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^{1}H NMR AND INFRARED SPECTRA OF TRIMETHYLPLATINUM(IV) COMPLEXES OF β-DIKETONES, THIO-β-DIKETONES, AND β-IMINOKETONES

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SUMMARY

The ^{1}H NMR and infrared spectra of a number of β-diketone, thio-β-diketone, and β-iminoketone derivatives of trimethylplatinum(IV) have been recorded. The spectra indicate that in the parent compounds $[Pt(CH_3)_3L]_2$, (L = β-iminoketone or thio-β-diketone) the β-iminoketones bridge via the γ-carbon atom as found in β-diketone complexes, while the thio-β-diketones bridge via sulfur atoms. Complexes of the type $[Pt(CH_3)_3LR]$ (R = a neutral unidentate ligand) and $[Pt(CH_3)_3BipyL]$ (Bipy = 2,2′-bipyridine) have also been studied.

INTRODUCTION

Since the discovery of the compound $[Pt(CH_3)_3Acac]_2$ in 1928[1], interest has been shown in the β-diketone complexes of trimethylplatinum(IV) due to the variety of bonding modes found for these ligands. In all known cases these compounds have been found to be dimeric in solution[2,3]. The compounds were initially assumed to have bridging oxygen atoms[2], but X-ray structural determinations[4-6] showed that the β-diketone functions as a tridentate ligand, bonding through both oxygen atoms to one platinum atom and through the central (γ) carbon atom to the second platinum atom. These compounds reacted readily with a number of nitrogen donor atom ligands[7] giving species of the types $[Pt(CH_3)_3\beta\text{-DiketonatoR}]$ (R = unidentate neutral nitrogen-donor ligand) and $[Pt(CH_3)_3\beta\text{-Diketonato}]_2R$ (R = bridging bidentate nitrogen-donor ligand)[8]. In these compounds the β-diketone acts as a bidentate coordinating via the two oxygen atoms. The compound $[Pt(CH_3)_3AcacBipy]$ (Bipy = 2,2′-bipyridine) however, was shown to contain a unidentate acetylacetonate group bound only through the γ-carbon atom[9,10]. The corresponding 1,10-phenanthroline complex apparently has a similar structure[7].

Since β-diketone ligands have been found to coordinate via the γ-carbon atom, either as unidentates or tridentates[11], it seemed of interest to determine whether similar types of bonding are possible for related ligands where one or both of the oxygen groups of the β-diketone has been replaced by groups such as S or NR, or whether the electronic structures of these latter ligands are modified sufficiently to require a change in the mode of coordination from that found for β-diketone compounds.

In the present paper, a number of trimethylplatinum(IV) compounds of β-diketones, thio-β-diketones, and β-iminoketones* have been prepared and their NMR and infrared spectra investigated.

RESULTS AND DISCUSSION

^1H *NMR spectra*

β-Diketone complexes. The NMR spectra of a number of complexes of the type $[Pt(CH_3)_3\beta\text{-diketonato}]_2$ have been examined[12-14]. The compounds showed evidence for ligand exchange[13], and variable temperature studies indicated that the exchange mechanism involved cleavage of the Pt–γ-carbon bonds[14]. The rate of exchange in $[Pt(CH_3)_3Acac]_2$ has been determined[15]. The spectrum of $[Pt(CH_3)_3Acac]_2$ at −21.5° is recorded in Table 1 for comparison with the other compounds in this paper. Kite and Truter[7] prepared compounds of the formula $[Pt(CH_3)_3\beta\text{-DiketonatoR}]$, where R was a unidentate neutral nitrogen-donor ligand. In these compounds the β-diketone acted as a simple bidentate, coordinated via the two oxygen atoms[7]. The ^1H NMR spectra of such complexes with symmetrical β-diketones should show two methyl platinum triplets in the intensity ratio of 2/1. Kite *et al.*[13] found the compound $[Pt(CH_3)_3DibmPy]$ (where Dibm = anion of diisobutyrylmethane) exhibited this pattern, but $[Pt(CH_3)_3AcacQuin]$ (Quin = quinoline) gave only a single triplet, which was considered due to rapid exchange of the quinoline ligand on the NMR time scale. The spectrum of $[Pt(CH_3)_3AcacNH_3]$ was reported[13] to be difficult to interpret satisfactorily.

Table 1 lists the ^1H NMR spectra of the compounds $[Pt(CH_3)_3AcacR]$, where R = NH_3, CH_3NH_2, 3,5-lutidine, quinoline, dimethyl sulfide, and triphenylphosphine. At 34–36° the compounds R = NH_3, CH_3NH_2, and 3,5-lutidine show the expected 2/1 intensity ratio of methyl triplets, although the peaks are somewhat broad in the ammine compound. The compound R = PPh_3 shows a similar 2/1 ratio of methyl peaks, with each peak split into a doublet due to coupling between ^{31}P ($I=\frac{1}{2}$, 100% abundance) and the methyl protons. $^3J(^{31}P\text{–Pt–C–H})$ for the *trans*-methyl group (8.4 Hz) is slightly greater than that for the *cis*-methyl groups (7.6 Hz). The compound where R = quinoline shows a very broad triplet at 34° which sharpens considerably on heating to 59°. On cooling to 9°, the expected 2/1 ratio of triplets is observed. Such behaviour is consistent with rapid exchange of the quinoline ligand, but the complex nature of the quinoline absorption precludes direct confirmation of such a mechanism by observation of coupling between the α-proton of the ligand and ^{195}Pt. However, a small coupling ($J \approx 2$ Hz) between the central (γ) proton of the acetylacetonate ligand and ^{195}Pt is observed throughout the temperature range examined, so that breaking of Pt–O bonds seems unlikely.

Direct evidence for ligand exchange is obtained from the spectrum of $[Pt(CH_3)_3Acac(CH_3)_2S]$. At 34°, the methyl-platinum region consists of a sharp triplet.

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* The ligands (with their abbreviated names) used in this work are as follows: Anion of 4-hydroxy-3-penten-2-one = Acac; 3-hydroxy-1-phenyl-2-buten-1-one = Bzac; 3-hydroxy-1,3-diphenyl-2-propen-1-one = Bzbz; 4-mercapto-3-penten-2-one = Sacac; 3-mercapto-1-phenyl-2-buten-1-one = Sbzac; 3-mercapto-1,3-diphenyl-2-propen-1-one = Sbzbz; 4-mercapto-3-pentene-2-thione = Sacsac; 4-amino-3-penten-2-one = AcacNH; 4-methylamino-3-penten-2-one = $AcacNCH_3$.

TABLE 1

^{1}H NMR SPECTRA OF β-DIKETONE COMPLEXES OF TRIMETHYLPLATINUM(IV) IN $CDCl_3$

Compound	*Temp (°C)*	*No. of PtCH$_3$ peaks*	*Ratio*	*Trans atom*	*J(Pt–CH$_3$)*	*τ(PtCH$_3$)*	*τ(H$_γ$)*	*J(Pt–H$_γ$)*	*τ(lig–CH$_3$)*	
$[Pt(CH_3)_3Acac]_2$	34	1			74.8	8.99	5.37	42.0	8.02	
	−21.5	2	2	O	75.1	8.97	5.35		8.00	
			1	C	73.3	9.06				
$[Pt(CH_3)_3AcacNH_3]$	34	2	2	O	74.3	9.12	4.82	2.5	8.07	
			1	N	73.6	9.31				
$[Pt(CH_3)_3AcacCH_3NH_2]$	34	2	2	O	74.3	9.17	4.82	2.5	8.07	
			1	N	71.7	9.34				
$[Pt(CH_3)_3AcacQuin]$	59	1			73.5	8.90	5.01	2.0	8.19	
	9	2	2	O	74.0	8.88	5.00		8.17	
			1	N	73.0	8.98				
$[Pt(CH_3)_3AcacLut]$	34	2	2	O	74.0	9.01	4.98	2.5	8.09	τ(Lut–CH_3) 7.67
			1	N	71.2	9.19				
$[Pt(CH_3)_3Acac(CH_3)_2S]$	34	1			73.7	9.11	4.78	2.0	8.07	τ[$(CH_3)_2S$] 7.83
	−20	2	2	O	74.2	9.12	4.76		8.05	^3J(H–C–S–Pt) 9.9 Hz
			1	S	71.7	9.10				
$[Pt(CH_3)_3AcacPPh_3]$	34	2	2	O	74.2	8.97	5.37	2.0	8.31	^3J(P–Pt–CH_3) 7.6
			1	P	60.4	9.11				8.4
$[Pt(CH_3)_3BipyAcac]$	34	2	2	N	68.8	9.03	6.05	51.3	8.51	
			1	C	63.8	9.73				
$[Pt(CH_3)_3PhenAcac]$	34	2	2	N	69.2	8.78	5.97	51.5	8.69	
			1	C	64.0	9.71				
$[Pt(CH_3)_3BzacLut]$	34	3	1	O	74.3	8.89	4.26		7.97	τ(Lut–CH_3) 7.71
			1	O	74.0	8.93				
			1	N	71.2	9.10				
$[Pt(CH_3)_3BzbzLut]$	34	2	2	O	74.5	8.82	3.63			τ(Lut–CH_3) 7.74
			1	N	71.2	9.03				

