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Polyhedron 26 (2007) 3271–3276
POLYHEDRON
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Synthesis and spectral characterization of some complexes of platinum(II) containing η^2-methyleugenol

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Received 7 February 2007; accepted 3 March 2007
Available online 21 March 2007

Abstract

Several complexes of the formula *trans*-[Pt(Meug)(Am)Cl_2], Meug: methyleugenol (4-allyl-1,2-dimethoxybenzene), a η^2-coordinated olefin, and Am: ammine, methylamine, diethylamine, *o*-toluidine, *m*-toluidine, *p*-toluidine, *o*-anisidine, *m*-anisidine and *p*-anisidine have been prepared. UV, IR, Raman, ^{1}H NMR, ^{13}C NMR and 2D NMR spectra of the complexes were recorded and analyzed.

Keywords: Platinum complexes; Olefin complexes; Methyleugenol; ^{1}H NMR; ^{13}C NMR

1. Introduction

Platinum–olefin complexes quite long ago attracted the attention of chemists [1,2]. Various olefin ligands have been used. Amongst the arylolefin ligands, phenylethylene (styrene) and substituted phenylethylenes were widely studied [3,4], but phenylpropylenes were rare. Today substituted phenylpropylenes, which are easily available from natural resources, have been used as valuable starting materials in various synthetic processes [5]. In many cases transition metals-olefin complexes are present as key intermediates.

Eugenol, izoeugenol and methyleugenol (4-allyl-1,2-dimethoxybenzene) represents interesting phenylpropylenes, extracted from essential clove oil, which can be transformed into coniferyl aldehyde, coniferyl alcohol, vanilin and vanillic acid, compounds commonly used in the flavour and fragrance industry [6]. In this paper we describe some platinum(II) complexes containing methyleugenol, which are prepared as follows:

$$K[Pt(C_2H_4)Cl_3] \xrightarrow{\text{Methyleugenol}} \underset{(\mathbf{1})}{K[Pt(Meug)Cl_3]} \xrightarrow{\text{Amine}} \underset{(\mathbf{2})\text{–}(\mathbf{10})}{\textit{trans}\text{-}[Pt(Meug)(Am)Cl_2]}$$

Meug: Methyleugenol (4-allyl-1,2-dimethoxybenzene, formula I).
Am: NH_3 (**2**), CH_3NH_2 (**3**), $(C_2H_5)_2NH$ (**4**), *o*-$CH_3C_6H_4NH_2$ (**5**), *m*-$CH_3C_6H_4NH_2$ (**6**), *p*-$CH_3C_6H_4NH_2$ (**7**), *o*-$CH_3OC_6H_4NH_2$ (**8**), *m*-$CH_3OC_6H_4NH_2$ (**9**), *p*-$CH_3OC_6H_4NH_2$ (**10**).

2. Results and discussion

The complexes [Pt(Meug)(Am)Cl_2] were prepared by replacement of a Cl ligand from K[Pt(Meug)Cl_3] (**1**) by an amine, Am. According to the *trans*-effect, the Cl ligand in the opposite position to Meug is replaced by the amine. For volatile amines such as methylamine, diethylamine and NH_3, the reaction was carried out at 10–15 °C, with 1.2 mmol of amine per 1 mmol of **1**. For toluidines and anisidines, the reaction was carried out at 25–30 °C, with 1.1 mmol of amine per 1 mmol of **1**. The neutral complexes [Pt(Meug)(Am)Cl_2] precipitate out and can be easily

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doi:10.1016/j.poly.2007.03.017

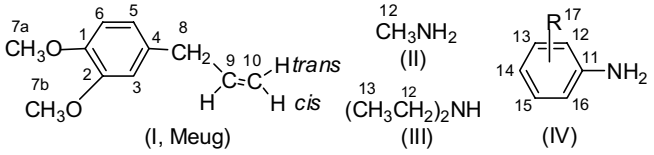
isolated, then purified by recrystallizing from aqueous EtOH solution.

