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Synthesis and characterization of liquid platinum compounds

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Abstract

Liquid platinum complexes were obtained with a ligand with alkyl chains that attach to the coordination plane perpendicularly and herewith render a close packing of the molecules difficult for certain chain lengths. Bis(O,O'-dialkyldithiophosphato)platinum(II) complexes, Pt(C_x dtp)₂, where the alkyl chains are methyl (x = 1), ethyl (x = 2), propyl (x = 3), butyl (x = 4), pentyl (x = 5), hexyl (x = 6), heptyl (x = 7), dodecyl (x = 12), and octadecyl (x = 18), were investigated. The platinum compounds were synthesized via two routes: reaction of tetrachloroplatinate(II) with ammonium-O,O'-dialkyldithiophosphates or oxidative addition of (O,O'-dialkylthiophosphoryl)disulfides to tris(styrene)platinum(0). The melting temperatures as a function of the alkyl chain length show a minimum for the complex with pentyl groups. The complexes with pentyl and hexyl groups are liquid at room temperature, and the complexes with butyl and heptyl groups melt only slightly above room temperature. Depending on the complex, the low melting temperatures are induced by an unfavorable packing of the molecules in the solid state, reflected in a low melting enthalpy, or melting entropy. The molecular weights of the liquid complexes are between 700 and 800 and, therefore, extraordinarily high for liquid metal compounds. Depending on the alkyl groups, the complexes decompose at 172–241°C. Crystals of bis(O,O'-diethyldithiophosphato)platinum(II), Pt(C_2 dtp)₂, are monoclinic, space group $P2_1/n$, a = 8.90, b = 8.70, c = 12.45 Å, $\alpha = \gamma = 90^\circ$, $\beta = 100.89^\circ$, and Z = 4. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Platinum complexes; Dithiophosphato complexes; Liquid complexes

1. Introduction

Transition metal compounds are usually solid under ambient conditions. Liquid transition metal complexes are also known and they find interest, e.g. in the preparation of thin layers by chemical vapor deposition (CVD) [1] or of polymer-inorganic nanocomposites [2]. Examples of liquid transition metal compounds are TiCl₄, VCl₄, SnCl₄, VOCl₃, CrO₂Cl₂, ReO₃Cl, MoF₆, ReF₆, H₂Fe(CO)₄, Fe(CO)₅, Ni(CO)₄, Ru(CO)₅, Os(CO)₅, Zn(CH₃)₂, Cd(CH₃)₂, Hg(CH₃)₂, Zn(CH₂-CH₃)₂, Cd(CH₂CH₃)₂, Hg(CH₂CH₃)₂, Ti(N(CH₂CH₃)₂)₄, Ti-(N(CH₂CH₃)₂)₄, Zr(N(CH₂CH₃)₂)₄, Nb(OCH₂CH₂CH₂-CH=CH₂)₅, Ta(OCH₂CH₂CH₂CH=CH₂)₅, and alkylsubstituted ferrocenes [1,3–6]. To our knowledge, liquid complexes of platinum have not been described to date. Here, we present a study of liquid platinum complexes of the type bis(O,O'-dialkyldithiophos-phato)platinum(II), where the alkyl chains are positioned perpendicularly to the coordination plane. The intermolecular interactions in such complexes are dominated by van der Waals interactions, and hence, the resulting melting temperatures might be governed by critical balances between steric effects (crystal packing) in the solid structure and the melting entropy, both depending on the alkyl chain lengths.

In the following, we describe liquid platinum complexes with O,O'-dialkyldithiophosphate ligands. Dithiophosphoric acids and their derivatives have been extensively studied since the beginning of this century [7–9]. O,O'-Dialkyldithiophosphoric acids have been employed as flotation reagents for the recovery of metals from their solutions [10,11] and O,O'-dialkyldithiophosphates have been used as pesticides and for chemical warfare [12–14], while metal complexes with O,O'-dialkyldithiophosphates have found application as antioxidants, oil-additives [15–19], coloring and bioactive agents [15–21]. Finally, O,O'-dialkyldithio-

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phosphate complexes have been reported for almost each of the naturally occurring metals [22-31]. In the case of platinum(II), only the bis(O,O'-diethyldithiophosphate) complex has been well characterized [29], although X-ray crystal data have not been presented. To our knowledge, the possibility of preparing liquid metal complexes with bis(O,O'-dialkyldithiophosphate) as ligands has not yet been recognized.