On cooling to $-20°$, the expected 2/1 intensity ratio is observed. The methyl peak of the dimethyl sulfide ligand, which is broad at 34°, is a sharp triplet at $-20°$ due to coupling between the methyl protons and ^{195}Pt ($J \approx 10.0$ Hz), which indicates exchange of the dimethyl sulfide ligand at the higher temperature. The compounds with R$=$NH$_3$, CH$_3$NH$_2$, and 3,5-lutidine all show exchange phenomena at higher temperatures in high boiling solvents such as nitrobenzene or tetrachloroethylene. The compound [Pt(CH$_3$)$_3$AcacPPh$_3$] tends to decompose at temperatures above 120° rather than undergo exchange. A rough order of increasing ease of exchange of the group R in [Pt(CH$_3$)$_3$AcacR] is PPh$_3$ < 3,5-lutidine < CH$_3$NH$_2$ < NH$_3$ < quinoline < dimethyl sulfide. Preliminary experiments with methyl benzyl sulfide indicate a similar ease of exchange to that of the dimethyl sulfide ligand and it is apparent that for this system neutral ligands with S donor atoms are more labile than those with N donor atoms. The lability of the quinoline probably results from a combination of low base strength and steric effects due to the bulkiness of the ligand. The coupling constant for the methyl group *trans* to O is remarkably constant throughout the series (73.5 to 74.3 Hz) suggesting that there is little *cis* influence from the R groups. The coupling constant for the methyl group *trans* to R is strongly dependent on the R group as has been found for other trimethylplatinum(IV) compounds[13,16,17]. Values range from 73.6 Hz for R$=$NH$_3$ to 60.4 Hz for R$=$PPh$_3$. In general, the values are of the same order as found for these ligands in other trimethylplatinum(IV) compounds[16-18], although there is some evidence for effects from the ligands in the *cis* positions. For example, for the compounds with R$=$NH$_3$ and R$=$CH$_3$NH$_2$ the coupling constants for methyl groups in *trans* positions are 73.6 and 71.7 Hz respectively, which are somewhat higher than those found in the compounds [Pt(CH$_3$)$_3$BipyR]ClO$_4$[17] (71.7 and 69.6 Hz respectively) and the compounds $[\mathrm{Pt(CH_3)_3R_3}]^+$[16] (71.0 and 68.4 Hz respectively). Similarly the value for R$=$PPh$_3$ (60.4 Hz) may be compared with those for [Pt(CH$_3$)$_3$Bipy PPh$_3$]ClO$_4$ (58.5 Hz)[17] and a range of bis(phosphine) complexes (56–59 Hz)[18]. The value of 71.7 Hz for the methyl group *trans* to dimethyl sulfide indicates that the *trans* influence of organic sufides is of the same order as is found for amines.

In each of the compounds [Pt(CH$_3$)$_3$AcacR] a small coupling ($J \approx 2$Hz) is observed between ^{195}Pt and the central (γ) proton of the acetylacetonate ligand. Kite *et al.*[13] have noted such a coupling in the compounds which they examined. As also noted by Kite *et al.*[13], there is no evidence for coupling between ^{195}Pt and the methyl protons of the ligand, although such splitting occurs in platinum(II) complexes of acetylacetone[19].

Little information may be obtained from the chemical shift values of the protons due to the range of electronic environments produced by the ligands R. In general, however, those compounds with R groups containing aromatic rings have the methyl platinum protons deshielded compared to those compounds with R groups having no unsaturation. The methyl groups of the acetylacetone are on the other hand slightly shielded.

Comparison between the chemical shifts of the central proton in [Pt(CH$_3$)$_3$-Acac]$_2$ and [Pt(CH$_3$)$_3$AcacR] (R$=$NH$_3$, CH$_3$NH$_2$) reveals an upfield shift in the dimer of ≈ 0.5 ppm (Table 1). Such a difference may be the result of the central proton having a more saturated character in the tridentate ligand than in the normal bidentate form. The compounds with unsaturated R groups show upfield shifts for the central proton, suggesting shielding effects from the aromatic rings.

The effect of substituting methyl groups of acetylacetone by phenyl groups is shown in the spectra of the compounds [Pt$(CH_3)_3$BzacLut] and [Pt$(CH_3)_3$BzbzLut] (Table 1). Comparison with the spectrum of [Pt$(CH_3)_3$AcacLut] shows that the coupling constant values for the methyl platinum protons are not altered appreciably by the substitution, but the chemical shift values decrease by 0.1–0.2 ppm due to deshielding of these protons. The central proton resonance is affected to a larger extent, being shifted by $\approx$0.7 ppm as each phenyl group is inserted.

Kite and Truter[7] reported that [Pt$(CH_3)_3$BipyAcac] and [Pt$(CH_3)_3$PhenAcac] were too insoluble in organic solvents for interpretable PMR spectra to be obtained. We have found both compounds to be moderately soluble in chloroform and nitrobenzene, giving spectra which are readily interpretable in terms of the same structure as in the solid state[9,10]. Table 1 lists the observed spectra in $CDCl_3$. Both compounds give the expected 2/1 intensity ratio of methyl triplets. The coupling constants $^2J(^{195}Pt–CH_3)$ for the methyl groups *trans* to the γ-carbon atom are 63.8 Hz for the 2,2′-bipyridine compound and 64.0 Hz for the 1,10-phenanthroline compound. In both compounds the γ-proton couples with ^{195}Pt with a magnitude of $\approx$51 Hz which is substantially greater than that observed in [Pt$(CH_3)_3$Acac]$_2$ (42.0 Hz). Such data provide evidence for a stronger Pt–C bond in these compounds than in [Pt$(CH_3)_3$Acac]$_2$[17,20,21].

The influence of the aromatic rings of 2,2′-bipyridine and 1,10-phenanthroline is evident in the large upfield shifts of $\approx$0.6 ppm for the *cis*-methyl platinum protons, the acetylacetonate methyl protons, and the central proton resonance compared with those of [Pt$(CH_3)_3$Acac]$_2$. Similar shifts in the *cis* methyl group were observed in a number of 2,2′-bipyridine complexes of trimethylplatinum(IV)[17].

Thio-β-diketone complexes. The ^{1}H NMR spectra in $CDCl_3$ of a number of trimethylplatinum(IV) complexes of monothio-β-diketones appear in Table 2. The spectra of [Pt$(CH_3)_3$SacacLut] and [Pt$(CH_3)_3$SacacPPh$_3$] are readily interpreted on the basis of Sacac functioning as a bidentate through O and S atoms. Three nonequivalent methyl platinum triplets would be anticipated for this structure and three are in fact observed for the lutidine complex. In the case of [Pt$(CH_3)_3$SacacPPh$_3$] each of the three peaks is split into a doublet due to coupling with ^{31}P.

Two of the methyl peaks in [Pt$(CH_3)_3$SacacLut] have coupling constants of 76.8 and 60.9 Hz, which are almost identical with values of 76.5 and 60.9 Hz found in [Pt$(CH_3)_3$SacacPPh$_3$], so that these resonances are assigned to the methyl groups *trans* to the Sacac ligand. The third coupling constant for each compound (71.9 Hz for R = Lut, and 61.2 Hz for R = PPh$_3$) is consistent with the value found for the corresponding Acac compound [Pt$(CH_3)_3$AcacR] (71.2 and 60.4 Hz respectively).

