Inorganica Chimica Acta, 111 (1986) 99–106

Complexes of Binucleating Ligands.
XVIII. Complexes Incorporating Two Independent Species at a (Pd(II))$_2$ Site Normally Occupied by a Bridge. The Crystal Structure of a Complex with Chloride and Glycine Ester Bound at the (Pd(II))$_2$ Site

T. E. CROSSLEY, B. F. HOSKINS, I. A. S. McDONALD and R. ROBSON*

Department of Inorganic Chemistry, University of Melbourne, Parkville, Vic. 3052, Australia

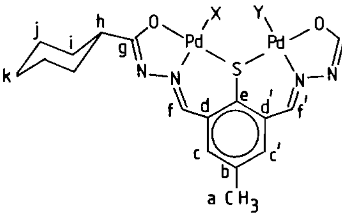
Received March 21, 1985

Abstract

The three atom acetate bridge of $LPd_2(CH_3CO_2)$, in which L^{3-} is a previously described binucleating ligand, can be displaced by two separate ligands to give stable, isolable, so-called non-bridged complexes. One of the two separate ligands is an anion and the other a neutral nitrogen donor in the examples discovered so far, *viz.*, $LPd_2(Cl)(NH_2R)$ (where R = $CH_2COOC_2H_5$, $CH_2C_6H_5$, $CH_2C_6H_4{\cdot}pNO_2$), $LPd_2(Cl)(NH_3)$, $LPd_2(N_3)(NH_3)$, and $LPd_2(CH_3CO_2)$(1-n-propyliminazole). NMR evidence indicates that in solution $LPd_2(CH_3CO_2)$(1-n-propyliminazole) is exceptional in that the acetate and iminazole units exchange positions at the $(Pd(II))_2$ site at a significant rate at room temperature, whereas in all other examples no such exchange is apparent. An X-ray structure analysis of $LPd_2(Cl)(NH_2CH_2COOC_2H_5){\cdot}CHCl_3{\cdot}(H_2O)_{2.5}$ has shown that Cl and ethyl glycinate groups are bonded independently to separate Pd atoms at the site normally occupied by bridging groups. The crystals are triclinic, space group $P\bar{1}$, with a = 10.128(3), b = 12.498(2), c = 15.804(3) Å, α = 93.33(1), β = 95.98(2), γ = 103.54(2)°.

Introduction

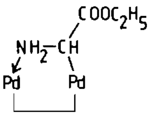
Two areas in which complexes of binucleating ligands may prove interesting or useful are the promotion of bond formation between two initially independent species attached to adjacent metal centres to generate a bridge and the reverse of this process. One could envisage that such bridge creation or destruction might constitute important steps in possible catalytic cycles promoted by appropriate complexes of binucleating ligands. It was therefore of interest to us to develop binucleating systems providing a bimetallic site capable of accommodating not only a range of bridging species but also two separate ligands in what we shall call non-bridged complexes. Using the binucleating ligand (referred to below as L^{3-}) shown in the generalized non-bridged complex **I**, we have demonstrated the capacity of the LPd_2^+ system to accommodate 1 atom, 2 atom and 3 atom bridging species [1–4]. NMR evidence has been presented which supports the existence of a short-lived non-bridged intermediate complex in which a dimethylsulphoxide molecule is coordinated to one palladium of the LPd_2^+ unit, whilst the conjugate base of maleimide is attached to the adjacent metal centre [1]. The present report is concerned with the synthesis and characterisation of some long-lived, isolable, non-bridged derivatives of LPd_2^+ and the crystal structure of one of them is described.



I

Results and Discussion

The first and best characterised example of an isolable complex incorporating two separate ligands at the bimetallic site of LPd_2^+ was discovered accidentally in a reaction intended to generate the 2 atom N,C bridged complex, **II**. A number of N,C bridged



II

---

*Author to whom correspondence should be addressed.

0020-1693/86/$3.50

complexes related to **II** have previously been obtained by bridge substitution reactions upon $LPd_2(CH_3CO_2)$ in which the outgoing acetate was a sufficiently strong base to deprotonate the incoming carbon donor [2, 4]. In an attempt to obtain **II**, $LPd_2(CH_3CO_2)$ in chloroform was treated with an aqueous solution of glycine ethyl ester hydrochloride to which one equivalent of hydroxide had been added. The product isolated unexpectedly incorporated chlorine, having the composition $LPd_2(Cl)(NH_2CH_2COOC_2H_5)$.

The IR spectrum of this compound showed, in addition to the familiar pattern arising from LPd_2^+, ν_{NH} at 3170 and 3080 cm^{-1}, $\nu_{C=O}$ at 1730 cm^{-1} and ν_{C-O} at 1220 cm^{-1} which suggests that the ester group is uncoordinated and that the glycine unit is bound at least through the amino group. The ^1H NMR spectrum of $LPd_2(Cl)(NH_2CH_2COOC_2H_5)$ in $CDCl_3$ clearly indicated the incorporation of one intact glycine ester unit per LPd_2^+ unit, not deprotonated as in the case of **II**. The NH_2 protons appeared as a broad multiplet at 4.62 ppm and the glycine CH_2 group adjacent to nitrogen as a two proton approximate triplet at 3.69 ppm which, on D_2O exchange, was replaced by a singlet as the NH_2 resonance disappeared. The most useful feature of the spectrum arising from protons in L^{3-} was a pair of singlets at 8.22 and 7.97 ppm originating from the imine protons (H_f and $H_{f'}$ in **I**) in significantly different environments. This differentiation between the two 'halves' of L^{3-} extended as far as the aromatic protons, H_c and $H_{c'}$ in **I**, which appeared as an incompletely resolved AB quartet with the two main components at 7.39 and 7.36 ppm.

