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Note

Synthesis and characterisation of four-membered ring platinalactam complexes derived from 2-cyanoacetylurea; crystal structure of [Pt{N(CONH₂)C(O)CH(CN)}(PPh₃)₂]

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Abstract

The reactions of *cis*-[PtCl₂L₂] [L = PPh₃ or L₂ = dppe (Ph₂PCH₂CH₂PPh₂)] with cyanoacetylurea [NCCH₂C(O)NHC(O)NH₂] and triethylamine gives the platinalactam complexes [Pt{N(CONH₂)C(O)CH(CN)}L₂]. A single-crystal X-ray diffraction study on the triphenylphosphine complex confirms the presence of the four-membered platinalactam ring; the urea substituent is involved in intra- and intermolecular hydrogen bonding, forming a dimer in the solid state. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Four-membered rings which contain a metal atom and an amide group in the ring system (metallalactam complexes) are quite rare in the literature. A number of four-membered ring metallalactam complexes of platinum(II) and palladium(II) 1, 2 have been synthesised by reaction of halide complexes $[MCl_2L_2]$ (L = phosphine ligand or $L_2 =$ cyclo-octadiene) with organic amides in the presence of a base [silver(I) oxide]; amides investigated to date are N-cyanoacetylurethane [1,2], acetoacetanilide [3] and 2-benzoylacetanilide [4]. In this Note we extend our studies to the synthesis of platinalactam complexes 3 from the more highly functionalised precursor cyanoacetylurea, NCCH₂C(O)NHC(O)NH₂. This was of interest because of the possibility of forming a platinaureylene complex 4, and for the nature of the hydrogen bonding in the product formed. Platinaureylene complexes have previously been synthesized from ureas, by the same Ag_2O methodology [5], and by other routes [6–8].

2. Results and discussion

2.1. Synthesis of platinalactam complexes

The reactions of the platinum(II) chloride complexes *cis*-[PtCl₂(PPh₃)₂] and [PtCl₂(dppe)] (dppe = Ph₂PCH₂CH₂PPh₂) with cyanoacetylurea and excess triethylamine in refluxing methanol gives the platinalactam complexes **3** in good yields. The reactions proceed rapidly, and the products can be isolated from the byproduct $Et_3NH^+Cl^-$ and excess Et_3N simply by the addition of excess water, in which the platinum complexes are insoluble. Previous syntheses of platinalactam complexes have used silver(I) oxide as a base [1–4], so the triethylamine method is a viable alternative. It is noteworthy that no ureylene complex **4** was observed; presumably the Pt–NH group of **4** is less stable than the

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Pt–N–C(O) group in 3, where the Pt–N bond is stabilisised by two electron-withdrawing carbonyl groups. The attempted synthesis of the analogous bis(triphenylphosphine) palladium complex was unsuccessful, with ³¹P NMR showing the formation of a complex mixture of products.

In the ¹H NMR spectrum of **3a** a broad resonance is observed at δ 4.5, assigned to the exchangeable urea protons. The PtCH proton appears as a doublet of doublets due to coupling to both P atoms, with ¹⁹⁵Pt satellites. The ${}^{31}P{}^{1}H{}$ NMR spectrum of **3a** shows the expected AB spin system of two nonequivalent PPh₃ ligands, with the phosphorus *trans* to the higher *trans* influence CH(CN) group showing the smaller ${}^{1}J(PtP)$ value (2543 versus 3742 Hz). Comparison of the ³¹P NMR data of 3a and 3b with the corresponding cyanoacetylureylene-derived complexes 1 [3] indicates that the $N(CO_2Et)$ and $N(CONH_2)$ substituents have very similar trans influences, but with the latter being slightly higher, as shown by the smaller values of ${}^{1}J(PtP)$ for P atoms *trans* to this group in **3a** and **3b**. In the ¹³C{¹H} NMR spectrum of **3a**, the PtCH carbon (δ 11.5) gives the expected doublet of doublets due to phosphorus coupling, with additional coupling to ¹⁹⁵Pt (388 Hz). For comparison, in cyanoacetylurea, the CH₂ carbon appears at δ 30.6 (in DMSO-d₆) indicating shielding on platination. The cyano carbon (δ 121.7, c.f. δ 119 in cyanoacetylurea) gives a doublet due to phosphorus coupling, with additional platinum coupling (${}^{3}J(PC)$ 6.5, ${}^{2}J(PtC)$ 49.4). The lactam carbonyl (δ

