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Dinuclear palladium complexes incorporating amidato, carbamato and urea bridging groups

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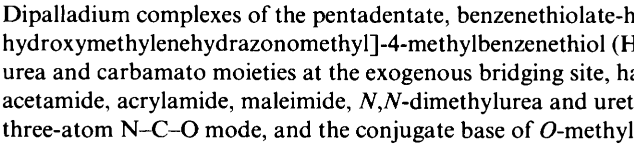
Dipalladium complexes of the pentadentate, benzenethiolate-hinged binucleating ligand 2,6-bis[(cyclohexyl)-hydroxymethylenehydrazonomethyl]-4-methylbenzenethiol (H_3L), incorporating amidato and alkyl-substituted urea and carbamato moieties at the exogenous bridging site, have been prepared. The conjugate bases of acetamide, acrylamide, maleimide, *N*,*N*-dimethylurea and urethane bridge the two palladium atoms in a three-atom N–C–O mode, and the conjugate base of *O*-methylisourea is co-ordinated *via* a N–C–N bridging mode, at the bridging site of LPd_2^+. A dinuclear complex cation is generated when *O*-methylisourea is incorporated as a neutral species at the bridging site, although the nature of the co-ordination mode is not clear. The structure of an amidato-*N*,*O* bridged complex has been established by a single-crystal X-ray diffraction study. It is the first example of a complex containing co-ordinated maleimide, $[Pd_2L(C_4H_2NO_2)]$. The relevance of these complexes to possible intermediates for the urease-catalysed hydrolysis of urea is discussed.

The enzymatic hydrolysis of urea by the nickel(II)-containing enzyme urease apparently proceeds *via* the formation of carbamate ion [equation (1)].[1] In contrast, the non-enzymatic

$$H_2NCONH_2 + H_2O \longrightarrow (H_2NCO_2^- + NH_4^+) \longrightarrow CO_2 + 2NH_3 \quad (1)$$

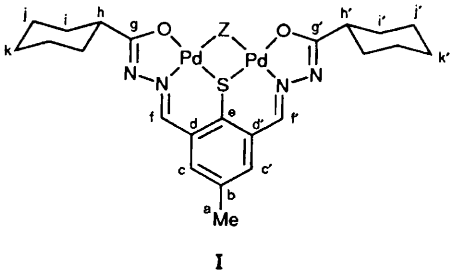
degradation of urea in aqueous media proceeds *via* an elimination reaction yielding the sole products ammonia and cyanic acid [equation (2)].[2]



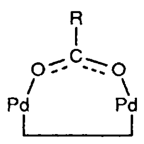
(2)

Clarke and Wilcox[3] have shown that the magnetic properties of Jack bean urease suggest that the distance between the nickel centres in the dinickel active site is sufficiently close to allow bridging co-ordination modes for substrates, and Dixon *et al.*[4] have proposed a mechanism for the urease-catalysed hydrolysis of urea, and other closely related substrates, which involves the concerted action of two nickel ions. The crucial intermediate in this proposal is one in which the nucleophile, a hydroxide ion, is co-ordinated to one Ni^{II} and the substrate, urea (or an amide derivative), is co-ordinated to the adjacent Ni^{II}. Subsequent nucleophilic attack at the substrate's central carbon atom (additionally activated towards nucleophiles by virtue of the Lewis acidity of the nickel ion to which it is co-ordinated) by the co-ordinated hydroxide ion, followed by loss of ammonia, results in a co-ordinated carbamate (or carboxylic acid). This mechanism requires that the two nickel ions per 96 000-dalton subunit of urease are within 6 Å of each other. It is reminiscent of a mechanism we have proposed for the hydrolysis of nitriles catalysed by sulfur-hinged dinuclear palladium complexes,[5,6] and suggested to us that these dipalladium complexes may serve as functional models for the dinickel active site of urease. Our intention was to prepare complexes incorporating urea, carbamate [the initial product in the urease-catalysed reaction (1)] and some of their alkylated derivatives at the bridging site of these dimetallic complexes. Both urea and carbamate are ambidentate, being potentially capable of O and/or N co-ordination as mono-/bi-/tri-dentate ligands. Thus the characterization of complexes containing urea-type ligands in their various binding modes will aid in establishing the most efficient mode for activation of the central carbon atom towards attack by nucleophiles. There exist, however, few examples of complexes incorporating urea. So far only monodentate co-ordination of urea *via* the oxygen atom to a variety of metal ions, M^{III} = Cr, Mn, Co, Ru or Rh and M^{II} = Mn, Co, Ni, Cu or Zn, and less commonly *via* the nitrogen atom to M^{III} = Co, Ru or Rh and M^{II} = Ni, Cu or Pt is known.[7] To the best of our knowledge bridging bidentate urea and carbamate co-ordination to two metal ions has not been reported. In particular, complexes incorporating a carbamate-type ligand bridging between two metal ions are important model compounds for the dinuclear mechanism proposed by Dixon *et al.*[4]