In the ^{13}C NMR spectrum of $LPd_2(Cl)(NH_2CH_2COOC_2H_5)$ all the carbon atoms of L^{3-} (see **I** for labelling) could be accounted for satisfactorily by comparison with earlier unambiguously assigned ^{13}C spectra of other LPd_2^+ derivatives as follows: $C_{g,g'}$, 184.5, 183.5; $C_{f,f'}$, 150.4, 148.1; $C_{c,c'}$, 140.1; C_b, 136.0; $C_{d,d'}$, 132.5, 131.8; C_e, 122.8; $C_{h,h'}$, 40.4, 39.5; $C_{i,i'}$, 31.3, 30.8; $C_{j,j',k,k'}$, 25.9; C_a, 20.4 ppm. Again, the inequivalence of the two 'halves' of L^{3-} was apparent. Resonances arising from carbon atoms in the glycine ester unit are assigned as follows: terminal C of C_2H_5, 14.1; C adjacent to N, 45.2; methylene C of C_2H_5, 61.8; carboxyl C, 169.8 ppm.

All of the evidence for $LPd_2(Cl)(NH_2CH_2COOC_2H_5)$ then is consistent with a structure in which chloride is bound to one metal centre and glycine ester is N-bonded to the adjacent metal and this is confirmed by the X-ray crystallographic results presented below.

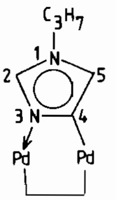
Other complexes of the type $LPd_2(Cl)(NH_2R)$ (where R = H, $CH_2C_6H_5$ and $CH_2C_6H_4 \cdot pNO_2$) could be obtained from $LPd_2(CH_3CO_2)$ and the amine hydrochloride using the same two phase reaction conditions employed above for the glycine ester derivative. Their spectroscopic properties, discussed below, support structures analogous to that of the glycine ester derivative. Low solubilities precluded the recording of ^{13}C NMR spectra for these derivatives.

In the IR spectra the NH stretching bands were generally weak and broad: $LPd_2(Cl)(NH_2CH_2C_6H_5)$, 3150, ~3040(?) cm^{-1}; $LPd_2(Cl)(NH_2CH_2C_6H_4 \cdot pNO_2)$, 3180, 3100(?) cm^{-1}; $LPd_2(Cl)(NH_3)$, 3200–3300 (broad and ill-defined), 3050(?) cm^{-1}. The possibility that the band of lower frequency (queried above) in each of these three cases and also in the case of the glycine ester derivative is associated with C–H rather than N–H stretching cannot be entirely discounted, but, comparison with the IR spectra of many other LPd_2^+ derivatives supports the view that these bands are associated with N–H stretching, in which case they probably roughly correspond to vibrations of the N–H involved in H-bonding to the adjacent chloro ligand.

The ^1H NMR spectra of all three of these chloroamine complexes indicate the inclusion of one intact amine (or ammonia) per LPd_2^+ unit. $LPd_2(Cl)(NH_2CH_2C_6H_5)$ in its ^1H NMR spectrum shows a broad four proton signal at ~4.9 ppm corresponding to the superimposed resonances of the NH_2 and the benzylic CH_2 groups. D_2O exchange leads to the replacement of this broad signal by a two proton singlet at 4.86 ppm arising from the benzylic CH_2 now decoupled from the amino group. In the case of $LPd_2(Cl)(NH_2CH_2C_6H_4 \cdot pNO_2)$ the NH_2 appears as a broad multiplet at ~4.5 ppm and the benzylic CH_2 as an approximate triplet at 4.18 ppm which becomes a sharp singlet on D_2O exchange as the NH_2 resonance disappears. The NH_3 of $LPd_2(Cl)(NH_3)$ appears as a broad resonance at 3.45 ppm. In each of these three cases, as in the case of the glycine ester derivative, a pair of singlets is observed for the two inequivalent imine protons of L^{3-} (H_f and $H_{f'}$ in **I**) as follows: $LPd_2(Cl)(NH_2CH_2C_6H_5)$, 8.23 and 8.34 ppm; $LPd_2(Cl)(NH_2CH_2C_6H_4 \cdot pNO_2)$, 7.99 and 8.10 ppm; $LPd_2(Cl)(NH_3)$, 7.95 and 8.18 ppm. The aromatic protons of the *p*-nitrophenyl group in $LPd_2(Cl)(NH_2CH_2C_6H_4 \cdot pNO_2)$ give rise to a well defined quartet with components at 7.72, 7.81, 8.07 and 8.16 ppm.

A complex of composition $LPd_2(N_3)(NH_3)$ could be isolated either from reaction of $LPd_2(Cl)(NH_3)$ with azide ion in chloroform-methanol or from a two phase reaction between $LPd_2(CH_3CO_2)$ in chloroform and an aqueous mixture of NH_4ClO_4 and NaN_3 to which one equivalent of hydroxide had been added. In the IR spectrum of this complex, azido bands were located at 2020 cm^{-1} ($\nu_{N_3 asym}$) and 1260 cm^{-1} ($\nu_{N_3 sym}$) [5], but, as in the case of $LPd_2(Cl)(NH_3)$ the ν_{NH} bands were broad and ill-defined in the range 3060–3340 cm^{-1}. $LPd_2(N_3)(NH_3)$ showed in its ^{1}H NMR spectrum a pair of singlets at 8.19 and 8.04 ppm arising from the imine protons (H_f and $H_{f'}$ in **I**) in different environments and a broad three proton NH resonance at 3.35 ppm. Low solubilities again precluded the recording of a ^{13}C NMR spectrum. There can be little doubt that this complex contains azide bound to one palladium and ammonia bound to the other.

