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Homoleptic binuclear platinum compounds with $C_6F_5S^-$ and $C_6HF_4S^-$

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Abstract

By reacting $[Pt(SR)_2COD]$ with $K_2[Pt(SR')_4]$ (R and R' $= C_6F_5$ or p-C_6HF_4) platinum(II) homoleptic binuclear compounds with bridging fluorothiolate groups are obtained. Compounds bearing mixed ligands show a variety of isomers in solution.

Introduction

In recent years there has been an increasing interest in binuclear complexes since they appear to be active in a variety of chemical processes [1]. Among this class of compounds there are very few examples of fluorinated species and as a result of our long standing interest in fluorothiolate derivatives, we have set up a program to obtain a number of such compounds [2].

Binuclear platinum(II) complexes of the type $[Pt_2A_2B_4]^{2-}$ where A and B are anionic ligands can form one single isomer $[Pt_2(\mu\text{-}A)_2B_4]^{2-}$ with two A bridges, two isomers $[Pt_2(\mu\text{-}A)(\mu\text{-}B)AB_3]^{2-}$ with A and B bridges and three isomers $[Pt_2(\mu\text{-}B)_2A_2B_2]^{2-}$ with two B bridges. Most of the previously reported complexes of this type have the $(\mu\text{-}A)_2$ bridge structure [3, 4].

In this paper we report [5] the synthesis of the binuclear complexes $[Pt_2(SR)_2(SR')_4]^{2-}$ ($R = R' = C_6F_5$ (**1**) or p-C_6HF_4 (**2**); $R = C_6F_5$, $R' = p$-C_6HF_4 (**3**); $R = p$-C_6HF_4, $R' = C_6F_5$ (**4**)) which adopt a variety of structures in solution. Compound **1** has been obtained recently by an alternative synthetic route [6].

Preparation of the new starting materials $K_2[Pt(SC_6HF_4)_4]$ (**5**), $[Pt(SC_6F_5)_2COD]$ (**6**) and $[Pt(SC_6HF_4)_2COD]$ (**7**) where COD = 1,5-cyclooctadiene are also described.

Experimental

The starting compounds $Pb(SC_6F_5)_2$ [7], $K_2[Pt(SC_6F_5)_4]$ [8], $[PtCl_2COD]$ [9] and $[Pt(SCF_3)_2COD]$ [10] were prepared by previously published methods.

IR spectra were recorded over the 4000–200 cm^{-1} range on a Perkin-Elmer 1330 with a Data Station 1300, as CsI pellets. NMR spectra were recorded on a Varian VXR-300S as hexadeuteroacetone solutions (external TMS $\delta = 0$, ^1H and CCl_3F $\delta = 0$, ^{19}F). Electric conductivities were measured in acetonic solutions with a YSI-32 digital conductimeter.

Elemental analyses were determined by Galbraith Labs., Inc., USA.

All manipulations were carried out routinely under a dry oxygen-free nitrogen atmosphere by standard vacuum and Schlenk techniques with solvents purified and dried by standard procedures.

Synthesis of $K_2[Pt_2(\mu\text{-}SC_6F_5)_2(SC_6F_5)_4]$ (1)

A solution of $[Pt(SC_6F_5)_2COD]$ (0.081 g, 0.115 mmol) in acetone (20 ml) was added to a solution containing $K_2[Pt(SC_6F_5)_4]$ (0.123 g, 0.115 mmol) in acetone (20 ml). Under reflux, the solution turned yellow slowly. The course of the reaction was followed by thin layer chromatography (TLC) using silica gel. After 58 h, the solvent was distilled off, the solid residue washed with benzene and the product crystallized from acetone. Yield 81%.

Synthesis of $K_2[Pt_2(\mu\text{-}SC_6HF_4)_2(SC_6HF_4)_4]$ (2)

Complex **2** was prepared as **1**, from $[Pt(SC_6HF_4)_2COD]$ (0.087 g, 0.131 mmol) and $K_2[Pt(SC_6HF_4)_4]$ (0.13 g, 0.130 mmol). Yield 89%.

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Synthesis of $K_2[Pt_2(SC_6F_5)_2(SC_6HF_4)_4]$ (3)

Complex **3** was prepared as **1**, from $[Pt(SC_6F_5)_2COD]$ (0.081 g, 0.115 mmol) and $K_2[Pt(SC_6HF_4)_4]$ (0.114 g, 0.114 mmol). Yield 80%.