Coupling constants for methyl groups *trans* to oxygen donor ligands are usually found to lie in the range 73–81 Hz[13,17], so that the values of 76.5 and 76.8 Hz obtained above are probably due to the methyl groups *trans* to the oxygen of the Sacac ligand. Such values are higher than those found in the compounds [Pt$(CH_3)_3$AcacR] [$^2J(Pt–CH_3) \approx 74.2$ Hz] and may indicate a slightly weaker Pt–O bond in the Sacac complexes. The value of 60.9 Hz must then be assigned to the methyl group *trans* to the sulfur atom of Sacac. This value may be compared with those found for methyl groups *trans* to unidentate sulfur bonded ligands in the complexes [Pt$(CH_3)_3$BipySCN][17] ($J \approx 70.5$ Hz) and [Pt$(CH_3)_3$Acac$(CH_3)_2$S] ($J \approx 71.8$ Hz). From these values it

TABLE 2

^{1}H NMR SPECTRA OF THIO-β-DIKETONE COMPLEXES OF TRIMETHYLPLATINUM(IV) IN $CDCl_3$

Compound	*No. of $PtCH_3$ peaks*	*Ratio*	*Trans atom*	*$J(Pt-CH_3)$*	*$\tau(PtCH_3)$*	*$\tau(H_\gamma)$*	*$\tau(lig-CH_3)$*	
$[Pt(CH_3)_3Sacac]_2$	3	1	S	74.4	9.17	3.58	7.84, 7.86	
		1	S	62.3	9.05			
		1	O	80.6	8.75			
$[Pt(CH_3)_3SacacLut]$	3	1	O	76.8	9.10	3.82	7.77, 7.99	$\tau(Lut-CH_3)$ 7.68
		1	S	60.9	9.08			
		1	N	71.9	9.10			
$[Pt(CH_3)_3SacacPPh_3]$	3	1	O	76.5	9.20	4.18	7.98, 8.24	$^3J(P-Pt-CH_3)$ 7.3
		1	S	60.9	9.02			7.3
		1	P	61.2	8.94			8.1
$[Pt(CH_3)_3BipySacac]$	2	2	N	70.1	8.72	4.18	7.80, 8.23	
		1	S	64.8	9.65			
$[Pt(CH_3)_3Sbzac]_2$[a]	3	1	S	74.0	9.09		7.74	
		1	S	63.8	8.90			
		1	O	80.6	8.65			
$[Pt(CH_3)_3SbzacLut]$	3	1	O	76.5	9.01	3.18	7.65	$\tau(Lut-CH_3)$ 7.73
		1	S	60.9	8.96			
		1	N	72.0	9.03			

[Pt(CH$_3$)$_3$BipySbzac]	2	2	N	70.2	8.67	3.57	7.68	
		1	S	64.8	9.66			
[Pt(CH$_3$)$_3$Sbzbz]$_2$[a]	3	1	S	74.8	9.12			
		1	S	64.4	9.64			
		1	O	80.7	8.62			
[Pt(CH$_3$)$_3$SbzbzLut]	3	1	O	76.8	8.92	2.86		τ(Lut-CH$_3$) 7.73
		1	S	61.1	8.88			
		1	N	72.2	8.92			
[Pt(CH$_3$)$_3$BipySbzbz]	4	4	N	70.0	8.67	3.41		τ(Ph) 3.06
		2	S	65.0	9.71			
		2	N	70.0	8.90			
		1	C	65.2	9.93			
[Pt(CH$_3$)$_3$Sacsac]$_2$[b]	6	1	S	74.2	8.58	3.84	Complex pattern	
		1	S	71.6	8.82	4.11		
		1	S	67.0	8.93			
		1	S	66.8	9.40			
		1	S	70.0	9.54			
		1	S	68.0	9.73			
[Pt(CH$_3$)$_3$SacsacPPh$_3$]	2	2	S	62.9	9.33	3.26	7.98	^3J(P–Pt–CH$_3$) 6.9
		1	P	62.9	9.09			7.9

[a] Assumed to be dimers. [b] Dimer, two isomers.

is apparent that the platinum–sulfur bond strength is greater in the Sacac complex.

The PMR spectrum of the parent compound $[Pt(CH_3)_3Sacac]_2$ (known to be dimeric from molecular weight measurements) is less readily interpreted. Three major methyl platinum triplets in the intensity ratio of 1/1/1 with $^2J(^{195}Pt–CH_3)$ values of 80.6, 74.4, and 62.3 Hz are observed along with some weak peaks. Several modes of bonding are possible for the Sacac ligand, each of which would give rise to a set of three non-equivalent methyl groups. The ligand may coordinate via the central (γ) carbon atom as was observed for $[Pt(CH_3)_3Acac]_2$, or may bridge through either the oxygen or sulfur atoms. The carbon bonded species may be eliminated since coupling of the central proton resonance with ^{195}Pt, which would have been expected to be of the order of 42 Hz as observed for $[Pt(CH_3)_3Acac]_2$, is absent.

Trimethylplatinum(IV) complexes with bridging oxygen atoms are known for $[Pt(CH_3)_3Sal]_2$[22] (Sal = salicylaldehyde) and $[Pt(CH_3)_3Oxine]_2$[23] (Oxine = 8-hydroxyquinoline), and for the latter compound the oxygen atom bridges unsymmetrically as shown by the observation of different coupling constants for the *trans*-methyl groups (76.0 and 80.4 Hz)[13]. A trimethylplatinum(IV) species with bridging sulfur atoms has been postulated for $[Pt(CH_3)_3SCN]_4$ ($J \approx 75.0$ Hz)[24]. The values of 80.6, 74.4 and 62.3 Hz are somewhat difficult to interpret in terms of either mode of bridging. Values of 80.6 and 74.4 Hz would be consistent with the presence of a bridging oxygen atom, but it seems unlikely that a lower $^2J(^{195}Pt–CH_3)$ coupling constant (and hence stronger Pt–O bond) would be obtained in a bridging species as compared with the simple bidentate Sacac (76.5 Hz). If the compound does bridge through sulfur, the bond must be highly unsymmetrical with coupling constants for *trans*-methyl groups of 74.4 and 62.3 Hz, and the bridge would be expected to be cleaved quite readily. This latter mode of bonding must be favoured in view of the tendency of platinum to coordinate more readily with sulfur donor atoms than with oxygen donor atoms.

The compounds $[Pt(CH_3)_3Sbzac]_2$ and $[Pt(CH_3)_3Sbzbz]_2$, although far less soluble than $[Pt(CH_3)_3Sacac]_2$ in $CDCl_3$, show a similar pattern of three non-equivalent methyl groups and the coupling constant values are quite similar to those of $[Pt(CH_3)_3Sacac]_2$ {80.6, 74.0 and 63.8 Hz for $[Pt(CH_3)_3Sbzac]_2$ and 80.7, 74.8, and 64.4 Hz for $[Pt(CH_3)_3Sbzbz]_2$}. It is reasonable to assume that these compounds are also dimeric with a similar bridged structure. The electronic structures of the thio-β-diketone ligands are apparently sufficiently different from those of the corresponding β-diketones to preclude the formation of γ-carbon bonded tridentate species.

If the compounds have sulfur bridges, two isomers are possible as shown in Fig. 1, L = oxygen. The weak peaks observed in the spectrum of $[Pt(CH_3)_3Sacac]_2$ are almost certainly due to a second isomer, since reaction of the sample with lutidine in an NMR tube yields only peaks due to $[Pt(CH_3)_3SacacLut]$. The spectra of the compounds $[Pt(CH_3)_3Sbzac]_2$ and $[Pt(CH_3)_3Sbzbz]_2$ which are much less soluble than the Sacac complex are interpretable in terms of only one isomer.

The NMR spectra obtained do not allow unequivocal assignment to a particular isomer. They do, however, provide evidence for *S*-bridged species as opposed to *O*-bridged species from observation of chemical shift values. Substitution of a phenyl group for the methyl group on the C=O carbon atom as in $[Pt(CH_3)_3Sbzac]_2$ causes a downfield shift of roughly equal magnitude for each of the three methyl proton triplets (Table 2). Substitution of a phenyl group at the C=S carbon atom also

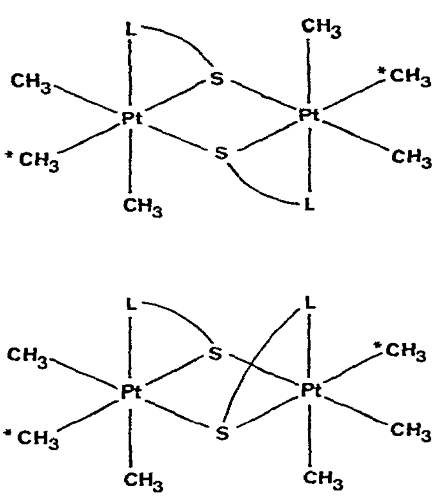


Fig. 1. Possible isomers of $[Pt(CH_3)_3Thio\text{-}\beta\text{-diketone}]_2$ (L = O) and $[Pt(CH_3)_3Sacsac]_2$ (L = S).

as in $[Pt(CH_3)_3Sbzbz]_2$ results in a large upfield shift (≈ 6 ppm) of one of the methyl platinum resonances. Such an effect would be expected for the labelled (*) methyl groups (Fig. 1) which, according to models, lie quite near to this second phenyl group in both isomers with bridging S atoms. For bridging O atoms, such an effect would be anticipated in the compound $[Pt(CH_3)Sbzac]_2$ as well as in $[Pt(CH_3)_3\text{-}Sbzbz]_2$.