It has been reported previously that $LPd_2(CH_3CO_2)$ reacts with 1-n-propyliminazole in boiling benzene-methanol to give the 2 atom NC bridged species **III**, which crystallises in pure form when the solution is cooled [2]. Prolonged heating of $LPd_2(CH_3CO_2)$ and 1-n-propyliminazole in refluxing benzene gives L_2Pd_3 [1] as the main product, but if the mixture is heated for only a short time (<10 min.) the crystalline solid which separates on cooling has the composition $LPd_2(CH_3CO_2)(C_3H_7 \cdot C_3H_3N_2)$. Evidence presented below indicates that in this complex the acetate is bound in a monodentate fashion to one palladium and the intact, neutral 1-n-propyliminazole is bound to the adjacent metal centre.

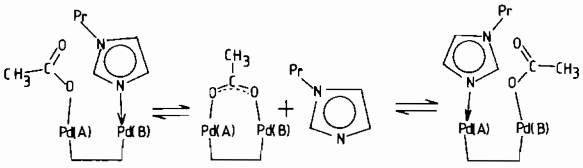


III

The 3 atom bridging acetate group of $LPd_2(CH_3CO_2)$ gives rise to strong IR bands at 1540 cm^{-1} ($\nu_{CO_2 asym}$) and 1420 cm^{-1} ($\nu_{CO_2 sym}$). These bands have disappeared from the IR spectrum of $LPd_2(CH_3CO)_2(C_3H_7 \cdot C_3H_3N_2)$ to be replaced by bands at 1620 cm^{-1} ($\nu_{CO_2 asym}$) and 1315 cm^{-1} ($\nu_{CO_2 sym}$). This large separation of the asymmetric and symmetric stretching frequencies constitutes very strong evidence that the acetate has become monodentate [6].

$LPd_2(CH_3CO_2)(C_3H_7 \cdot C_3H_3N_2)$ dissolves in chloroform at room temperature to give a solution from which (if the concentration is sufficient) $LPd_2(CH_3CO_2) \cdot 2CHCl_3$ then crystallises without removal of solvent or change in temperature. It appears that the acetate-bridged complex and the non-bridged complex coexist in equilibrium in solution, the solid non-bridged complex separating in preference to the bridged complex from benzene solution, and the solid bridged complex (as the chloroform solvate) separating preferentially from chloroform solution. This behaviour presumably arises from differences in the relative solubilities of the bridged and non-bridged species in the two solvents and also, possibly, from differences in the position of the solution equilibrium in two solvents.

A solution of $LPd_2(CH_3CO_2)(C_3H_7 \cdot C_3H_3N_2)$ in $CDCl_3$ gives an ^{1}H NMR spectrum identical to that of an equimolar mixture of $LPd_2(CH_3CO_2)$ and 1-n-propyliminazole, the most outstanding feature of which is the 'disappearance' of the acetate CH_3 resonance. This resonance, which in $LPd_2(CH_3CO_2)$ appears as a sharp singlet at 2.29 ppm, is in fact present but very much broadened, we presume by the exchange **IV** ⇌ **V** ⇌ **VI**, and is almost lost in the broad intense cyclohexyl-derived signal. When successive ^{1}H NMR spectra are recorded for solutions of $LPd_2(CH_3CO_2)$ in $CDCl_3$ to which increasing proportions of 1-n-propyliminazole (in the range 0–1 molar equivalents) have been added, the stepwise broadening and eventual collapse of the acetate signal can be clearly seen. In the ^{1}H NMR spectrum of $LPd_2(CH_3CO_2)(C_3H_7 \cdot C_3H_3N_2)$ in $CDCl_3$ at 50 °C the acetate resonance is beginning to emerge from the broad cyclohexyl-derived background as a still broad band at 2.16 ppm and in deuteronitrobenzene at 90 °C the acetate resonance is well defined at 2.04 ppm, although under these forcing conditions complicated secondary processes also occur and so the spectrum had to be recorded as soon as the solution had equilibrated at 90 °C.



IV **V** **VI**

Other features of the ^{1}H NMR spectra of $LPd_2(CH_3CO_2)(C_3H_7 \cdot C_3H_3N_2)$, though less pronounced, are also consistent with the exchange **IV** ⇌ **VI**; thus, whilst the other non-bridged complexes described above show two distinct singlets arising from the two imine protons (H_f and $H_{f'}$ in **I**) in different environments,, these protons in $LPd_2(CH_3CO_2)(C_3H_7 \cdot C_3H_3N_2)$ appear in the room temperature spectrum as a significantly broadened two proton singlet at 8.04 ppm which detectably sharpens when the temperature is raised to 50 °C.

Broadening of resonances originating in the 1-n-propyliminazole unit is also apparent at room temperature as a result of exchange between the coordinated and free condition; *e.g.* the approximate triplet at 3.94 ppm arising from the propyl CH_2 directly attached to nitrogen is broadened significantly at room temperature and detectably sharpened at 50 °C. The situation with regard to the aromatic iminazole protons is more complicated, as detailed below. Free 1-n-propyliminazole in its ^{1}H NMR spectrum shows the three aromatic protons as distinct one proton multiplets at 7.46, 7.06 and 6.90 ppm assigned to H2, H5 and H4 respectively (for iminazole numbering see **III**) by comparison with the assignments previously made for 1-methyliminazole [7]. Deuteration studies showed unambiguously that in the ^{1}H NMR spectrum of the 2 atom N,C bridged complex, **III**, H2 and H5 appeared as distinct multiplets at 7.61 and 6.82 ppm [2]. Only two of the three aromatic protons of the iminazole ring are immediately apparent in the room temperature ^{1}H NMR spectrum of $LPd_2(CH_3CO_2)(C_3H_7{\cdot}C_3H_3N_2)$ in $CDCl_3$, namely a one proton multiplet at 6.89 ppm and a broad one proton signal at ~7.1 ppm. Integration shows that the signal from a third iminazole proton is present as a very broad resonance which is almost lost under the aromatic band of L^{3-} at 7.41 ppm and the $CHCl_3$ band at 7.26 ppm. At 50 °C the 6.89 ppm signal remains little changed, the ~7.1 ppm signal sharpens to a well defined one proton multiplet at 7.09 ppm and the 'lost' iminiazole proton begins to emerge as a still broad multiplet at 7.53 ppm. Despite the fact that we are unable to make specific assignments with regard to these three protons, this behaviour is entirely consistent with the proposed exchange, the chemical shifts of two of the protons (*i.e.* the two protons giving rise to the 7.53 and 7.09 ppm bands in the 50 °C spectrum, presumably H2 and H4) being more affected upon coordination than that of the third proton (*i.e.* the proton giving rise to the 6.89 ppm band, presumably H5).