173.9) shows coupling to both ¹⁹⁵Pt and ³¹P while the urea carbonyl (δ 156.0) shows coupling only to the *trans* PPh₃ ligand giving a doublet (*J* 5.6 Hz). Overall the NMR spectroscopic features of **3a** are comparable to those of the related lactam complex **1** (M = Pt, L = PPh₃) [1].

Electrospray mass spectrometry has also been used to characterise complexes **3a** and **3b**, which give strong [MH]⁺ and weaker [2MH]⁺ ions in their positive-ion electrospray mass spectra at low cone voltages (ca. 20 V) using MeCN-H₂O as the mobile phase solvent. At cone voltages of 40 V and higher, fragmentation occurs, with the fragment ions [MH-NH₃]⁺, [MH-HNCO]⁺, and [L₂Pt(NCO)]⁺ (L = PPh₃ or L₂ = dppe) observed for both complexes, formed by fragmentation of the urea group and metalacycle. Thus, for complex **3a**, the ion [(Ph₃P)₂(NCO)]⁺ was observed at m/z 761. There was no evidence for the alternative fragment ions [L₂Pt(CH₂CN)]⁺, which for L = PPh₃ would have m/z759.

As with previously characterised platinalactam complexes derived from *N*-cyanoacetylurethane (1) the IR stretching frequency of the cyanide group shifts on complex formation [1]. In cyanoacetylurea, the CN stretch is observed at 2270 cm⁻¹, while in **3a** it is observed at 2211 cm⁻¹.

2.2. X-ray structure of $[Pt\{N(CONH_2)C(O)CH(CN)\}-(PPh_3)_2]$ (3a)

Fig. 1 shows the atom labeling scheme for the complex, and selected bond lengths and angles are given in Table 1. The structure determination confirms the formulation of the complex as a four-membered ring platinalactam. The geometry about the platinum is a distorted square plane; the N(1)-Pt-C(2) angle is acute



Fig. 1. Molecular structure of $[Pt{N(CONH_2)C(O)CH(CN)}(PPh_3)_2]$ (3a) showing the atom numbering scheme. Thermal displacement ellipsoids are depicted at 50% probability. The phenyl hydrogen atoms, dichloromethane and diethyl ether of crystallisation have been omitted for clarity.

for

Table 1 Selected bond lengths (\AA) and bond angles (°) $[Pt{N(CONH_2)C(O)CH(CN)}(PPh_3)_2]$ (3a)

Pt-N(1)	2.071(4)	Pt-C(2)	2.105(4)
Pt-P(1)	2.2467(11)	Pt-P(2)	2.3375(11)
N(1)-C(1)	1.371(6)	N(1)–C(4)	1.401(6)
N(2)–C(3)	1.143(7)	N(3)–C(4)	1.349(7)
O(1)-C(1)	1.220(6)	O(2)–C(4)	1.230(6)
C(1)–C(2)	1.529(6)	C(2)–C(3)	1.442(7)
P(1)–C(11)	1.826(5)	P(1)-C(21)	1.834(5)
P(1)-C(31)	1.813(5)	P(2)–C(41)	1.827(5)
P(2)-C(51)	1.841(5)	P(2)-C(61)	1.826(5)
N(1)-Pt-C(2)	65.94(17)	N(1)–Pt–P(1)	162.51(11)
C(2) - Pt - P(1)	96.62(13)	N(1)-Pt-P(2)	99.97(11)
C(2)-Pt-P(2)	165.48(13)	P(1) - Pt - P(2)	97.35(4)
C(1)–N(1)–C(4)	124.5(4)	C(1)-N(1)-Pt	98.6(3)
C(4)-N(1)-Pt	135.9(3)	O(1)-C(1)-N(1)	130.2(5)
O(1)-C(1)-C(2)	126.7(4)	N(1)-C(1)-C(2)	103.1(4)
C(3)–C(2)–C(1)	112.4(4)	C(3)-C(2)-Pt	113.8(3)
C(1)-C(2)-Pt	92.2(3)	N(2)-C(3)-C(2)	178.9(6)
O(2)–C(4)–N(3)	123.0(5)	O(2)-C(4)-N(1)	119.9(4)
N(3)-C(4)-N(1)	117.2(4)		

