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Synthesis and Characterization of a 3-Thio-2,4-pentanedionate Pt(II) Complex; Bis(dimethylphenylphosphine)[2,4-pentanedione-3-thiolato(2−)-*O*,*S*]-platinum(II) Prepared by S–S Bond Cleavage of 2,3-Dithio-1,1,4,4-tetraacetylbutane

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Synopsis. 3-Thio-2,4-pentanedionate (tac) complex of platinum(II), [Pt(tac)(PMe$_2$Ph)$_2$], has been prepared by treating [PtCl(PMe$_2$Ph)$_3$][PF$_6$] with 2,3-dithio-1,1,4,4-tetraacetylbutane in a KOH/methanol-acetone mixed solution. This complex has been characterized by IR, ^{1}H, ^{13}C, and ^{31}P NMR, secondary ion mass and ESR spectroscopy and cyclic voltammetry.

Linkage modes of 1,1,2,2-tetraacetylethane(dahd= 3,4-diacetyl-2,4-hexadiene-2,5-diol) to Rh(I) and Pd(II) as well as Pt(II) as bifunctional *O*$_2$-chelates and a (C^3,O')-chelate, respectively, have been formerly established.[1–3] The dahd dianion in acidic condition favors symmetrical *O*-bonding bifunctional chelation, while in basic condition it prefers the (C^3,O')-chelate. In them, the metal-carbon bonded [Pt(dahd-C^3,O')(SEt$_2$)$_2$] exhibits its unusual behavior.[3] An inversion of one sulfur atom arranged at the trans position to C^3 accompanies a bond dissociation the rearrangement of which may proceed via an intermolecular pathway. An extention of these previous findings has been investigated for the linkage mode of its dithio derivative: 2,3-dithio-1,1,4,4-tetraacetylbutane. A basic treatment of the sulfur compound gave an S–S bond cleavaged product, 3-thio-2,4-pentanedionate dianion (tac^{2-}), whose bonding mode to platinum(II) is, however, unknown so far.

This paper deals with a convenient synthesis of the 3-thio-2,4-pentanedionate Pt(II) complex, [Pt(tac)(PMe$_2$Ph)$_2$], by an alkaline treatment of 2,3-dithio-1,1,4,4-tetraacetylbutane with [PtCl(PMe$_2$Ph)$_3$][PF$_6$]; the complex has been characterized using ^{1}H, ^{13}C, ^{31}P NMR and SIMS spectroscopy.

Experimental

2,3-Dithio-1,1,4,4-tetraacetylbutane (H$_2$dttb): H$_2$dttb was prepared by a method described in the literature.[4] Found: C, 45.28; H, 5.14%. Calcd for C$_{10}$H$_{14}$O$_4$S$_2$: C, 45.79; H, 5.38%. IR(Nujol mull): ν(C$\doteq$O)+ν(C$\doteq$O) 1548(br). ^{1}H NMR (CDCl$_3$): δ_{Me}=2.37, δ_{OH}=17.00.

[PtCl(PMe$_2$Ph)$_3$][BF$_4$] and Its PF$_6^-$ Salt: 1.7 g of *cis*-PtCl$_2$(PMe$_2$Ph)$_2$[5] was dissolved in acetone (partial suspension), and 0.62 g of AgBF$_4$ was added to the solution, producing AgCl (0.4 g; 94% per Pt atom). After filtration of AgCl, the solution was evaporated to give a pale-orange oil, which was dried in vacuo (1.5 g; 84%). Found: C, 32.91; H, 3.69%. Calcd for C$_{16}$H$_{22}$ClP$_2$BF$_4$Pt: C, 32.37; H, 3.74%. 0.6 g of the [Pt$_2$Cl$_2$(PMe$_2$Ph)$_4$][BF$_4$]$_2$ product was dissolved in acetone, and 0.13 g of PMe$_2$Ph was added to the solution. This solution was then evaporated to give an orange oil, which was dried in vacuo (0.72 g; 100%). Found: C, 38.34; H, 4.51%. Calcd for C$_{24}$H$_{35}$OClBF$_4$Pt with a solvation of H$_2$O: C, 38.44; H, 4.71%. ^{31}P{^{1}H} NMR(CDCl$_3$) shows a typical AB spin system: δ_A=16.86, δ_B=−3.94 ppm with J(A-B)=21.8, J(^{195}Pt-A)=3496.8 and J(^{195}Pt-B)=2310.9 Hz. An analogous PF$_6$ salt was prepared by reacting *cis*-PtCl$_2$(PMe$_2$Ph)$_2$ (1.0 g) with PMe$_2$Ph (0.3 g) and NH$_4$PF$_6$ (0.3 g) in a methanol-acetone solution (yield: 1.4 g; 93%).