Attempts to record the ^{13}C NMR spectrum of $LPd_2(CH_3CO_2)(C_3H_7{\cdot}C_3H_3N_2)$ were thwarted by low solubility and in the time taken to accumulate sufficient data the main L^{3-}-derived featurs to emerge were those of L_2Pd_3 [1].

Attempts to isolate solid non-bridged products of the form $LPd_2(CH_3CO_2)(X)$, in which X = pyridine or acetonitrile, were unsuccessful, unchanged $LPd_2(CH_3CO_2)$ being retrieved. However, NMR evidence suggests that, in the case of pyridine, a significant but probably small equilibrium concentration of the non-bridged complex is formed in solution. Thus, when increasing amounts of d^5-pyridine are added to $CDCl_3$ solutions of $LPd_2(CH_3CO_2)$ a much less dramatic effect upon the acetate CH_3 resonance is observed than when 1-n-propyliminazole is added, but nevertheless relatively large additions (several molar equivalents) of d^5-pyridine do produce significant broadening of the acetate resonance. Presumably, the non-bridged $LPd_2(CH_3CO_2)(C_5D_5N)$ is significantly less stable and present in equilibrium to a smaller extent than $LPd_2(CH_3CO_2)(C_3H_7{\cdot}C_3H_3N_2)$ as a result of the greater steric bulk of the six membered pyridine ring compared with the five membered iminazole.

The X-ray structure analysis of $LPd_2(Cl)(NH_2CH_2COOC_2H_5){\cdot}CHCl_3{\cdot}(H_2O)_{2.5}$ revealed that the crystals contain discrete molecules of the binuclear species $LPd_2(Cl)(NH_2CH_2COOC_2H_5)$ together with chloroform and water molecules of solvation as is shown in Fig. 1. The important bond distances and angles, together with their estimated standard deviation (e.s.d.) values, are listed in Tables I and II respectively and the numbering scheme used is shown in Fig. 2. The closest intermolecular contact distances between the binuclear units agree with those predicted from the sum of the van der Waals radii of the

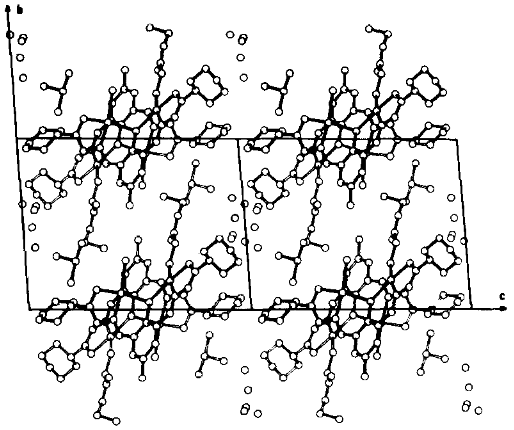


Fig. 1. The packing arrangement in the crystals of $LPd_2(Cl)NH_2CH_2COOC_2H_5){\cdot}CHCl_3{\cdot}(H_2O)_{2.5}$ as viewed down the *a*-axis.

TABLE I. Interatomic Distances (Å)

Atoms	Distance	Atoms	Distance
Pd(1)–O(1)	2.02(1)	C(15)–S	1.75(2)
Pd(1)–Cl(1)	2.303(5)	C(14)–C(16)	1.45(3)
Pd(1)–S	2.272(5)	C(16)–N(3)	1.31(3)
Pd(1)–N(2)	1.92(1)	N(3)–N(4)	1.39(2)
Pd(2)–N(5)	2.05(2)	N(4)–C(17)	1.33(3)
Pd(2)–O(2)	1.99(1)	C(17)–O(2)	1.29(2)
Pd(2)–N(3)	1.95(1)	C(17)–C(18)	1.49(3)
Pd(2)–S	2.253(4)	C(18)–C(19)	1.25(5)
O(1)–C(1)	1.32(3)	C(19)–C(20)	1.56(6)
C(1)–C(2)	1.53(4)	C(20)–C(21)	1.30(6)
C(2)–C(3)	1.46(4)	C(21)–C(22)	1.31(6)
C(3)–C(4)	1.49(4)	C(22)–C(23)	1.56(6)
C(4)–C(5)	1.35(6)	C(23)–C(18)	1.48(6)
C(5)–C(6)	1.40(6)	N(5)–C(24)	1.49(3)
C(6)–C(7)	1.55(5)	C(24)–C(25)	1.44(4)
C(7)–C(2)	1.48(4)	C(25)–O(3)	1.24(3)
C(1)–N(1)	1.28(3)	C(25)–O(4)	1.26(3)
N(1)–N(2)	1.46(2)	O(4)–C(26)	1.47(2)
N(2)–C(8)	1.29(2)	C(26)–C(27)	1.51
C(8)–C(9)	1.48(3)	C(28)–Cl(2)	1.72(3)
C(9)–C(10)	1.42(2)	C(28)–Cl(3)	1.74(3)
C(9)–C(15)	1.40(2)	C(28)–Cl(4)	1.66(3)
C(10)–C(11)	1.37(3)		
C(11)–C(12)	1.53(2)	Bridging Distances	
C(11)–C(13)	1.38(2)		
C(13)–C(14)	1.37(2)	Pd(1)•••Pd(2)	3.987(2)
C(14)–C(15)	1.41(3)	Cl(1)•••N(5)	3.14(1)