The molar conductivity (μ) of 10^{-4} M K[Pt(Meug)Cl_3] solution is 95 Ω^{-1} cm^2 mol^{-1}. The molar conductivity (μ) of a $5.10^{-5} - 10^{-4}$ M solution of *trans*-[Pt(Meug)(Am)Cl_2] is in the range 15–22 Ω^{-1} cm^2 mol^{-1}, indicating its non-electrolytic nature (Table 1).

The electronic spectra of the synthesized complexes are given in Table 1. All the examined complexes are slight soluble. Their spectra were recorded at a concentration as small as 10^{-4} M in 96% by volume aqueous EtOH. Thus only charge-transfer and ligand spectra were obtained.

In Table 1, the *v*(Pt–N), *v*(Pt–Cl) values were taken from the Raman spectra. Because the intensity of *v*(NH) in the Raman spectra was too weak, the *v*(NH) value was taken from the IR spectra. These values are in general agreement with those in the literature [1,7].

The NMR data of the examined compounds are presented in Tables 2–4. The numeration of the examined compounds for the analysis of the NMR spectra is as follows:



The assignment of the NMR signals is based on their chemical shift, spin-spin splitting patterns, HMQC, HMBC and NOESY spectra. For example, the assignment of some ambiguous signals from the ^{13}C NMR spectrum of complex **8** and then the signals of H7a, H7b, H17 have been assigned as illustrated in Fig. 1.

In Fig. 1, the signals of all the protons, except H-7a, H-7b and H-17, have been unambiguously assigned, the signals of ring carbons are thus identified. Two cross peaks *a* and *b* of H-16 (7.29 ppm) show that two signals at 152.0 and 127.0 ppm belong to C-12 and C-14, respectively. Two cross peaks *c*, *d* of H-14 (7.15 ppm) show signals of C-12 (152.0), C-16 (124.1). Two cross peaks *e*, *f* of H-13 (6.98 ppm) show signals of C-11 (130.52), C-15 (121.81). Two cross peaks *g*, *h* of H-5 (6.96 ppm) show signals of C-1 (148.83), C-3 (113.88). Two cross peaks *i*, *k* of H-6 (6.86 ppm) show signals of C-2 (150.11), C-4 (132.3). Two cross peaks *l*, *m* of H-15 (6.88 ppm) show signals of C-11 (130.52), C-13 (112.88). The cross peaks of C-12, C-2 and C-1, in turn, allow one to distinguish the signals of H-17, H-7b and H-7a.

Upon coordination to Pt(II), the resonances of the ethylenic protons (H-9, H-10 *cis* and H-10 *trans*, Table 2) are upfield in comparison to those of non-coordinated methyleugenol (5.86, 4.96 and 4.98 ppm, respectively). The ^{195}Pt satellites in the signals from H-9 are broadened beyond detection, but two satellites in the signals from H-10 *cis* and H-10 *trans* are clear, with a $^2J_{PtH}$ value of 60–70 Hz (Table 2). The resonances of the ethylenic carbons (C-9, C-10) are upfield too (Table 4). These indicate that methyleugenol is present as an η^2-coordinated olefin.

For non-coordinatinated methyleugenol, two protons H-8 (formula I) give rise to a doublet at 3.22 ppm with $^3J = 6.5$ Hz, but in the spectra of the examined complexes we usually observed one doublet of doublets centered at 3.38–3.55 ppm for H-8a and another doublet of doublets centered at 3.01–3.21 ppm for H-8b. This is expected since upon coordination to Pt(II), atom C-9 becomes a chiral center, and H-8a and H-8b become diastereotopic.