Bis(dimethylphenylphosphine)(2,4-pentanedione-3-thiolato)platinum(II), [Pt(tac)(PMe$_2$Ph)$_2$]: 1.7 g of [PtCl(PMe$_2$Ph)$_3$][PF$_6$] was dissolved in acetone; to the solution a methanol solution of KOH 0.25 g and H$_2$dttb 0.57 g were added as the pale-yellow solution turned orange. The solution was stirred for 30 minutes under N$_2$ as a white solid precipitated (0.5 g: 200% per Pt atom as a summation of KCl and KPF$_6$ salts). After filtration, the solution was developed by TLC (silica) in CH$_2$Cl$_2$-acetone. A yellow band was eluted and recrystallized from CH$_2$Cl$_2$-hexane (0.79 g; 61%). Found: C, 41.84; H, 4.81%. Calcd for C$_{21}$H$_{28}$O$_2$P$_2$SPt: C, 41.93; H, 4.69%. M.W. (CH$_2$Cl$_2$) 664(602). The other species, showing orange and brown layers (TLC), have not been characterized.

Dipotassium 3-Thio-2,4-pentanedionate, K$_2$tac(CH$_3$OH): 1 g of H$_2$dttb was dissolved in CH$_3$OH and to the solution 0.43 g of KOH in CH$_3$OH was added as the solution turned orange. The solution was reduced in volume under reduced pressure to about 5 cm^3. The addition of diethyl ether to the residual solution, by allowing it to stand in a refrigerator overnight, gave a pale-orange solid (ca. 0.5 g). The product was further reprecipitated from methanol-diethyl ether (the product was moisture sensitive, and a slight weight loss was accompanied in its elemental analysis). Found: C, 28.62; H, 4.34%. Calcd for C$_6$H$_{11}$O$_{3.5}$SK$_2$ with a solvation of CH$_3$OH and H$_2$O: C, 28.89; H, 4.45%. IR(Nujol mull): ν(C$\doteq$O)+ν(C$\doteq$C)1580(vs) cm^{-1}. ^{1}H NMR (CD$_3$OD): δ_{Me}=2.08 .

Cyclic Voltammetry of [Pt(tac)(PMe$_2$Ph)$_2$]: A cyclic voltammograph of [Pt(tac)(PMe$_2$Ph)$_2$] was produced in acetone [1.16 and 1.74 mM (1 M=1 mol·dm^{-3})], 0.1 M TEAP at a platinum electrode or a glassy carbon electrode using a BAS voltammograph CV-27 and a Ag/AgCl reference electrode. An irreversible oxidation wave was observed, in which the corresponding cathodic wave was small. The anodic peak potential at 100 mV s^{-1} for the wave was E_p=+0.46 V. Controlled-potential coulometry at +0.60 V using a YANACO Potentiostat Model V8 revealed that a total of 0.94 electrons was involved in this oxidation. The nature of the reaction, via an electrochemical reaction, is not known at this time.

Elemental analyses were performed at the Micro Analytical Center, Kyoto University. IR spectra were recorded on a Hitachi 260-10 infrared spectrometer. ^{1}H NMR spectra at 90 MHz, ^{13}C at 22.66 MHz, and ^{31}P{^{1}H} at 36.36 MHz were recorded on a Hitachi R-90H FT NMR(90.04 MHz) operating in the Fourier transform mode. The SIMS spectrum was produced using a Hitachi M-80 mass spectrometer and

Table 1. IR, ^{1}H and ^{31}P{^{1}H} NMR Data of [Pt(tac)(PMe$_2$Ph)$_2$]

Chracteristic bands (IR)$^{a)}$			^{1}H$^{b)}$					^{31}P$^{c)}$		
ν(C=C) or ν(C=C)	ν(C-O)	ν(C-S)	δ_{Me}(tac)	J(P-H)	δ_{Me}(PMe$_2$Ph)	J(P-H)	J(^{195}Pt-H)	(PMe$_2$Ph)	J(Pt-P)	J(P-P)
1621(s)	1488(vs)	1262	2.42	1.8	1.74	12.5	39	−6.88(d)	2790.8	26.4
	1475(vs)		2.48	1.8	1.64	13.0	26	−26.52(d)	3354.0	

a) Measured in CH$_2$Cl$_2$. b) Measured in CDCl$_3$. Chemical shifts are relative to Me$_4$Si at 0.00.
c) Measured in CDCl$_3$. Chemical shifts are relative to 85% H$_3$PO$_4$ at 0.00.