at 65.94(17)°, but is comparable to those found in similar metallalactam structures (64-67°) [1,3]. The P(1)-Pt-P(2) angle is more obtuse [97.35(4)°] to accommodate the steric bulk of the PPh₃ ligands. The Pt-P bond lengths reflect the relative *trans* influences of the trans atoms; Pt-P(1) [2.2467(11) Å] (trans to the low trans influence nitrogen) is shorter than Pt-P(2) (2.3375(11) Å), trans to the high trans influence C(2). The coordination sphere around the platinum atom, and the ring system, is highly planar, with no atom lying more than 0.022(2) Å from the least-squares plane. The Pt-N (2.071(4) Å) and Pt-C (2.105(4) Å) bonds of **3a** are slightly longer than those of the related cyanoacetylurethane complex $Pt{N(CO_2Et)C(O)CH}$ -(CN) (cod)] (cod = 1.5-cvclo-octadiene) of type 1 [Pt-N 2.016(6), Pt-C 2.069(8) Å] [1] due to the higher trans influence of the PPh₃ ligand compared to cod [9].

The main feature of interest in the structure of 3a is the urea substituent, which is coplanar with the platinacycle. The urea nitrogen N(3) oriented such that H(3a) forms an intramolecular hydrogen bond to the lactam oxygen O(1) [O(1)...H(3a) 1.988 Å]. H(3b) forms an intermolecular hydrogen bond to a symmetry equiva-



Fig. 2. Hydrogen bonding in $[Pt{N(CONH_2)C(O)CH(CN)}(PPh_3)_2]$ (3a); (a) plan view, (b) side view. Phenyl rings are omitted for clarity.

lent of O(2') [O(2)...H(3b) 2.123 Å], giving rise to a loosely-bound dimeric species in the solid state (Fig. 2a), where the dimer is located about the crystallographic inversion center at coordinates (1, 0.5, 1). The bond lengths for the cyanoacetylurea moiety are not unusual. A side view of the intermolecular contacts (Fig. 2b) shows that the hydrogen bonding is not in a planar arrangement, but has the molecules lying stepped to one another. Because of this intermolecular interaction, H(3a) and H(3b) are not positioned opposite each other. As can be seen in Fig. 2, H(3b) is bent out of the plane of the platinalactam, oriented so that it can more readily hydrogen bond to O(2'). A conformational calculation of the torsion angles [O(2)-C(4)-N(3)-H] has H(3a) at 170.3° and H(3b) at 22.1°. If H(3b) was directly opposite H(3a) a torsion angle of about 10° for O(2)-C(4)-N(3)-H(3b) might be expected. Hydrogen-bonded distances and angles are summarised in Table 2.

Table 2

Hydrogen bonds ^a (with $H \cdots A < r(A) + 2.000$ Å) and angles ($D \cdots H \cdots A$ angle > 100°) for [$Pt\{N(CONH_2)C(O)CH(CN)\}(PPh_3)_2$] (**3a**) ^b

D-H	D–H (Å)	H…A (Å)	D…H…A (°)	D…A (Å)	А
N(3)-H(3a)	0.901	1.988	137.45	2.721	O(1)
N(3)-H(3b)	0.861	2.123	161.93	2.954	O(2)

^a D-H = H bond donor, A = H bond acceptor.

^b Symmetry operator = [-x+2, -y+1, -z+2].