It is interesting that in ^1H NMR and ^{13}C NMR spectra of *trans*-[Pt(Meug)(Et_2NH)Cl_2] (**4**), recorded in d_6-acetone, two CH_2 groups of diethylamine give rise to two complicated proton signals (one multiplet centered at 2.88 ppm and another at 3.17 ppm, H12a and H12b in Fig. 2) and two ^{13}C signals at 49.67 and 49.69 ppm; two CH_3 groups give rise to two triplets (one centered at 1.400 and another at 1.395 ppm) and the two ^{13}C signals are at 14.67 and 14.74 ppm. This anomaly also happens in the spectra of **4** recorded in CD_3CN. It is noted that we have just prepared *trans*-[Pt(Saf)(Et_2NH)Cl_2] (**4a**) and *trans*-[Pt(Saf)(Me_2-NH)Cl_2] (**4b**) (Saf: 4-allyl-1,2-methylendioxybenzene, Et: $-CH_2CH_3$, Me: CH_3). In the spectra of **4a** recorded in d_6-acetone, two CH_2 groups of diethylamine give rise to two complicated proton signals (one multiplet centered at

Table 1
Molar conductivity (μ), the main bands in UV-, IR- and Raman spectra of the synthesized complexes

Compound	μ, Ω^{-1} cm^2 mol^{-1}	λ_{max} (nm)/log ε	*v* (NH) (IR, cm^{-1})	*v* (Pt–N) (Raman cm^{-1})	*v* (Pt–Cl) (Raman cm^{-1})
1	95	231/4.25; 284/3.38; 341/3.37			330
2	22	240/3.98; 280/3.82	3274, 3191	525	335
3	21	230/3.78; 279/3.17	3270, 3221	525	336
4	20	231/4.03; 279/3.90	3224	492	334
5	15	232/4.16; 276/3.86	3225, 3203	485	333
6	18	232/4.06; 279/3.75	3302, 3225	470	332
7	16	230/4.27; 274/4.00	3282, 3220	489	340
8	19	233/4.25; 283/3.96	3248, 3213	489	331
9	17	230/3.78; 281/3.27	3283, 3233	485	338
10	18	225/4.43; 279/4.16	3293, 3229	502	340

Table 2
The resonances of protons H-3 to H-9 of the examined complexes, δ (ppm), J (Hz)

Compound (solvent)	H-3	H-5	H-6	H-7a	H-7b	H-8a	H-8b	H-9
1	7.36 d	6.93 dd	6.91 d	3.87 s	3.89 s	2.90 dd	3.49 dd	5.21 m
(CD_3OD)	^4J 1.5	^3J 8, ^4J 1.5	^3J 8	[a]	[a]	^2J 15, ^3J 6.5	^2J 15, ^3J 7	
2	6.87 s	6.89 dd	6.84 d	3.89 s	3.87 s	3.21 dd	3.55 dd	5.60 m
($CDCl_3$)		^3J 8, ^4J 1.5	^3J 8			^2J 15, ^3J 8	^2J 15, ^3J 6	
3	6.87 d	6.89 dd	6.84 d	3.89 s	3.87 s	3.21 dd	3.52 dd	5.59 m
($CDCl_3$)	^4J 1.5	^3J 8, ^4J 1.5	^3J 8			^2J 15, ^3J 7.5	^2J 15, ^3J 6.5	
4	7.02 d	6.92 dd	6.90 d	3.83 s	3.78 s	3.19 dd	3.43 dd	5.45 m
(CD_3COCD_3)	^4J 2	^3J 8, ^4J 2	^3J 8			^2J 15, ^3J 7.5	^2J 15, ^3J 6.5	
5	6.97 s	6.92 dd	6.88 d	3.78 s	3.76 s	3.09 dd	3.42 dd	5.53 m
(CD_3COCD_3)		^3J 8.5, ^4J 1.5	^3J 8.5			^2J 15, ^3J 6	^2J 15, ^3J 7.5	
6	6.99 d	6.95 dd	6.77 d	3.78 s	3.75 s	3.01 dd	3.39 dd	5.40 m
(CD_3CN)	^4J 2	^3J 8, ^4J 2	^3J 8			^2J 15, ^3J 6.5	^2J 15, ^3J 8	
7	6.97 s	6.94 dd	6.78 d	3.79 s	3.75 s	3.01 dd	3.38 dd	5.39 m
(CD_3COCD_3)	^4J 2	^3J 8, ^4J 2	^3J 8			^2J 15, ^3J 6	^2J 15, ^3J 8	
8	7.00 d	6.96 dd	6.86 d	3.80 s	3.76 s	3.03 dd	3.40 dd	5.44 m
(CD_3CN)	^4J 1.5	^3J 8, ^4J 1.5	^3J 8			^2J 15, ^3J 6	^2J 15, ^3J 7.5	
9	7.03 d	6.92 dd	6.81 d	3.79 s	3.78 s	3.08 dd	3.45 dd	5.42 m
(CD_3COCD_3)	^4J 2	^3J 8.5, ^4J 2	^3J 8.5			^2J 15, ^3J 6.5	^2J 15, ^3J 7.5	
10	7.01 d	6.95 dd	6.80 d	3.79 s	3.75 s	3.06 dd	3.41 dd	5.38 m
(CD_3COCD_3)	^4J 2	^3J 8, ^4J 2	^3J 8			^2J 15, ^3J 6.5	^2J 15, ^3J 7.5	

