Complexes of Trimethylplatinum(IV) with Butane-2,3-dione Monoxime

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The dimeric complex of butane-2,3-dione monoxime (Hbdm) with trimethylplatinum(IV), [{$PtMe_3$(bdm)}$_2$] **1**, and its pyridine (py) and 2,2′-bipyridyl (bipy) adducts [$PtMe_3$(bdm)(py)] and [$PtMe_3$(bdm)(bipy)], show three different configurations for the ionised monoxime ligand. Dimer **1** forms a fluxional solvated monomer in co-ordinating solvents. Its solution-state stereodynamics in CD_3OD have been measured by two-dimensional exchange NMR spectroscopy and a 'windscreen-wiper' mechanism proposed which is novel in trimethylplatinum(IV) chemistry.

There is much current interest in the pronounced physiological effects of butane-2,3-dione monoxime (Hbdm), which have recently been reviewed.[1] As ligands monoximes have received much less attention than *vic*-dioximes; Hbdm is reported to form weaker complexes than *vic*-dioximes and few well characterised complexes of this ligand have been reported.[2] Attempts to make a palladium(II) complex were unsuccessful,[3] but complexes with Cr^{III}, Mn^{II}, Fe^{III}, Co^{II}, Ni^{II} and Cu^{II} have been reported.[4] Data are consistent with the monoxime reacting as an ionised bidentate ligand forming [M(bdm)$_2$] and [M(bdm)$_3$], but no structural evidence was presented.

By contrast, we now report that trimethylplatinum(IV) forms a well defined dimeric complex [{$PtMe_3$(bdm)}$_2$] **1** with the ionised ligand, and treatment of this dimer with pyridine (py) or 2,2′-bipyridyl (bipy) gives the 1 : 1 adducts [$PtMe_3$(bdm)(py)] **2** and [$PtMe_3$(bdm)(bipy)] **3**. In the solid state, dimer **1** has the hydroxo–oxime configuration. In solution, **1** becomes a solvated monomer retaining the hydroxo–oxime form in CD_3OD, while in $(CD_3)_2CO$ and $(CD_3)_2SO$ the ligand has the carbonyl–oxime configuration found in the pyridine complex **2**. In each case, ^1H NMR spectroscopy reveals the configuration of the monoximate ligand in solution unambiguously.

Experimental

Iodotrimethylplatinum(IV) was prepared by the literature method.[5] Butane-2,3-dione monoxime (Aldrich Chemical Company) was used as supplied. Trimethylplatinum(IV) sulfate was made[6] as described below.

Preparations.—$(PtMe_3)_2SO_4\cdot4H_2O$. Moist Ag_2SO_4 (made by adding $Na_2SO_4\cdot10H_2O$ to $AgNO_3$ in water) was added to a stirred suspension of [$(PtMe_3I)_4$] (2.0 g, 5.45 mmol) in benzene–acetone (80 cm^3, 60 : 40 v/v) and the reactants refluxed for *ca.* 18 h. After filtration to remove AgI and unreacted Ag_2SO_4, the solvent was removed *in vacuo* to yield a beige solid (1.46 g, 83%) which was characterised by ^1H NMR and IR spectroscopy.

[{$PtMe_3$(bdm)}$_2$] **1**. A solution of butane-2,3-dione monoxime (500 mg, 5 mmol) in water (10 cm^3) was added to a stirred solution of $(PtMe_3)_2SO_4\cdot4H_2O$ (400 mg, 0.62 mmol) in water (10 cm^3). A pale yellow solution was obtained. On the addition of solid sodium acetate (0.5 g) the colour deepened, and an orange precipitate formed, which was filtered off, washed with water and dried in air. Recrystallisation from acetone–light petroleum (b.p. 40–60 °C) gave orange *crystals* of [{$PtMe_3$(bdm)}$_2$] **1** (320 mg, 85%), m.p. 132–134 °C (decomp.) [Found: C, 24.4; H, 4.85; N, 4.15%; *M* (in methanol, ebulliometer) 350. $C_7H_{15}NO_2Pt$ requires C, 24.7; H, 4.45; N, 4.15%; *M* (monomer) 340].

