Positively Charged Pd_2 Complexes of a New Thiophenoxide-hinged Binucleating Ligand. The Crystal and Molecular Structure of μ-{4-Methyl-2,6-bis[2-(2-pyridyl-κ*N*)ethylimino-κ*N*-methyl]thiophenolato-1κ*S*:2κ*S*}-bis[dichloropalladium(II)] Chloride–Water–Methanol (1/1/0.5)†

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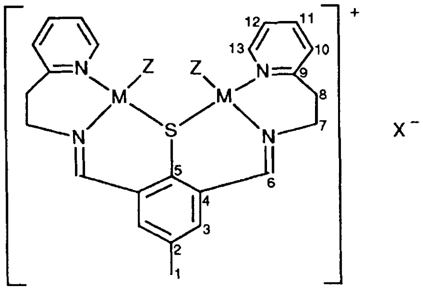
The Schiff-base condensation of 2-(*N*,*N*-dimethylcarbamoylthio)-5-methylisophthaldehyde with 2-(2-aminoethyl)pyridine, in the presence of Pd^{2+}, gives the complex $[Pd_2LCl_2]Cl{\cdot}H_2O{\cdot}0.5CH_3OH$ (**1a**), where L = 4-methyl-2,6-bis[2-(2-pyridyl)ethyliminomethyl]thiophenolate, and a monopalladium monoaldehyde complex, (**2**). The structure of (**1a**) was established by a single-crystal *X*-ray diffraction study: the crystals are monoclinic, space group *Cc*, with $a = 24.186(4)$, $b = 14.911(2)$, $c = 15.299(2)$ Å, $\beta = 104.87(1)°$; refined to $R = 0.026$ for 5 067 reflections [$I \geqslant 3\sigma(I)$] collected by counter methods. The structure of $[Pd_2LCl_2]^+$ reveals two chloride ions at the exogenous bridging site of the complex, one bound to each palladium. Spectroscopy suggests an analogous structure for $[Pd_2L(CH_3CO_2)_2]PF_6$.

A number of examples[1] of unusual reactions occurring at bimetallic sites in complexes of binucleating ligands afford encouragement that many other metal pair-promoted processes await invention or discovery. One general type of process that might be anticipated involves the bringing together of two separate species at the bimetallic site to undergo subsequently some sort of condensation. The demonstration that it is possible to bind two separate species to adjacent metals is significant in this regard, lending credence to such intermediates in the overall condensation process. The only reported example of such a species identified unambiguously by *X*-ray crystallography involves a chloride attached to one metal and a glycine ester N-co-ordinated to its neighbour.[2] These two ligands, however, cannot be regarded as strictly independent because they are clearly associated by an N–H···Cl hydrogen bond; it is possible that the hydrogen bonding in this case is crucial to the binding of the two species to adjacent metals. Presented here is a crystallographically characterized complex of a binucleating ligand in which two unquestionably independent species are bound at the bimetallic site.

Results and Discussion

The new binucleating ligand, L^-, used in this work is represented in the generalized derived complex (**1**), formulated $[M_2LZ_2]X$. The initial objective in choosing this monoanionic ligand was to study the effect of the positive charge in its Pd_2L^{3+} derivatives upon the catalysis of nitrile hydration, the earlier Pd_2 catalysts for this reaction being derived from trianionic binucleating ligands.[1e,f] Unfortunately complexes of L^- proved unsuitable for this purpose because of facile ligand hydrolysis under the conditions of the reaction.

The synthetic approach to Pd_2L^{3+} derivatives in the Scheme of first isolating the S-protected ligand precursor, (**III**), which was then intended to be subjected to metal-promoted S-deprotection followed by complex formation (a procedure which has generally worked well in the synthesis of several related systems), could not be used because we were unable to isolate (**III**) in pure form. The ^1H n.m.r. spectrum ($CDCl_3$) of a 1:3 mixture of 2-(*N*,*N*-dimethylcarbamoylthio)-5-methylisophthalaldehyde, (**I**), and 2-(2-aminoethyl)pyridine, (**II**), indicated complete conversion of the dialdehyde into the diimine after 1 h in boiling $CDCl_3$ (in particular all trace of the aldehydic resonance at δ 10.79 had disappeared). Nevertheless, many attempted preparations of (**III**) in a range of different solvents failed to yield a pure solid.