[a] Because of methanol.

Table 3
The resonances of protons H-10 to H-17 of the examined complexes, δ (ppm), J (Hz)

Compound[a]	H-10 *cis*	H-10 *trans*	H-12	H-13	H-14	H-15	H-16	Others
1	4.30 d	4.46 d						
(a)	^3J 7.5, J_{PtH} 70	^3J 7.5, J_{PtH} 70						
2	4.62 dd, ^2J 1,	4.69 dd, ^2J 1,						3.55 s: NH_3
(b)	^3J 8, J_{PtH} 65	^3J 14, J_{PtH}65						
3	4.56 dd,^2J 1,	4.69 dd,^2J 1,	2.66 t,					3.85 s: NH_2
(b)	^3J 7.5, J_{PtH} 70	^3J 14, J_{PtH} 70	^3J 6.5					
4	4.40 dd, ^2J 1.5,	4.53 dd, ^2J 1.5	3.17 m,	1.400 t,				5.28 s: NH
(c)	^3J 8, J_{PtH} 68	^3J 14, J_{PtH} 64	2.88 m	1.395 t				
5	4.44 d	4.54 d		7.13 dd	7.08 td	7.07 td	7.24 dd	
(c)	^3J 8, J_{PtH} 68	^3J 14, J_{PtH} 68		^3J 6.5, ^4J 2	^3J 7, ^4J 2	^3J 7, ^4J 2	^3J 7, ^4J 2	2.28 s: H-17
6	4.43 d	4.55 d	7.08 s		7.03 d	7.19 t	7.06 d	6.40 s: NH_2
(d)	^3J 7.5, J_{PtH} 68	^3J 14, J_{PtH} 68			^3J 7.5	^3J 7.5	^3J 8	2.31 s:H-17
7	4.42 d	4.53 d	7.15 d	7.11 d		7.11 d	7.15 d	6.39 s: NH_2
(c)	^3J 7.5, J_{PtH} 65	^3J 14, J_{PtH} 65	^3J 8.5	^3J 8.5		^3J 8.5	^3J 8.5	2.30 s: H-17
8	4.44 d	4.57 d		6.99 dd	7.15 td	6.87 td	7.29 dd	6.16 s: NH_2
(d)	^3J 7, J_{PtH} 65	^3J 15, J_{PtH} 65		^3J 8, ^4J 1.5	^3J 8, ^4J 1.5	^3J 8, ^4J 1.5	^3J 8, ^4J 1.5	3.83 s: H-17
9	4.41 dd, ^2J 1.5	4.54 dd, ^2J 1.5	7.07 t		6.88 dd	7.26 t	7.02 d	7.35 s: NH_2
(c)	^3J 7.5, J_{PtH} 65	^3J 14, J_{PtH} 65	^4J 2		^3J 8.5, ^4J 2	^{3}J8.5	^3J 8.5	3.80 s: H-17
10	4.37 dd, ^2J 1.5	4.49 dd, ^2J 1.5	7.34 d	6.87 d		6.87 d	7.34 d	7.25 s: NH_2
(c)	^3J 7.5, J_{PtH} 65	^3J 14, J_{PtH} 65	^3J 9	^3J 8		^3J 8	^3J 9	3.81 s: H-17

[a] Solvent, a: CD_3OD, b: $CDCl_3$, c: CD_3COCD_3, d: CD_3CN.