Of the parent compounds, only $[Pt(CH_3)_3Sacac]_2$ is sufficiently soluble in $CDCl_3$ to allow observation of the central proton resonance. This resonance lies at τ 3.58, a value consistent with the ligand having a structure similar to that of a bidentate, since the absorption lies in the region of that observed for $Ni(Sacac)_2$ (τ 3.59)[25]. The value is somewhat lower than those found in $[Pt(CH_3)_3SacacLut]$ (τ 3.82) and $[Pt(CH_3)_3SacacPPh_3]$ (τ 4.18), where some shielding of the central proton by the aromatic rings of 3,5-lutidine and triphenylphosphine would be expected. Such values may be contrasted with those of the acetylacetonate system, where the central proton in $[Pt(CH_3)_3Acac]_2$ lies in the same region as that in $[Pt(CH_3)_3AcacPPh_3]$.

The spectra of $[Pt(CH_3)_3SbzacLut]$ and $[Pt(CH_3)_3SbzbzLut]$ are readily interpretable in terms of a structure similar to that for $[Pt(CH_3)_3SacacLut]$. Coupling constants indicate the presence of methyl groups *trans* to oxygen (76.5 and 76.8 Hz respectively), sulfur (60.9 and 61.1 Hz), and the lutidine nitrogen (72.0 and 72.2 Hz). The effect on chemical shifts of successive substitution of the thioacetylacetone methyl groups by phenyl groups is similar to that observed in the acetylacetone complexes. The γ-carbon proton is deshielded by 0.6 ppm with the introduction of one phenyl group and a further 0.3 ppm with the second phenyl group.

The NMR spectrum of $[Pt(CH_3)_3BipySacac]$ has two methyl-platinum triplets in the intensity ratio of 2/1. The coupling constants are 70.1 Hz for the more intense peak, which is indicative of methyl groups *trans* to 2,2′-bipyridine[17], and 64.8 Hz, which would be consistent with the presence of either a methyl group *trans* to a γ-carbon atom {*cf.* 63.8 Hz in $[Pt(CH_3)_3BipyAcac]$} or to a sulfur atom. Since coupling of the central proton with ^{195}Pt is not observed {*cf.* 51.3 Hz for $[Pt(CH_3)_3Bipy\text{-}$

Acac]} it appears that the Sacac ligand is coordinating via the sulfur atom in this compound. Such a mode of bonding has been reported for fluorinated monothio-β-diketones in a number of Ni^{II}, Pd^{II} and Pt^{II} complexes[26].

The chemical shift value of the central proton (τ 4.18) may support the absence of a Pt–γ-carbon bonded ligand, since it lies in the same region as that of [$Pt(CH_3)_3$-SacacPPh$_3$] (τ 4.18) whereas the central proton resonance of [$Pt(CH_3)_3$BipyAcac] (τ 6.05) was found well upfield from that of [$Pt(CH_3)_3$AcacPPh$_3$] (τ 5.37), presumably due to the more saturated nature of the central proton in the γ-carbon bonded species. Thus in the reaction of [$Pt(CH_3)_3$Sacac]$_2$ with 2,2′-bipyridine, the platinum–oxygen bond and the sulfur bridge are broken, but the platinum–sulfur bond must be sufficiently stable to prevent rearrangement to the γ-carbon bonded species.

The spectrum of [$Pt(CH_3)_3$BipySbzac] resembles that of [$Pt(CH_3)_3$BipySacac] in both coupling constants and chemical shifts, so that a sulfur bonded Sbzac ligand is presumably present. The NMR spectrum of the product of reaction between [$Pt(CH_3)_3$-Sbzbz]$_2$ and 2,2′-bipyridine, however, indicates the presence of two isomers in a 2/1 ratio, each isomer exhibiting two methyl platinum triplets in the intensity ratio of 2/1. The spectrum attributed to the major isomer is similar to those of [$Pt(CH_3)_3$Bipy-Sacac] and [$Pt(CH_3)_3$BipySbzac], both in chemical shifts and coupling constants and may thus be assigned to a compound with sulfur bonded Sbzbz. The second component has coupling constant values of similar magnitude to the major component (70.0 and 65.2 Hz as compared with 70.0 and 65.0 Hz) but both peaks are shifted ≈0.2 ppm to higher field. This second component is probably a Bipy complex with the Sbzbz ligand bonding in a different way. Bonding via the oxygen atom seems unlikely in view of the value of 65.2 Hz for the *trans*-methyl group, and the only other likely mode of bonding would be via the γ-carbon atom. A value of 65.2 Hz would not be inconsistent with a methyl group *trans* to γ-carbon {63.8 Hz for [$Pt(CH_3)_3$BipyAcac]}, but it is unusual that such a species would form in only this system, unless the platinum–sulfur bond in the Sbzbz compound is sufficiently weakened by the electron-withdrawing properties of the phenyl groups of the ligand. Although a peak at τ 3.41 could be assigned to the central proton resonance of the Sbzbz ligand for the major component of the mixture, that for the minor component could not be assigned with certainty, and probably lies under phenyl group absorptions.

One interesting feature of the phenyl absorptions is the presence of a single sharp resonance at τ 3.06 consistent with the presence of freely rotating phenyl groups. In all other phenyl-substituted thio-β-diketone complexes studied the phenyl group absorptions were invariably split into 2/2/1 multiplets. The ratio of this peak to the methyl peaks of the minor component of the mixture is consistent with the phenyl resonance being due to the minor component.

The spectrum of [$Pt(CH_3)_3$SacsacPPh$_3$] is consistent with the presence of bidentate Sacsac. Two sets of methyl resonances (triplets split by ^{31}P into sextets) in the intensity ratio of 2/1 are observed, each with a coupling constant of 62.9 Hz. The coupling of the methyl protons with ^{31}P is again slightly larger for the *trans*-methyl group (7.9 Hz) than for the *cis*-methyl groups (6.9 Hz). Only one Sacsac methyl resonance is present as anticipated. The central proton resonance is at τ 3.26, higher than that found in Ni(Sacsac)$_2$[25] (τ 2.94) which probably indicates shielding by the phenyl groups of the triphenylphosphine as was observed for the analogous Acac and Sacac complexes.

The compound $[Pt(CH_3)_3SacsacLut]$ gives only very broad methyl platinum peaks, indicating that the 3,5-lutidine group is undergoing exchange at ambient temperatures, so that the Sacsac ligand evidently has a greater *cis* effect on the Pt–N bond than Sacac and Acac in the corresponding compounds.

The compound $[Pt(CH_3)_3Sacsac]_2$ gives a spectrum which is difficult to interpret completely. A total of six methyl triplets is observed, all of approximately equal intensity. Such a pattern may be interpreted in terms of two isomeric forms each with three non-equivalent CH_3 groups. If a similar S-bridged structure to that obtained with the monothio-β-diketones is present, two isomers are possible as shown in Fig. 1, L = sulfur.

Two resonances of about equal intensity are observed at τ 3.84 and 4.11 and these are presumably due to the central protons. There is no evidence for coupling with ^{195}Pt for either resonance, so that it is highly unlikely that γ-carbon bonded species are present in $[Pt(CH_3)_3Sacsac]_2$. The chemical shift values are, however, substantially higher than that found in the bis(bidentate) complex $Ni(Sacsac)_2$ (τ 2.94)[25], and even that in $[Pt(CH_3)_3SacsacPPh_3]$ (τ 3.26).

Reference to the coupling constants in Table 2 reveals a range of values from 66.8 to 74.2 Hz, all of which are substantially higher than those found for methyl groups *trans* to S in $[Pt(CH_3)_3SacsacPPh_3]$ where the ligand functions as a bidentate. Due to the fairly similar coupling constants obtained it is difficult to assign any of the methyl platinum resonances either to a particular isomer or to a particular environment within an isomer.

As expected, the Sacsac methyl region consists of a number of partially overlapping peaks, indicating that the methyl groups of the ligands are probably non-equivalent in the compounds.

The inability of the compound $[Pt(CH_3)_3Sacsac]_2$ to react with 2,2′-bipyridine is consistent with the strength expected for the Pt–S bond, and agrees with the observations for the thio-β-diketone complexes where, in general, the Pt–S bond remains unbroken on reaction with 2,2′-bipyridine.

β-Iminoketone complexes. The compounds $[Pt(CH_3)_3AcacNHL]$ (L = 3,5-lutidine, triphenylphosphine) give spectra readily interpretable in terms of monomeric species containing AcacNH as a bidentate ligand. Three methyl platinum triplets are observed for the complex where L = Lut, and three sextets for L = PPh_3 due to coupling between the methyl protons and ^{31}P. Again, $^3J(P\text{–}Pt\text{–}CH_3)$ for the methyl group *trans* to phosphorus (8.7 Hz) is greater than that for the *cis*-methyl groups which are *trans* to nitrogen (7.4 Hz) and oxygen (7.2 Hz). For $[Pt(CH_3)_3AcacNHPPh_3]$, the coupling constants of the methyl groups are 72.3, 63.2, and 62.0 Hz which are assigned to methyl groups *trans* to oxygen, nitrogen, and phosphorus respectively. The value of 63.2 Hz for the methyl *trans* to nitrogen is significantly lower than is normally observed for methyl groups *trans* to nitrogen-bonded ligands[13,17]. A similar lowering of coupling constants was noted earlier for methyl groups *trans* to sulfur in the thio-β-diketone complexes. For $[Pt(CH_3)_3AcacNHLut]$, the coupling constant for the methyl group *trans* to N is 63.0 Hz, but it is difficult to assign the other peaks since the coupling constants are similar (72.7 and 73.2 Hz).