2. Experimental

2.1. General

Phosphorus pentasulfide and the different alcohols were bought from Fluka (Buchs, Switzerland). Potassium tetrachloroplatinate(II) was either prepared according to the literature [32,33] or purchased, as was platinum(II) dichloride, from Johnson–Matthey (Zurich, Switzerland).

Tris(styrene)platinum(0) was synthesized and purified in situ by slightly modifying a procedure from the literature [34,35]. *cis*-Dichlorobis(styrene)platinum(II)

Table 1

Crystal data and structure refinement for	$Pt(C_2dtp)$	2
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Empirical formula	$C_8H_{20}O_4P_2PtS_4$
Formula weight	282.76
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_{1}/n$
Unit cell dimensions	
a (Å)	8.899(6)
$b(\mathbf{A})$	8.695(5)
$c(\dot{A})$	12.454(10)
α (°)	90
β(°)	100.89
γ (°)	90
Volume (Å ³)	946.3(11)
Ζ	4
D_{calc} (g cm ⁻³)	1.985
Absorption coefficient (mm^{-1})	8.028
F(000)	544
Crystal size (mm)	$0.5 \times 0.1 \times 0.1$
θ Range for data collection (°)	2.60-22.02
Index ranges	$-8 \le h \le 9, \ 0 \le k \le 8,$
-	$0 \le l \le 11$
Reflections collected	890
Independent reflections	890 $[R_{int} = 0.0000]$
Absorption correction	integration
Max./min. transmission	0.534, 0.413
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	890/0/89
Goodness-of-fit on F^2	0.966
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0339, wR_2 = 0.0777$
R indices (all data)	$R_1 = 0.0396, wR_2 = 0.0793$
Extinction coefficient	0.028(2)
Largest difference peak and hole (e $Å^{-3}$)	1.363 and -1.642

(3.00 g, 6.3 mmol) in distilled styrene (120 ml) was treated with triphenylsilane (3.29 g, 12.6 mmol). The solution was stirred for 30 min. Thereafter a solution of concentrated ammonia (30 ml) and water (250 ml) was added and the solution was stirred vigorously for 90 min. The two phases were separated in a separation funnel. The organic phase was shaken with 250 ml water and again separated from the aqueous phase. The organic phase was percolated through a column of 4 cm diameter filled with 15 cm Alox basic (activity I). After the solution had passed the Alox, the column was washed with distilled styrene (150 ml), and this eluate was combined with the first fraction, yielding a solution of tris(styrene)platinum(0) in styrene. To analyze the platinum content, 5 g of the solution were evaporated and the black residue was dissolved in aqua regia (10 ml). The orange solution was diluted with 0.1 M hydrochloric acid (700 g) and analyzed with atomic absorption spectroscopy. The platinum mass concentrations in the styrene solutions fell in the range of 0.47-0.58%.

Elemental analyses were performed by the Laboratorium für Organische Chemie of ETH Zürich. NMR spectra were obtained on Bruker dpx 200 and Bruker dpx 300 spectrometers (300.1, 81.0 and 64.5 MHz for ¹H, ³¹P and ¹⁹⁵Pt NMR spectra, respectively). For ¹H NMR spectra, tetramethylsilane (TMS) was used as internal standard and for ³¹P and ¹⁹⁵Pt NMR spectra, H₃PO₄ 85% and Na₂PtCl₆, respectively, as external standard. Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) were performed on a Perkin–Elmer Series 7 apparatus. UV–Vis spectra were measured on a Perkin–Elmer Lambda 900 device.

2.2. X-ray crystallography

Suitable crystals for X-ray analysis were grown by diffusion of hexane into a solution of bis(diethyldithiophosphato)platinum(II), $Pt(C_2dtp)_2$, in dichloromethane at room temperature (r.t.). Crystal data and details of the structure refinement of $Pt(C_2dtp)_2$ are summarized in Table 1. The data were collected on a Syntex P21 four circles diffractometer (graphitemonochromated Mo K α radiation) at r.t. using the ω/θ scan mode. Absorption correction was applied to the data using integration. Transmission factors were 0.413 (min.) and 0.534 (max.). The structure was solved using the program SHELXS-86 [36] and refined by full-matrix least-squares on F^2 using SHELXL-93 [37]. The H atoms were included in calculated positions and treated as 'riding atoms'.

2.3. Preparation of ammonium (O,O')-dialkyldithiophosphates

Phosphorus pentasulfide (4.44 g, 20 mmol) and the respective alcohols (70 mmol) were stirred at 70°C for 3 h.