Table 2. ^{13}C{^{1}H} NMR datum of [Pt(tac)(PMe$_2$Ph)$_2$] and 2,3-Dithio-1,1,4,4-tetraacetylbutane (dttb-H$_2$)$^{a)}$

	tac					PMe$_2$Ph		
	C^1	C^2	C^3	C^4	C^5	C^1	C$^{1'}$	C^2
H$_2$-dttb	24.51	197.60	106.19					
[Pt(tac)(PMe$_2$Ph)$_2$]	25.66	194.66	109.76	179.96	29.79	16.04	15.96	12.71
	(4.84)	(3.46)	(8.29,	(9.33,		(43.53)	(44.22)	(35.93)
	[59.42]	[28.56]	2.77)	3.11)		[37.31]	[36.62]	[20.39]

a) Measured in CDCl$_3$. Chemical shifts are relative to Me$_4$Si at 0.00. J(P-C) and J(^{195}Pt-C) are in parentheses and bracket respectively.

3-nitrobenzylalcohol or glycerin as a matrix and Xe gas as the first ion source. The molecular weight was obtained using a CORONA Molecular Weight Apparatus M-117 (vapor pressure osmometry) at 30 °C in CH$_2$Cl$_2$. The ESR spectra of the solid were recorded on a Varian E Line Century Series EPR spectrometer, and the diamagnetism of the complex was affirmed.

Results and Discussion

2,3-Dithio-1,1,4,4-tetraacetylbutane (H$_2$dttb) in solution has a dienolic form (Experimental section). The crystal structure of its tri-thio analog, 2,3,4-trithio-1,1,5,5-tetraacetylpentane, has been established by X-ray diffraction studies4) to have a dienolic form, which is in analogy with 1,1,2,2-tetraacetylethane (H$_2$dahd). These previous findings may give rise to a question concerning its linkage mode to the metal: whether it may be stabilized in a form of bifunctional O_2-chelates or another, for example (S,O)-chelates. Unexpectedly, an alkaline treatment of [PtCl(PMe$_2$Ph)$_3$][PF$_6$] with H$_2$dttb in methanol-acetone gave a diamagnetic 2,4-penatanedione-3-thiolato Pt(II) complex, [Pt(tac)(PMe$_2$Ph)$_2$][tac(2−)=3-thio-2,4-pentanedionate], which was produced via a S-S bond cleavage of the dttb dianion.

^{1}H, ^{31}P{^{1}H} NMR and IR spectral data of [Pt(tac)(PMe$_2$Ph)$_2$] are shown in Table 1, and ^{13}C{^{1}H} NMR datum in Table 2. ^{31}P NMR shows an AB spin system with J(^{195}Pt-P$_A$)=3354 and J(^{195}Pt-P$_B$)=2791 Hz. These values are apart from a trans configuration, but rather close to cis configuration for the two phosphorous atoms.6,7) Me-protons of PMe$_2$Ph appeared as two resonances, showing that the structure of the complex has low symmetry. Me protons of the tac also appear as two resonances with doublet patterns respectively, which may arise from a coupling with phosphorous nuclei at their trans positions. Its ^{13}C NMR spectrum shows that the circumstances around one acetyl group is distinct from the other. Resonances at 24.5 and 19.7 are due to C^1 and C^2, and each resonance appears as a doublet pattern accompanying ^{195}Pt satellites. The resonance pattern is in accordance with those observed for [Pt(dahd-C^3,O')(PMe$_2$Ph)$_2$] and is consistent with one carbonyl in an enol-form being bound to Pt(II). However, resonance at 180.0 arising from C^4 is in a region close to that of ketonic carbonyl;8,9) it appeared as a quartet pattern which may arise from a long-range coupling with two phosphorous nuclei. A single resonance at 29.8 is due to C^5. In both resonances no ^{195}Pt satellites could be observed, indicating that the ketonic carbonyl is liberated from the metal. IR bands at 1488 and 1475 cm^{-1} can be assigned to ν(C-O) and 1262 cm^{-1} to ν(C-S), the latter of which is in a region close to that found in the thiolato complex.10) A

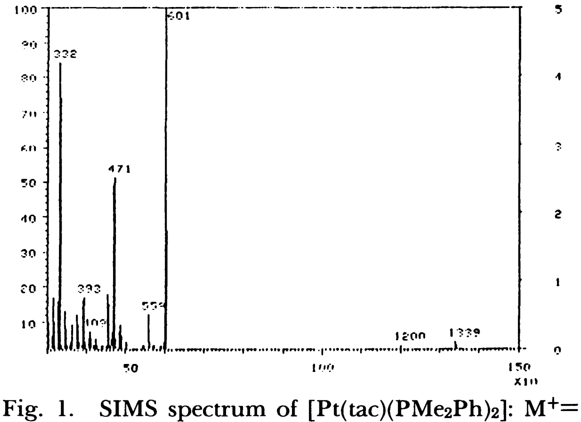


Fig. 1. SIMS spectrum of [Pt(tac)(PMe$_2$Ph)$_2$]: M$^+$=601, [M−tac]$^+$=471, [M−tac−PMe$_2$Ph]$^+$=332.