[$PtMe_3$(bdm)(py)] **2**. A mixture of [$PtMe_3$(bdm)] (60 mg, 0.176 mmol) and pyridine (0.5 cm^3) was stirred in benzene (10 cm^3) for 2 h. The deep orange solution was reduced *in vacuo* to 5 cm^3 and *n*-hexane added. On cooling, deep orange *crystals* of [$PtMe_3$(bdm)(py)] **2** (52 mg, 70%) precipitated, m.p. 184–185 °C (decomp.) (Found: C, 34.5; H, 4.80; N, 6.70. $C_{12}H_{20}N_2O_2Pt$ requires C, 34.3; H, 4.80; N, 6.70%).

[$PtMe_3$(bdm)(bipy)] **3**. Compound [$PtMe_3$(bdm)] (102 mg, 0.3 mmol) was added to a stirred solution of 2,2′-bipyridyl (47 mg, 0.3 mmol) in benzene (10 cm^3). The mixture was refluxed for 1 h. The pale yellow solid that formed was filtered off, washed with cold benzene and light petroleum (b.p. 40–60 °C) and dried *in vacuo* to give pale yellow *crystals* (140 mg, 95%), m.p. 174–176 °C (decomp.) (Found: C, 41.35; H, 4.90; N, 8.70. $C_{17}H_{23}N_3O_2Pt$ requires C, 41.1; H, 4.65; N, 8.45%).

Proton NMR spectra were recorded on a Bruker AM250 Fourier-transform spectrometer operating at 250.13 MHz. Spectra were recorded in $(CD_3)_2CO$, $(CD_3)_2SO$, CD_3OD or $CDCl_3$ solution, with chemical shifts quoted relative to tetramethylsilane as internal standard. Two-dimensional exchange spectra were obtained using the NOESYPH automation program.[7] Signal intensities were obtained by integration of the four most intense rows. Integrations were performed four times and average values used to evaluate the rate data *via* the D2DNMR program.[8] NMR probe temperatures were controlled by a standard B-VT 1000 unit. The probe temperatures were periodically checked against a digital thermometer (Comark): they are considered accurate to ± 1 °C. Activation parameters were extracted from a least-squares fitting of the Eyring and Arrhenius plots. The errors quoted are those defined by Binsch and Kessler.[9]

Infrared spectra were recorded as CsI discs on a Nicolet Magna FT-IR spectrometer in the region 4000–200 cm^{-1}. Fast atom bombardment (FAB) mass spectra of the complexes dissolved in a matrix of 3-nitrobenzyl alcohol were obtained by Dr. J. A. Ballantine on a VG AutoSpec Instrument operating at 25 kV energy. Elemental analyses were carried out by Butterworth Laboratories Ltd., Teddington, Middlesex. Melting points were obtained on a Gallenkamp digital apparatus and are uncorrected.

Results and Discussion

Analytical figures and spectroscopic evidence indicate that the three complexes have the structures illustrated in Fig. 1. The parent complex [{$PtMe_3$(bdm)}$_2$] **1** is isolated in high yield as

Table 1 Infrared data (cm^{-1}) for the trimethylplatinum(IV) complexes with butane-2,3-dione monoxime

Complex	σ(OH)(Δ$σ_{\frac{1}{2}}$)[a]	σ(Me)	σ[b]	σ(PtC)	σ(PtN)
1 $[\{PtMe_3(bdm)\}_2]$	3230 (280)	2964, 2897, 2815	1594	599, 583, 544	453
2 $[PtMe_3(bdm)(py)]$	—	2954, 2894, 2812	1602, 1553	593, 578, 556	461, 445
3 $[PtMe_3(bdm)(bipy)]$	—	2953, 2895, 2812	1654	582, 571, 537	459, 419

[a] Half-height width (cm^{-1}). [b] See text for assignment.