The suspensions were filtered and the residues were washed with dichloromethane (50 ml). Greenish oils (white solid in the case of the substance with octadecyl chains) were isolated after removal of the solvent, and it is assumed that these substances predominantly consist of the (O,O')-dialkyldithiophosphoric acids **1**. They were diluted with hexane (50 ml), and anhydrous ammo-

nia was subsequently bubbled through the solution for 5 min under stirring. The white ammonium (O,O')-dialkyldithiophosphates (2) precipitated and were filtered, washed with hexane $(2 \times 50 \text{ ml})$ and dried. The overall yields of 2 were ca. 50%, consistent with those of similar reactions reported by Wystrach et al. [38]. Elemental analyses and NMR data are collected in Tables 2 and 3.

Table 2 Elemental analysis of ammonium (O, O')-dialkyldithiophosphates

Alkyl group	С		Н		0		S	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Methyl	13.71	13.65	5.75	5.65	18.26	18.20	36.60	36.54
Ethyl	23.64	23.64	6.94	6.77	15.74	15.84	31.55	31.66
Propyl	31.16	31.07	7.84	7.71	13.83	14.09	27.72	27.81
Butyl	37.05	36.95	8.55	8.37	12.34	12.36	24.72	24.45
Pentyl	41.79	41.73	9.12	9.13	11.13	11.32	22.31	22.28
Hexyl	45.69	45.75	9.58	9.56	10.14	10.35	20.33	20.53
Heptyl	48.95	48.76	9.98	9.81	9.31	9.08	18.67	18.71
Dodecyl	59.58	59.43	11.25	11.03	6.61	6.88	13.25	13.02
Octadecyl	66.31	66.12	12.06	12.13	4.91	4.90	9.83	9.62

Table 3

NMR chemical shifts (ppm) and coupling constants, J (Hz), in DMSO-d⁶ of ammonium (O,O')-dialkyldithiophosphates ^a

Alkyl group	¹ H ^b					³¹ P
	α-CH ₂	β-CH ₂	-CH2-	-CH ₃	$\mathrm{NH_4^+}$	
Methyl				3.38	7.12	118.7
				6H, d	4H, s	S
				J = 14.3		
Ethyl	3.79			1.12	7.11	114.4
	4H, $d \times q$			6H, t	4H, s	S
	J = 9.0, 7.1			J = 7.1		
Butyl	3.69	1.52		0.85	7.11	114.7
	4H, $d \times t$	4H, m		6H, t	4H, s	S
	$J = 8.5, \ 6.8$			J = 7.4		
Propyl	3.73	1.49	1.31	0.88	7.11	114.7 s
	4H, $d \times t$	4H, m	4H, m	6H, t	4H, s	
	$J = 8.4, \ 6.5$			J = 7.2		
Pentyl	3.72	1.50	1.28	0.87	7.13	114.8
	4H, $d \times t$	4H, m	8H, m	6H, t	4H, s	S
	$J = 8.4, \ 6.6$			J = 6.7		
Hexyl	3.72	1.49	1.27	0.86	7.09	114.7
	4H, $d \times t$	4H, m	12H, m	6H, t	4H, s	S
	$J = 8.4, \ 6.6$			J = 6.6		
Heptyl	3.72	1.49	1.26	0.86	7.09	114.7
	4H, $d \times t$	4H, m	16H, m	6H, t	4H, s	S
	$J = 8.4, \ 6.6$			J = 6.5		
Dodecyl	3.70	1.47	1.23	0.84	7.07	114.6
	4H, $d \times t$	4H, m	36H, m	6H, t	4H, s	S
	$J = 8.5, \ 6.6$			J = 6.4		
Octadecyl	3.69	1.47	1.22	0.84	7.07	114.6
-	4H, $d \times t$	4H, m	60H, m	6H, t	4H, s	S
	J = 8.5, 6.5			J = 6.4		

^a s, singlet; d, doublet; t, triplet; m, multiplet.

^b J refers to $J(^{1}H-^{1}H)$.

2.4. Preparation of bis(O,O'-dialkylthiophosphoryl)disulfides

O,O'-dialkyldithiophosphoric acids **1** were prepared as described above and diluted with water (100 ml). The pH value was adjusted with 1 M KOH to 8, and KNO₂ (3.86 g, 40 mmol) was added to the solution to which 95% sulfuric acid (4.96 g, 40 mmol) was slowly admixed. The solutions were stirred at 50°C for 2 h. The bis(O,O'-dialkylthiophosphoryl)disulfides (**3**) were extracted with CH₂Cl₂ (3 × 100 ml) and dried over MgSO₄. The solvent was then removed, yielding greenish oils (white solid in the case of the substance with octadecyl chains), which were purified by flash chromatography (SiO₂/CH₂Cl₂). The global yields of **3** were 50%. Elemental analyses and NMR data are collected in Tables 4 and 5, respectively.