(**1a**) Z = X = Cl
(**1b**) Z = CH_3CO_2, X = PF_6

The alternative direct approach to the complexes involving imine formation, metal-promoted S-deprotection, and complex formation, all in a 'one-pot' reaction was not straightforward. Solids isolated from reactions of compounds (**I**) and (**II**) and either $[PdCl_4]^{2-}$ or $[PdCl_2(C_6H_5CN)_2]$ in proportions appropriate for the formation of Pd_2L^{3+} derivatives in a variety of solvents invariably proved to be mixtures of $[Pd_2LCl_2]Cl$, (**1a**), and the mononuclear complex (**2**).

Complex (**2**) was obtained free from (**1a**) from the reaction of compounds (**I**), (**II**), and $[PdCl_4]^{2-}$ in equimolar proportions. If substantial amounts of water were present in the reaction mixture (**2**) free of (**1a**) was also obtained from proportions of reactants appropriate for formation of Pd_2L^{3+} derivatives; the specimen of (**2**) used for elemental analysis (see Experimental section) was obtained in this way.

In its i.r. spectrum complex (**2**) showed an intense aldehydic ν(C=O) band at 1 672 cm^{-1} and a relatively weak imine ν(C=N) band as a shoulder at *ca.* 1 620 cm^{-1} on a pyridine-ring vibration at 1 605 cm^{-1}. The proportions, judged by i.r. spectroscopy, of

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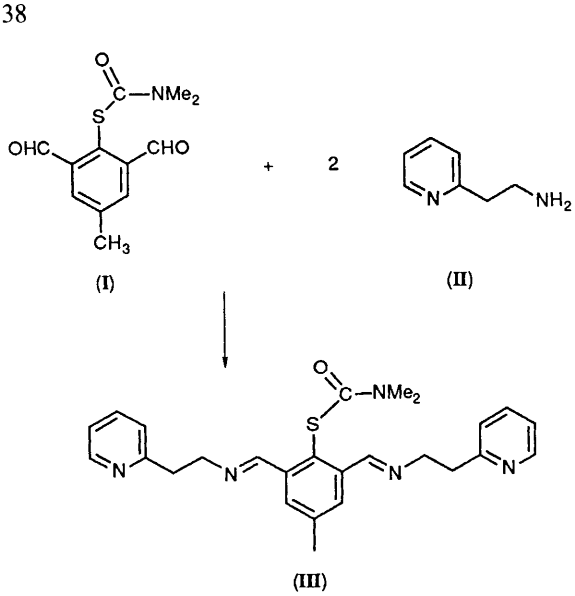
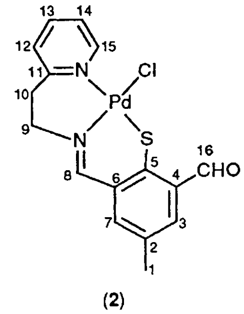
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



Scheme.



(2)

(**1a**) and (**2**) in the mixtures obtained from many attempted preparations of chloro Pd_2L^{3+} derivatives were variable. The mixture containing the least proportion of (**2**), obtained from the reaction between the dialdehyde and amine in chloroform using $[PdCl_2(C_6H_5CN)_2]$ as the metal source, revealed ν(C=N) of $[Pd_2LCl_2]Cl$ as a band at 1 625 cm^{-1} clearly separated, in this case, from the pyridine-ring vibration. All attempts to recrystallize these mixed products merely increased the proportion of (**2**). Clearly one imine link in $[Pd_2LCl_2]Cl$ is very fragile and the *X*-ray crystallographic analysis, described below, points to the reason for this. We were unable to isolate a sample of $[Pd_2LCl_2]Cl$ completely free of (**2**) except for the single crystal hand-picked for the *X*-ray study.