Synthesis of $K_2[Pt_2(SC_6HF_4)_2(SC_6F_5)_4]$ (4)

Complex **4** was prepared as **1**, from $[Pt(SC_6HF_4)_2COD]$ (0.1 g, 0.15 mmol) and $K_2[Pt(SC_6F_5)_4]$ (0.161 g, 0.15 mmol). Yield 80%.

Synthesis of $K_2[Pt(SC_6HF_4)_4]$ (5)

HSC_6HF_4 (2.64 g, 20 mmol) was added to a solution containing $K_2[PtCl_4]$ (1.0 g, 2.4 mmol) in water (10 ml). The solution immediately turned red and after 1 h stirring the solvent was distilled off and the product crystallized from ethanol. Yield 75%.

Synthesis of $[Pt(SC_6F_5)_2COD]$ (6)

$Pb(SC_6F_5)_2$ (0.273 g, 0.45 mmol) in acetone (10 ml) was added to a solution containing $[PtCl_2COD]$ (0.168 g, 0.45 mmol) in acetone (15 ml). The solution slowly turned yellow and after 12 h stirring the $PbCl_2$ formed was filtered off and the product crystallized by slow evaporation of the solvent. Yield 94%.

Synthesis of $[Pt(SC_6HF_4)_2COD]$ (7)

This compound was prepared as **6** using $Pb(SC_6HF_4)_2$ (0.304 g, 0.54 mmol) and $[PtCl_2COD]$ (0.2 g, 0.54 mmol). Yield 96%.

Results and discussion

By modifying the method published by Beck *et al.* [8], potassium tetrachloroplatinate ($K_2[PtCl_4]$) reacts with p-C_6HF_4SH (1:4) as shown in eqn. (1) to give the corresponding tetrathiolato derivative.

$$K_2[PtCl_4] + p\text{-}C_6HF_4SH \longrightarrow K_2[Pt(SC_6HF_4)_4](\mathbf{5}) + 4HCl \quad (1)$$

Methatetical reactions of $[PtCl_2(COD)]$ with $Pb(SR)_2$, $R = C_6F_5$ or p-C_6HF_4, proceed according to eqn. (2), affording the corresponding fluorothiolate-containing species.

$$[PtCl_2(COD)] + Pb(SR)_2 \longrightarrow [Pt(SR)_2(COD)] + PbCl_2 \quad (2)$$

$R = C_6F_5$ (**6**) or p-C_6HF_4 (**7**)

Obtention of binuclear complexes was attempted by interacting the metallo-ligands $[Pt(SR)_2(COD)]$ with potassium tetrachloroplatinate as indicated in eqn. (3). The reaction proceeds however to the formation of polymeric species first reported by Beck *et al.* [8].

$$[Pt(SR)_2(COD)] + K_2[PtCl_4] \longrightarrow [PtCl_2COD] + [Pt(SR)_2]_n + 2KCl \quad (3)$$

Since the role of the tetrachloroplatinate seems to be determinant in this reaction, it was decided to treat $[Pt(SR)_2(COD)]$ with $K_2[Pt(SR')_4]$ ($R = C_6F_5$, p-C_6HF_4 or CF_3; $R' = C_6F_5$, p-C_6HF_4).

Reactions between aryl-containing substituents afforded, according to eqn. (4), binuclear compounds of the type $K_2[Pt(SR)(SR')_2]_2$.

$$[Pt(SR)_2(COD)] + K_2[Pt(SR')_4] \longrightarrow K_2[Pt(\mu\text{-}SR)(SR')_2]_2 + COD \quad (4)$$

R and $R' = C_6F_5$ and/or p-C_6HF_4 (**1**–**4**)