2.87 ppm and another at 3.18 ppm) and two ^{13}C signals at 49.67 and 49.71 ppm; two CH_3 group give rise to one proton signal (at 1.408 ppm) but two ^{13}C signals (at 14.64 and 14.74 ppm). In the spectra of **4b** recorded in d_6-acetone, two CH_3 groups of dimethylamine give rise to two proton signals (at 2.65 and 2.70 ppm) and two ^{13}C signals (at 40.09 and 41.99 ppm). The analogous appearance was still observed when d_6-acetone was replaced by CD_3CN or CD_3Cl. Whilst for *cis*-[Pt(Morpholine)(Et_2NH)Cl_2], the two CH_2 groups of ethylamine give rise to one proton signal, and the two CH_3 groups of ethylamine also give rise to one proton signal [7], for *trans*-[$PtCl_2(C_2H_4)(Et_2NH)$] the two CH_2 groups of ethylamine give rise to one carbon signal (at 48.979 ppm), and the two CH_3 groups of ethylamine also give rise one carbon signal (at 14.699 ppm) and one proton signal (at 1.573 ppm). This asks the question, what causes the two ethyl groups in *trans*-[Pt(Meug)(Et_2NH)Cl_2] to become non-equivalent?

To answer this, we recorded NOESY spectra of **4**, **4a**, **4b**, **7** and **8**. The signals of H-9, H-10 *cis and* H-10 *trans* of all the 10 complexes are shaped and resolved. The cross peaks *n* and *p* (Fig. 2) indicate that only group CH_2-a (H-12a) is adjacent

Table 4
^{13}C NMR signals of complexes **1**–**10**, δ (ppm) (For numeration of the C atoms see formula I–IV, for solvents see Table 2)

	1	2	3	4	5	6	7	8	9	10
C-1	148.97	149.08	147.81	149.21	149.06	148.80	148.89	148.83	148.10	148.79
C-2	150.38	150.41	149.03	150.52	150.39	150.08	150.17	150.11	150.40	150.08
C-3	114.29	113.87	112.24	114.07	113.11	112.74	112.90	113.88	111.70	112.74
C-4	133.74	132.56	131.03	132.24	132.08	132.26	132.39	132.30	130.68	132.30
C-5	122.10	121.62	120.84	121.81	121.83	121.84	121.89	121.47	121.83	121.85
C-6	113.21	113.08	111.49	113.28	113.85	113.79	113.93	112.85	113.07	113.83
C-7a	56.58	56.18	55.97	56.27	56.21	56.32	56.42	56.25	56.08	56.30
C-7b	56.54	56.08	55.97	56.12	56.08	56.28	56.34	56.27	55.76	56.27
C-8	39.87	40.14	40.10	40.13	39.70	39.80	39.82	39.89	40.01	39.77
C-9	92.11	98.01	99.71	99.21	101.44	100.48	100.45	99.64	101.08	100.62
C-10	65.20	69.26	69.35	69.19	70.08	69.21	69.20	68.45	70.04	69.19
C-11					146.39	140.82	138.52	130.52	132.29	133.30
C-12			32.22	49.71	132.12	127.18	130.67	152.00	116.48	124.30
				49.67						
C-13				14.74	121.87	140.31	122.66	112.88	161.23	115.29
				14.67						
C-14					127.46	120.10	135.99	126.98	113.63	158.55
C-15					128.05	123.38	122.66	121.81	113.92	115.29
C-16					131.59	130.05	130.67	124.11	131.00	124.30
C-17					19.13	21.41	20.94	56.83	56.21	56.21