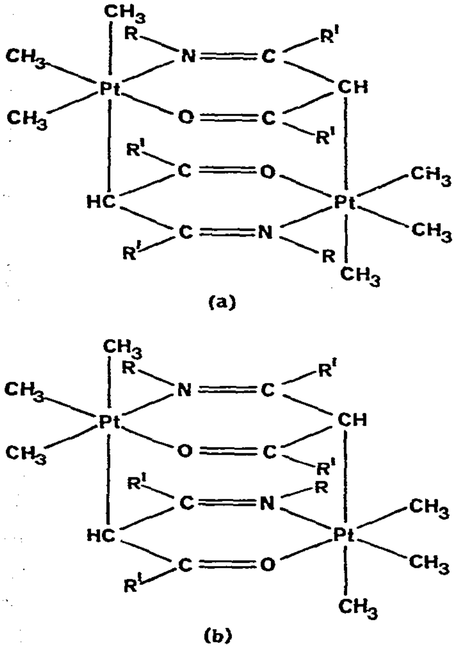
The NMR spectral data for $[Pt(CH_3)_3AcacNH]_2$, found to be dimeric in $CDCl_3$ solution, are shown in Table 3. At 34°, a single, sharp methyl platinum triplet with a coupling constant of 70 Hz is observed, indicating an exchange phenomenon

TABLE 3

^{1}H NMR SPECTRA OF β-IMINOKETONE COMPLEXES OF TRIMETHYLPLATINUM(IV) IN $CDCl_3$

Compound	*Temp.* (°C)	*No. of $PtCH_3$ peaks*	*Ratio*	*Trans atom*	*$J(Pt-CH_3)$*	*$\tau(PtCH_3)$*	*$\tau(H_\gamma)$*	*$J(Pt-H_\gamma)$*	*$\tau(lig\text{-}CH_3)$*	
$[Pt(CH_3)_3AcacNH]_2$	−15	3	1	C	71.1	9.24	6.20	44.4	7.98, 8.12	$^4J(H-N-C-C-H)$ 2.2 Hz
			1	N	62.4	9.27				
			1	O	73.6	9.32				
$[Pt(CH_3)_3AcacNCH_3]_2$	−15	3	1	N	64.8	9.12	6.15	49.5	Complex pattern	$^3J(H-C-N-Pt)$ 16.0 Hz
			1	O	74.2	9.21				
			1	C	70.4	9.23				
$[Pt(CH_3)_3AcacNHLut]$	34	3	1	N	72.7	9.22	5.38		8.10	$\tau(Lut\text{-}CH_3)$ 7.61 $^4J(H-N-C-C-H)$ 2.2 Hz
			1	O	73.2	9.25				
			1	N	63.0	9.30				
$[Pt(CH_3)_3AcacNHPPh_3]$	34	3	1	N	63.2	9.07	5.72		8.31, 8.44	$^3J(P-Pt-CH_3)$ 7.4, 8.7 7.2
			1	P	62.0	9.11				
			1	O	72.3	9.35				$^4J(H-N-C-C-H)$ 2.2 Hz
$[Pt(CH_3)_3AcacNCH_3Lut]$	34	3	1	N	72.2	9.14	5.43		8.13, 8.16	$\tau(Lut\text{-}CH_3)$ 7.68 $^3J(H-C-N-Pt)$ 15.0 Hz
			1	N	64.3	9.19				
			1	O	72.4	9.23				

at this temperature. On cooling to −15°, three main methyl platinum triplets in the intensity ratio of 1/1/1, together with some weak peaks are observed. The major peaks are consistent with the β-iminoketone ligand functioning as a tridentate through oxygen and nitrogen to one platinum atom, and via the central (γ) carbon atom to a second platinum atom, analogous to the bonding mode in the β-diketone complexes. Such a mode of bonding is confirmed by observation of coupling between the central proton and ^{195}Pt($J \approx 44.4$ Hz) at −15°. At 34°, the absorption is broad with no satellites, so that the exchange behaviour probably involves breaking of the Pt–γ-carbon bond as found with the β-diketone complexes[14]. Since $[Pt(CH_3)_3AcacNH]_2$ is capable of existing in two isomeric forms, as indicated in Fig. 2 with R=H and R′=CH_3, the weak peaks observed in the spectrum may indicate the presence of a second isomer.



(a)

(b)

Fig. 2. Possible isomers of $[Pt(CH_3)_3AcacNR]_2$ (R′=CH_3, R=H or CH_3).

The methyl platinum peaks in the spectrum of $[Pt(CH_3)_3AcacNH]_2$ at −15° exhibit coupling constants of 73.6, 71.1 and 62.4 Hz. The values of 73.6 and 62.4 Hz are assigned to the methyl groups *trans* to oxygen and nitrogen respectively, by comparison with the values found in the triphenylphosphine derivative. The value of 71.1 Hz, which is of the same order as those found for CH_3 *trans* to γ-carbon in the compounds $[Pt(CH_3)_3$-β-Diketonato$]_2$ (71.0–75.5 Hz)[14], is then assigned to the methyl group *trans* to γ-carbon.

The spectra of the three AcacNH compounds show a slight splitting of the central proton of the AcacNH ligand (J 2.2 Hz) which is due to coupling between the central proton and the proton on the nitrogen atom.

The spectrum of $[Pt(CH_3)_3AcacNCH_3]_2$ indicates a similar dimeric γ-carbon bonded species to that for $[Pt(CH_3)_3AcacNH]_2$. At 34° the spectrum exhibits a single methyl platinum triplet and a broad central proton resonance. The spectrum at $-15°$ consists of three equally intense methyl triplets with coupling constants of 74.2, 70.4, and 64.8 Hz. These may be assigned to the methyl groups *trans* to oxygen, γ-carbon, and nitrogen respectively. At $-15°$ the central proton couples to platinum-195 with a magnitude of 49.5 Hz, indicating a stronger Pt–C bond[20,21] in this complex as compared with those of $[Pt(CH_3)_3AcacNH]_2$ (44.4 Hz) and $[Pt(CH_3)_3\beta\text{-Diketonato}]_2$ (41-42.5 Hz). The *N*-methyl group couples to ^{195}Pt throughout the temperature range studied indicating there is no rapid dissociation of the Pt–N bond in $[Pt(CH_3)_3AcacNCH_3]_2$. The magnitude of the coupling is 16.0 Hz.

The derivative $[Pt(CH_3)_3AcacNCH_3Lut]$ has three methyl platinum triplets of equal intensity with coupling constants of 72.4, 72.2 and 64.3 Hz. As for the corresponding AcacNH complex, it is difficult to distinguish between methyl groups *trans* to oxygen and lutidine, but the value of 64.3 Hz may be assigned to the methyl *trans* to nitrogen.

The central proton resonances in $[Pt(CH_3)_3AcacNH]_2$ and $[Pt(CH_3)_3AcacNCH_3]_2$ both lie substantially at higher field than those of their lutidine derivatives, which parallels the behaviour of the central proton resonances in the acetylacetone system.

Comparison of the coupling constants for the methyl group *trans* to lutidine in the series of complexes studied, $[Pt(CH_3)_3LLut]$ ($L=\beta$-diketonate, thio-β-diketonate, or β-iminoketonate) shows a small *cis* influence from the L ligand. Values vary from 71.2 Hz for $L=\beta$-diketonate to 72.7 Hz for $L=\beta$-iminoketonate. A similar effect is observed in the phosphine complexes, with values ranging from 60.4 Hz for L= Acac to 62.9 Hz for L=Sacsac. The order is similar in each case.

Infrared spectra

The compounds studied show peaks characteristic of methyl–platinum vibrations and vibrations of the β-diketone, thio-β-diketone and β-iminoketone ligands. Only a few of the modes of the latter ligands are dependent on their type of coordination, the remainder being relatively unchanged from those of the normal bidentate ligands found in other metal complexes[27]. These modes are listed in Table 4 together with the Pt–C stretching frequencies. Bands due to 3,5-lutidine, 2,2′-bipyridine and triphenylphosphine are relatively invariant and are not recorded.