Table 2 Proton NMR data[a] for the trimethylplatinum(IV) complexes with butane-2,3-dione monoxime

Complex	Solvent	T/K	*trans* Atom[b]	δ(PtMe)	^2J(PtH)/Hz	Oxime δ(J/Hz)
1	CD_3OD	273	1 N	0.85	63.4	1.99 [3 H, m, ^4J(PtH) 4.2]
			1 O	1.11	76.8	2.52 (≈2 H, m, NCH_2)
			1 O (CD_3OD)	0.62	83.2	4.85 (1 H, br, OH)
	$(CD_3)_2SO$	303	1 N	0.76	63.9	1.83 [3 H, m, ^4J(PtH) 4.1]
			1 O	0.95	76.4	2.47 (3 H, s, $OCCH_3$)
			1 S [$(CD_3)_2SO$]	0.59	69.3	
	$(CD_3)_2CO$	258	1 N	0.79	63.1	1.82 [3 H, m, ^4J(PtH) 4.4]
			1 O	1.06	76.7	2.44 (3 H, s, $OCCH_3$)
			1 O [$(CD_3)_2CO$]	0.51	83.7	
2[c]	$CDCl_3$	303	1 N	0.89	63.9	1.85 [3 H, m, ^4J(PtH) 4.1]
			1 O	1.16	76.6	2.36 (3 H, s, $COCH_3$)
			1 N	0.61	72.2	
3[d]	$CDCl_3$	303	1 N (bdm)	0.29	70.3	1.55 (3 H, s, NCH_3)
			2 N	1.29	69.4	1.67 (3 H, s, $COCH_3$)

[a] Chemical shifts quoted relative to $SiMe_4$ as an internal standard. [b] Data for oxime nitrogen atom quoted first. [c] Pyridine signals, *ortho*, δ 8.48, 2 H, ^3J(PtH) 11.8, $^3J(HH_m)$ 6.36, ^4J(HH) 1.58; *meta*, δ 7.36, 2 H, $^3J(HH_p)$ 7.6, $^3J(HH_o)$ 6.4; *para*, δ 7.79, 1 H, $^3J(HH_m)$ 7.6, ^4J(HH) 1.58. [d] 2,2′-Bipyridyl signals, H_A, δ 8.93, ^3J(PtH) 13.2, ^3J(HH) 5.46, ^4J(HH) 0.73; H_D, δ 8.20, ^3J(HH) 8.08; H_C, δ 8.06, ^3J(HH) 8.08, ^3J(HH) 8.47, ^4J(HH) 0.73; H_B, δ 7.64, ^3J(HH) 8.47, ^3J(HH) 5.46 Hz; H atoms labelled as in Fig. 1.

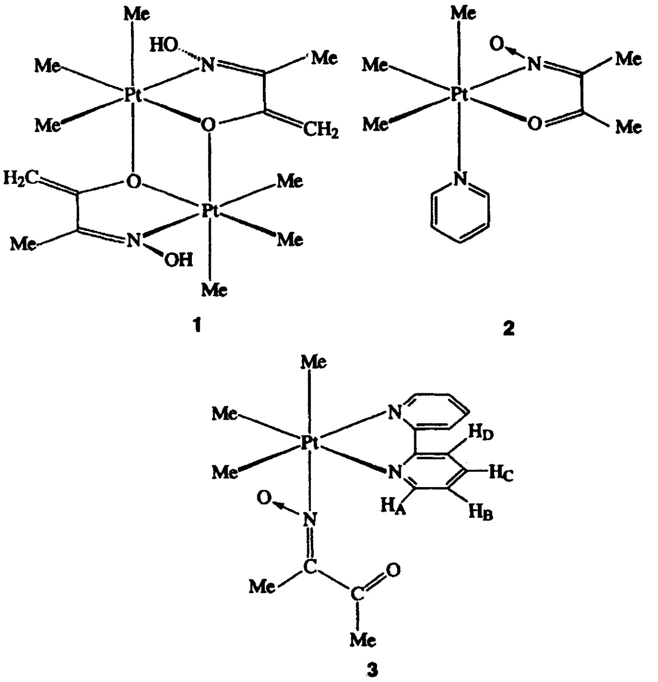

Fig. 1 Configurations of complexes of butane-2,3-dione monoxime (Hbdm) $[\{PtMe_3(bdm)\}_2]$ **1**, $[PtMe_3(bdm)(py)]$ **2** and $[PtMe_3(bdm)(bipy)]$ **3**