TABLE II. Bond Angles (°)

Atoms	Angle	Atoms	Angle
O(1)–Pd(1)–N(2)	80.6(5)	C(8)–C(9)–C(10)	111.4(13)
N(2)–Pd(1)–S	91.2(4)	C(10)–C(9)–C(15)	120.3(16)
S–Pd(1)–Cl(1)	98.5(2)	C(15)–C(9)–C(8)	127.9(13)
Cl(1)–Pd(1)–O(1)	89.9(3)	C(9)–C(10)–C(11)	121.8(14)
N(5)–Pd(2)–S	91.4(4)	C(10)–C(11)–C(12)	120.3(15)
S–Pd(2)–N(3)	96.4(4)	C(12)–C(11)–C(13)	122.4(17)
N(3)–Pd(2)–O(2)	80.7(5)	C(13)–C(11)–C(10)	117.2(14)
O(2)–Pd(2)–N(5)	91.2(5)	C(11)–C(13)–C(14)	122.6(17)
Pd(2)–N(5)–C(24)	117.7(13)	C(13)–C(14)–C(16)	112.7(17)
N(5)–C(24)–C(25)	113.8(19)	C(16)–C(14)–C(15)	125.8(14)
O(3)–C(25)–C(24)	124(2)	C(15)–C(14)–C(13)	121.4(14)
C(24)–C(25)–O(4)	113(2)	C(14)–C(15)–S	125.3(11)
O(4)–C(25)–O(3)	122(3)	S–C(15)–C(9)	117.6(14)
C(25)–O(4)–C(26)	126(2)	C(9)–C(15)–C(14)	116.7(13)
O(4)–C(26)–C(27)	101.6(12)	C(14)–C(16)–N(3)	130.6(17)
Pd(1)–S–C(15)	109.6(6)	C(16)–N(3)–N(4)	115.1(12)
C(15)–S–Pd(2)	111.4(6)	N(4)–N(3)–Pd(2)	114.7(9)
Pd(2)–S–Pd(1)	123.5(2)	Pd(2)–N(3)–C(16)	129.9(11)
Pd(1)–O(1)–C(1)	109.5(10)	N(3)–N(4)–C(17)	110.0(12)
O(1)–C(1)–C(2)	114.5(19)	N(4)–C(17)–C(18)	119.0(18)
C(2)–C(1)–N(1)	120.9(19)	C(18)–C(17)–O(2)	116(2)
N(1)–C(1)–O(1)	124.6(16)	O(2)–C(17)–N(4)	124.5(16)
C(1)–C(2)–C(3)	111(2)	C(17)–C(18)–C(19)	119(2)
C(3)–C(2)–C(7)	118(3)	C(19)–C(18)–C(23)	101(3)
C(7)–C(2)–C(1)	113(2)	C(23)–C(18)–C(17)	111(3)
C(2)–C(3)–C(4)	112(2)	C(18)–C(19)–C(20)	115(3)
C(3)–C(4)–C(5)	116(4)	C(19)–C(20)–C(21)	105(3)
C(4)–C(5)–C(6)	122(4)	C(20)–C(21)–C(22)	110(4)
C(5)–C(6)–C(7)	116(3)	C(21)–C(22)–C(23)	112(3)
C(6)–C(7)–C(2)	108(3)	C(22)–C(23)–C(18)	112(4)
C(1)–N(1)–N(2)	110.4(14)	C(17)–O(2)–Pd(2)	109.8(12)
N(1)–N(2)–C(8)	112.7(12)	Cl(2)–C(28)–Cl(3)	108.3(17)
C(8)–N(2)–Pd(1)	133.2(11)	Cl(3)–C(28)–Cl(4)	113.4(18)
Pd(1)–N(2)–N(1)	114.0(8)	Cl(4)–C(28)–Cl(2)	113.2(15)
N(2)–C(8)–C(9)	125.8(13)		

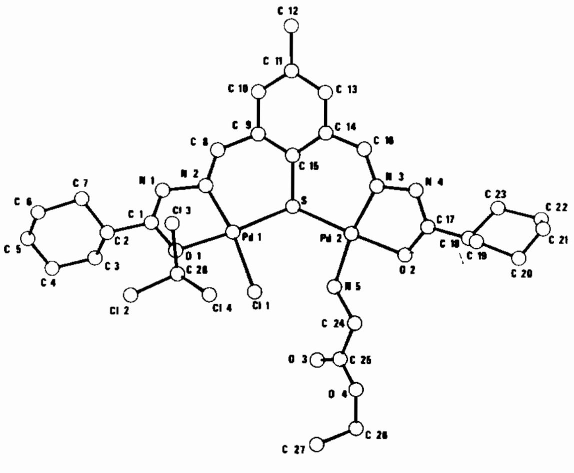


Fig. 2. The atomic arrangement and numbering scheme used for $LPd_2(Cl)(NH_2CH_2COOC_2H_5){\cdot}CHCl_3$.

relevant atoms with one exception. The short N(1)--N(5) ($\bar{x}$, $\bar{y}$, 1 – z) distance, 3.01 Å, is attributed to the formation of a hydrogen bond between these two atoms; the resulting association of pairs of binuclear molecules can be seen from Fig. 1. As with other complexes of LPd_2^+ which have crystallised from chloroform solution, crystals of $LPd_2(Cl)(NH_2CH_2COOC_2H_5)$ also contain molecules of this solvent. In this case, one chloroform molecule is present in the asymmetric unit and is weakly hydrogen bonded to a terminal O-atom of the binucleating ligand: O(1)···H(28) 2.45 Å. The crystals contain at least one other solvent species, methanol and/or water, present in a disordered form which has inhibited their identification. These are situated about the line (x, ½, 1) and lie between pairs of centrosymmetrically related chloroform molecules; this will be discussed further in the Experimental section.