C=O stretching frequency. The C=O stretching frequency of the acetylacetonate ligand has been found to depend strongly on its mode of coordination. In complexes containing bidentate oxygen-bonded acetylacetone, ν(C=O) is generally found[28] in the range 1570–1600 cm^{-1}. For platinum(II) complexes with unidentate *C*-bonded acetylacetone groups, the frequency is usually much higher due to the predominance of the diketo tautomer of acetylacetone[19]. Where the ligand functions as a tridentate, the value found tends to be intermediate between those for the unidentate and bidentate species[29]. In the present work, bands at 1580, 1639, 1635 and 1613 cm^{-1} are assigned to ν(C=O) in $[Pt(CH_3)_3AcacLut]$, $[Pt(CH_3)_3BipyAcac]$, $[Pt(CH_3)_3PhenAcac]$ and $[Pt(CH_3)_3Acac]_2$ respectively. The values are consistent with those reported by Kite and Truter[7], and agree with the above observations.

In the compounds $[Pt(CH_3)_3AcacNR]_2$ ($R=H$ and CH_3) which also contain tridentate ligands, bands assignable to ν(C=O) appear at 1612 cm^{-1} in both cases.

TABLE 4

INFRARED DATA FOR COMPLEXES OF β-DIKETONES, THIO-β-DIKETONES, AND β-IMINOKETONES

Compound	$\nu(C{=}O)$	$\nu(C{-}S)$	$\pi(C{-}H)$	$\nu(Pt{-}C)$
$[Pt(CH_3)_3Acac]_2$	1613 vs.		835 vs	586 w, 568 w
$[Pt(CH_3)_3AcacLut]$	1601 (sh), 1580 vs		768 s	585 m (sh)
$[Pt(CH_3)_3BipyAcac]$	1639 s			585 w, 553 m
$[Pt(CH_3)_3PhenAcac]$	1635 s		560 w	560 w
$[Pt(CH_3)_3Sacac]_2$	1620 vs	690 s	820 vs	561 m
$[Pt(CH_3)_3SacacLut]$	1561 vs	722 s	801 vs	585 vw, 574 wm, 560 w
$[Pt(CH_3)_3SacacPPh_3]$	1565 vs	726 m	797 m	572 vw
$[Pt(CH_3)_3BipySacac]$	1649 s	723 m		577 m, 550 w
$[Pt(CH_3)_3Sbzac]_2$	1570 s, 1561 (sh)	667 s	840 m	563 m
$[Pt(CH_3)_3SbzacLut]$	1542 (sh), 1531 s	727 s	818 m	582 vw, 570 w
$[Pt(CH_3)_3BipySbzac]$	1612 m	735 m		579 w, 559 m
$[Pt(CH_3)_3Sbzbz]_2$	1562 s	708 s	790 m	568 vw, 559 w
$[Pt(CH_3)_3SbzbzLut]$	1533 s	730 s	765 s	593 w, 561 w
$[Pt(CH_3)_3BipySbzbz]$	1622 m	731 m		578 w, 550 w
$[Pt(CH_3)_3Sacsac]_2$		658 m, 663 m (sh)	818 s	557 m
$[Pt(CH_3)_3SacsacLut]$		752 s	825 s	563 w
$[Pt(CH_3)_3SacsacPPh_3]$		757 m	816 m	558 w
$[Pt(CH_3)_3AcacNH]_2$	1612 vs		832 vs	585 w, 575 w, 560 w
$[Pt(CH_3)_3AcacNHLut]$	1600 vs		759 s	582 w, 577 w (sh) –
$[Pt(CH_3)_3AcacNCH_3]_2$	1612 vs		813 s	577 w, 572 w, 562 w
$[Pt(CH_3)_3AcacNCH_3Lut]$	1596 s			582 w, 575 w

The value drops to 1600 cm^{-1} for $[Pt(CH_3)_3AcacNHLut]$ and 1596 cm^{-1} for $[Pt(CH_3)_3AcacNCH_3Lut]$ so that the behaviour of ν(C=O) is similar to that observed in the β-diketone system.

In the compound $[Pt(CH_3)_3Sacac]_2$ ν(C=O) appears at 1620 cm^{-1} which is in the region expected for *C*-bonded species, but NMR evidence indicates that the compound contains bridged sulfur ligands. The high value for ν(C=O) in this compound must indicate some tendency for the ligand to coordinate in the keto tautomer when the sulfur is bridging. In the lutidine and triphenylphosphine derivatives, the value falls below 1600 cm^{-1} (1561 and 1565 cm^{-1} respectively) where it has been observed in other complexes with bidentate Sacac[30]. NMR evidence indicates that the compound $[Pt(CH_3)_3BipySacac]$ contains a unidentate *S*-bonded ligand. The ν(C=O) peak occurs at 1649 cm^{-1}, which indicates the presence of a non-bonded carbonyl group.

The compounds $[Pt(CH_3)_3Sbzac]_2$ and $[Pt(CH_3)_3Sbzbz]_2$ have no bands above 1600 cm^{-1}, ν(C=O) occurring at 1570 and 1562 cm^{-1} respectively. The values are higher than those for the 3,5-lutidine derivatives with bidentate thio-β-diketones (1531 and 1533 cm^{-1} respectively) so that some tendency towards the keto tautomer probably exists in these dimers as is found for $[Pt(CH_3)_3Sacac]_2$. The 2,2′-bipyridine derivatives $[Pt(CH_3)_3BipySbzac]$ and $[Pt(CH_3)_3BipySbzbz]$ both exhibit peaks above 1600 cm^{-1} which indicate the presence of free carbonyl groups.

C–S stretching frequency. C–S stretching frequencies have been found[30] between 690 and 721 cm^{-1} in a number of metal complexes of Sacac. In the compound $[Pt(CH_3)_3Sacac]_2$, a band at 690 cm^{-1} may be assigned to this vibration. In the lutidine and triphenylphosphine derivatives bands at 722 and 726 cm^{-1} respectively are assigned to this mode. The lower value for this frequency in $[Pt(CH_3)_3Sacac]_2$ may be a result of the bridging S atom in this compound. The corresponding Sbzac and Sbzbz compounds show a similar variation in frequencies of ν(C–S).

In a number of metal complexes with bidentate Sacsac[31], ν(C–S) was assigned in the range 696–706 cm^{-1} and ν(C–S) + ν(C–CH_3) between 738 and 751 cm^{-1}. In $[Pt(CH_3)_3Sacsac]_2$, a doublet at 658 and 663 cm^{-1} is assigned to ν(C–S). No bands are observed between 700 and 800 cm^{-1}. In the lutidine and triphenylphosphine derivatives, peaks are observed at 752 and 757 cm^{-1} respectively, but no peaks below 700 cm^{-1} are ascribable to ν(C–S). However, peaks of the neutral ligands tend to interfere in this region. The low value for ν(C–S) in $[Pt(CH_3)_3Sacsac]_2$ may again be an indication of bridging sulfur atoms.

C(γ)–H bending. Kite and Truter[7] observed bands at 778 and 776 cm^{-1} in $[Pt(CH_3)_3AcacNH_3]$ and $[Pt(CH_3)_3AcacPy]$ which they assigned to π(C–H) for bidentate acetylacetonate. In $[Pt(CH_3)_3AcacLut]$ a band assignable to this vibration appears at 768 cm^{-1}. In $[Pt(CH_3)_3Acac]_2$, a very strong band occurs at 835 cm^{-1} as was noted by Kite and Truter[7]. An intense broad band has been found in a number of other β-dicarbonyl complexes of trimethylplatinum(IV), and is assigned to C(γ)–H bending. The complexes $[Pt(CH_3)_3AcacNR]_2$ (R = H and CH_3) show a similar intense broad band above 800 cm^{-1}, while $[Pt(CH_3)_3AcacNH\ Lut]$ has π(C–H) below 800 cm^{-1}.

It may be noted that while the spectra of all trimethylplatinum(IV) compounds containing tridentate ligands include an intense band above 800 cm^{-1}, the platinum(II) compound $Cu[PtAcac_2Cl]_2$[29], where the ligand is also a tridentate, showed no parallel absorption in this region.

The spectrum of each of the thio-β-diketone complexes includes a band assignable to π(C–H) (see Table 4).

Methyl–platinum vibrations. The C–H stretching region exhibits in each case three bands characteristic of trimethylplatinum complexes[17,32] and these are relatively invariant. The methyl bending and rocking vibrations are in general obscured by ligand absorptions. Values for ν(Pt–C) are generally found between 550 and 600 cm^{-1} in trimethylplatinum(IV) complexes[17,32]. For the present compounds, as many as three peaks assignable to ν(Pt–C) appear in this region. Previously it has been found for the series of compounds $[Pt(CH_3)_3BipyX]$ and $[Pt(CH_3)_3Lut_2X]$[17] that two bands were usually observed and these appeared consistent with one band being predominantly due to the CH_3 group *trans* to N donors, the other to the CH_3 *trans* to the X group. Similar observations may be made here. For $[Pt(CH_3)_3Acac]_2$, peaks appear at 586 and 568 cm^{-1}. The former may be associated with methyl groups *trans* to O, and the latter with CH_3 *trans* to C. In the lutidine derivatives, $[Pt(CH_3)_3AcacLut]$, only a single peak appears at 585 cm^{-1} (CH_3 *trans* to N) as a shoulder on the intense band at 600 cm^{-1} which belongs to Acac. In the compounds $[Pt(CH_3)_3BipyAcac]$ and $[Pt(CH_3)_3PhenAcac]$, bands above 550 cm^{-1} appear at 585, 553 cm^{-1} (CH_3 *trans* to O, C) and 560 cm^{-1} (CH_3 *trans* to C) respectively.