Table 3

Crystal, collection and refinement data for $[Pt{N(CONH_2)C(O)CH(CN)}(PPh_3)_2]$ (3a)

Empirical formula	C ₄₀ H ₃₃ N ₃ O ₂ P ₂ Pt. CH ₂ Cl ₂ . 0.5(C ₂ H ₅) ₂ O
Formula weight	966.71
Crystal system	triclinic
Space group	$P\overline{1}$
Unit cell dimensions	
a (Å)	10.9488(1)
b (Å)	12.8958(2)
<i>c</i> (Å)	17.5272(3)
α (°)	72.796(1)
β (°)	73.69(1)
γ (°)	66.19(1)
V (Å ³)	2125.65(5)
Ζ	2
$D_{\rm c} ({\rm g \ cm^{-3}})$	1.510
Diffractometer	Siemens SMART CCD
Radiation, wavelength (Å)	Mo K α , $\lambda = 0.71073$
Temperature (K)	203(2)
Crystal size (mm)	$0.45 \times 0.40 \times 0.30$
θ Range for data collection (°)	$1.76-27.49 \ (-13 \le h \le 14, \ -15 \le k \le 16, \ 0 \le l \le 22)$
Reflections collected	20978
Independent reflections	9205 $[R_{(int)} = 0.0202]$
Absorption coefficient (mm ⁻¹)	3.541
Max., min. transmission factors	0.4164, 0.2987
F(000)	962
Solution by	direct methods
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	9205/3/481
Goodness-of-fit on F^2	1.141
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0348, \ wR_2 = 0.0991$
R indices (all data)	$R_1 = 0.0374, \ wR_2 = 0.1013$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0520P)^2 + 7.0112P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest difference peak (e $Å^{-3}$)	2.881 [1.14 Å from C(84)]
Largest difference hole (e $Å^{-3}$)	-2.719
Programs used	SHELXS-97 and SHELXL-97 [15]

Strong hydrogen bonding involving the urea substituent is not unexpected. Ureas are strongly hydrogen-bonded in the solid state [10] and platinum complexes containing strongly hydrogen bonding ligands are of interest for the diversity of hydrogenbonded motifs which are displayed [11].

Complex **3a** crystallises with one molecule of dichloromethane and one half of a diethyl ether; these two solvent molecules occupy voids in the crystal lattice and have no contacts closer than C(70)-O(2) (3.257 Å) and O(3)-C(22) (3.532 Å) with the platinalactam complex.

3. Experimental

3.1. General

General procedures and instrumentation were as previously described [4]. All reactions and recrystallisations were carried out in solvents that were distilled prior to use but were not deoxygenated. The complex [PtCl₂(cod)] was synthesised by the literature procedure [12], and the complexes cis-[PtCl₂(PPh₃)₂] and [PtCl₂(dppe)] were synthesised from it by ligand substitution with a stoichiometric quantity of the phosphine in dichloromethane [13]. Cyanoacetylurea was used as supplied from Aldrich.