The noteworthy feature of the binuclear $LPd_2(Cl)(NH_2CH_2COOC_2H_5)$ molecule is that the LPd_2^+ core has incorporated two independent donor groups, *viz.* the chloride and ethyl glycinate groups. The donor groups are bonded to separate palladium centres, as shown in Fig. 2, and occupy the sites normally filled by a bridging group, such as acetate [8]. This geometry has confirmed the spectroscopic evidence for the non-bridged mode of coordination mentioned earlier. In order to achieve this previously unobserved coordination mode, the LPd_2^+ core adopts the V-shaped geometry shown in Fig. 3 which allows the chloride and nitrogen donor atoms to be accommodated comfortably; the distance between these atoms is 3.14 Å. The Pd(1)–Cl(1) interatomic distance of 2.303(5) Å compares well with those found for other strongly bonded Cl–Pd complexes and the Pd(2)–N(5) distance of 2.05(2) Å is typical of such bonds. With the exception of the terminal methyl group the ethyl glycinate ligand is essentially planar with an average deviation from planarity of 0.073 Å exhibited by the six non-hydrogen atoms. A torsional angle of 84.5° is observed at the O(4)–C(26) link in order to relieve the steric repulsion between the terminal methyl group at C(27) and the carbonyl oxygen atom, O(3). The distance between these atoms, 3.17 Å, is considerably larger than that which would be expected in the case of a planar arrangement, ~2.3 Å.

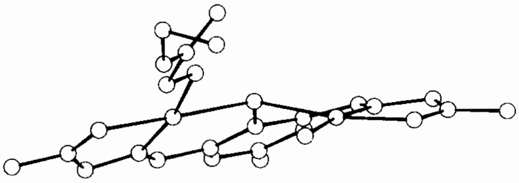


Fig. 3. The V-shape of the $LPd_2(Cl)(NH_2CH_2COOC_2H_5)$ unit.

The Cl and $NH_2CH_2COOC_2H_5$ groups are associated through a hydrogen bonding scheme involving the Cl(1) and N(5) atoms which form a pseudo three-atom N–H···Cl bridge. The bite distance between the donor atoms is 3.14 Å, which is very much larger than the average value of 2.25 Å observed for the corresponding three atom carboxylate systems [8]. This feature leads to considerable buckling of the LPd_2^+ core with a concomitant increase in the Pd···Pd separation [3.987 Å *cf.* av. 3.677 Å for $LPd_2(CH_3CO_2)$]. If the cyclohexyl rings are ignored the atoms of the LPd_2^+ core lie in two distinct planes. This geometry, which is also evident in one of the acetate bridged species [8], is illustrated in Fig. 3. The valley dividing these planes lies across the Pd(1)–S and C(8)–C(9) bonds and the dihedral angle, 30.7°, between them is slightly greater than the value observed for the non-solvated acetate bridged complex of av. 27.9°. The asymmetric V-shape of the LPd_2^+ core is enabled by the twist about one bond in particular. In the solvated acetate bridged structure the Pd–S–Pd group is aligned symmetrically with the toluene residue. In $LPd_2(Cl)(NH_2CH_2COOC_2H_5)$, however, a twist, ~17°, has occurred about the thiophenoxide link [C(15)–S] such that Pd(2) lies in the plane of the toluene residue whilst Pd(1) is located well above it.

Experimental

$LPd_2(Cl)(NH_2R)$ (where R = $CH_2COOC_2H_5$, $CH_2C_6H_5$, $CH_2C_6H_4{\cdot}pNO_2$ or H)

A solution of $LPd_2(CH_3CO_2)$ (1 molar proportion) dissolved in the minimum volume of chloroform at room temperature was stirred vigorously for 20 h with an aqueous phase consisting of the amine hydrochloride (5 molar proportions) dissolved in the volume of 0.2 M NaOH required to provide 4 molar proportions of hydroxide. After removal of the aqueous phase, the chloroform layer was dried over Na_2SO_4 and evaporated to small volume. Addition of diethyl ether precipitated the product which was recrystallised from chloroform–petrol (b.p. 60–80°) and dried in vacuum at 135 °C.

$LPd_2(Cl)(NH_2CH_2COOC_2H_5)$. Yield, 80%. *Anal.* Found: C, 42.2; H, 5.1; N, 9.1; Cl, 4.9; S, 3.8. Calcd. for $C_{27}H_{38}ClN_5O_4SPd_2$: C, 41.7; H, 4.9; N, 9.0; Cl, 4.6; S, 4.1

$LPd_2(Cl)(NH_2CH_2C_6H_5)$. Yield, 65%. *Anal.* Found: C, 46.1; H, 4.8; N, 8.9; S, 4.2; Cl, 4.7. Calcd. for $C_{30}H_{38}ClN_5O_2SPd_2$: C, 46.1; H, 4.9; N, 9.0; S, 4.1; Cl, 4.5.

$LPd_2(Cl)(NH_3)$. Yield, 88%. *Anal.* Found: C, 40.3; H, 4.4; N, 9.0; S, 4.8; Cl, 4.7. Calcd. for $C_{23}H_{32}ClN_5O_2SPd_2$: C, 40.0; H, 4.7; N, 10.0; S, 4.6; Cl, 5.1.