described above. In methanol solution it is monomeric (ebulliometer). However the FAB mass spectrum shows a molecular ion at m/z 681 which corresponds to the dimer $\{[PtMe_3(bdm)]_2H\}^+$, with consistent observed and calculated isotope patterns. Intense fragmentation peaks are observed at m/z 341 and 240, corresponding to $[PtMe_3(bdm)H]^+$ and $[PtMe_3]^+$ respectively. Compound **1** is insoluble in non-co-ordinating solvents, but is moderately soluble in acetone (see below), from which it can be crystallised, and is very soluble in MeOH, EtOH and Me_2SO. Proton NMR data (see below) show that **1** is a solvated monomer in these solvents. It reacts readily with both pyridine and 2,2′-bipyridyl to yield the 1:1 adducts, deep orange $[PtMe_3(bdm)(py)]$ **2** and pale yellow $[PtMe_3(bdm)(bipy)]$ **3**, respectively.

The IR spectrum of **1** shows a strong, broad band at 3230 cm^{-1} that shifts on deuteriation to 2365 cm^{-1}. Since the analytical figures show that no water is present, this band implies that the butane-2,3-dione monoxime ligand in **1** has an ionised hydroxo-oxime (C=N–OH) configuration (Fig. 1), with intermolecular hydrogen bonding in the solid state. A sharp band at 1594 cm^{-1} can be tentatively assigned to a combination of C=N and C=C stretching modes. Bands due to the Pt–C and Pt–N stretches may also be tentatively assigned (Table 1).

The ^1H NMR data for **1**–**3** in solution are shown in Table 2. The spectrum of **1** in CD_3OD at 303 K reveals slightly exchange-broadened signals in the Pt–Me region. This line broadening disappears on cooling. The ^1H NMR spectrum of **1** at 273 K is shown in Fig. 2. The spectrum shows Pt–Me signals in the range δ 0.6–1.2, and ligand alkyl signals in the range δ 1.9–2.6. In addition, a broad band at *ca.* δ 4.85, which exchanges with the solvent, may be tentatively assigned to the ligand OH environment. The Pt–Me region shows three signals, with ^{195}Pt satellites, in a 1:1:1 intensity ratio. The highest frequency signal is assignable to the methyl *trans* to the carbonyl oxygen atom of the ligand, and the lowest frequency signal to the methyl *trans* to the oxygen of the solvent on the basis of their ^2J(PtH) scalar coupling constants.[10,11] The central resonance [^2J(PtH) = 63.4 Hz] is attributed to the methyl *trans* to the oximate nitrogen by comparison with corresponding complexes with *vic*-dioximates.[12] The ^2J value indicates a very strong Pt–N bond {*cf.* 66.5 Hz for $[PtMe_3(bipy)(H_2O)]^+$}.[13] In the ligand alkyl region, two signals are observed in an approximately 2:3 intensity ratio. The lower frequency signal (δ 1.99) shows scalar coupling to ^{195}Pt [^4J(PtH) = 4.2 Hz] and is assigned to the methyl group β to the oxime nitrogen. The AB quartet expected for the O–C=CH_2 group appears initially as a complex seven-line multiplet that gradually disappears on standing, the methylene protons being sufficiently acidic to exchange with the OD of the