3.2. Synthesis of [Pt{N(CONH₂)C(O)CH(CN)}(PPh₃)₂] (3a)

A mixture of *cis*-[PtCl₂(PPh₃)₂] (500 mg, 0.633 mmol), cyanoacetylurea (250 mg, 1.97 mmol) and triethylamine (ca. 0.5 ml) in methanol (25 ml) was refluxed for 1 h to give a white suspension in a pale yellow solution. The mixture was cooled to room temperature, the white solid **3a** was filtered, washed with cold methanol (5 ml), water (10 ml) and diethyl ether (10 ml) and dried to give 349 mg (65%) of **3a**. Found: C, 57.1; H, 4.0; N, 4.8. C₄₀H₃₃N₃O₂P₂Pt requires: C, 56.9; H, 3.9; N, 5.0%. IR: ν (CN) 2211(s), ν (CO) 1683(s), 1652(s) cm⁻¹. M.p. 274–276°C (dec.). ¹H NMR: δ 7.54–7.03 (*m*, 30H, Ph), 4.50 (*s*, br, 2H, NH₂), 1.65 [*dd*, 1H, PtCH, ³*J*(PH_{*trans*}) 8, ³*J*(PH_{*cis*}) 3, ²*J*(PtH) 61]. ¹³C{¹H} NMR: δ 173.9 [*d*, ring CO, ³*J*(PC) 6.2, ²*J*(PtC) ca. 120], 156.0 [*d*, urea CO, ³*J*(PC) 5.6], 134.7– 127.5 (*m*, Ph), 121.7 [*d*, CN, ³*J*(PC) 6.5, ²*J*(PtC) 49.4] 11.5 [*dd*, PtCH, ²*J*(PC_{trans}) 74, ²*J*(PC_{cis}) 2, ¹*J*(PtC) 388]. ³¹P{¹H} NMR: AB spin system, δ 17.2 [*d*, ¹*J*(PtP trans C) 2530, ²*J*(PP) 18], 11.8 [*d*, ¹*J*(PtP trans N) 3722, ²*J*(PP) 18]. ESMS (cone voltage 20 V, MeCN–H₂O solution) [MH]⁺ (*m*/*z* 845, 100%), [2MH]⁺ (*m*/*z* 1689, 10%); cone voltage 40 V, [(Ph₃P)₂Pt(NCO)]⁺ (*m*/*z* 761, 60%), [MH–HNCO]⁺ (*m*/*z* 802, 15%), [MH–NH₃]⁺ (*m*/*z* 828, 15%), [MH]⁺ (845, 100%).

3.3. Synthesis of [*Pt*{*N*(*CONH*₂)*C*(*O*)*CH*(*CN*)}(*dppe*)] (**3b**)

Following the method for **3a**, [PtCl₂(dppe)] (88 mg, 0.13 mmol), cyanoacetylurea (18 mg, 0.15 mmol) and triethylamine (ca. 0.5 ml) gave **3b** (68 mg, 73%). The product was recrystallised from dichloromethane–diethyl ether and dried under vacuum prior to elemental analysis. Found: C, 49.6; H, 4.0; N, 5.7. $C_{30}H_{27}N_3O_2P_2Pt$ requires: C, 50.1; H, 3.8; N, 5.9%. IR: v(CN) 2202(s), v(CO) 1616 (br, s) cm⁻¹. M.p. 151–154°C (dec.). ³¹P{¹H} NMR: AB spin system, δ 45.1 [s, ¹J(PtP trans C) 2525, ²J(PP) unresolved], 38.6 [s, ¹J(PtP trans N) 3432, ²J(PP) unresolved]. ESMS (cone voltage 20 V, MeCN–H₂O solution): [MH]⁺ (m/z 719, 100%). [2MH]⁺ (m/z 635, 25%), [MH–HNCO]⁺ (m/z 676, 20%), [MH–NH₃]⁺ (702, 40%), [MH]⁺ (m/z 719, 100%).

3.4. X-ray structure of [Pt{N(CONH₂)C(O)CH(CN)}-(PPh₃)₂] (**3***a*)

Suitable crystals for an X-ray diffraction study were grown by vapor diffusion of diethyl ether into a dichloromethane solution of the complex. Preliminary cell parameters and the crystal orientation matrix were obtained from a collection of 45 standard frames. Accurate intensity data were collected over a sphere of reciprocal space and were corrected for Lorentz and polarisation effects. A semiempirical absorption correction was applied to the data [14]. The position of the platinum atom was determined by Patterson methods. All other non-hydrogen atoms were located from the difference Fourier maps of successive refinement cycles. Hydrogen atoms H(3a) and H(3b) were located from the residual electron density map. Electron density that was assigned to the solvents of crystallisation (dichloromethane and diethyl ether) was initially refined with a variable site occupancy factor. This indicated that the dichloromethane had about 90% occupancy, and was subsequently refined with full occupancy, while the diethyl ether had about 50% occupancy, and was modelled in the final refinement cycle with a 50% site occupancy factor. Attempts to include the significant electron density located near the diethyl ether (1.14 Å from C(84)) in the model resulted in unreasonable thermal motion parameters for the nearby atoms. It is likely that this residual density is due to disorder of the diethyl ether. Crystal data, together with collection and refinement details are given in Table 3.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure described in this paper have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 151652. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

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