$LPd_2(N_3)(NH_3)$

A suspension of $LPd_2(CH_3CO_2)$ (0.101 g) in chloroform (2 cm^3) was stirred vigorously at room temperature with a mixture of NH_4ClO_4 (0.074 g) and NaN_3 (0.020 g) in 0.192 M NaOH (1.5 cm^3). Within a minute or so all the suspended $LPd_2(CH_3CO_2)$ dissolved then shortly thereafter copious pale yellow solid suddenly precipitated. After being stirred for 0.75 h the mixture was treated with petrol (60–80°, 5 cm^3) and the stirring was continued for a further 0.5 h. The precipitate was collected directly from the 2 liquid phase mixture and was washed first with water then with a 1:1 chloroform–petrol mixture. The crude yellow solid (0.094 g) was recrystallised from chloroform–methanol to give feathery pale yellow crystals which were collected, washed with chloroform–methanol mixture and dried in vacuum at 80 °C. Yield, 0.064 g. *Anal.* Found: C, 39.3; H, 4.6; N, 15.9; S, 4.3; Pd, 30.4.

Calcd. for $C_{23}H_{32}N_8O_2SPd_2$: C, 39.6; H, 4.6; N, 16.1; S, 4.6; Pd, 30.5.

$LPd_2(CH_3CO_2)(C_3H_7 \cdot C_3H_3N_2)$

A solution of $LPd_2(CH_3CO_2)$ (0.200 g) and 1-n-propyliminazole (0.032 g) in benzene (7 cm^3) was heated under reflux for 5 min. Upon being cooled the solution precipitated fine yellow crystals which were collected, washed with 2:1 benzene–petrol and dried in vacuum at 80 °C. No satisfactory recrystallisation medium could be found for this compound. Yield, 0.175 g. *Anal.* Found: C, 46.3; H, 5.4; N, 10.4. Calcd. for $C_{31}H_{42}N_6O_4SPd_2$: C, 46.1; H, 5.2; N, 10.4.

Crystallography

Crystal data

$LPd_2(Cl)(NH_2CH_2CO_2C_2H_5) \cdot CHCl_3 \cdot (H_2O)_{2.5}$ $C_{28}H_{40}Cl_4N_5O_4Pd_2S$, $2.5H_2O$, M = 941.7, triclinic, a = 10.128(3), b = 12.498(2), c = 15.804(3) Å, α = 93.33(1), β = 95.98(2), γ = 103.54(2)°, U = 1927.1 Å^3, D_m = 1.612(15) g cm^{-3}, Z = 2, D_c = 1.623 g cm^{-3}, $F(000)$ = 950.0, space group $P\bar{1}$ (C_i^1, No. 2), Mo$K\bar{\alpha}$ radiation (graphite monochromated) ($\lambda_{\bar{\alpha}}$ = 0.71069 Å), μ(Mo$K\bar{\alpha}$) = 12.5 cm^{-1}. Oscillation and Weissenberg photographs, Enraf-Nonius CAD-4F diffractometer. Crystal dimensions ±(100) 0.343, ±(010) 0.028, ±(001) 0.043 mm from crystal centre; min. and max. transmission factors 0.8639 and 0.9324.

Crystals of $LPd_2(Cl)(NH_2CH_2CO_2C_2H_5) \cdot CHCl_3 \cdot H_2O)_{2.5}$ were obtained as red, elongated needles by the slow evaporation of a solution of the complex in a 2:1 chloroform-methanol mixture. As the crystals were very sensitive to solvent loss the one used for the data collection was sealed in a Lindemann glass tube together with a small amount of mother liquor. Intensities were measured in the ω:2θ scan mode at 294 K for 7547 reflections in the range $2.0 \leqslant 2\theta \leqslant 50.0°$. The data were scaled according to the average variation of the intensities of three reference reflections, measured every 1800 s of X-ray exposure time, each of which displayed an average intensity of approximately 90% of their original values at the end of the data collection. A redetermination of the unit cell parameters after the data collection showed that these were all within 1.0 e.s.d. of the initial values. The data were corrected for absorption [9(a), 10], Lorentz and polarization effects and the amalgamation of equivalent terms gave 6761 unique structure amplitudes (R_{amal} 0.023). Of these 3242 satisfied the designated criterion of observability, $I \geqslant 1.0\sigma(I)$, reflecting the relatively weak scattering nature of the crystals which was evident from the preliminary photographic survey. No allowance was made for extinction.

