) and electronic spectra along with magnetic data indicate a four-coordinated planar geometry for these derivatives similar to that reported for analogous dialkyl dithiophosphates of platinum(II). With ligands like triphenyl-phosphine/-arsine, the above derivatives form coloured (yellow to brown) 1:1 solid adducts which are soluble in halocarbons ($CHCl_3$ and CH_2Cl_2).

Introduction

In contrast to considerable published work on transition metal complexes of dialkyl dithiophosphoric acids [1] including those of palladium and platinum [2–4], the ligating properties of cyclic alkylene dithiophosphoric acids towards metallic and organometallic species have been little explored [5–8]. Our continuing interest in transition metal complexes of cyclic alkylene dithiophosphoric acids [9–11] led us to investigate the synthesis and characterization of platinum(II) alkylene dithiophosphates and their adducts with ligands containing group V donor atoms. The structural features of these derivatives have been discussed with the help of IR NMR (^1H and ^{31}P), electronic spectral and magnetic susceptibility measurements.

Experimental

Reaction of 2,3-Butylene Dithiophosphoric Acid with Potassium Tetrachloroplatinate(II)

Bis(2,3-butylene dithiophosphato)platinum(II) was obtained as a brown precipitate by heating a mixture of potassium chloroplatinate (0.363 g, 0.874 mmol in ~10 ml water) with 2,3-butylenedithiophosphoric acid (0.362 g, 1.966 mmol in ~10 ml ethanol) to boiling. The product was crystallised from dichloromethane/acetone mixture.

Reaction of Ammonium Tetramethylethylene Dithiophosphate with Potassium Tetrachloroplatinate(II)

Potassium tetrachloroplatinate (0.242 g, 0.583 mmol in ~15 ml water) was mixed with ammonium tetramethylethylene dithiophosphate (0.348 g, 1.51 mmol in ~15 ml water) and the solution was heated to boiling. A yellow precipitate, which separated out, was crystallised from dichloromethane/acetone mixture.

Relevant data for the similar synthesis of other compounds are given in Table I.

Reaction of Bis(tetramethylethylene Dithiophosphato)platinum(II) with Triphenylphosphine in 1:1 Molar Ratio

Triphenylphosphine (0.065 g, 0.248 mmol) dissolved in dichloromethane was added slowly to bis(tetramethylethylenedithiophosphato)platinum(II) (0.141 g, 0.228 mmol) dissolved in hot dichloromethane. On addition of triphenylphosphine, the yellow colour of the solution became lighter. After addition of 10–15 ml acetone the mixture was kept at 0 °C. Light yellow crystals separated out.

The triphenylarsine adduct of bis(tetramethylethylenedithiophosphato)platinum(II) was prepared by a similar method.

IR spectra were recorded as KBr pellets in the range 4000–200 cm^{-1}. ^1H NMR spectra were recorded in $CDCl_3$ on an X-L-100 A spectrometer, using TMS as an internal standard. ^{31}P NMR spectra were recorded in $CDCl_3$ on a Bruker 500 MHz spectrometer, using 85% H_3PO_4 as an external standard. Electronic spectra were recorded in $CHCl_3$ with an S.P. 8-100 UV–Vis Pye spectrophotometer.

Results and Discussion

Potassium tetrachloroplatinate(II) reacts readily with ammonium *O,O*-alkylene dithiophosphates in 1:2 molar ratio to afford yellow to brown complexes of the type

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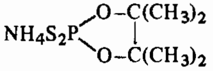
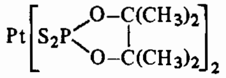
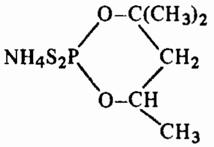
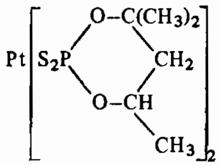
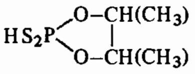
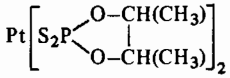
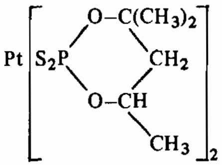
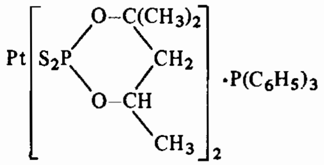
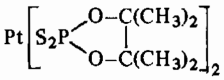
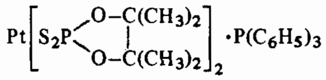
TABLE I. Reactions of Potassium Tetrachloroplatinate(II) with *O,O*-alkylene Dithiophosphates/Phosphoric Acid and Dialkyl Dithiophosphates