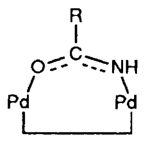
Reported here is a series of dipalladium complexes of the benzenethiolate-hinged pentadentate compound, 2,6-bis[(cyclohexyl)hydroxymethylenehydrazonomethyl]-4-methylbenzenethiol (H_3L). The dinuclear framework is depicted by **I**, and will be referred to as LPd_2Z, where Z represents the bridging site. Earlier work has shown that a wide variety of three-, two- and one-atom bridges (*e.g.* acetate, pyrazole and iodide respectively) can be incorporated at the Pd_2 site, Z.[8–12] Interestingly, and extremely relevant to the work here, is that two separate species can be also accommodated, one bonded to each metal centre, in complexes of L[12] and a related benzenethiolate-hinged binucleating ligand;[13] this fact is



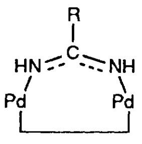
I



II



III



IV

important with respect to modelling the urease-catalysed mechanism proposed by Dixon *et al.*[4] Clearly, sensible models for this mechanism must allow for the binding of two separate species as well as bridging species. The structural features of several complexes incorporating three-atom, two-atom and non-bridged (*e.g.* a chloride ion bound to each palladium atom) species at the bridging site Z of the binucleating ligand in **I**, L^{3-}, have been established by X-ray crystallography.[11,12,14,15] The intermetallic distances typically imposed by this hinged dinuclear system are in the range 3.6–4 Å. The complexes investigated here include urea-, carbamato- and amidato-type bridging groups which span the two palladium atoms and represent the first reported examples of bridging co-ordination by some of these ligands. Generally the complexes incorporating alkyl derivatives of both urea and carbamate showed solubility properties more amenable to solution spectroscopic characterization than did their corresponding non-alkylated derivatives. The alkyl groups provided also spectroscopic handles to aid in establishing the co-ordination modes of the species occupying the bridging site, Z.

Results and Discussion

Complexes which incorporate bidentate bridging carboxylate, amide and amidine groups at the site, Z, of LPd_2^+ **I** are prototypes for O–C–O, O–C–N and N–C–N three-atom bridging co-ordination (represented by **II**, **III** and **IV**, respectively). The recognition of these three types of co-ordination modes was important in the analysis of the complexes prepared in the present work containing carbamate- and urea-derived moieties at the bridging site of LPd_2^+. We have previously reported examples of all three classes of complex: $[Pd_2L(O_2CR)]$ (R = H, Me or Et),[7] $[Pd_2L(HNOCR)]$ (R = Me[5] or Ph[8]), $[Pd_2L(HNNHPh)]$.[8] The work here involves the extension of this series to include LPd_2^+ complexes incorporating further examples of amidato bridging species as well as urea- and carbamato-derived bridging groups.

Proton and ^{13}C NMR data for the binucleating ligand component of the amidato-, carbamato- and urea-bridged complexes are listed in Table 1. The carbon atoms of L^{3-} are labelled as in **I** and directly attached protons are labelled with the same subscripts, *e.g.* the aromatic protons of L^{3-} are labelled H_c and $H_{c'}$. Corresponding data relating to the bridging component, Z, in LPd_2Z are presented in Table 2. In most cases the two palladium centres within the dinuclear unit are rendered inequivalent by attachment to bridging units carrying the two distinguishable donor atoms, O and N; the inequivalence of the two halves of L^{3-} is apparent in both the ^{13}C and ^1H NMR spectra, generally extending as far as carbons c and c′, i and i′ and hydrogens f and f′. In these cases, the ^1H NMR spectra show two separate 'imine' resonances (H_f and $H_{f'}$), whilst in the ^{13}C NMR spectra a 'doubling up' of the resonances due to carbon atoms c, c′, d, d′, f, f′, g, g′, h, h′ and i, i′ is often observed. By contrast complexes containing bridging species with two equivalent donor centres (**II** and **IV**) show a single resonance for the two H_f protons and single lines for the pairs of carbons of the type c, d, f–i.

Amidato-bridged complexes

The amidato-bridged complexes, where Z in **I** represents the conjugate bases of acetamide ($MeCONH^-$), acrylamide ($CH_2CHCONH^-$) and maleimide ($C_4H_2NO_2^-$) were prepared by substitution of the μ-$MeCO_2^-$ in $[Pd_2L(O_2CMe)]$.[8] The complexes $[Pd_2L(HNOCMe)]$ and $[Pd_2L(C_4H_2NO_2)]$ have been reported previously,[5,8] however unpublished NMR data for the former are included here along with the new crystal structure of the latter, see below. The amidato-bridged complexes show three-atom N–C–O bridging, and this is verified by the crystal structure. The ^1H and ^{13}C NMR signals pertaining to the alkene atoms of the bridge in $[Pd_2L(HNOCCHCH_2)]$ indicate that there is no interaction of the alkene group with the palladium atoms; co-ordination to the bridging site is exclusively *via* the acrylamide oxygen and nitrogen atoms.

Carbamato-bridged complex

The reaction of $[Pd_2L(O_2CMe)]$ with an excess of urethane (ethyl carbamate) in the presence of base in a mixture of methanol and benzene under reflux yields $[Pd_2L(HNOCOEt)]$ as a yellow, crystalline solid. The two palladium atoms are rendered inequivalent by the attachment to the two different donor atoms (N and O) of the bridging species. The ^1H NMR spectrum shows resonances at δ 8.16 and 8.04 which are assigned to the imine protons, H_f and $H_{f'}$, of the unsymmetrically bridged complex represented by **III**, R = OEt. The ^{13}C NMR spectrum shows the expected 'doubling up' of some of the resonances. The IR spectrum shows a N–H stretching band at 3380 cm^{-1} and a band at 1595 cm^{-1} originating from the O–C–N system of the bridging group.

