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A DTA and XPS Study of '*cis*-Platin'

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Much interest is focussed on the chemistry of *cis*-diamminedichloroplatinum(II), '*cis*–platin', and structurally related complexes in the context of cancer chemotherapy [1–5].

Some controversy is associated with the interpretation of existing thermal analysis data for *cis*-platin and related complexes. Wendlandt and Smith [6] have reported dissociation temperatures of 228 and 227 °C for *cis*- and *trans*-$[(NH_3)_2Cl_2Pt]$, respectively. Nikolaev [7] has reported two sharp exothermic peaks in the DTA of *cis*-platin at 215 and 275 °C preceeding the main endothermic peak at 340 °C. Nikolaev [7] assigns these exothermic peaks to *cis–trans* isomerisation with decomposition of the *trans* complex at 340 °C. An independent DTA study of *trans*-platin indicated initial decomposition at 230 °C [8]. Wendlandt [9] has reported a TG/DTA study of tetraammineplatinum(II)chloride, which is consistent with ammonia loss commencing at 180 °C and formation of *trans*-platin as an intermediate at 260 °C which subsequently decomposes at 320 °C yielding a platinum metal residue at 350 °C. Block *et al.* [10] have reported a TG study of *trans*-platin which indicates that decomposition of this complex commences at 220 °C. The TG data for $(NH_3)_4PtCl_2$, as obtained by Wendlandt [9] and Block *et al.*, [10] have essentially been confirmed by Kinoshita *et al.* [11]. Thus, from the existing thermal analysis data for *cis*-platin and related complexes it is apparent that the temperatures corresponding to *cis–trans* isomerisation and *trans*-platin decomposition require confirmation.

The present letter reports a further DTA study of *cis*-platin and *cis–trans* isomerisation and decomposition DTA assignments are confirmed from an XPS study of *cis*-platin and the product formed at the temperature corresponding to the end of the initial DTA endotherm.

Experimental

Diamminedichloroplatinum(II) was obtained from David Bull Laboratories, Clayton, Vic., Australia. *Anal.* Calc. for $(NH_3)_2Cl_2Pt$: Cl, 23.6; N, 9.33. Found, Cl, 23.4; N, 9.38%.

Infrared spectra were recorded in the range 4000–250 cm^{-1} on a Perkin-Elmer 457 Grating Infrared Spectrophotometer using the KBr pellet method, with band calibration relative to polystyrene.

Differential thermal analysis (DTA) was obtained using a Rigaku-Denki Thermal Analysis System (Type 8085), employing platinum sample pans, a 10 mg sample mass, a heating rate of 5 °C min^{-1} and a static air atmosphere. Alumina was used as the thermally inert reference.

The XPS spectra were recorded on a spectrometer previously described by Kemeny *et al.* [12] using Mg Kα photons of 1253.6 eV energy and at 10^{-6}–10^{-7} HPa ($\simeq$Torr). All samples were mounted on a double-sided copper sample holder and were in the form of a fine powder adhered to double sided adhesive tape. All binding energies (E_b^F) were calibrated relative to the $Cu(2p_{3/2})$ binding energy level of 932.50 eV, relative to the spectrometer Fermi level [13].

Results and Discussion

A typical DTA thermogram for '*cis*-platin' is shown in Fig. 1. A sharp endothermic peak is exhibited at 335 °C followed immediately by a sharp exothermic peak at 366 °C.

Core level binding energies: $E_b^F(Pt(4d_{5/2,3/2}))$ and $E_b^F(Cl(2p))$ for *cis*-platin and the product obtained immediately prior to the DTA exotherm of *cis*-

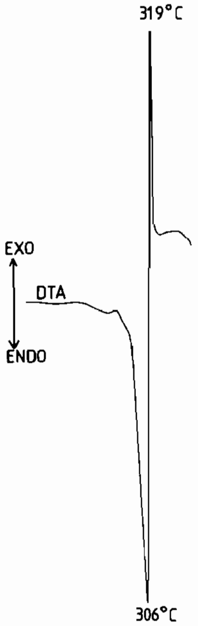

Fig. 1. Typical DTA thermogram for *cis*-platin.

