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Mono- and di-nuclear platinum(II) complexes containing O- and N-bonded acetamide

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Abstract

The preparation, characterization, and interconversion reactions of a series of novel O- and N-bonded acetamide and deprotonated N- and N,O-bonded acetamido derivatives of platinum(II)-terpy (terpy = 2,2′:6′,2″-terpyridine) are described. The X-ray structures of the mononuclear N-acetamido and an unusual di-nuclear N,O-acetamido species are also reported.

Keywords: Platinum(II) complex; Acetamide; Linkage isomers; X-ray structures

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Acetamide is able to act as either an O- or N-donor ligand, depending on the nature of the metal centre. Hard metal ions such as cobalt(III) [1], chromium(III) [2], ruthenium(III) [3], and rhodium(III) [4], typically bond to the O-atom, while softer Lewis acids such as platinum(II) and palladium(II) show only a weak affinity for O-coordination and prefer to coordinate to the N-atom [5,6]. Indeed, O-bonded amide complexes such as those of platinum(II) are readily able to isomerize intramolecularly to the thermodynamically stable N-bonded isomer [7]. The facile hydrolysis of acetonitrile in the platinum(II) coordination sphere provides another route to N-acetamide complexes [5]. Two of the most significant features of N-acetamide complexes include the potential for metallation to stabilize both the amide and iminol tautomers, each of which have been observed for platinum(II) complexes [8], and the tendency for deprotonated acetamido complexes to form di-nuclear species containing a bridging N,O-acetamido ligand [5], a phenomenon that has also been recently reported for palladium(II) [9].

Herein we report the preparation and characterization of a series of novel acetamide complexes of platinum(II)-terpy (terpy = 2,2′:6′,2″-terpyridine), including an unusual example in which deprotonated acetamide acts as a bridging bidentate ligand coordinated to two metal centres via both its N- and O-atoms. The terpy ligand sufficiently stabilizes all the platinum(II) complexes such that the O- and N-bonded acetamide and deprotonated N- and N,O-bonded acetamido derivatives can be isolated and fully characterized.

Treatment of the labile precursor $[Pt(MeCN)(terpy)](OTf)_2$ with acetamide afforded the O-acetamide derivative **1** in excellent yield (91%) (Scheme 1) [10]. The complex was found to undergo a linkage isomerization reaction to afford **2** in quantitative yield [11]. This process was readily effected by heating **1** in acetone solution at 50 °C for 1 h or by allowing the complex to stand in acetone solution for 36 h at room temperature. The intramolecular conversion of the kinetic O-bonded acetamide complex **1** to the thermodynamically stable N-bonded isomer **2** has been previously reported for the analogous diethylenetriamine system [7], and demonstrates the particular affinity of platinum(II) for N- rather than O-donor ligands. The isomerization reaction was confirmed by means of

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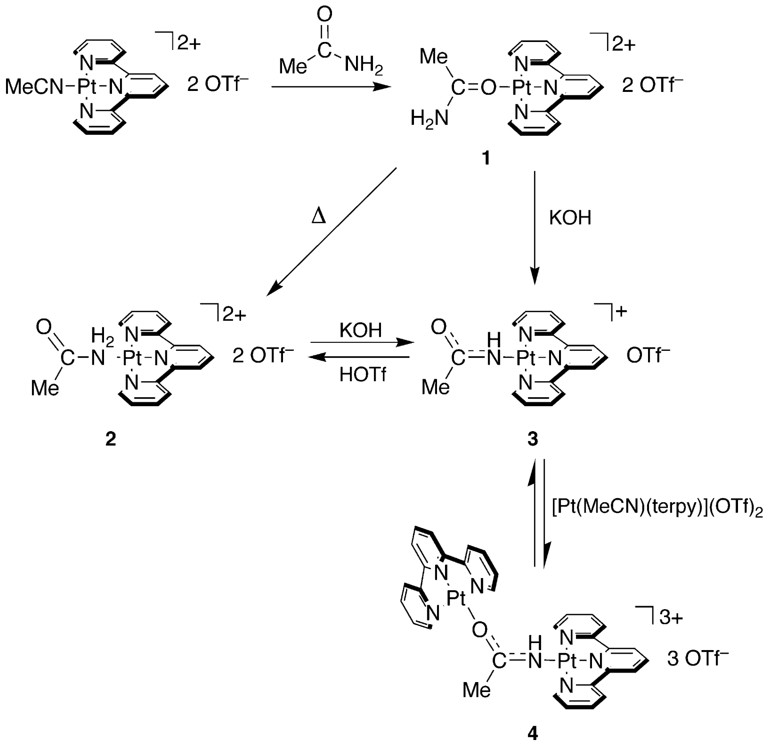