Urea-bridged complexes

The acetate bridge of $[Pd_2L(O_2CMe)]$ can be exchanged for the conjugate base of *N*,*N*-dimethylurea in the presence of base in a mixture of methanol and benzene under reflux. The NMR spectral data for $[Pd_2L(HNOCNMe_2)]$, recovered from this reaction as a yellow, crystalline solid, indicate the N–C–O bridging mode, **III** (R = NMe_2), analogous to the above-mentioned amidato- and urethane-bridged complexes, for the deprotonated *N*,*N*-dimethylurea ligand. The inequivalence of the two halves of L^{3-} is apparent in both the ^1H and ^{13}C NMR spectra. The ^1H spectrum shows singlets at δ 8.16 and 8.04 which are attributed to the chemically inequivalent imine protons, H_f and $H_{f'}$. The ^{13}C NMR spectrum shows two resonances for some of the corresponding carbon atoms of each half of L^{3-} (C_f and $C_{f'}$, C_d and $C_{d'}$ and C_h and $C_{h'}$). The chemical shift difference between other pairs of corresponding carbon atoms (for example, C_g and $C_{g'}$, C_c and $C_{c'}$ and C_b and $C_{b'}$) is not resolved. The IR spectrum is dominated by a broad band centred at 1505 cm^{-1} which is attributed to urea-derived ν(CO) and ν(CN), along with an intense L^{3-}-derived band. A peak at 3400 cm^{-1} is assigned to urea ν(NH). The NMR data do not eliminate entirely the possibility of a N–C–N bridging mode for the conjugate base of *N*,*N*-dimethylurea. However, this mode would disrupt the preferred planarity of the urea ligand since a tetrahedral arrangement would be imposed upon the nitrogen atom of the co-ordinated dimethylamino group. It is anticipated that the increase in π-electron delocalization, over four atoms in **III** (R = NMe_2), in contrast to three atoms in a μ-Me_2NCONH *N*,*N*′-bridged complex, favours the former arrangement.

X-Ray structural studies of urea and substituted derivatives have shown that the hydrogen atoms (or alkyl groups) are coplanar with the C, N and O atoms. This indicates π-electron delocalization about the C–O and both C–N bonds. Thus restricted rotation about the *exo*-C–NMe_2 bond, due to the appreciable double-bond character of this bond, should, in principle, render the two methyl groups inequivalent. A difference in the chemical shift of the two *exo*-methyl groups of $[Pd_2L(HNOCNMe_2)]$ is not evident in the room-temperature ^1H NMR spectrum. The spectrum ($CDCl_3$) recorded at −55 °C shows also one single resonance attributable to the

Table 1 The NMR features originating in L^{3-} (see **I** for atom labelling)

	^{1}H NMR (δ)		^{13}C NMR (δ)									
Complex	H_f	H_c	C_g	C_f	C_c	C_b	C_d	C_e	C_h	C_i	$C_{j,k}$	C_a
$[Pd_2L(HNOCMe)]^a$	8.15 8.06	7.41	183.6	149.1 148.6	140.3 140.1	136.1	132.1 131.9	121.4	40.4	31.3 40.2	26.1 26.0	20.5
$[Pd_2L(HNOCCHCH_2)]^a$	8.13 8.01	7.39	182.9	148.5 148.3	140.4	136.1	131.7 131.4	120.7	40.2 40.0	31.1	26.1 25.8	20.4
$[Pd_2L(C_4H_2NO_2)]^{a,b}$	8.19 7.94	7.42	184.5 183.6	150.8 148.3	140.2	136.9	132.6 131.6	121.2	40.1	31.2	26.1 25.9	20.5
$[Pd_2L(HNOCOEt)]^a$	8.16 8.04	7.40	183.9 183.7	149.3 148.5	140.2 140.0	136.2	132.1	121.6	40.2 40.0	31.1	26.0	20.3
$[Pd_2L(HNOCNMe_2)]^a$	8.16 8.04	7.37	183.6	148.9 148.4	139.9	136.1	132.2 131.9	121.8	40.4 40.1	31.2	26.1 26.0	20.6
$[Pd_2L\{(HN)_2COMe\}]^c$	8.16	7.37	183.5	148.5	140.2	135.5	132.2	122.1	40.3	31.1	26.1 25.9	20.4
$[Pd_2L(MeOCNHNH_2)]^{+d}$	8.22	7.84	181.7	150.8	141.3	135.4	130.5	120.7		30.6	25.7	19.8

[a] Spectrum recorded in $CDCl_3$. [b] Data from ref. 11. [c] Proton NMR spectrum recorded in $CDCl_3$, ^{13}C recorded in $(CD_3)_2SO$. [d] Compensating anion HSO_4^-, recorded in $(CD_3)_2SO$.