2.5. Preparation of bis(O,O'-dialkyldithiophosphato)platinum(II)

(a) Potassium tetrachloroplatinate(II) (415 mg, 1 mmol) and the respective ammonium (O,O')-dialkyl-dithiophosphates (2) (3 mmol) were stirred in water (50 ml) at 60°C for 1 h. The water was removed and the

Table 4 Elemental analysis of bis(*O*,*O*'-dialkyldithiophosphoryl)disulfides

products were purified by flash chromatography (SiO_2/CH_2Cl_2) and dried. Yields 90–95%. The elemental analyses and NMR data of the complexes are presented in Tables 6 and 7, respectively.

(b) The respective bis(O,O'-diethyldithiophosphoryl)disulfides (**3**) (190 mg, 0.51 mmol) were added to a solution of tris(styrene)platinum(0) [35] (2% Pt in styrene, 5 g, 0.51 mmol) and stirred for 15 min. The styrene was removed under reduced pressure at r.t. and the solid residue was purified by chromatography (SiO₂, 1:1 CH₂Cl₂/hexane). The yields of the bis(O,O'-dialkyl-dithiophosphate)platinum(II) complexes (**4**) were 85–90%.

3. Results and discussion

3.1. Syntheses and chemical analyses

The preparation of metal O,O'-dialkyldithiophosphate complexes usually involves the reaction of metal halides or acetates with dithiophosphoric acids or their salts [22,23]. We have prepared the bis(O,O'-dialkyldithiophosphato)platinum(II) complexes **4** by two different reaction paths (Fig. 1). The first route follows

Alkyl group	С		Н	Н		0		S	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
Ethyl	25.94	25.66	5.44	5.38	17.28	17.06	34.62	34.40	
Hexyl	48.46	48.55	8.81	8.52	10.76	10.49	21.56	21.31	
Dodecyl	61.89	61.69	10.82	10.88	6.87	7.06	13.77	14.06	
Octadecyl	68.19	67.97	11.76	11.59	5.05	5.04	10.11	10.00	

Table 5

NMR chemical shifts (ppm) and coupling constants, J (Hz), in CDCl₃ of bis(O,O'-dialkyldithiophosphoryl)disulfides ^a

Alkyl group	¹ H ^b						
	α-CH ₂	β-CH ₂	-CH2-	-CH ₃			
Methyl	4.24			1.41	86.0		
	8H, m			12H, $d \times t$ J = 7.1, 0.8	S		
Hexyl	4.16	1.74	1.34	0.90	86.7		
·	8H, m	8H, m	24H, m	12H, t J = 6.5	S		
Dodecyl	4.16	1.74	1.27	0.88	86.7		
-	8H, m	8H, m	72H, m	12H, t J = 6.4	S		
Octadecyl	4.16	1.74	1.26	0.88	86.7		
	8H, m	8H, m	120H, m	12H, t $J = 6.4$	s		

^a s, singlet; d, doublet; t, triplet; m, multiplet.

^b J refers to $J(^{1}H-^{1}H)$.

Table 6 Elemental analysis of bis(O,O'-dialkyldithiophosphate)platinum(II) complexes

Alkyl group	С		Н	Н		0		S	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
Methyl	9.43	9.62	2.37	2.13	12.56	12.77	25.17	25.23	
Ethyl	16.99	17.11	3.56	3.41	11.32	11.51	22.68	22.60	
Propyl	23.19	23.21	4.54	4.41	10.30	10.26	20.63	20.64	
Butyl	28.36	28.20	5.35	5.23	9.44	9.64	18.92	19.13	
Pentyl	32.73	32.81	6.04	6.07	8.72	8.91	17.48	17.39	
Hexyl	36.49	36.69	6.63	6.58	8.10	8.29	16.24	16.04	
Heptyl	39.75	40.01	7.15	7.02	7.56	7.60	15.16	14.96	
Dodecyl	51.17	51.18	8.95	8.80	5.68	5.83	11.38	11.24	
Octadecyl	59.10	59.69	10.02	9.85	4.37	4.38	8.76	8.72	

Table 7

Chemical shift values (ppm) and coupling constants, J (Hz), in CDCl₃ for bis(O, O'-dialkyldithiophosphate)platinum(II) complexes ^a