TABLE III. Final Atomic Fractional Coordinates

Atom	*x/a*	*y/b*	*z/c*
Pd(1)	0.1455(1)	0.0908(1)	0.41970(9)
Pd(2)	0.3814(1)	0.1614(1)	0.64359(8)
S	0.2396(4)	0.0406(3)	0.5435(3)
O(1)	0.032(1)	0.1107(9)	0.3112(7)
C(1)	–0.030(2)	0.013(2)	0.272(1)
C(2)	–0.118(3)	0.017(2)	0.188(2)
C(3)	–0.250(3)	0.037(3)	0.204(1)
C(4)	–0.339(4)	0.040(4)	0.123(2)
C(5)	–0.336(4)	–0.035(4)	0.059(2)
C(6)	–0.214(5)	–0.063(3)	0.043(2)
C(7)	–0.116(4)	–0.073(3)	0.123(2)
N(1)	–0.021(2)	–0.079(1)	0.300(1)
N(2)	0.082(1)	–0.061(1)	0.3747(8)
C(8)	0.111(2)	–0.151(1)	0.397(1)
C(9)	0.224(2)	–0.159(1)	0.462(1)
C(10)	0.259(2)	–0.262(1)	0.451(1)
C(11)	0.371(2)	–0.283(1)	0.497(1)
C(12)	0.401(2)	–0.397(1)	0.487(2)
C(13)	0.448(2)	–0.200(1)	0.556(1)
C(14)	0.419(2)	–0.099(1)	0.567(1)
C(15)	0.303(2)	–0.076(1)	0.522(1)
C(16)	0.515(2)	–0.025(2)	0.631(1)
N(3)	0.517(1)	0.075(1)	0.6621(8)
N(4)	0.627(1)	0.123(1)	0.7235(9)
C(17)	0.608(2)	0.216(2)	0.760(1)
C(18)	0.714(2)	0.281(3)	0.828(1)
C(19)	0.825(4)	0.334(4)	0.807(2)
C(20)	0.923(6)	0.409(3)	0.881(3)
C(21)	0.974(4)	0.342(3)	0.927(3)
C(22)	0.876(5)	0.275(4)	0.959(2)
C(23)	0.763(5)	0.208(4)	0.888(3)
O(2)	0.509(1)	0.260(1)	0.7359(8)
Cl(1)	0.2103(6)	0.2795(4)	0.4502(3)
N(5)	0.244(2)	0.258(1)	0.6476(9)
C(24)	0.298(2)	0.377(2)	0.679(2)
C(25)	0.195(3)	0.439(2)	0.677(2)
O(3)	0.070(2)	0.396(1)	0.664(2)
O(4)	0.242(2)	0.540(1)	0.700(2)
C(26)[a]	0.164	0.618	0.728
C(27)[a]	0.110	0.652	0.644
C(28)	0.271(3)	0.275(2)	0.226(2)
Cl(2)	0.165(1)	0.3026(7)	0.1417(6)
Cl(3)	0.316(1)	0.153(1)	0.1980(6)
Cl(4)	0.405(2)	0.380(1)	0.2586(7)
O(5)[a]	0.577	0.357	0.050
O(6)[a]	0.562	0.476	0.043
O(7)[a]	0.637	0.577	0.058
O(8)[a]	0.585	0.614	0.007
O(9)[a]	0.549	0.598	0.066

[a] As these atoms were held constant during final refinement, no e.s.d.s have been calculated.

The structure was solved by normal Fourier methods and refined by the use of a full-matrix least-squares procedure, based on $\Sigma w\Delta^2$. Unit weights were initially used but subsequently the weighting scheme $w = k[\sigma^2(F_o) + g|F_o|]^{-1}$ was applied, where the final values of k and g were 0.0428 and 0.0060 respectively; R and R_w at convergence were both

0.077. During the course of the refinement a region of attenuated electron density, which contained five peaks corresponding to values of approximately 1.5 e Å^{-3}, were observed in the difference maps. These have been treated as disordered oxygen atoms of water molecules, although the possibility of disordered methanol could not be ruled out; either would be consistent with the measured density. Because attempts to refine the coordinates of the disordered oxygen atoms failed to give convergence these atoms were held at fixed positions which corresponded to the sites of the peaks. The site occupation factor was set at 0.5 for each disordered atom and only their isotropic temperature factors were allowed to vary. The difference maps also indicated disorder in the region of the ethyl moiety of the ethyl glycinate ligand. Since the coordinates of these atoms also failed to converge their coordinates were held constant at the sites of the highest electron density and their individual isotropic temperature factors were allowed to vary; this treatment was supported by the bond angle of 101.6° at C(26) and the distance of 1.51 Å for the bond C(26)–C(27). Anisotropic thermal parameters were applied to all other atoms and hydrogen atoms were included at their calculated positions.

The inclusion of the water-oxygen atoms in the model markedly improved the previously poor agreement between the F_o and F_c values of a number of reflections, with the result that only two reflections now have a $\Delta F/\sigma(F_o)$ ratio greater than 3.0 but each of these is less than 4.0. Similarly there was a reduction in the magnitude of a number of high ripples centred around the palladium atoms from the maximum value of 2.5 to 1.9 e Å^{-3}.

Both the coefficients for the neutral atomic scattering curve and the corrections for anomalous dispersion for palladium were taken from refs. [9(b), 9(c)] while those collected by Sheldrick [10] were used for the remaining atoms. All calculations were performed using the SHELX-76 system [10]. The atomic coordinates and their estimated standard deviations for the non-hydrogen atoms are listed in Table III. Listings of anisotropic temperature factors, hydrogen atom coordinates, mean plane data and the observed and calculated structure factors derived from the final set of parameters have been deposited with the Editor-in-Chief.

Acknowledgement

We acknowledge the Commonwealth of Australia for the award of a post-graduate scholarship to one of us (I.A.S.McD.).

References

1 M. Louey, P. D. Nichols and R. Robson, *Inorg. Chim. Acta, 47,* 87 (1981).

2 R. Robson, *Inorg. Chim. Acta, 57,* 71 (1982).

3 R. Robson, *Inorg. Chim. Acta, 85,* 195 (1984).

4 T. E. Crossley, P. Davies, M. Louey, R. Robson and T. N. Huckerby, *Inorg. Chim. Acta, 85,* 199 (1984).

5 K. Nakamoto, 'The Infrared Spectra of Inorganic and Coordination Compounds, 2nd edn.', Wiley, New York, 1970, p. 192.

6 G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev., 33,* 227 (1980).

7 G. S. Reddy, R. T. Hobgood and J. H. Goldstein, *J. Am. Chem. Soc., 84,* 336 (1962).

8 B. F. Hoskins and I. A. S. McDonald, *Aust. J. Chem., 37,* 725 (1984).

9 'International Tables for X-Ray Crystallography, Vol. 4', Kynoch Press, Birmingham, 1974, (a) p. 58; (b) p. 100; (c) p. 150.

10 G. M. Sheldrick, 'SHELX-76', Program for Crystal Structure Determination, University of Cambridge, 1976.