Table 2 The NMR features originating in the exogenous bridging group*

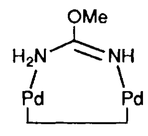
	^{1}H NMR (δ)	^{13}C NMR (δ)
$[Pd_2L(HNOCMe)]^a$	2.28 (s, 3 H, CH_3), 5.68 (br s, 1 H, NH)	24.8 (CH_3), 172.2 (amide C)
$[Pd_2L(HNOCCHCH_2)]^a$	4.40 (br s, 1 H, NH), 6.34–5.53 (complex m, CH_2CH)	160.5 (amide C), 130.8, 124.8, (CH_2CH)
$[Pd_2L(C_4H_2NO_2)]^{a,b}$	6.73 (q, J = 5.5 Hz, Δν = 51.2 Hz, CHCH)	186.0, 179.1 (C=O), 137.0, 136.0 (CHCH)
$[Pd_2L(HNOCOEt)]^a$	1.25 (t, 3 H, CH_3), 4.13 (q, 2 H, CH_2), 4.40 (br s, 1 H, NH)	14.4 (CH_3), 62.9 (CH_2), 160.5 (amide C)
$[Pd_2L(HNOCNMe_2)]^a$	3.00 (s, 6 H, CH_3), 3.99 (br s, 1 H, NH)	37.9 (CH_3), 161.8 (amide C)
$[Pd_2L\{(HN)_2COMe\}]^c$	3.73 (s, 3 H, CH_3), 3.90 (br s, 1 H, NH)	54.1 (CH_3), 159.3 (amide C)
$[Pd_2L(MeOCNHNH_2)]^{+d}$	3.92 (s, 3 H, CH_3), 8.39 (br s, 1 H, NH)	37.9 (CH_3), 162.3 (amide C)

* Footnotes as for Table 1.

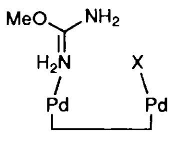
protons of the two methyl groups of the bridging species. It is possible that, even at −55 °C, rotation of the dimethylamino group about the *exo*-C–N bond is not sufficiently restricted to render the *gem*-methyl groups diastereotopic and, therefore, the chemical shifts for the protons of each methyl group still cannot be resolved. Another possibility is that the chemical shifts of the protons of each methyl group are coincidently the same.

The acetate bridge of $[Pd_2L(O_2CMe)]$ was exchanged easily for the conjugate base of *O*-methylurea by reaction with neutral *O*-methylisourea generated *in situ* from the hydrogensulfate salt of the latter and tetrabutylammonium hydroxide in a methanol–benzene mixture. Symmetrical N–C–N co-ordination as in **IV** (R = OMe) for the bridging species in $[Pd_2L\{(HN)_2COMe\}]$ is supported by the presence of a single resonance at δ 8.16 attributed to H_f and $H_{f'}$ in its ^{1}H NMR spectrum. The ^{13}C NMR spectrum of the complex lacks any 'doubling up' of carbon resonances.

The reaction of $[Pd_2L(O_2CMe)]$ with the hydrogensulfate salt of *O*-methylisourea, in a boiling solution of methanol and benzene, gave a salt formulated as $[Pd_2L(MeOCNHNH_2)][HSO_4]$. The spectral evidence suggests that a neutral *O*-methylisourea ligand is co-ordinated at the bridging site *via* either, or both, of two possible bridging modes, **V** and **VI** (X = H_2O or MeOH). The IR spectrum shows an intense band at 1700 cm^{-1} which may be consistent with the stretching vibration of the C=N bond in either **V** or **VI**. Both these bonds (C=N, in **V** or **VI**) are expected to show an increased bond order relative to the free hydrogensulfate salt of *O*-methylisourea and its conjugate base in $[Pd_2L\{(HN)_2COMe\}]$ arising from the inability of one of the urea nitrogen atoms to be involved in π-electron delocalization. The N–H stretching absorptions in the IR spectrum of $[Pd_2L(MeOCNHNH_2)][HSO_4]$ occur at 3350 and 3150 cm^{-1} and are relatively more intense than those in the spectrum of $[Pd_2L\{(HN)_2COMe\}]$. The NMR data for $[Pd_2L(MeOCNHNH_2)][HSO_4]$ are of poor quality due to the general insolubility of the complex and cannot be used to assign unambiguously the co-ordination mode of neutral *O*-methylisourea. However a single resonance at δ 8.22 is attributed to H_f and $H_{f'}$ in the ^{1}H NMR spectrum. The ^{13}C NMR spectrum [in $(CD_3)_2SO$], although not well resolved, appears to lack any 'doubling up' of the resonances. These data imply that a symmetrical bridging unit is incorporated at the bridging site of LPd_2^+ which, at first sight, is not consistent with either **V** or **VI**. However, it is possible that rapid proton exchange, relative to the NMR time-scale, between the co-ordinated imine and amine nitrogen atoms of **V** renders the corresponding carbon atoms of L^{3-} chemically equivalent. Alternatively, fast exchange of the monodentate groups of **VI** [X = $(CD_3)_2SO$], between the palladium atoms, possibly *via* **V**, may also render this complex symmetrical on the NMR time-scale. Pertinent to these results is the observation of linkage isomerization (*i.e.* between co-ordination by the two nitrogen atoms) reported for the *N*-co-ordinated urea in $[Pt(dien)(NH_2CONH_2)]^{2+}$ to account for its broadened NMR spectrum.[7] Given that Pd is generally more labile than Pt, similar fluxionality (*e.g.* linkage isomerization) seems feasible for the neutral *O*-methylisourea ligand of our system.