Compound (**I**) with 2 mol equivalents of (**II**) in the presence of palladium(II) acetate and tetrabutylammonium hexafluorophosphate in dichloromethane–methanol at room temperature gave $[Pd_2L(CH_3CO_2)_2]PF_6$, (**1b**). Spectroscopic evidence supports structure (**1b**), analogous to that determined crystallographically for $[Pd_2LCl_2]Cl$. The ^1H n.m.r. spectrum in $(CD_3)_2SO$ shows a single acetate-derived six-proton resonance at δ 1.86 and the ^{13}C n.m.r. spectrum in the same solvent shows a single acetate-methyl resonance at 23.6 p.p.m. and a single carboxylate resonance at 176.1 p.p.m., consistent with structure (**1b**). In the i.r. spectrum ν_{sym}(OCO) appears at 1 370 cm^{-1} and ν_{asym}(OCO) is one contributor, together with the imine ν(C=N) and the pyridine-ring vibration, to an intense broad absorption with two barely resolved maxima in the 1 605—1 630 cm^{-1} region. Such widely spaced acetate bands are consistent with the monodentate co-ordination proposed in (**1b**).[3]

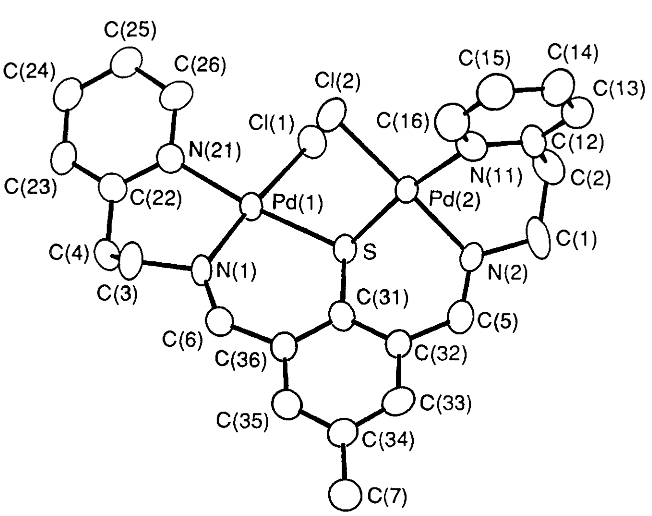


Figure 1. The atom arrangement for cation 1 of $[Pd_2LCl_2]Cl{\cdot}H_2O{\cdot}0.5CH_3OH$ together with the numbering scheme used for both independent cations

Table 1. Selected interatomic distances (Å) and angles (°) for the two independent cations of $[Pd_2LCl_2]Cl{\cdot}H_2O{\cdot}0.5CH_3OH$

	Cation 1	Cation 2
Pd(1) $\cdots$ Pd(2)	3.798(1)	3.891(1)
Pd(1)-S	2.241(2)	2.255(2)
Pd(1)-Cl(1)	2.319(2)	2.314(2)
Pd(1)-N(1)	2.018(5)	2.017(6)
Pd(1)-N(21)	2.089(6)	2.115(6)
Pd(2)-S(1)	2.270(2)	2.283(2)
Pd(2)-Cl(2)	2.294(3)	2.285(3)
Pd(2)-N(2)	2.016(6)	2.031(6)
Pd(2)-N(11)	2.061(7)	2.070(6)
S-C(31)	1.738(7)	1.754(7)
S-Pd(1)-Cl(1)	81.9(1)	82.3(1)
S-Pd(1)-N(1)	94.5(2)	93.6(2)
S-Pd(1)-N(21)	171.7(2)	172.2(2)
Cl(1)-Pd(1)-N(1)	174.4(2)	174.5(2)
Cl(1)-Pd(1)-N(21)	89.9(2)	90.2(2)
N(1)-Pd(1)-N(21)	93.8(3)	93.8(3)
S-Pd(2)-Cl(2)	95.9(1)	94.7(1)
S-Pd(2)-N(2)	84.7(2)	85.8(2)
S-Pd(2)-N(11)	171.9(3)	173.5(2)
Cl(2)-Pd(2)-N(2)	176.9(2)	177.5(2)
Cl(2)-Pd(2)-N(11)	92.1(3)	91.8(2)
N(2)-Pd(2)-N(11)	87.3(3)	87.7(3)
Pd(1)-S-Pd(2)	114.7(1)	118.1(1)
Pd(1)-S-C(31)	113.7(3)	113.5(3)
Pd(2)-S-C(31)	97.0(3)	99.0(3)