The spectra of $[Pt(CH_3)_3Sacac]_2$, $[Pt(CH_3)_3Sbzac]_2$ and $[Pt(CH_3)_3Sbzbz]_2$ include only a single medium intensity band between 560 and 570 cm^{-1}, and this may be associated with methyl *trans* to sulfur. In the lutidine derivatives peaks are observed at 560–570 cm^{-1} (methyl *trans* to S) as well as peaks above 570 cm^{-1} attributable to methyl *trans* to O and N. For the bipyridine complexes two bands, one at ≈578 cm^{-1}

(CH$_3$ *trans* to N) and one between 560 and 550 cm^{-1} (CH$_3$ *trans* to S) are observed.

For the compounds [Pt(CH$_3$)$_3$AcacNR]$_2$ (R=H and CH$_3$) three peaks are observed at ≈580 cm^{-1} (CH$_3$ *trans* to O), ≈570 cm^{-1} (CH$_3$ *trans* to N) and ≈560 cm^{-1} (CH$_3$ *trans* to C). In the lutidine derivatives, the lowest peaks are at ≈576 cm^{-1}, consistent with CH$_3$ *trans* to O and N donors.

EXPERIMENTAL

Preparations of complexes of trimethylplatinum(IV) have almost invariably employed [PtI(CH$_3$)$_3$]$_4$ as starting material. In particular, complexes of ligands with oxygen donor atoms such as β-diketones[1-3], salicylaldehyde[22], and 8-hydroxyquinoline[23] have usually been prepared by the action of the appropriate thallium(I) compound on [PtI(CH$_3$)$_3$]$_4$. In the present work the compound [Pt(CH$_3$)$_3$]$_2$SO$_4$·4H$_2$O has been found to be a convenient starting material. Metal derivatives of the

TABLE 5

ANALYTICAL DATA

Compound	*C(%)*		*H(%)*		*N(%)*		*Pt(%)*	
	Calcd.	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*
Pt(CH$_3$)$_3$Acac	28.3	28.3	4.7	4.6			57.5	57.4
Pt(CH$_3$)$_3$Acac NH$_3$	27.0	26.8	5.4	5.4	3.9	3.8	54.7	54.7
Pt(CH$_3$)$_3$AcacCH$_3$NH$_2$	29.2	28.9	5.7	5.7	3.8	3.7	52.7	52.1
Pt(CH$_3$)$_3$Acac Lut	40.4	40.5	5.6	5.7	3.1	3.2	43.7	44.0
Pt(CH$_3$)$_3$Acac Quin	43.6	43.8	4.9	5.0	3.0	3.0	41.6	41.1
Pt(CH$_3$)$_3$Acac(CH$_3$)$_2$S	29.9	30.2	5.5	5.7			48.6	49.1
Pt(CH$_3$)$_3$Acac PPh$_3$	51.9	51.9	5.2	5.2				
Pt(CH$_3$)$_3$Bipy Acac	43.6	43.7	4.9	5.0	5.6	5.6	39.4	39.0
Pt(CH$_3$)$_3$Phen Acac	46.2	46.0	4.7	4.7	5.4	5.4	37.6	37.8
Pt(CH$_3$)$_3$Sacac	27.0	26.9	4.5	4.5			54.9	54.7
Pt(CH$_3$)$_3$Sacac Lut	38.9	38.8	5.4	5.5	3.0	3.1	44.9	44.9
Pt(CH$_3$)$_3$Sacac PPh$_3$	50.6	50.6	5.1	5.2				
Pt(CH$_3$)$_3$Bipy Sacac	42.3	42.0	4.7	4.7	5.5	5.3	38.1	38.1
Pt(CH$_3$)$_3$Sbzac	37.4	37.6	4.3	4.4			46.7	47.1
Pt(CH$_3$)$_3$Sbzac Lut	45.8	46.0	5.2	5.3	2.7	2.8	37.2	36.9
Pt(CH$_3$)$_3$Bipy Sbzac	48.2	48.2	4.6	4.7	4.9	4.9	34.0	33.9
Pt(CH$_3$)$_3$Sbzbz	45.1	45.1	4.2	4.2			40.7	40.6
Pt(CH$_3$)$_3$Sbzbz Lut	51.2	51.3	5.0	5.2	2.4	2.4	33.3	33.5
Pt(CH$_3$)$_3$Bipy Sbzbz	52.9	52.5	4.4	4.8	4.4	4.5	30.7	30.3
Pt(CH$_3$)$_3$Sacsac	25.9	26.2	4.3	3.9			52.5	52.0
Pt(CH$_3$)$_3$Sacsac Lut	37.6	37.6	5.3	5.3	2.9	3.0	40.8	40.7
Pt(CH$_3$)$_3$Sacsac PPh$_3$	49.3	49.2	4.9	5.1				
NiSacac$_2$	41.6	41.2	4.9	4.9				
NiSbzac$_2$	58.1	57.9	4.4	4.4				
NiSbzbz$_2$	67.1	66.3	4.1	4.2				
NiSacsac$_2$·	37.4	37.4	4.4	4.5				
Pt(CH$_3$)$_3$AcacNH	28.4	28.3	5.1	5.1	4.1	3.9	57.7	57.6
Pt(CH$_3$)$_3$AcacNHLut	40.4	40.7	5.9	6.0	6.3	6.2	43.8	43.8
Pt(CH$_3$)$_3$AcacNHPPh$_3$	52.0	51.7	5.4	5.3	2.3	2.2		
Pt(CH$_3$)$_3$AcacNCH$_3$	30.7	30.5	5.4	5.5	4.0	3.9	55.4	55.6
Pt(CH$_3$)$_3$AcacNCH$_3$Lut	41.8	41.6	6.1	6.3	6.1	5.8	42.5	43.0

ligands were found to react quite readily with $[Pt(CH_3)_3]_2SO_4 \cdot 4H_2O$ in ethanol or acetone to produce the required compounds generally in good yield. The sodium derivatives were found to be most convenient for the preparation of β-diketone complexes, while the nickel complexes readily gave the thio-β-diketone species. Both sodium and nickel derivatives were used in the preparation of β-iminoketone complexes.

Analytical data for the compounds are listed in Table 5.

Complexes of β-diketones

Sodium acetylacetonate was prepared by the method of Hatch and Sutherland[33] and recrystallized twice from ethanol.

$[Pt(CH_3)_3Acac]_2$. $[Pt(CH_3)_3]_2SO_4 \cdot 4H_2O$ (1.0 g) was treated with sodium acetylacetonate (0.5 g) in 95% ethanol (10 ml). On heating the solution sodium sulfate precipitated rapidly. The solution was evaporated to dryness and the residue extracted with boiling n-hexane. On concentration of the hexane solution and cooling, colorless needles of $[Pt(CH_3)_3Acac]_2$ were formed. The product was contaminated with $[Pt(OH)(CH_3)_3]_4$ which was readily removed by careful recrystallization of the product from n-hexane. Yield 80%.

A molecular weight determination in benzene (osmometrically) confirmed the compound to be dimeric. Calculated for $[Pt(CH_3)_3Acac]_2$ 679; found 661.

$[Pt(CH_3)_3AcacR]$ ($R=NH_3$, CH_3NH_2, 3,5-lutidine, dimethyl sulfide, triphenylphosphine). Kite and Truter[7] have reported the preparation of a number of complexes of this type. Their reaction conditions, however, involve heating the reactants for at least one hour. We have found that the reactions go to completion almost instantaneously.

The compounds with $R=NH_3$ and CH_3NH_2 were prepared by passing the gaseous amine into a hot n-hexane solution of $[Pt(CH_3)_3Acac]_2$. A white precipitate formed immediately, but passage of gas was continued for several minutes. The solution was cooled and the product filtered off and washed with cold n-hexane. Yield 90–95%.

The compounds with R = 3,5-lutidine and R = dimethyl sulfide were prepared by addition of excess ligand to an n-hexane solution of $[Pt(CH_3)_3Acac]_2$. The 3,5-lutidine complex crystallized on concentration of the solution and cooling (yield 90%), but the dimethyl sulfide compound was very soluble in n-hexane and was obtained by careful evaporation to dryness of the solution. It decomposed slowly in the solid state, liberating dimethyl sulfide. The triphenylphosphine complex was obtained by reacting a 1/1 mole ratio of $[Pt(CH_3)_3Acac]_2$ and PPh_3 in n-hexane, concentrating the solution and filtering off the crystals which formed. Yield 90%.