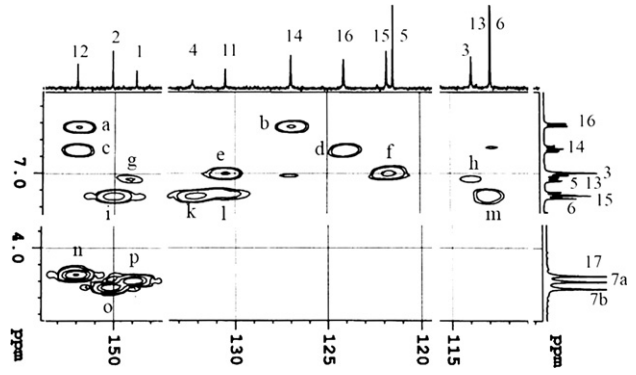


Fig. 1. A part of the HMBC spectrum of [Pt(Meug)(*o*-CH_3O-$C_6H_4NH_2$)Cl_2] (**8**).

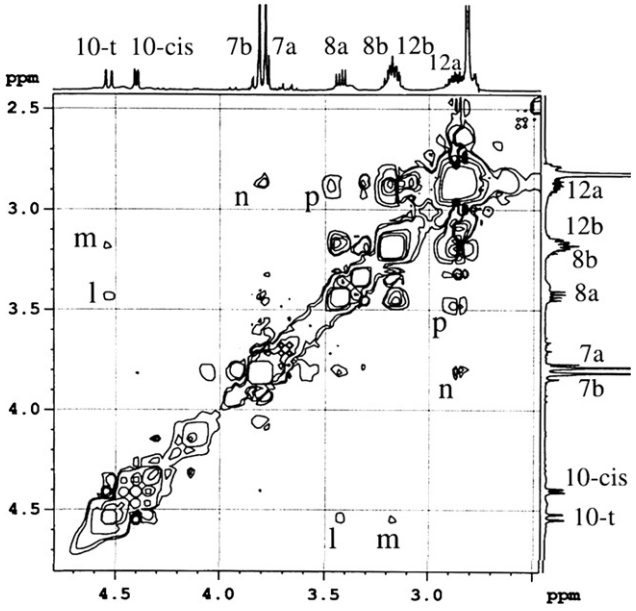


Fig. 2. A part of the NOESY spectrum of [Pt(Meug)(Et_2NH)Cl_2] (**4**).

to the protons H-7b and H-8a, while group CH_2-b (H-12b) is not. This demonstrates that a rotation around the coordination axes (Pt–olephin bond and Pt–N bond) does not occur on the NMR timescale at the recorded temperature. Thus the atom Pt becomes asymmetrical.

3. Experimental

Elemental analysis: Pt was analyzed according to the weight method [8], and C, H, N analyses were performed at the Ho Chi Minh City Center of Analytical Service. Experimentation used an automatic elemental analyzer. The molar conductivity was measured using a conductivity Meter HI 88119 N. The UV spectra were recorded on a GCB Instrument-2855 spectrophotometer. The Raman spectra were carried out on a Micro Raman LABRAM in the range 4000–100 cm^{-1}, using excited radiation at 632.8 nm from a heli-neon laser. The IR spectra were recorded on an IMPACK-410 NICOLET spectrometer in KBr discs in the range 400–4000 cm^{-1}. The NMR spectra were recorded on a Bruker AVANCE 500 MHz, all at 298–300 K, with TMS as the internal standard in a suitable solvent (Tables 2 and 3).

3.1. 4-Allyl-1,2-dimethoxybenzene (Methyleugenol, Meug)

Methyleugenol is prepared by reaction of eugenol (from *Ocimum Sanetum* L.) with dimethyl sulfate in alkaline medium, Bp. (15 mm Hg), 125–126 °C; (125–127 °C, according to [9]). ^1H NMR ($CDCl_3$, δ, ppm, J, Hz, formula I): 6.61, d, ^4J 1.8, 1H: H3; 6.62, dd, ^3J 8, ^4J 1.8, 1H: H5; 6.68, d, ^3J 8, 1H: H6; 3.73, s, 3H, 3.75, s, 3H: H7a, H7b; 3.22, d, ^3J 6.5, 2H: H8; 5.86, m, 1H: H9; 4.96, m, *J cis* 7, 1H: H10 *cis*; 4.98, m, *J trans* 12.5, 1H: H10 *trans*.