	¹ H ^b				³¹ P ^c	¹⁹⁵ Pt ^c
	α-CH ₂	β-CH ₂	CH ₂	-CH ₃		
$Pt(C_1dtp)_2$ (4.1)	3.91			3.91	108.0	-4005
	8H, d			12H, d	d	t
	J = 14.9			J = 14.9	J = 449	J = 449
$Pt(C_2dtp)_2$ (4.2)	4.31			1.42	102.5	-3987
	8H, $d \times q$			12H, t	d	t
	J = 9.4, 7.1			J = 7.1	J = 445	J = 445
$Pt(C_3dtp)_2$ (4.3)	4.19	1.79		0.99	102.2	-3992
	8H, $d \times t$	8H, m		12H, t	d	t
	J = 8.9, 6.6			J = 7.4	J = 445	J = 445
$Pt(C_4 dtp)_2$ (4.4)	4.23	1.74	1.43	0.95	102.7	- 3991
	8H, $d \times t$	8H, m	8H, m	12H, t	d	t
	J = 8.8, 6.6			J = 7.3	J = 444	J = 444
$Pt(C_5 dtp)_2$ (4.5)	4.22	1.76	1.25-1.45	0.92	102.7	- 3991
	8H, $d \times t$	8H, m	16H, m	12H, t	d	t
	$J = 8.8, \ 6.7$			J = 7.0	J = 444	J = 444
$Pt(C_6 dtp)_2$ (4.6)	4.22	1.75	1.28-1.45	0.90	102.1	- 3991
	8H, $d \times t$	8H, m	24H, m	12H, t	d	t
	J = 8.9, 6.7			J = 6.8	J = 444	J = 444
$Pt(C_7 dtp)_2$ (4.7)	4.21	1.75	1.28-1.42	0.89	101.9	- 3989
	8H, $d \times t$	8H, m	32H, m	12H, t	d	t
	J = 8.9, 6.7			J = 6.8	J = 444	J = 444
$Pt(C_{12}dtp)_{2}$ (4.12)	4.21	1.75	1.26-1.45	0.88	102.7	- 3991
12 1/2 /	8H, $d \times t$	8H, m	72H, m	12H, t	d	t
	J = 8.8, 6.7			J = 6.7	J = 444	J = 444
$Pt(C_{18}dtp)_2$ (4.18)	4.21	1.75	1.25-1.45	0.88	102.0	- 3991
	8H, $d \times t$	8H, m	120H, m	12H, t	d	t
	J = 8.7, 6.7	,	*	J = 6.7	J = 444	J = 444

^a s, singlet; d, doublet; t, triplet; m, multiplet.

^b J refers to $J(^{1}H-^{1}H)$.

^c J refers to $J(^{195}\text{Pt}-^{31}\text{P})$.

the common procedure for short-chain compounds [9,23,38], which we have modified for longer alkyl chains in order to avoid solubility and emulsion problems during the syntheses: an excess of phosphorus pentoxide reacts with primary alcohols to produce O,O'-dialkyldithiophosphoric acids 1. Since compounds 1 are slowly oxidized by atmospheric oxygen, no attempt was made to purify them; they were used as

crude products for the conversion into the ammonium O,O'-dialkyldithiophosphates (2) with anhydrous ammonia. The complexes 4 were prepared from 2 and potassium tetrachloroplatinate(II). The compounds 2 have to be present in excess in order to avoid the formation of dichloro-bridged complexes [27].

As an alternative reaction, bis(O,O'-dialkylthiophos-phoryl)disulfides (3) were first formed by oxidation of



Fig. 1. Reaction scheme for the preparation of $Pt(C_x dtp)_2$ complexes.



Fig. 2. UV–Vis spectrum of $Pt(C_6dtp)_2$ in dichloromethane. Also indicated in the Figure are the absorption maxima and extinction coefficients (in brackets, M^{-1} cm⁻¹).



Fig. 3. Molecular structure and selected bond lengths and bond angles of $Pt(C_2dtp)_2$. Hydrogen atoms are omitted for clarity.

1. This conversion can be induced by irradiation with visible light [39] or oxidative agents [21,40]. We selected the method involving nitrous acid [40] and modified the procedure in order to facilitate the handling of the long-chain products. As a result, higher yields than those reported in the literature were obtained. The compounds **3** were converted into the platinum complexes **4** by oxidative addition to tris(styrene)platinum(0). As can be expected, the sulfur–sulfur bond, which mimics the cysteine CSSC skeleton [41], is very sensitive towards reduction.