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TABLE I. XPS Data for *Cis*- and *Trans*-Platin

Sample	E_b (eV)		
	Pt($4d_{5/2}$)	Pt($4d_{3/2}$)	Cl(2p)
Platinum (metal)	314.5	331.5	–
cis-Platin	313.8	330.9	196.1
trans-Platin	312.7	329.8	197.2

platin are recorded in Table I. It should be noted that the Pt($4d_{5/2,3/2}$) core level binding energies were determined in preference to Pt(4f) binding energies, since the 4d level has a higher cross-section per electron compared with the 4f level [14], and hence $E_b{}^F$(Pt(4d)) is more susceptible to structural changes than $E_b{}^F$(Pt(4f)). Typical Pt($4d_{5/2,3/2}$) XPS spectra for the *cis*- and *trans*-platin complexes are shown in Figs. 2 and 3, respectively.

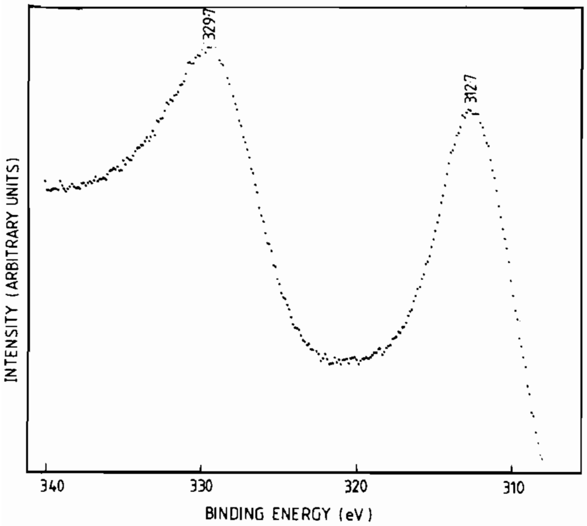

Fig. 2. Typical Pt($4d_{5/2,3/2}$) XPS spectra for *cis*-platin.

The infrared spectra of *cis*-platin and the product obtained during differential thermal analysis of *cis*-platin are summarised in Table II. These spectra correspond very closely to those reported by Poulet *et al.* [15] for *cis*- and *trans*-platin, respectively.

The DTA, XPS and infrared spectral data collectively are consistent with *cis–trans* isomerisation of *cis*-platin at 306 °C and decomposition of *trans*-platin at 319 °C. With respect to the XPS data (Table I), Pt($4d_{5/2,3/2}$) core level binding energies for *trans*-platin are less than those for the *cis* isomer, whereas an opposite trend is apparent for the corresponding Cl(2p) core level binding energies. These data are consistent with a lower electron density on Pt and a higher electron density on Cl^- for *cis*-platin relative to *trans*-platin due to the asymmetric electron withdrawing effect of *cis*-orientated Cl^- ligands in *cis*-platin.

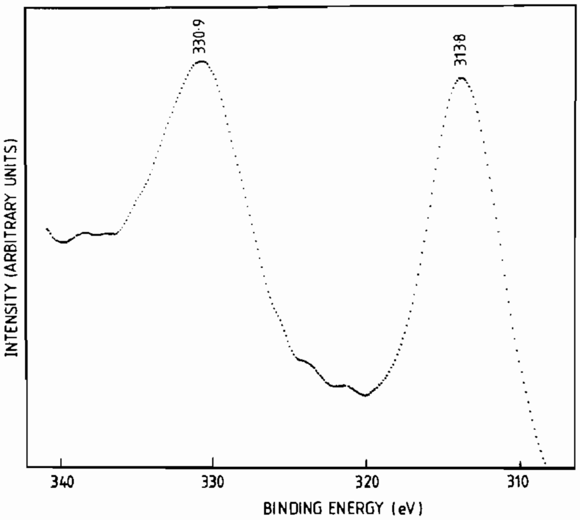

Fig. 3. Typical Pt($4d_{5/2,3/2}$) XPS spectra for *trans*-platin.

TABLE II. Infrared Spectral Data (cm^{-1}) for *cis*- and *trans*-platin

Assignment	*cis*-Platin (cm^{-1})	*trans*-Platin (cm^{-1})
νPt–Cl	323, 330	328
νPt–N	510	507
ν(N–H)	805	805
$\delta(NH_3)_{sym}$	1300, 1315	1290
$\delta(NH_3)_{assym}$	1530, 1610	1525, 1615
$\nu(NH_3)_{sym}$	3200	3200
$\nu(NH_3)_{assym}$	3280	3280

It is clear from the present thermal analysis data that the thermal stability of *cis*- and *trans*-platin is greater than previously reported [6–8, 10].

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