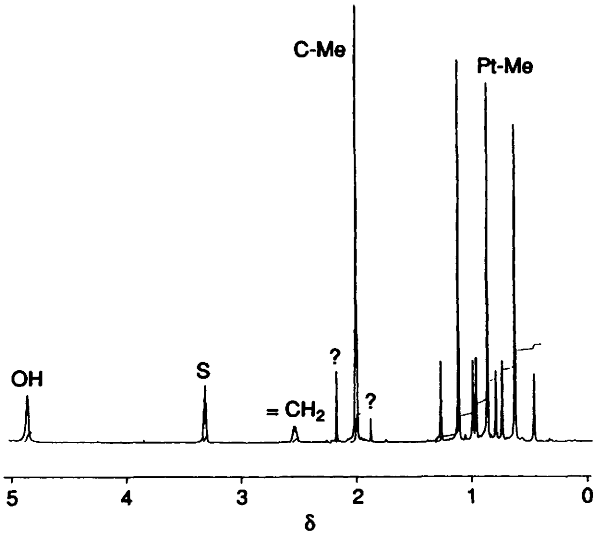

Fig. 2 The ^1H NMR spectrum of **1** in CD_3OD at 273 K showing the hydroxo–oxime structure; S = residual solvent signal

solvent (CD_3OD). The complexity of this multiplet is attributed to the additional presence of O–C=CHD groups (two types), the hydrogen signals of which exhibit splitting due to HD spin–spin coupling.

On warming the CD_3OD solution of **1** reversible dynamic broadening of the two signals from the platinum methyls *trans* to oxygen is observed. The central (*trans* N) Pt–Me resonance remains sharp at all temperatures, indicating that the monoximate ligand is bound to the metal *via* the Pt–N bond throughout, as shown by the retention of the (Pt–N=C–CH_3) ^4J(PtH) scalar coupling at elevated temperatures. The low boiling point of the solvent frustrated the acquisition of a full set of temperature-dependent NMR spectra, and so dynamic information was sought by two-dimensional exchange spectroscopy (2D EXSY). Six EXSY experiments were performed at different temperatures in the range 288–313 K. Since the fluxional process involves changes in solvent interactions (see below), the fluxional kinetics are likely to be concentration dependent, so all dynamic NMR experiments were performed on the same sample. Compound **1** is stable in solution and no evidence of decomposition is observed in its spectra. The 2D EXSY spectrum of **1** at 303 K is shown in Fig. 3. This clearly reveals the presence of cross peaks between the two PtMe signals due to methyl groups *trans* to oxygen, whilst no exchange is observed with the central (*trans* N) resonance. The Eyring activation parameters calculated from the 2D EXSY data (Table 3) are as follows: $\Delta H^{\ddagger} = 132.3 \pm 10.2$ kJ mol^{-1}, $\Delta S^{\ddagger} = 195 \pm 34$ J K^{-1} mol^{-1}, $\Delta G^{\ddagger}$ (298.15 K) = 74.3 ± 0.07 kJ mol^{-1}

The sizeable positive $\Delta S^{\ddagger}$ value observed for this fluxional rearrangement suggests a partially dissociated transition state in which the oxygen atom (but not the nitrogen atom) is disconnected from the metal moiety. It is proposed that the exchange of the two *trans*-oxygen Pt–Me signals arises from a 'windscreen-wiper' movement of the chelate ligand as depicted in Fig. 4. The involvement of the solvent is supported by the solvent dependence of the rate of the fluxional process. This is illustrated in Fig. 5 where it can be seen qualitatively that the stereodynamics are much more rapid in $(CD_3)_2CO$ than in CD_3OD or $(CD_3)_2SO$ (in which the solvent is believed to be S-co-ordinated, see below). The rate of the fluxion of **1** at room temperature in $(CD_3)_2CO$ is such that the Pt–Me (*trans*-O) and (*trans*-solvent) signals have coalesced to a broad band centred near the Pt–Me (*trans*-N) signal. Furthermore, the latter signal exhibits some slight exchange broadening, implying that at high rates of the 'windscreen-wiper' fluxion there is also some tendency either for dissociation of the complex or for intramolecular scrambling involving all three PtMe groups. A quantitative comparison of the exchange kinetics in the different solvents was thought unlikely to be informative because of the concentration dependence of the rates and because of the different structural form of the complex in $(CD_3)_2CO$ and $(CD_3)_2SO$. In both of these solvents, the ligand displays *two* methyl signals and no methylene signal. The lower frequency signal shows coupling to ^{195}Pt ($^4J \approx 4$ Hz) and this is attributed to the N=CMe group. The other signal is a singlet, and is assigned to an O=CMe group. Thus compound **1** would appear to exist in two forms dependent on the solvent, a hydroxo–oxime configuration in CD_3OD [Fig. 6(*a*)] and a carbonyl–oxime configuration in $(CD_3)_2CO$ and $(CD_3)_2SO$ [Fig. 6(*b*)].