In the following, the individual bis(O,O'-dialkyldithiophosphato)platinum(II) complexes are designated as $Pt(C_x dtp)_2$, where x denotes the number of carbon atoms in the respective alkyl chains. Complexes with x = 1, 2, 3, 4, 5, 6, 7, 12, and 18 were prepared. Their elemental composition agrees with the expected values (Table 6). The purity of the substances is also manifested in ¹H, ³¹P, and ¹⁹⁵Pt NMR spectra. Chemical shifts and coupling constants are collected in Table 7. The spectra fully agree with the surmised structures. For example, the ¹H NMR spectra confirm the presence of the alkyl chains and the ¹⁹⁵Pt-³¹P couplings (J = 440-450 Hz) are visible in both the ³¹P and ¹⁹⁵Pt spectra. The ¹⁹⁵Pt spectra are characterized by a triplet at around -4000 ppm, proving that the platinum atoms are coordinated with two of the bidentate ligands, and the ³¹P spectrum shows the corresponding platinum satellites. The chemical shifts in the ³¹P spectra lie close together except that of $Pt(C_1dtp)_2$. The ¹⁹⁵Pt shifts are practically identical for the complexes with x > 1 and differ slightly but not relevantly for $Pt(C_1dtp)_2$. As the electronic structure around the platinum atoms is very similar in all complexes, all $Pt(C_x dtp)_2$ compounds exhibit virtually identical UV-Vis spectra and molar extinction coefficients. As an example, Fig. 2 shows the absorption spectrum of $Pt(C_6dtp)_2$. Despite the apparent simplicity of this spectrum, the interpretation is not easy due to contradictory explanations in the literature stemming from different energy level sequences in the molecular orbital scheme [25,42]. Due to their lone pair electrons, the $C_x dtp^$ ligands exert a strong nephelauxetic effect [24,27]. The character of the binding in complexes 4 is dominated by σ -type bonds, while π interactions are of minor importance [24,25,27].

Pt(C₂dtp)₂ was obtained as crystals suitable for examination with X-ray diffraction. Fig. 3 shows the elucidated structure, Table 8 lists selected bond lengths and angles, and Table 1 contains the crystal data for Pt(C₂dtp)₂. The molecule consists of a square-planar platinum(II) complex with a crystallographic center of inversion and a non-crystallographic C_2 axis. The phosphorus atoms are out of the plane defined by the four Pt–S bonds. The Pt–S distances (2.33 Å) are longer than the Ni–S distances (2.23 Å) in Ni(C₂dtp)₂ [43,44], Table 8

Bond lengths (Å) and angles (°) for $Pt(C_2dtp)_2$ (atomic coordinates will be deposited in the Cambridge Crystallographic Data Center)^a

Bond lengths	
Pt−S(2) # 1	2.325(3)
Pt-S(2)	2.325(3)
Pt−S (1) # 1	2.332(4)
Pt-S(1)	2.332(4)
S(2)-P	1.998(4)
P–O(1)	1.558(7)
P-O(2)	1.564(7)
P-S(1)	2.007(4)
O(1)-C(1)	1.462(14)
O(2)–C(3)	1.444(13)
C(3)–C(4)	1.33(2)
C(2)–C(1)	1.42(2)
Bond angles	
S(2) # 1-Pt-S(2)	180.0
S(2) # 1-Pt-S(1) # 1	84.19(10)
$S(2)-Pt-S(1) \neq 1$	95.81(10)
S(2) # 1-Pt-S(1)	95.81(10)
S(2)–Pt–S(1)	84.19(10)
S(1) # 1 - Pt - S(1)	180.0
P-S(2)-Pt	86.89(14)
O(1)-P-O(2)	96.8(4)
O(1)–P–S(2)	114.3(3)
O(2)–P–S(2)	114.8(4)
O(1)–P–S(1)	115.1(3)
O(2)–P–S(1)	114.1(4)
S(2)–P–S(1)	102.4(2)
C(1)-O(1)-P	121.6(7)
C(3)–O(2)–P	122.4(7)
C(4)-C(3)-O(2)	112.8(13)
C(2)-C(1)-O(1)	110.4(10)
P–S(1)–Pt	86.51(14)

^a Symmetry transformations used to generate equivalent atoms: # 1 - x, -y, -z.

as expected since platinum(II) has a larger diameter than the nickel(II) cation [3]. Otherwise, the P-S and P-O bond lengths (2.00 and 1.56 Å, respectively) and the S-P-S, O-P-O and S-P-O bond angles (102.4, 96.8 and 114.8°, respectively) are similar to those in related compounds [43-47]. Fig. 4 shows the packing of the $Pt(C_2dtp)_2$ molecules in the unit cell. The shortest intermolecular Pt–Pt distance is 8.19 Å, which excludes any metal-metal interaction. The tetrahedral arrangement around the phosphorus atoms hinders any overlap of the metal orbitals and prevents a parallel stacking of the planar units around the platinum atoms. As a consequence, the structure and the intermolecular interactions in the solid state and, therefore, the melting temperatures are expected to be influenced significantly by the packing of the alkyl chains.