V



VI

Expectations that the central carbon atom of the *O*-methylisourea-derived ligand in $[Pd_2L(MeOCNHNH_2)][HSO_4]$ might show an increased reactivity towards nucleophiles compared to the central carbon atom of the deprotonated, anionic bridging species in $[Pd_2L\{(HN)_2COMe\}]$

were not realized. There was no evidence of either methyl ester hydrolysis or ethanolysis to give $[Pd_2L(ROCNHNH_2)][HSO_4]$, R = H or Et, when $[Pd_2L(MeOCNHNH_2)][HSO_4]$ was heated in solvent mixtures containing a significant proportion of water or ethanol under reflux. The starting material was recovered unchanged.

The two *O*-methylisourea-derived complexes, $[Pd_2L[\{(HN)_2COMe\}]$ and $[Pd_2L(MeOCNHNH_2)][HSO_4]$ can be interconverted; that is, treatment of a solution of the former in methanol with 1 molar equivalent of sulfuric acid generates the latter. Conversely, treatment of a methanolic solution of the latter with 1 molar equivalent of base generates the former.

The isolation and characterization of complexes incorporating unsubstituted urea proved significantly more difficult than for the alkyl-substituted derivatives. Identification of reaction products by NMR spectroscopy was severely hampered by their general insolubility. The reaction of $[Pd_2L(O_2CMe)]$ with an excess of urea in mixtures of benzene and methanol, or chloroform and methanol, gives two distinct products. Shorter reaction times tend to favour a complex which we have formulated as $[Pd_2L(CN_2OH_3)]$ where $CN_2OH_3^-$ represents the conjugate base of urea (product A). Bands at 3320 and 3340 [ν(NH)] and at 3420 cm^{-1} [ν(OH)] in the IR spectrum of product A support the N–C–N bridging mode **IV** (R = OH) rather than N–C–O bridging as in **III** (R = NH_2), consistent with the general preference of palladium(II) for nitrogen over oxygen donors. The complex $[Pd_2L(CN_2OH_3)]$ is relatively insoluble, however, adequate ^1H NMR spectra, in both $CDCl_3$ and $(CD_3)_2SO$ could be obtained given relatively long accumulation times. The spectrum suggests that the urea ligand in $[Pd_2L(CN_2OH_3)]$, in solution, and in contrast to the structure suggested by the solid-state IR spectrum is coordinated as a mixture of the linkage isomers **III** (R = NH_2) and **IV** (R = OH). Three resonances due to imine protons (H_f and $H_{f'}$) and two resonances due to the aromatic protons (H_c and $H_{c'}$) are observed. The pair of singlets with similar integrated intensities at δ 8.52 and 8.43 [in $(CD_3)_2SO$] are assigned to the unsymmetrically bridged N–C–O isomer **III** (R = NH_2). The singlet at δ 8.39 is assigned to the symmetrical N–C–N-bridged isomer **IV** (R = OH). The integrated intensities of these signals suggest a higher concentration of the N–C–O- compared to that of the N–C–N-bridged isomer. The observation of two resonances due to H_c and $H_{c'}$ is consistent with this proposal; the more intense signal at δ 7.92 is attributed to isomer **III** (R = NH_2) and the weaker signal at δ 7.83 to **IV** (R = OH). Three broad peaks between δ 3 and 7 are consistent with the four types of NH and OH protons expected for a mixture of the two linkage isomers.

On many occasions a product with significantly different spectral characteristics to those of $[Pd_2L(CN_2OH_3)]$ was obtained from reaction mixtures in which a high proportion of methanol was present in the solvent mixture and/or a smaller excess of urea was used (product B). It was noted also that $[Pd_2L(CN_2OH_3)]$ could be converted into product B simply by heating it, for 30 min, in a mixture of chloroform and methanol under reflux. The back reaction was never observed. The nitrogen analysis of product B is low compared to that of $[Pd_2L(CN_2OH_3)]$ (see Experimental section). We believe that nucleophilic attack at a N–C–O-bridging urea, **III** (R = NH_2), by water or methanol to give the conjugate base of carbamic acid, **III** (R = OH) or methyl carbamate, **III** (R = OMe), offers a feasible explanation for these results. The ^1H NMR spectrum of product B was of extremely poor quality due to its low solubility in the available solvents. However, the IR spectrum lends support to the formulation **III** (R = OH or OMe). The pattern observed in the OH and NH region of the spectrum is markedly different to that in the spectrum of $[Pd_2L(CN_2OH_3)]$. A weak peak, at 3270 cm^{-1}, which may be due to ν(NH) of **III** (R = OH or OMe), is superimposed on a broad band due to water of solvation. This is very similar to the pattern observed in the spectra of complexes with isostructural bridging species; for example, $[Pd_2L(HNOCOEt)]$, **III** (R = OEt) and the acetamide- and acrylamide-bridged complexes **III** (R = Me or $CHCH_2$, respectively). Unfortunately, the evidence so far is insufficient to assign, unequivocally, the bridging group and its co-ordination mode in product B.