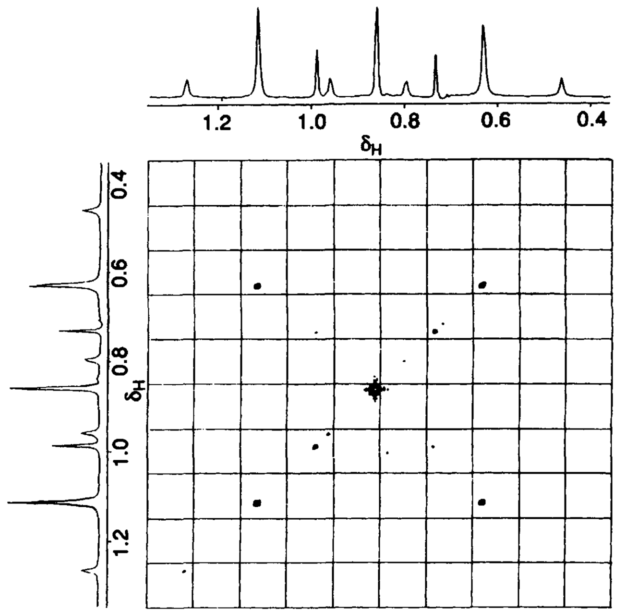

Fig. 3 The ^1H NMR two-dimensional EXSY spectrum of **1** in CD_3OD at 303 K showing the exchange between the Pt–Me (*trans*-O) and Pt–Me (*trans*-solvent) signals. Mixing time was 0.45 s

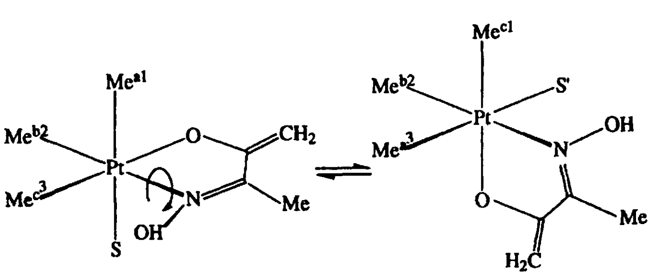

Fig. 4 Proposed 'windscreen-wiper' fluxion of **1** in organic solvents. The numbers refer to the sites of the *fac*-orientated methyl groups, the letters identify the chemical environments of the methyl groups

Table 3 Two-dimensional EXSY data for $[\{PtMe_3(bdm)\}_2]$ **1**

T/K	Mixing time/s	Rate*/s^{-1}
288	2.0	0.067
293	1.5	0.232
298	0.75	0.691
303	0.45	1.91
308	0.25	3.71
313	0.075	5.49

* First-order rate constants for the fluxional rearrangement of **1** in CD_3OD: uncertainties *ca.* ± 10%.