3.2. Thermal analyses

Melting temperatures were measured with DSC after careful purification of the products. The phase transitions were also observed with optical microscopy at the respective temperatures. The melting process is accompanied by a vanishing of birefringence. The melting process is reversible in DSC and optical microscopy except for $Pt(C_1dtp)_2$, which obviously melts under decomposition at 171°C (as a result, the enthalpy change at 171°C is negative $(-174 \text{ kJ mol}^{-1})$ in the calorimetric measurements, and the mass of $Pt(C_1dtp)_2$ in TGA decreases at 172°C). In the other cases, however, decomposition occurs at least 68°C above the melting temperature of the respective complexes (cf. Figs. 5 and 6). No mass loss was observed below 190°C, i.e. the substances do not contain significant amounts of low-boiling compounds, e.g. solvents. As an example, Fig. 7 shows the mass loss of $Pt(C_6dtp)_2$, in a range 50-800°C. Mass is lost in two steps. The loss at 225°C corresponds to the mass of the alkyl groups, suggesting that predominantly bis(dithio-meta-phosphato)platinum(II) is left. The mass remaining after the second step at 650°C corresponds to the mass of platinum(II) sulfide which might be finally left. The stability of the $Pt(C_ydtp)_2$ complexes increases with the length of the alkyl chains. There is a 69°C difference between the temperature of decomposition of $Pt(C_1dtp)_2$ and that of $Pt(C_{18}dtp)_2$, the latter being more stable.

Fig. 5 presents the melting temperatures of the $Pt(C_x dtp)_2$ complexes as a function of the length of the alkyl chains. For compounds with alkyl chains ranging from methyl (x = 1) to pentyl (x = 5), the melting temperatures decrease with increasing alkyl chain length. This effect is probably connected with less favorable packing in the solid state with increasing chain length. An increase in melting entropy induced by the increased conformational freedom of the longer chains in the melt must also be considered and is discussed below. There is only a barely perceptible odd–even effect in contrast to that observed in the melting temperatures of alkanes and many substituted alkanes with low chain lengths.

For $x \ge 7$, differences in the packing of the molecules in the solid state become probably less important and the melting temperatures increase with increasing molecular weight; the longer chains might enhance the van der Waals interactions and render the melting temperatures higher. The melting temperatures of Pt(C₇dtp)₂, 1-octanoic acid, 1-heptanol, 1-aminoheptane, and heptane (29, -8, -34, -18, and -91° C, respectively) markedly differ from each other. However, the melting temperature of $Pt(C_{18}dtp)_2$ (67°C) is close to the melting temperatures of 1-nonadecanoic acid (69°C), and to the values of 1-octadecanol (60°C) and 1-aminooctadecane (53°C), and differs only by 29°C from octadecane. The influence of the alkyl chains seems to dominate in $Pt(C_{18}dtp)_2$; indeed it is expected from standard bond lengths and angles that roughly 90% of the volume of $Pt(C_{18}dtp)_2$ is filled by alkyl groups.



Fig. 4. Crystal structure of $Pt(C_2dtp)_2$ in the (010) and (100) orientations.

A more detailed picture of the melting behavior of the $Pt(C_x dtp)_2$ complexes arises from the energy required for the melting of the substances (Table 9). The melting enthalpy was determined by DSC and the calorimetric data were further used to calculate the melting entropy (Table 9). For $x \le 6$, the melting enthalpies exhibit an odd-even effect. They are similar for x = 2, 4, and 6 (ca. 35 kJ mol⁻¹). However, the melting entropies of $Pt(C_4dtp)_2$ and $Pt(C_6dtp)_2$ are ca. 50% above the value of $Pt(C_2dtp)_2$. This implies that the sharp decrease in the melting temperatures from $Pt(C_2dtp)_2$ to $Pt(C_4dtp)_2$ and $Pt(C_6dtp)_2$ (ca. 100°C) is mainly due to the entropy gained by the increased conformational freedom of the longer alkyl chains. The melting entropies of $Pt(C_4dtp)_2$ and $Pt(C_6dtp)_2$ are virtually identical, and the slight difference of the melting



Fig. 5. Melting temperatures (°C) of $Pt(C_xdtp)_2$ complexes. $Pt(C_1dtp)_2$ melts under decomposition. The dotted line represents an empirical fit.