Earlier work[16–18] on monodentate O- and N-bound urea and urethane derivatives in pentaaminecobalt(III) complexes did not indicate that the central carbon atom of these moieties show increased susceptibility to nucleophilic attack when coordinated. Apart from the different linkage isomers characterized, hydrolysis of the cobalt complex resulted in cleavage of the metal–ligand bonds rather than ligand hydrolysis or alcoholysis.[16–18] The possible hydrolysis of the unsubstituted urea ligand in our system, as described above, may indicate that bidentate co-ordination of urea to the two Lewis-acid centres of LPd_2^+ instead of one in the pentaaminecobalt(III) complexes may activate the central carbon atom to a greater extent towards attack by nucleophiles. This result may be relevant to the mechanism by which the dinickel active site of urease catalyses the hydrolysis of urea.

Crystal and molecular structure of $[Pd_2L(C_4H_2NO_2)]\cdot CHCl_3$

The asymmetric unit of the structure consists of one molecule of $[Pd_2L(C_4H_2NO_2)]$ and one of solvent chloroform. Fig. 1 shows the molecular geometry and the atomic numbering scheme used. The molecules of $[Pd_2L(C_4H_2NO_2)]$ are hydrogen bonded to the molecules of chloroform through one of the oxygen atom termini of L^{3-} [O(1)···C(28) 3.12 Å]. Selected interatomic bond distances and angles are listed in Table 3.

The overall geometry of $[Pd_2L(C_4H_2NO_2)]$ is similar to that of the closely related three-atom, acetate-bridged complex of L^{3-}, $[Pd_2L(O_2CMe)]$.[14] The complex is folded about the C(15)–S bond so that the molecule is V-shaped, with the square co-ordination planes about the palladium atoms tilted towards each other by an angle of 27.5°. The distance between the palladium atoms is 3.703 Å which is comparable to that in other dipalladium complexes of L^{3-}.[14,15] The geometry around the palladium atoms is distorted somewhat from square planar with angles between the donor atoms in the range 79.7(5)–97.9(4)°. This is the first reported complex incorporating a maleimidate bridging group between two metal centres. However complexes containing the closely related bridges glutarimide-[19–21] and succinimide-*N*,*O*[22–24] are known. One of these is a dipalladium complex.[23] The seven non-hydrogen atoms of the maleimidate bridging group are coplanar within 0.031 Å. Interestingly there is no significant difference in the C–O

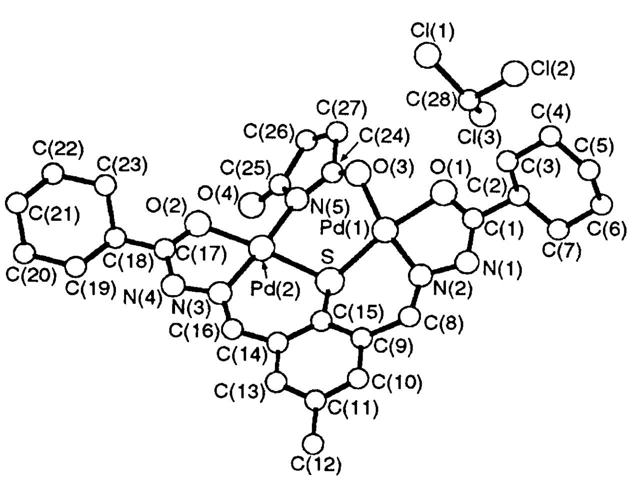


Fig. 1 The atomic arrangement and numbering scheme used for $[Pd_2L(C_4H_2NO_2)]\cdot CHCl_3$

Table 3 Selected interatomic distances (Å) and angles (°) for $[Pd_2L(C_4H_2NO_2)]\cdot CHCl_3$

Pd(1)–O(1)	2.04(1)	C(14)–C(15)	1.40(2)
Pd(1)–O(3)	2.07(1)	C(14)–C(16)	1.44(2)
Pd(1)–S	2.242(5)	C(16)–N(3)	1.33(2)
Pd(1)–N(2)	1.93(1)	C(15)–S	1.76(2)
Pd(2)–N(5)	2.06(1)	N(3)–N(4)	1.36(2)
Pd(2)–O(2)	2.01(1)	N(4)–C(17)	1.31(2)
Pd(2)–N(3)	1.96(1)	C(17)–O(2)	1.28(2)
Pd(2)–S	2.218(5)	O(3)–C(24)	1.20(3)
O(1)–C(1)	1.29(2)	C(24)–N(5)	1.35(3)
C(1)–N(1)	1.28(2)	N(5)–C(25)	1.35(3)
N(1)–N(2)	1.42(2)	C(25)–O(4)	1.18(3)
N(2)–C(8)	1.32(2)		
C(8)–C(9)	1.49(2)	Pd(1) ··· Pd(2)	3.703(2)
C(9)–C(15)	1.39(2)	O(3) ··· N(5)	2.33(3)
O(1)–Pd(1)–N(2)	79.9(5)	N(3)–Pd(2)–O(2)	79.7(5)
N(2)–Pd(1)–S	92.6(4)	O(2)–Pd(2)–N(5)	92.0(5)
S–Pd(1)–O(3)	97.9(4)	Pd(2)–S–Pd(1)	112.3(2)
O(3)–Pd(1)–O(1)	89.4(5)	O(3)–C(24)–N(5)	132.7(15)
N(5)–Pd(2)–S	92.0(4)	Pd(1)–O(3)–C(24)	128.6(12)
S–Pd(2)–N(3)	96.2(4)	C(24)–N(5)–Pd(2)	126.0(15)

bond lengths of the maleimide carbonyl groups, even though one of the carbonyl oxygen atoms, O(3), is co-ordinated to Pd(1) and the other, O(4), is unco-ordinated. This indicates extensive π-electron delocalization in the O–C–N–C–O moiety.