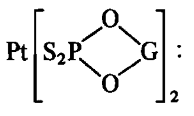
Reactants (g (mmol))		Product (g, %)	Colour (Melting point, °C)	PMR Spectral Shifts[a] (δ)
A	B			
K_2PtCl_4 0.242(0.583)	 0.348(1.518)	 0.305, 85	light yellow (260, decomp.)	1.5(s)
K_2PtCl_4 0.432(1.04)	 0.658(2.86)	 0.598, 95	light brown (240, decomp.)	1.4–2.2(m), 22H(CH_2, CH_3) 4.65–5.05(m), 2H(H)
K_2PtCl_4 0.363(0.874)	 0.362(1.966)	 0.423, 87	dark brown (245, decomp.)	1.45–1.55(d), 12H(CH_3) 4.2–4.6(m), 4H(CH)
K_2PtCl_4 0.372(0.896)	$NaS_2P(OC_2H_5)_2$ 0.466(2.24)	$Pt[S_2P(OC_2H_5)_2]_2$ 0.418, 83	yellow (122)	1.4(t), 6H(CH_3) 4.15–4.50(m), 2H(CH)
K_2PtCl_4 0.328(0.790)	$NH_4S_2P(OC_3H_7^i)_2$ 0.458(1.98)	$Pt[S_2P(OC_3H_7^i)_2]_2$ 0.383, 80	shining yellow (140)	1.35–1.55(d), 12H(CH_3) 4.8–5.2(m), 2H(CH)
$P(C_6H_5)_3$ 0.113(0.431)	 0.234(0.379)	 0.217, 66	yellowish (251, decomp.)	
$P(C_6H_5)_3$ 0.065(0.248)	 0.141(0.228)	 0.201, 98	light yellow (268, decomp.)	1.4(s), 24H(CH_3) 1.5(s) 7.4–7.9, 15H(C_6H_5)

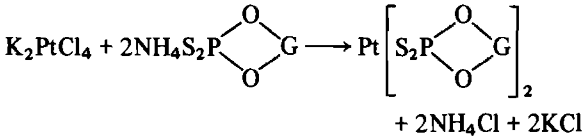
(continued)

TABLE I. (continued)

Reactants (g (mmol))		Product (g, %)	Colour (Melting point, °C)	PMR Spectral Shifts[a] (δ)
A	B			
$As(C_6H_5)_3$ 0.378(1.23)	$Pt\left[S_2P\begin{matrix}O-C(CH_3)_2\\ \mid\\ O-C(CH_3)_2\end{matrix}\right]_2$ 0.117(0.189)	$Pt\left[S_2P\begin{matrix}O-C(CH_3)_2\\ \mid\\ O-C(CH_3)_2\end{matrix}\right]_2 \cdot As(C_6H_5)_3$ 0.135, 77	yellowish white (273, decomp.)	1.5(s), 24H(CH_3) 7.35–7.80(m), 15H(C_6H_5)

[a] d, doublet; m, multiplet; s, singlet.





(where G = $-(CH_3)_2C\cdot C(CH_3)_2-$; $-CH(CH_3)(CH_3)CH-$; $-(CH_3)_2C\cdot CH_2\cdot CH(CH_3)-$)

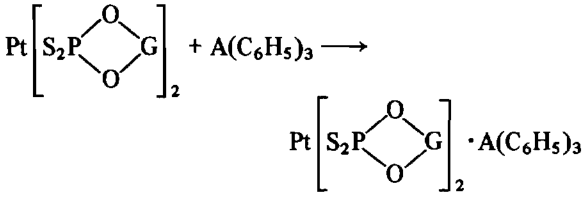
A slight excess of the ligand is taken to avoid the formation of bridged complexes.

The above compounds are soluble in halocarbons and can be recrystallised from a dichloromethane/acetone mixture.

Two representative examples of dialkyl dithiophosphates have also been prepared to compare the NMR spectral (^{31}P and ^1H) and magnetic properties with those of the cyclic derivatives. These have been obtained by treatment of potassium chloroplatinate(II) with $MS_2P(OR)_2$ ($M = Na$ or NH_4; $R = C_2H_5$ or $C_3H_7{}^i$)

$$2MS_2P(OR)_2 + K_2PtCl_4 \longrightarrow Pt[S_2P(OR)_2]_2 + 2MCl + 2KCl$$

The 1:1 adducts of bis(alkylene dithiophosphates) of platinum(II) with triphenyl-phosphine/-arsine have been readily obtained by heating a mixture of the two components in dichloromethane and then cooling to 0 °C.

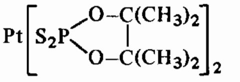
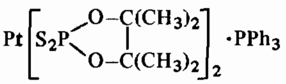
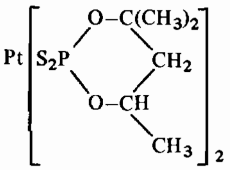
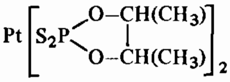


(A = P or As)

IR Spectra (Table II)

IR spectra of the platinum bis(alkylene dithiophosphates) show two bands in the regions 1140–975 and 900–790 cm^{-1} which may be assigned to (P)–O–C and P–O–(C) stretching modes [12], while the strong bands in the region 930–925 cm^{-1} are due to dioxaphospholane and dioxaphosphorinane ring vibrations [13, 14]. A strong band due to ν(P=S) observed in the region 710–670 cm^{-1} in the spectra of *O,O*-alkylene dithiophosphoric acids and their ammonium salts is shifted to lower frequency by ~50 cm^{-1} in the corresponding platinum derivatives. The bands observed in the region 595–495 cm^{-1} are attributed to P–S symmetric and asymmetric vibrations. The Pt–S vibrations appear in the region 370–310 cm^{-1}.