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Fig. 6. Decomposition temperatures (°C) of $Pt(C_x dtp)_2$ complexes. The dotted line represents an empirical fit.



Fig. 7. TGA diagram of Pt(C₆dtp)₂.

Table 9

Melting enthalpies (ΔH) and melting entropies (ΔS) of bis(O,O'-dialkyldithiophosphato)platinum(II) complexes

Alkyl group	$\Delta H (\mathrm{kJ}\mathrm{mol}^{-1})$	$\Delta S (\text{J mol}^{-1} \text{ K}^{-1})$
Ethyl	32.2	80.9
Propyl	18.3	54.0
Butyl	37.1	122
Pentyl	12.4	47.7
Hexyl	34.3	120
Heptyl	41.7	138
Dodecyl	150	474
Octadecyl	187	550

marked difference in the melting temperature of $Pt(C_3dtp)_2$ and $Pt(C_5dtp)_2$ (79°C) is due to an unfavorable packing of the $Pt(C_5dtp)_2$ molecules in the solid state.

The melting enthalpy and entropy of $Pt(C_7dtp)_2$ is 3.5 and 3 times, respectively, above the values of $Pt(C_5dtp)_2$ but only 25 and 15%, respectively, higher than the corresponding values of $Pt(C_6dtp)_2$. It seems that the molecules can fill the space between the planar units in $Pt(C_7dtp)_2$ better than in $Pt(C_5dtp)_2$. While the differences in melting enthalpy per mole of alkyl group between $Pt(C_7dtp)_2$ and heptane [3] is distinct (10.4 vs. 14.2 kJ mol⁻¹), the value of $Pt(C_{12}dtp)_2$ approaches that of dodecane [3] (37.6 vs. 36.6 kJ mol⁻¹). This suggests that the packing of the molecules in $Pt(C_{12}dtp)_2$ is largely determined by the alkyl chains. Since the alkyl chains are attached to a common central unit, the melting entropy per mole of alkyl chains of $Pt(C_{12}dtp)_2$ (119 J mol K⁻¹) is below the entropy gained upon melting of dodecane (139 J mol K^{-1}).

Remarkably, the complexes with pentyl (x = 5) and hexyl (x = 6) chains are liquid at r.t. They crystallize at - 14 and 13°C, respectively, which is not only evident from DSC but also clearly visible with an optical microscope equipped with a temperature control unit and a cooling stage. The complexes with butyl (x = 4) and hexyl (x = 6) chains are isolated as solids that melt only slightly above r.t. (30 and 29°C, respectively). To our knowledge, liquid metal complexes have not been reported so far with any platinum complex or with O,O'-dialkyldithiophosphates as ligands. Compared with the other liquid transition metal complexes, the molecular weights of $Pt(C_5dtp)_2$ and $Pt(C_6dtp)_2$ are extraordinarily high (733.83 and 789.94, respectively). It is often anticipated that the alkyl groups in metal compounds should be very short (methyl or ethyl) to obtain liquids since the van der Waals interactions increase with increasing molecular weight. However, steric effects may render close packing of the molecules more difficult with increasing chain length, and the melting entropy can also contribute to a decrease in melting temperature for intermediate chain lengths. The results with bis(O,O'-dialkyldithiophosphato) platinum(II) complexes suggest that intermediate alkyl chain lengths might generally render transition metal compounds liquid.

4. Conclusions

Bis(O,O'-dialkyldithiophosphato)platinum(II) compounds with alkyl chains containing 1-18 carbon atoms can be synthesized by reaction of tetrachloroplatinate(II) with ammonium-O,O'-dialkyldithiophosphates or oxidative addition of (O, O'-dialkylthiophosphoryl)disulfides to tris(styrene)platinum(0). The course of the melting temperatures of bis(O,O'-dialkyldithiophosphato)platinum(II) complexes exhibits a minimum at the complex with pentyl groups. This compound and the one with hexyl groups are liquid at r.t. (melting temperatures -14 and 13° C, respectively). The crystal structure of $Pt(C_2dtp)_2$ implies that the tetrahedral arrangement around the phosphorus atoms hinders any stacking of the molecules, which makes the formation of a dense packing of the molecules in the crystal more difficult for intermediate chain lengths, resulting in a decrease in melting temperature. In addition, the melting entropy can also contribute to the low melting temperatures. In $Pt(C_5dtp)_2$ the low melting enthalpy and in $Pt(C_6dtp)_2$ the relatively high melting entropy seem to be the decisive factors for the low melting temperatures. We expect that the concept applied here will also be useful for the development of other liquid metal complexes.

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