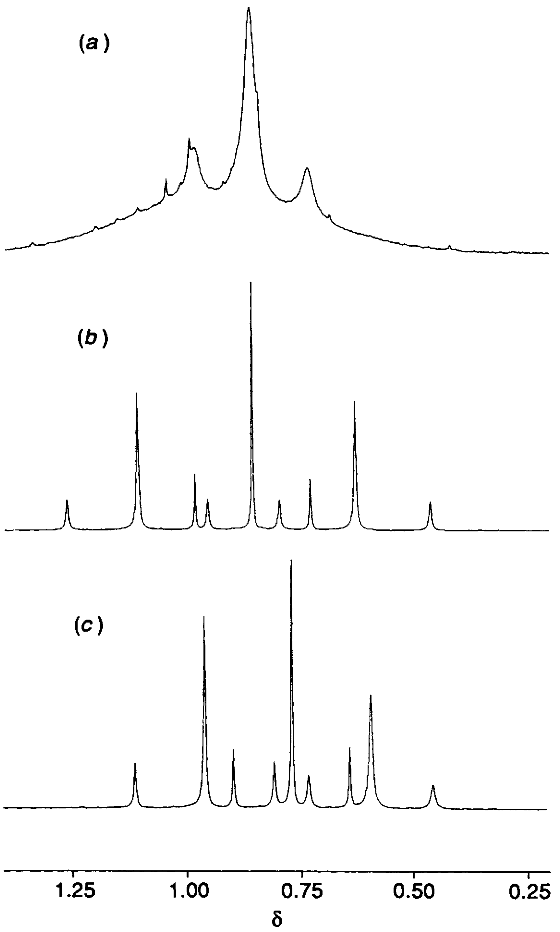

Fig. 5 The ^1H NMR spectra (PtMe region only) of solutions of **1** (17.9 g dm^{-3}) in $(CD_3)_2CO$ (*a*), CD_3OD (*b*) and $(CD_3)_2SO$ (*c*) at 303 K showing the relative rates of the 'windscreen-wiper' fluxion

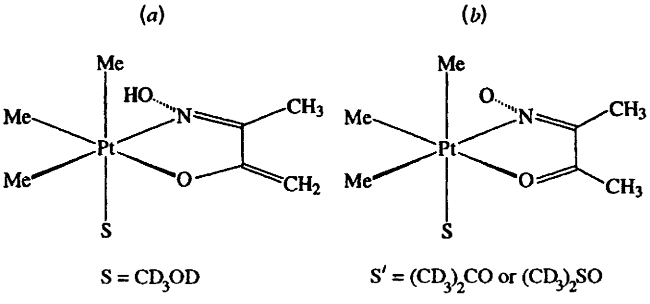

Fig. 6 The hydroxo–oxime (*a*) and carbonyl–oxime (*b*) forms of **1** in various solvents

Three Pt–Me signals are observed in $(CD_3)_2CO$ and $(CD_3)_2SO$, two of which show scalar couplings very close to the values in CD_3OD. The lowest frequency signal has significantly solvent-sensitive ^2J(Pt–H) values of 83.7 [in $(CD_3)_2CO$] and 69.3 Hz [in $(CD_3)_2SO$] (*cf.* 83.2 Hz in CD_3OD). The former is typical of methyl groups *trans* to weakly bonded solvent oxygen [*cf.* 80 Hz in $(PtMe_3)_2SO_4{\cdot}4H_2O$ in D_2O and $(CD_3)_2CO$] and may be compared to the corresponding values for acetone solvates of the β-diketone complexes $[\{PtMe_3(acac)\}_2]$ (Hacac = acetylacetone) and $[\{PtMe_3(dpacac)\}_2]$ (Hdpacac = 1,3-diphenylacetylacetone, acetylacetone = pentane-2,4-dione) in $(CD_3)_2CO$ solution of 82.4 and 82.6 Hz respectively.[11] In $(CD_3)_2SO$ a ^2J(Pt–H) value of 69.3 Hz indicates that $(CD_3)_2SO$ is S-bonded to the Pt {*cf.* ^2J(Pt–H) = 71.8 Hz for the methyl *trans* to the sulfur in $[PtMe_3(acac)(Me_2S)]$}.[14]

The pyridine and 2,2'-bipyridyl adducts [PtMe$_3$(bdm)(py)] **2** and [PtMe$_3$(bdm)(bipy)] **3** were made in high yield from the reaction of **1** with the nitrogen base. The IR spectrum of **2** (CsI disc) shows three bands in the C–H stretching region, three Pt–C stretches and one Pt–N stretch, consistent with the *fac*-octahedral geometry. The absence of an OH stretching mode implies that the bdm ligand has a different [C=N→O] configuration to that found in **1**. Strong bands at 764, 704, 654 and 642 cm^{-1} are characteristic of pyridine.[15] A band at 1553 cm^{-1} may be assigned to the stretching mode of the co-ordinated acyl group. The free C=O stretching mode at 1670 cm^{-1} in the free ligand is absent.