TABLE II. IR Spectral Data of Pt(II) *O,O*-Alkylene Dithiophosphates[a]

Compound	(P)–O–C	P–O–(C)	Ring vibrations	P=S	P–S	Pt–S
	1140m	875m	930s	645s	570w 495w	
	1040m	900s	930s	700s	540s	370w 325w
	1140m	870m	925s	640m	595w	360w 310w
	1035m	865m	930s	640s	560w	360w 310w
$Pt[S_2P(OC_2H_5)_2]_2$	1020s	815s		630s	530m	360s 310s
$Pt[S_2P(OC_3H_7^i)_2]_2$	975s	790		630s	535m	365w 315s

[a] b, broad; m, medium; s, strong; w, weak.

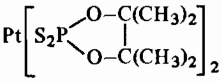
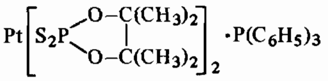
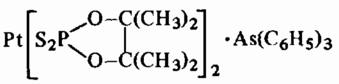
NMR Spectra

The ^1H NMR spectra show the characteristic resonances of the corresponding alkyl or alkylene as well as those of the aryl protons. The sharp singlet present at 3.7 ppm characteristic of the S–H proton in 2,3-butylene dithiophosphoric acid is absent in the ^1H NMR spectrum of the corresponding platinum(II) bis(2,3-butylene dithiophosphate) indicating the formation of a Pt–S bond. Tetramethylethylenedithiophosphoric acid and its metal complexes generally give only a singlet for all the methyl protons. In the case of bis(tetramethylethylene dithiophosphato)platinum(II) and its triphenylarsine adduct, only a singlet is observed at δ 1.5 ppm. However, in the corresponding triphenylphosphine adduct the methyl protons give two singlets of equal intensity.

The complex multiplet due to the protons of triphenyl-phosphine/-arsine moieties in the 1:1 adducts appear in the region δ 7.4–7.9 ppm.

The ^{31}P spectrum of bis(tetramethylethylene dithiophosphato)platinum shows a triplet at δ 111.17 ppm (Table III). The triplet is due to the coupling between ^{31}P and ^{195}Pt (^2J = 485.7 Hz). The spectrum of triphenylarsine adduct of this complex is quite similar to the above, with the ^{31}P triplet being centered at δ 111.95 ppm and $^2J(^{31}P–^{195}Pt)$ being 495 Hz. However, the corresponding triphenylphosphine adduct shows an interesting variation. In this case, the spectrum shows a singlet at 109.63 ppm for the dithiophosphate phosphorus and a triplet centered at δ 13.61 ppm with $^1J(^{31}P–^{195}Pt)$ = 3840.6 Hz, for the triphenylphosphine phosphorus. It seems that in this case, the presence of a strong one-bond coupling of platinum with triphenylphosphine phosphorus suppresses the two-bond coupling with dithiophosphate phosphorus.

TABLE III. ^{31}P Spectral Data of Pt(II) *O,O*-Alkylene Dithiophosphates

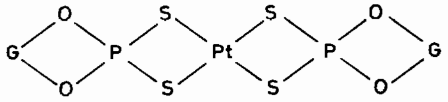
Compound	Chemical shift (δ)
$Pt[S_2P(OC_3H_7^i)_2]_2$	97.22
	111.17
	109.63, 13.61
	111.95

Electronic Spectral and Magnetic Measurements

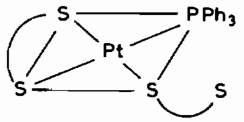
Electronic spectra of one representative compound bis(hexylenedithiophosphato)platinum(II) shows three transitions at 420, 288 and 246 nm. The similarity of these transitions to that reported earlier for dialkyl dithiophosphates of platinum(II) [15] indicates the four-coordination of the central platinum atom.

Magnetic measurements of bis(alkylenedithiophosphato)platinum(II) and their adducts show a diamagnetic nature of these complexes.

The above spectral and magnetic studies indicate the following square-planar structure for platinum(II) bis(*O*,*O*-alkylene dithiophosphates).



The geometry of 1:1 adducts can only be established either by X-ray diffraction (in the solid state) or low temperature ^{31}P NMR (in solution). However, the following geometry can be suggested tentatively on the basis of studies on analogous triphenylphosphine adducts of dialkyl dithiophosphato)platinum(II) [4].



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