3.2. Potassium trichloro(methyleugenol)platinat(II), K[Pt(Meug)Cl$_3$] (**1**)

To a stirred solution of 3.68 g (10 mmol) of Zeise's salt in 80 ml of ethanol was slowly added a solution of 2.5 ml (16 mmol) of methyleugenol in 20 ml of ethanol. The reaction mixture was stirred at 40–45 °C for an hour. Then it was allowed to cool to room temperature. Yellow plate crystals were collected and washed with cool water, then cool ethanol, and were then dried in a vacuum at 50 °C for 2 h. The yield was 4.15 g (80%). For ^{1}H and ^{13}C NMR see Tables 2–4. *Anal.* Calc. for $KPtC_{11}H_{14}O_2Cl_3$: Pt + K_2SO_4, 54.39; C, 24.46; H, 2.70. Found: Pt + K_2SO_4, 54.75; C, 24.18; H, 2.54%.

3.3. trans-Dichloro(methyleugenol)(ammine)platinum(II), [Pt(Meug)(NH$_3$)Cl$_2$] (**2**)

K[Pt(Meug)Cl$_3$] (0.518 g, 1 mmol) was dissolved in 16 ml of 50% by volume aqueous EtOH. To this solution 8 ml of 1.5 M NH_3 solution was slowly added over 30 minutes and stirred at 10–15 °C for an additional 3 h. The resulting yellow precipitate was collected, washed with a solution of 0.1 N HCl, cool water, cool ethanol and recrystallized from 75% by volume aqueous EtOH. The light yellow crystals were dried in a vacuum at 50 °C for 2 h. The yield was 0.32 g (70%). *Anal.* Calc. for [$PtC_{11}H_{17}NO_2Cl_2$]: Pt, 42.30; C, 28.63; H, 3.69; N, 3.04. Found: Pt, 42.58; C, 28.40; H, 3.88; N, 2.82%.

3.4. trans-Dichloro(methyleugenol)(methylamine)-platinum(II), [Pt(Meug)(MeNH$_2$)Cl$_2$] (**3**)

This complex was prepared starting from 0.52 g (1 mmol) K[Pt(Meug)Cl$_3$] and 1.3 ml aqueous solution of 30% methylamine (1.2 mmol), according to the procedure for the preparation of **2**. The yield was 0.36 g (75%), light yellow crystals. *Anal.* Calc. for [$PtC_{12}H_{19}NO_2Cl_2$]: Pt, 41.05; C, 30.32; H, 4.00; N, 2.95. Found: Pt, 41.30; C, 29.98; H, 4.12; N, 2.76%.

3.5. trans-Dichloro(methyleugenol)(diethylamine)-platinum(II), [Pt(Meug)(Et$_2$NH)Cl$_2$] (**4**)

This complex was prepared starting from 0.52 g (1 mmol) K[Pt(Meug)Cl$_3$], 0.13 ml (1.2 mmol) diethylamine, according to the procedure for the preparation of **2**. The yield was 0.36 g (70%), light yellow crystals. *Anal.* Calc. for [$PtC_{15}H_{25}NO_2Cl_2$] (%): Pt, 37.72; C, 34.82; H, 4.83; N, 2.71. Found: Pt, 37.58; C, 34.98; H, 4.62; N, 2.89%.

3.6. trans-Dichloro(methyleugenol)(o-toluidine)platinum(II), [Pt(Meug)(o-$CH_3C_6H_4NH_2$)Cl$_2$] (**5**)

This complex was prepared starting from 0.52 g (1 mmol) K[Pt(Meug)Cl$_3$], 0.12 ml (1.1 mmol) *o*-toluidine, at 25–30 °C, according to the procedure for the preparation of **2**. The yield was 0.44 g (80%), light yellow crystals. *Anal.* Calc. for [$PtC_{18}H_{23}NO_2Cl_2$]: Pt, 35.39; C, 39.20; H, 4.17; N, 2.54. Found: Pt, 35.52; C, 39.48; H, 4.32; N, 2.32%.