The ^1H NMR spectrum of **2** in $CDCl_3$ shows three Pt–Me signals, with ^{195}Pt satellites, in a 1 : 1 : 1 intensity ratio. Signals at δ 0.89 [^2J(PtH) = 63.9 Hz] and 1.16 [^2J(PtH) = 76.6 Hz] are assigned to the two non-equivalent equatorial Pt–Me environments resulting from the unsymmetrical nature of the chelate ligand (Fig. 1). These signals are attributed to the *trans*-N and *trans*-O platinum methyls respectively on the basis of their scalar coupling constants.[10,11] The signal at δ 0.61 [^2J(PtH) = 72.2 Hz] is assigned to the Pt–Me group *trans* to pyridine. In **2** both oximate methyls show a small low frequency shift to δ 1.85 and 2.36 compared to the unco-ordinated ligand (δ 1.93 and 2.40). The lower frequency signal shows ^{195}Pt coupling [^4J(PtH) = 4.1 Hz] and is assigned to the methyl group β to the oximate nitrogen on the basis that ^4J(PtH) coupling is observed through nitrogen in complexes of $Pt^{IV}Me_3$ with butane-2,3-dione dioxime,[12] but not through oxygen in [PtMe$_3$(acac)(py)].[11] The FAB mass spectrum of **2** is fully consistent with the proposed formulation, showing a parent ion at *m*/*z* 420 $(M + H)^+$.

The 2,2'-bipyridyl adduct **3** contains a monodentate N-co-ordinated oximato ligand (Fig. 1). The IR spectrum (CsI disc) shows no OH stretch but a strong band attributable to the C=O stretch of an unco-ordinated carbonyl group is observed at 1654 cm^{-1}. The *fac*-octahedral co-ordination geometry of the metal moiety is confirmed by the presence of three bands in the C–H stretching region (two due to the C–H stretching modes and one due to the overtone of the asymmetric vibration at *ca.* 1405 cm^{-1}).[16]

The FAB mass spectrum of **3** shows a molecular ion corresponding to $[M - bdm]^+$ (*m*/*z* 396). The ^1H NMR spectrum of **3** in $CDCl_3$ solution consists of three regions: (*i*) the Pt–Me region (*ca.* δ 0.2–1.3), (*ii*) the ligand oximato region (*ca.* δ 1.5–1.7) and (*iii*) the aromatic (bipyridyl) region (*ca.* δ 7.6–9.0). The platinum methyl region shows two signals, with ^{195}Pt satellites, in a 2 : 1 intensity ratio. These signals can be assigned unambiguously to the equatorial (*trans* bipy) and axial (*trans* N-bonded oximate) by their ^2J(PtH) coupling constants. The aromatic signals, which may be fully assigned, are characteristic[13,16] of a co-ordinated 2,2'-bipyridyl ligand bonded to $[Pt^{IV}Me_3]^+$.

Two oximato ligand methyl signals are seen in a 1 : 1 intensity ratio. The lower frequency signal is assigned to the methyl β to the oximate nitrogen by comparison with the spectra of **1** and **2**. However, no coupling to ^{195}Pt is observed, showing that long-range Pt–Me coupling is influenced strongly by the conformation of the oximate ligand. The higher frequency signal is attributed to the methyl of the oximate acyl group.

The above evidence clearly demonstrates that ionised butane-2,3-dione monoxime is a versatile ligand, displaying three distinct ligand bonding modes. The dimer **1** is clearly strongly bound, as it is preserved in the FAB mass spectrum and is only soluble in solvents in which it can form a solvated monomer. The behaviour in CD_3OD solution indicates that carbonyl methyl protons are sufficiently acidic (pK_a 9.30[17]), (*i*) for a proton to migrate to the oxime oxygen, and (*ii*) to exchange with OD in the solvent. The solvated monomers are stereochemically non-rigid, the kinetics being strongly solvent-dependent and a two-site 'windscreen-wiper' mechanism is proposed which is novel in trimethylplatinum(IV) chemistry.

Attempts to make the analogous compounds for the isoelectronic $[Re(CO)_3]^+$ were unsuccessful.

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