Conclusion

The isolation of urea- and carbamate-derived species exhibiting a variety of bidentate co-ordination modes supports the feasibility that some of these modes may be involved in the hydrolysis mechanism at the dinickel active site of urease. The mode of co-ordination of the urea ligand which would most favour its reaction with nucleophiles is yet to be established. However our suspicions of nucleophilic attack at the central carbon atom of $[Pd_2L(CN_2OH_3)]$ may be relevant in the elucidation of a mechanism of urea hydrolysis by the dinuclear nickel active site in urease, *i.e.* the 'double' activation of urea by virtue of co-ordination to two metal ions may be necessary to activate the central urea carbon atom enough for attack by hydroxide ion. All the bridging moieties used here are anticipated to show *syn-syn* co-ordination when incorporated into the LPd_2^+ system. This mode is apparently suitable for intermetallic separations in the range 3.6–4 Å. Bridging co-ordination of amidato-, carbamato- and urea-derived ligands *via syn-anti* or *anti-anti* modes will allow greater intermetallic separations.

Experimental

The NMR spectra were recorded with JEOL FX-100, FX-90Q or JNM GX-400 spectrometers, infrared spectra as KBr discs on a JASCO A302 spectrophotometer. Elemental analyses were performed by the Microanalytical Service, University of Queensland, St. Lucia, Australia and the Microanalytical Service, University of Otago, Dunedin, New Zealand. The complexes $[Pd_2L(O_2CMe)]$, $[Pd_2L(HNOCMe)]$ and $[Pd_2L(C_4H_2NO_2)]$ were prepared as described previously.[8]

Preparations

$[Pd_2L(HNOCCHCH_2)]$. The complex $[Pd_2L(O_2CMe)]$ (0.0792 g, 0.113 mmol) and acrylamide (0.0685 g, 0.964 mmol) were heated in a mixture of chloroform (4 cm^3) and methanol (0.5 cm^3) under reflux for 2 h, after which time methanol (3 cm^3) was added. On cooling orange crystals of $[Pd_2L(HNOCCHCH_2)]$ were deposited (0.0695 g, 87%) (Found: C, 44.0; H, 4.7; N, 9.8. $C_{26}H_{33}N_5O_3Pd_2S$ requires C, 44.1; H, 4.7; N, 9.9%).

$[Pd_2L(HNOCNMe_2)]$. The complex $[Pd_2L(O_2CMe)]$ (0.972 g, 0.138 mmol), *N,N*-dimethylurea (0.0692 g, 0.785 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) (0.0469 g, 0.308 mmol) were dissolved in benzene–methanol (1 : 1, 10 cm^3) at the boiling point. The solution was evaporated at atmospheric pressure to *ca.* half the original volume, then increasing amounts of methanol were added until crystallization commenced. The yellow needles of $[Pd_2L(HNOCNMe_2)]$ which separated were collected, washed with methanol and dried under vacuum at 80 °C (0.0702 g, 70%) (Found: C, 42.4; H, 5.0; N, 11.3; S, 4.6. $C_{26}H_{36}N_6O_3Pd_2S$ requires C, 43.1; H, 5.0; N, 11.6; S, 4.4%).

$[Pd_2L\{(HN)_2COMe\}]$. The hydrogensulfate salt of *O*-methylisourea (0.0378 g, 0.219 mmol) and tetrabutylammonium hydroxide (0.4 cm^3, 1 mol dm^{-3}, 0.4 mmol) dissolved in methanol (1 cm^3) were added to a solution of $[Pd_2L(O_2CMe)]$ (0.0624 g, 0.089 mmol) dissolved in hot benzene (4 cm^3). The solution changed from orange to pale yellow. Methanol (3–4 cm^3) was added to the boiling solution until crystallization of the product commenced. The solution was cooled and the yellow needles collected and washed with methanol (0.0618 g, 97%) (Found: C, 42.1; H, 4.9; N, 11.6. $C_{25}H_{34}N_6O_3Pd_2S$ requires C, 42.2; H, 4.8; N, 11.8%). Treatment of $[Pd_2L(MeOCNHNH_2)][HSO_4]$ with 1 molar equivalent of dbu or KOH in methanol gave an identical product.