3.7. trans-Dichloro(methyleugenol)(m-toluidine)-platinum(II), [Pt(Meug)(m-$CH_3C_6H_4NH_2$)Cl$_2$] (**6**)

This complex was prepared starting from 0.52 g (1 mmol) K[Pt(Meug)Cl$_3$], 0.118 g (1.1 mmol) *m*-toluidine, at 25–30 °C, according to the procedure for the preparation of **2**. The yield was 0.40 g (75%), light yellow crystals. *Anal.* Calc. for [$PtC_{18}H_{23}NO_2Cl_2$]: Pt, 35.39; C, 39.20; H, 4.17; N, 2.54. Found: Pt, 35.25; C, 39.37; H, 4.35; N, 2.65%.

3.8. trans-Dichloro(methyleugenol)(p-toluidine)-platinum(II), [Pt(Meug)(p-$CH_3C_6H_4NH_2$)Cl$_2$] (**7**)

This complex was prepared starting from 0.52 g (1 mmol) K[Pt(Meug)Cl$_3$], 0.118 g (1.1 mmol) *p*-toluidine, at 25–30 °C, according to the procedure for the preparation of **2**. The yield was 0.38 g (70%), light yellow crystals. *Anal.* Calc. for [$PtC_{18}H_{23}NO_2Cl_2$]: Pt, 35.39; C, 39.20; H, 4.17; N, 2.54. Found: Pt, 35.51; C, 39.38; H, 4.36; N, 2.72%.

3.9. trans-Dichloro(methyleugenol)(o-anisidine)-platinum(II), [Pt(Meug)(o-$CH_3OC_6H_4NH_2$)Cl$_2$] (**8**)

This complex was prepared starting from 0.52 g (1 mmol) K[Pt(Meug)Cl$_3$], 0.11 ml (1.1 mmol) *o*-anisidine, at 25–30 °C, according to the procedure for the preparation of **2**. The yield was 0.48 g (84%), light yellow crystals. *Anal.* Calc. for [$PtC_{18}H_{23}NO_3Cl_2$] (%): Pt, 34.39; C, 38.09; H, 4.06; N, 2.47. Found: Pt, 34.54; C, 38.22; H, 4.21; N, 2.33%.

3.10. trans-Dichloro(methyleugenol)(m-anisidine)-platinum(II), [Pt(Meug)(m-$CH_3OC_6H_4NH_2$)Cl$_2$] (**9**)

This complex was prepared starting from 0.52 g (1 mmol) K[Pt(Meug)Cl$_3$], 0.11 ml (1.1 mmol) *m*-anisidine, at 25–30 °C, according to the procedure for the preparation of **2**. The yield was 0.45 g (81%), light yellow crystals. *Anal.* Calc. for [$PtC_{18}H_{23}NO_3Cl_2$] (%): Pt, 34.39; C, 38.09; H, 4.06; N, 2.47. Found: Pt, 34.21; C, 38.25; H, 3.87; N, 2.62%.

3.11. trans-Dichloro(methyleugenol)(p-anisidine)-platinum(II), [Pt(Meug)(p-$CH_3OC_6H_4NH_2$] (**10**)

This complex was prepared starting from 0.52 g (1 mmol) K[Pt(Meug)Cl$_3$], 0.123 g (1.1 mmol) *p*-anisidine, at 25–30 °C, according to the procedure for the preparation of **2**. The yield was 0.46 g (82%), light yellow crystals. *Anal.* Calc. for [$PtC_{18}H_{23}NO_3Cl_2$] (%): Pt, 34.39; C, 38.09; H, 4.06; N, 2.47. Found: Pt, 34.26; C, 37.91; H, 4.26; N, 2.29%.

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