$[Pt(CH_3)_3AcacR]$ (R = 2,2′-bipyridine or 1,10-phenanthroline). A modification of the method of Lile and Menzies[34] was employed for the preparation of these compounds. $[Pt(CH_3)_3Acac]_2$ in n-hexane was treated with a one mole ratio of 2,2′-bipyridine (or 1,10-phenanthroline) in n-hexane. The product precipitated immediately in the form of yellow crystals. These were filtered off, washed with n-hexane, and air dried. Yield 90–95%.

$[Pt(CH_3)_3LLut]$ (L = Bzac and Bzbz). Excess lutidine was added to a chloroform suspension of crude $[Pt(CH_3)_3L]_2$ prepared by the addition of L to $[Pt(CH_3)_3Acac]_2$. The resultant solution was concentrated, and the product precipitated with

n-hexane. Yield 90%. The compounds $[Pt(CH_3)_3L]_2$ were insufficiently soluble for study by NMR.

Complexes of thio-β-diketones

Preparation of intermediates. $NiSacac_2$ was prepared by the method of Ouchi *et al.*[35] by passage of gasous HCl and H_2S into an ethanolic solution of $NiAcac_2$. The brown solid was recrystallized from methanol.

$NiSbzac_2$ (where Sbzac is $C_6H_5COCHCSCH_3$) has been prepared by Chaston *et al.*[36] by reaction of thiobenzoylacetone with nickel acetate. It may, however, be conveniently prepared by a method similar to that of the previous compound. Anhydrous nickel chloride (2.0 g) was refluxed with benzoylacetone (5.0 g) in absolute ethannol (80 ml) for 1 h. Hydrogen chloride gas was bubbled slowly through the solution for 20 min, then hydrogen sulfide for 1 h. The deep-brown solution was allowed to stand overnight, and brown crystals of the product separated out. These were recrystallized from a petroleum ether/acetone mixture. Yield 30%.

$NiSbzbz_2$ was prepared by a similar procedure to the above and recrystallized from acetone/petroleum ether. Yield 10%.

$NiSacsac_2$, prepared by the method of Barraclough *et al.*[25] and recrystallized from chloroform, was donated by Dr. R. F. Evans.

$[Pt(CH_3)_3Sacac]_2$. $[Pt(CH_3)_3]_2SO_4 \cdot 4H_2O$ (0.6 g) and $NiSacac_2$ (0.27 g) were dissolved in 95% ethanoi (10 ml) and the solution heated on a water bath. The solution rapidly became deep-red and a flocculent precipitate formed. The solution was evaporated to dryness and the residue extracted with boiling n-hexane. The orange-red n-hexane solution, on concentration and cooling, gave orange-brown crystals of the product. Yield 85%. Molecular weight in $CHCl_3$: found, 749; calcd. for dimer, 711.

$[Pt(CH_3)_3Sbzac]_2$. The compound was prepared by the above procedure and recrystallized from hexane as bright orange crystals. Yield 80%.

$[Pt(CH_3)_3Sbzbz]_2$. The compound was prepared by the above method, except that it was extracted with, and recrystallized from chloroform. The product was a bright orange-red solid. Yield 85%.

$[Pt(CH_3)_3Sacsac]_2$. This was prepared by the general procedure above. Due to its high solubility in organic solvents it was obtained by evaporation of the n-hexane extract. The product was a deep-red solid. Yield 80%. Molecular weight in $CHCl_3$: found, 730; calcd. for dimer, 743.

$[Pt(CH_3)_3$Thio-β-diketoneLut$]$ (Thio-β-diketone = Sacac, Sbzac, Sbzbz, Sacsac). $[Pt(CH_3)_3$ Thio-β-diketone$]_2$ (0.1 g) in n-hexane (5 ml) was treated with excess 3,5-lutidine. The solution was concentrated to a small volume and cooled to give crystals of the product. Yield 90–95%.

$[Pt(CH_3)_3$Thio-β-diketone$PPh_3]$ (Thio-β-diketone = Sacac, Sacsac). $[Pt(CH_3)_3$-Thio-β-diketone$]_2$ (0.1 g) in n-hexane (5 ml) was treated with a stoichiometric quantity of triphenylphosphine in n-hexane (2 ml) and the solution heated for 5 min. On concentration of the solution and cooling, crystals of the product separated. Yield 90–95%.

$[Pt(CH_3)_3$BipyThio-β-diketone$]$ (Thio-β-diketone = Sacac, Sbzac, Sbzbz). $[Pt(CH_3)_3$ Thio-β-diketone$]_2$ (0.1 g) in n-hexane (5 ml) was treated with a stoichiometric quantity of 2,2'-bipyridine in n-hexane (2 ml) and the solution heated for 5 min. Concentration of the solution and cooling gave the product as pale yellow crystals. Yield 80–85%.

Complexes of β-iminoketones

Preparation of intermediates. Ni(AcacNH)$_2$ was prepared by the method of Lacey[37], and recrystallized from 95% ethanol.

Acetylacetone methylimine was prepared by a modification of that of Holtzclaw *et al.*[38]. Acetylacetone (5 g) was treated with excess ethanolic methylamine, and the resultant yellow solution heated for several hours on a steam bath. The resultant orange liquid solidified on cooling. The solid was recrystallized from petroleum ether as colorless crystals in 70% yield.

[Pt(CH$_3$)$_3$AcacNH]$_2$. [Pt(CH$_3$)$_3$]$_2$SO$_4$·4H$_2$O (0.4 g) in 95% ethanol (5 ml) was treated with Ni(AcacNH)$_2$ (0.16 g) in 95% ethanol (5 ml). The colour of the mixture rapidly changed from red-brown to pale green on heating, and a flocculent precipitate formed. The solution was evaporated to dryness on the water bath and the residue extracted with chloroform. Concentration of the chloroform solution and cooling gave colorless crystals of the product which were filtered off, washed with n-hexane, and air-dried. Yield 85%. Molecular weight in CHCl$_3$: found, 636; calcd. for dimer, 677.

[Pt(CH$_3$)$_3$AcacNHLut]. [Pt(CH$_3$)$_3$AcacNH]$_2$ (0.1 g) in chloroform (3 ml) was treated with excess 3,5-lutidine and the mixture heated for several minutes. Concentration of the solution and addition of n-hexane gave the product as a white solid in 90% yield.

[Pt(CH$_3$)$_3$AcacNHPPh$_3$]. [Pt(CH$_3$)$_3$AcacNH]$_2$ (0.1 g) in chloroform (3 ml) was treated with triphenylphosphine (0.08 g) in chloroform (2 ml) and the solution heated for several minutes. Concentration of the solution and addition of n-hexane gave the product in 95% yield.

[Pt(CH$_3$)$_3$AcacNCH$_3$]$_2$. A non-aqueous procedure similar to that of Everett and Holm[39] was used for this preparation. [Pt(CH$_3$)$_3$]$_2$SO$_4$·4H$_2$O (0.5 g) was dissolved in tert-butanol (5 ml) and a mixture of sodium hydride (0.04 g) and acetylacetone methylimine (0.2 g) in tert-butanol (5 ml) added. A flocculent white solid precipitated immediately. The solution was evaporated to dryness and the residue extracted with chloroform. By careful recrystallization from chloroform, the product was obtained free from [PtOH(CH$_3$)$_3$]$_4$, but the yield was low (10%).

[Pt(CH$_3$)$_3$AcacNCH$_3$Lut]. [Pt(CH$_3$)$_3$AcacNCH$_3$]$_2$ (0.05 g) was dissolved in chloroform (5 ml) and an excess of 3,5-lutidine was added. Evaporation of the solution to dryness gave the product as a colorless solid.

Measurements

Nuclear magnetic resonance spectra. These were recorded at 60 MHz on a Varian A60 NMR spectrometer at a sample temperature of $34 \pm 2°$. The complexes were studied in saturated or near-saturated solutions on a sweep width of 500 Hz using tert-butanol as internal reference. τ values were obtained used τ(t-BuOH) = 8.72 ppm for CDCl$_3$. Spin–spin coupling constants are considered accurate to ± 0.5 Hz, and τ values to ± 0.01 ppm. Low temperature NMR spectra of the β-iminoketone complexes were recorded on a Jeol MH 100 using a sweep width of 540 Hz and TMS as internal reference. Spin–spin coupling constants are considered accurate to ± 0.5 Hz and τ values to ± 0.01 ppm.

Molecular weights. These were measured in CHCl$_3$ at 37° using a Hewlett–Packard model 302 vapour pressure osmometer.

Infrared spectra. These were recorded from 4000 to 400 cm^{-1} on a Perkin–Elmer Model 457 Spectrometer as Nujol and hexachlorobutadiene mulls between KBr discs. Frequencies are considered accurate to ± 2 cm^{-1}.

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