$[Pd_2L(MeOCNHNH_2)][HSO_4]$. The hydrogensulfate salt of *O*-methylisourea (0.1024 g, 0.595 mmol) dissolved in methanol (1 cm^3) was added to a solution of $[Pd_2L(O_2CMe)]$ (0.1122 g, 0.159 mmol) dissolved in boiling benzene (2.5 cm^3). The salt $[Pd_2L(MeOCNHNH_2)][HSO_4]$ precipitated immediately. The solution was left to stand several hours then the solid was collected and washed with methanol (0.1161 g, 90%) (Found: C, 38.5; H, 4.7; N, 10.6; S, 8.0. $C_{25}H_{36}N_6O_7Pd_2S_2$ requires C, 37.1; H, 4.5; N, 10.4; S, 7.9%). IR 1120 cm^{-1} (HSO_4^-). An identical product was isolated from a methanolic solution of $[Pd_2L\{(HN)_2COMe\}]$ treated with 1 molar equivalent of sulfuric acid.

$[Pd_2L(HNOCOEt)]$. Urethane (0.3399 g, 3.8 mmol) and dbu (0.0246 g, 0.162 mmol) were dissolved in methanol (4 cm^3) and added to a solution of $[Pd_2L(O_2CMe)]$ (0.0623 g, 0.088 mmol) dissolved in boiling benzene. After refluxing the solution for 15 min methanol (4 cm^3) was added and the solution allowed to cool. The yellow, crystalline product was collected and washed with methanol (0.0457 g, 71%) (Found: C, 42.9; H, 4.8; N, 9.8; Pd, 29.3. $C_{26}H_{35}N_5O_4Pd_2S$ requires C, 43.0; H, 4.9; N, 9.6; Pd, 29.3%).

$[Pd_2L(CN_2OH_3)]$. *Product A.* Urea (0.0633 g, 1.05 mmol) dissolved in methanol (2 cm^3) was added to a solution of $[Pd_2L(O_2CMe)]$ (0.0799 g, 0.113 mmol) dissolved in boiling chloroform (2 cm^3). The solution was refluxed for 2 h; yellow crystals grew on cooling, which were collected and washed with methanol (0.0547 g, 69%) (Found: C, 42.8; H, 5.2; N, 11.4. $C_{24}H_{32}N_6O_3Pd_2S$ requires C, 41.3; H, 4.6; N, 12.1%).

Product B. The complex $[Pd_2L(CN_2OH_3)]$ (0.0547 g, 0.0784 mmol) was heated in a mixture of methanol and chloroform (3 : 2) (10 cm^3) under reflux for 1 h, after which time the volume was reduced by boiling at atmospheric pressure and until orange crystals of the product started to form in the solution. The solid was collected and washed with methanol (0.0390 g) (Found: C, 43.9; H, 5.1; N, 9.8%).

Crystallography

Crystals of the maleimidate-bridged complex suitable for X-ray analysis were obtained as orange-red plates by the evaporation, over 1 week, of a methanol–chloroform solution of

Table 4 Crystal data and details of crystal structure determination for $[Pd_2L(C_4H_2NO_2)]\cdot CHCl_3$

Formula	$C_{27}H_{31}N_5O_4Pd_2S\cdot CHCl_3$
M	854.1
Crystal system	Triclinic
Space group	$P\bar{1}$ (C_i^1, no. 2)
a/Å	7.970(2)
b/Å	14.491(1)
c/Å	14.565(3)
α/°	96.40(1)
β/°	99.03(2)
γ/°	101.67(1)
U/Å^3	1609
Z	2
D_c/g cm^{-3}	1.763
D_m/g cm^{-3}	1.770
Crystal dimensions (distance in mm from the centroid)	±(1 0 0) 0.288 ±(0 1 0) 0.063 ±(0 0 1) 0.025
F(000)	856.0
Diffractometer	Enraf-Nonius CAD-4
μ(Cu-Kα)/cm^{-1}	118.8
Absorption correction (minimum, maximum transmission coefficients)	0.1682, 0.5753
2θ range/°	2.0–130.0
Scan mode	ω–2θ
Total no. reflections	6212
No. unique reflections	5489
No. unique reflections used in refinement	2981 [$I \geq \sigma(I)$]
R_{amal}	0.040
Function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Weighting scheme parameters in $w = k/[\sigma^2(F_o) + gF_o^2]$	$g = 0.0007$, $k = 1.4609$
Final R	0.069
Final R'	0.068

$[Pd_2L(C_4H_2NO_2)]$. One of these was sealed in a Lindemann glass tube with some of the mother-liquor. Oscillation and Weissenberg photographs using Cu-Kα (nickel filtered) radiation (λ_α = 1.5418 Å) showed that the crystals were triclinic. Crystal data and details of the structure determination are included in Table 4. The intensities of three reference reflections, measured every 1800 s of X-ray exposure time, were used to monitor the extent of any intensity variation or crystal decomposition. Towards the end of the data collection the average intensity of these reflections was 90% of that observed at the commencement. The data were corrected for this intensity variation, Lorentz-polarization effects, and absorption.[25,26] The crystal orientation was checked every 100 reflections during the data collection. No allowance was made for extinction. Analysis of the three-dimensional Patterson map gave the positions of both palladium atoms in the asymmetric unit. The positions of all the remaining non-hydrogen atoms were located in the subsequent difference electron-density maps (refinement performed on F). All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were kept fixed at calculated positions and with a thermal parameter of 0.10 Å^2.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/30.

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