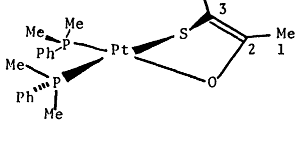
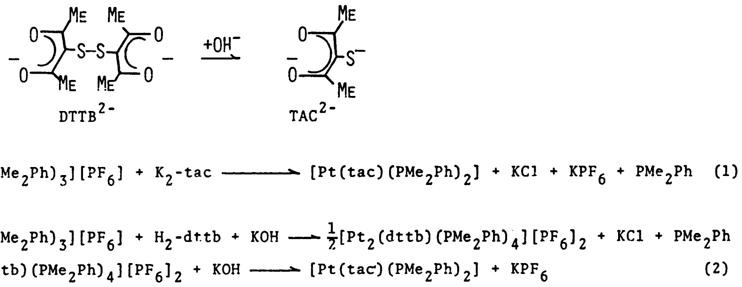


Fig. 2. Supposed structure of [Pt(tac)(PMe$_2$Ph)$_2$].



$$[\mathrm{PtCl(PMe_2Ph)_3][PF_6]} + \mathrm{K_2\text{-}tac} \longrightarrow [\mathrm{Pt(tac)(PMe_2Ph)_2}] + \mathrm{KCl} + \mathrm{KPF_6} + \mathrm{PMe_2Ph} \quad (1)$$

$$[\mathrm{PtCl(PMe_2Ph)_3][PF_6]} + \mathrm{H_2\text{-}dttb} + \mathrm{KOH} \longrightarrow \tfrac{1}{2}[\mathrm{Pt_2(dttb)(PMe_2Ph)_4][PF_6]_2} + \mathrm{KCl} + \mathrm{PMe_2Ph}$$
$$\tfrac{1}{2}[\mathrm{Pt_2(dttb)(PMe_2Ph)_4][PF_6]_2} + \mathrm{KOH} \longrightarrow [\mathrm{Pt(tac)(PMe_2Ph)_2}] + \mathrm{KPF_6} \quad (2)$$

Scheme 1.

band at 1621 cm^{-1} can, therefore, be assigned to ν(C=O) or ν(C=C), which is in a lower frequency region than the 1600—1700 region found in metal carbon bonded Pt(II) and Pd(II) complexes of β-diketone.[11,12] Its SIMS spectrum shows an explicit basal peak at M/Z=601 corresponding to the molecular ion (Fig. 1). The result of a molecular weight measurement was consistent with this SIMS data. These spectral data are in accordance with a square planar structure in which 3-thio-2,4-pentanedionate bonds Pt(II) with (S,O)-chelate, as shown in Fig. 2. Any other conceivable structure for $[\mathrm{Pt(tac)(PMe_2Ph)_2}]$, in which tac may retain an (O-H) or (S-H) group, can be neglected, since no corresponding ^{1}H NMR resonances have been observed in the region 0—20 ppm. It is also quite unlikely, judging from a molecular model, that the ketonic carbonyl may have any interaction with the metal from the apical site of the coordination tetragonal plane. In fact, by varying the temperature (20—50 °C), we did not observe any spectral change which should correspond to a coordination site exchange, as observed for five-coordinate complexes.[13,14]

$[\mathrm{Pt(tac\text{-}}S,O\mathrm{)(PMe_2Ph)_2}]$ produced via an S-S bond cleavage[15] of the dttb dianion may be given by supposing two reaction paths: first, the dttb dianion by an attack of OH$^-$ cause an S-S bond cleavage to form the tac dianion and a following metathesis of the complex; second, a dinuclear dttb complex, such as $[\mathrm{Pt_2(dahd)(PMe_2Ph)_4][BF_4]_2}$, is formed and a subsequent S-S bond cleavage occurs by and attack of the nucleophile OH$^-$, as attributed in Scheme 1. By treating $\mathrm{H_2dttb}$ with KOH in methanol, $\mathrm{K_2tac}$ could be obtained. By reacting $[\mathrm{PtCl(PMe_2Ph)_3][PF_6]}$ with $\mathrm{K_2tac}$, we have also obtained $[\mathrm{Pt(tac)(PMe_2Ph)_2}]$. No isolation of a dinuclear complex, such as $[\mathrm{Pt_2(dttb)(PMe_2Ph)_4][PF_6]_2}$, have yet succeeded. Another likely type of cleavage for the reaction is via the S-C bond of the dttb dianion. Yet, its details are uncertain at this time.

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