Scheme 1.

$^{195}Pt\{^1H\}$ NMR spectroscopy whereby the appearance of a signal at δ −2625 was accompanied by a disappearance of the resonance at δ −2319, consistent with the conversion from a PtN_3O to PtN_4 coordination sphere [12]. A downfield shift of the Me signal in the ^1H NMR spectrum ($\Delta\ \delta$ = ca. 0.2 ppm) and an upfield shift of the C=O signal in the $^{13}C\{^1H\}$ NMR spectrum ($\Delta\delta = 6.4$ ppm) were also observed during the conversion process. Complex **2** appears to exist as the amide rather than iminol tautomer as (a) no signal for the OH group of an iminol tautomer was observed in the ^1H NMR spectrum (even when scrupulously dried NMR solvents were used) and (b) the relative integrations of the NH:Me proton signals were found to be 2:3 rather than 1:3.

Complexes **1** and **2** were readily deprotonated by KOH to afford the N-acetamido derivative **3** which displays a singlet in the $^{195}Pt\{^1H\}$ NMR spectrum at δ −2609, consistent with a PtN_4 core [12], and a distinct molecular ion peak at m/z 486.1 in the ESI-MS corresponding to $[M-OTf]^+$ [13]. The ^1H NMR spectrum displays a significant shift of the NH signal from δ 8.79 to δ 8.35 during the conversion process which is consistent with the presence of free and coordinated amino groups, respectively; a 50% decrease in the intensity of this signal was also observed and is in accord with the deprotonation of the NH_2 group. In the preparation of **3** from **2**, the reaction was found to be completely reversible upon the addition of HOTf. However, the presence of the unusual di-nuclear species **4**, in which the N- and O-atoms of the acetamido ligand are coordinated to two platinum(II) centres, was detected by NMR spectroscopy irrespective of the mode of preparation of **3**. Complex **4** could also be prepared by the addition of one equivalent of $[Pt(MeCN)(terpy)](OTf)_2$ to **3** or by a direct reaction involving base hydrolysis of the coordinated acetonitrile in the precursor species $[Pt(MeCN)(terpy)](OTf)_2$ [14]. The di-nuclear species displayed the presence of two signals of approximately equal intensity at δ −2318 and δ −2607 in the $^{195}Pt\{^1H\}$ NMR spectrum, corresponding to the PtN_3O and PtN_4 cores, respectively [12]. Despite repeated attempts, a pure sample of **4** could not be prepared as it was always isolated with the mononuclear **3**; the inherent lability of the Pt–O bond in **4** would in part explain this phenomenon. X-ray diffraction studies confirmed that **4** co-crystallizes along with one molecule of **3** in the asymmetric unit [15]. The asymmetric unit additionally contains four triflate counter-ions, and eight sites modelled as partially-occupied water oxygen sites, with occupancies refined and then fixed at 0.5. The ORTEP structures of **3** and **4** are presented in Figs. 1 and 2, respectively.

In conclusion, we have shown that both mono- and di-nuclear platinum(II) derivatives of acetamide can be prepared conveniently from the O-acetamide derivative **1**. The complexes undergo a series of interesting transformations to afford the N-acetamide and deprotonated N-acetamido complexes and also a di-nuclear species containing a bridging N,O-acetamido ligand. We are now in the process of investigating the reactivities of these complexes towards a variety of substrates and the results of this study will be reported in due course.