TABLE 1. Physical properties

Compound	Colour	Analyses (%) calc./found		Melting point (°C)	Δ[a]
		C	H		
$K_2[Pt_2(\mu\text{-}SC_6F_5)_2(SC_6F_5)_4]$ (**1**)	orange	27.2		>250	184.45
		27.5			
$K_2[Pt_2(\mu\text{-}SC_6HF_4)_2(SC_6HF_4)_4]$ (**2**)	orange	29.2	0.41	>250	166.52
		29.12	<0.5		
$K_2[Pt_2(SC_6F_5)_2(SC_6HF_4)_4]$ (**3**)	orange	28.5	0.27	>250	167.97
		27.7	<0.5		
$K_2[Pt_2(SC_6HF_4)_2(SC_6F_5)_4]$ (**4**)	orange	27.9	0.13	>250	183.14
		27.48	<0.5		
$K_2[Pt(SC_6HF_4)_4]$ (**5**)	orange	27.8	0.9	>250	
		27.89	0.59		
$[Pt(SC_6F_5)_2COD]$ (**6**)	yellow	34.2	1.7	162–164d	
		33.88	2.0		
$[Pt(SC_6HF_4)_2COD]$ (**7**)	yellow	36.1	2.12	170–172d	
		36.12	2.4		

[a] Acetone, 1:1 electrolyte [11] $\Delta = 160$–$200\ cm^2\ ohm^{-1}\ mol^{-1}$.

TABLE 2. IR parameters

Compound	ν (cm^{-1})
1	1490vs, b; 1080vs, 965vs, 900vs, 852vs
2	1630s, b; 1490vs, 1435s, 1230s, 1170s, 915vs, 880s, 835s, 717s
3	1510s, 1480vs, 1170s, 975s, 910vs, 710s
4	1500vs, 1090s, 975vs, 910s, 860s
5	1625s, b; 1480vs, 1430s, 1220s, 1170s, 910vs, 885s, 710s
6	1480vs, 1435s, 1080vs, 975vs, 860vs
7	1630s, 1480vs, 1430vs, 1220s, 1170vs, 915vs, 895s, 830s, 715s

TABLE 3. NMR parameters

<table>
<tr><th rowspan="3">Compound</th><th colspan="6">^{19}F</th><th rowspan="3">^{1}H</th></tr>
<tr><th colspan="2">*ortho*</th><th colspan="2">*meta*</th><th colspan="2">*para*</th></tr>
<tr><th>bridge</th><th>terminal</th><th>bridge</th><th>terminal</th><th>bridge</th><th>terminal</th></tr>
<tr><td>**1**</td><td>−128.6</td><td>−131.1</td><td>−165.3</td><td>−166.5</td><td>−159.2</td><td>−164.4</td><td>7.1[a]</td></tr>
<tr><td>**2**</td><td>−128.5</td><td>−131.5</td><td>−141.8</td><td>−142.7</td><td></td><td></td><td>6.8[b]</td></tr>
<tr><td></td><td></td><td></td><td></td><td colspan="2">*meta–para*[c]</td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td></td><td>bridge</td><td>terminal</td><td></td><td></td></tr>
<tr><td>**3**</td><td>−128.0
−128.8</td><td>−130.8
−131.7</td><td></td><td>−139.7
−141.1
−141.7
−142.3
−159.8
−161.6
−163.4
−165.6
−166.0</td><td>−142.7
−164.7
−166.5</td><td></td><td>7.1[a]
6.8[b]</td></tr>
<tr><td>**4**</td><td>−128.3
−129.0</td><td>−129.9
−131.4</td><td></td><td>−141.6
−159.5
−165.4</td><td>−142.7
−143.2
−164.5
−166.0
−166.5
−167.3</td><td></td><td>7.2[a]
6.9[b]</td></tr>
<tr><td>**5**</td><td colspan="2">−135.3</td><td colspan="2">−145.7</td><td colspan="2"></td><td>6.7</td></tr>
<tr><td>**6**</td><td colspan="2">−132.8</td><td colspan="2">−166.1</td><td colspan="2">−160.0</td><td>5.1
2.7
2.5</td></tr>
<tr><td>**7**</td><td colspan="2">−133.1</td><td colspan="2">−143.3</td><td colspan="2"></td><td>6.9
5.1
2.7
2.5</td></tr>
</table>

[a] Bridge. [b] Terminal. [c] Superimposing signals.

Some properties of these compounds are shown in Table 1. IR frequencies and values of δ and J are collected in Tables 2, 3 and 4, respectively.

All products are air-stable crystalline solids, soluble in commonly used organic solvents. They give rise to conducting solutions characteristic of 2:1 electrolytes.

IR spectra are characteristic but unexceptional and only intense absorptions are reported.

Compounds bearing six equal fluorothiolate ligands can have but a single distribution of ligands. Accordingly, ^{19}F NMR spectra for **1** consist of two different sets of signals due to bridging and terminal SC_6F_5 groups with the expected 1:2 relative intensities. Within each set, the signals due to *ortho*, *meta* and *para* fluorines (relative intensities 2:2:1) are clearly distinguishable. No ^{19}F–^{195}Pt couplings are observed.

TABLE 4. NMR parameters

Compound	^{19}F			^{1}H		
	J_{o-m}	J_{o-p}	J_{p-m}	$J(H-F_o)$	$J(H-F_m)$	$J(H_v-Pt)$
1	27.46	10.00	27.46			
2	25.5			7.63[a]	10.82[a]	
				7.66[b]	10.85[b]	
5	26.7			7.89	10.53	
6	23.13	7.38	21.89			56.40
7	24.5			7.25	10.15	57.18

[a] Bridge. [b] Terminal.

Resonances arising from bridging thiolato groups are broad at room temperature, a fact which has been associated to a dynamic intramolecular process that exchanges *syn* and *anti* isomers through inversion at sulfur centers [6]. This interpretation implies that the Pt_2S_2 ring must lay in a plane.

The corresponding spectra of compound **2** show the same general features with absence of the *para* resonances which appear on the ^{1}H NMR spectra as two sets of signals (relative intensities 2:1). Each of these sets arise from the A part of a second order AMM'XX' magnetic system although they appear as a first order triplet of triplets.

At room temperature fluorine resonances arising from bridging fluorothiolates are also broad, probably reflecting a similar equilibrium between *syn* and *anti* isomers as found for compound **1**. No $^{19}F-^{195}Pt$ couplings are observed either.

Compounds bearing both $C_6F_5S^-$ and p-$C_6HF_4S^-$ substituents can give rise up to six different combinations of ligands around the metal centers. ^{19}F NMR spectra of both $K_2[Pt_2(SC_6F_5)_2(SC_6HF_4)_4]$ (**3**) and $K_2[Pt_2(SC_6HF_4)_2(SC_6F_5)_4]$ (**4**) show that more than two isomers are present in solution. Unfortunately some resonances overlap thus precluding the possibility of identifying each isomer. The presence of broad as well as resolved bridge signals indicates that *syn–anti* conversion is also present in these complexes.

Those reactions involving $[Pt(SCF_3)_2(COD)]$ afforded mixtures of ill-defined products in which the SCF_3 moiety is bonded to the cyclo-octadiene ring. These reactions are currently under investigation.

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References

1 C. Botteghi, R. Ganzerla, M. Lenarda and G. Moretti, *J. Mol. Catal.*, *40* (1987) 129.
2 J. García, H. Adams, N. Bailey, P. M. Maitlis and H. Torrens, *J. Chem. Soc., Chem. Commun.*, (1991) 74; D. Cruz-Garritz, J. García, C. Alvarez, R. A. Toscano, P. Poilblanc, A. Thorez and H. Torrens, *Transition Met. Chem.*, *16* (1991) 130; C. Claver, A. Masdeu, N. Ruiz, C. Foces-Foces, F. H. Cano, M. C. Apreda, L. A. Oro, J. García and H. Torrens, *J. Organomet. Chem.*, *398* (1990) 177.
3 A. F. Wells, *Structural Inorganic Chemistry*, Clarendon, Oxford, 1984, p. 1232, and refs. therein.
4 P. M. Maitlis, P. Espinet and M. J. H. Russell, in G. Wilkinson, F. G. A. Stone and E. W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Vol. 6, Pergamon, New York, 1982, Ch. 38.4, p. 306, and refs. therein.
5 H. Torrens, *Abstr., III Congreso Iberoamericano de Química Inorgánica, Zacatecas, Mexico, Apr. 1991*, p. 400.
6 R. Usón, J. Fornies, M. A. Usón and J. A. Apaolaza, *Inorg. Chim. Acta*, *187* (1991) 175.
7 M. E. Peach, *Can. J. Chem.*, *46* (1968) 2699.
8 W. Beck, K. Stetter, K. Tadros and K. Schawarzhens, *Chem. Ber.*, *100* (1967) 3944.
9 D. Drew and J. R. Doyle, *Inorg. Synth.*, *XIII* (1972) 47.
10 B. King and A. Efraty, *Inorg. Chem.*, *10* (1971) 1376.
11 R. J. Angelici, *Synthesis and Techniques in Inorganic Chemistry*, Saunders, Philadelphia, PA, 1986, p. 213.