Crystal and Molecular Structure of $[Pd_2LCl_2]Cl{\cdot}H_2O{\cdot}0.5CH_3OH$.—The crystal structure contains two crystallographically unique but chemically identical $[Pd_2LCl_2]^+$ units (cations 1 and 2) together with unco-ordinated chloride ions and methanol and water of solvation. The geometries for the cations are similar but not identical. The atomic arrangement for cation 1 together with the numbering scheme used for both cations is shown in Figure 1. Selected interatomic distances and bond angles are given in Table 1.

The geometry around the palladium atoms is distorted somewhat from square planar with angles between the donor atoms in the range 81.9(1)—95.9(1)° for cation 1 and 82.3(1)—

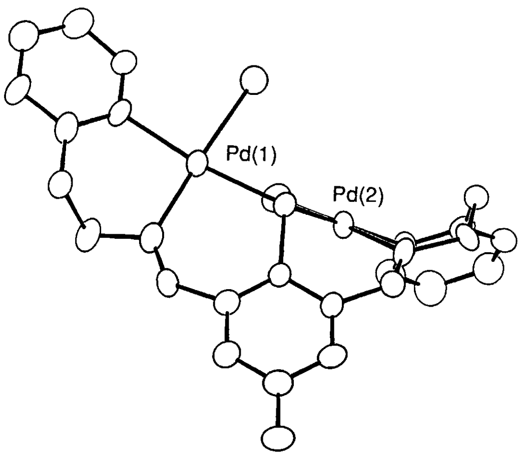


Figure 2. A view of cation 1 of $[Pd_2LCl_2]Cl{\cdot}H_2O{\cdot}0.5CH_3OH$ showing the marked twisting of the two metal atom co-ordination planes about the thiophenoxide hinge

94.7(1)° for cation 2. The geometry at the sulphur atom is markedly non-planar, the distances of the sulphur atom from the plane through its three bonded atoms being 0.713 and 0.662 Å for cations 1 and 2 respectively. Significant strain around the sulphur is evident in that it is displaced from the average plane of the benzene ring [C(31)—C(36)] to which it is attached by 0.206 Å in cation 1 and 0.239 Å in cation 2.

The factor dominating the conformation adopted appears to be the repulsive interaction between the two chloro ligands. Marked twisting of the two co-ordination planes around the hinging sulphur atom so that they are at angles of 75.3 (cation 1) and 77.0° (cation 2) to each other allows the chlorine atoms to be separated by 3.706(4) Å in cation 1 and 3.811(4) Å in cation 2. The Pd $\cdots$ Pd separations are 3.798(1) Å for cation 1 and 3.891(1) Å for cation 2. The side-arm twisting required for the Cl $\cdots$ Cl separations is not taken up equally by the two halves of the binucleating ligand; rather, the side arm associated with Pd(2) is very much more twisted out of the plane of the central aromatic unit than the other, as can clearly be seen in the view shown in Figure 2. The co-ordination plane of Pd(1) is at a dihedral angle of 10.7 (cation 1) and 17.1° (cation 2) to the central aromatic ring whereas the corresponding angles for the co-ordination plane of Pd(2) are 64.9 (cation 1) and 60.1° (cation 2).

The ready loss of one aminoethylpyridine unit from $[Pd_2LCl_2]Cl$ to liberate (**2**) is consistent with the pronounced twisting of one side arm revealed in the structural study. This ligand decompositon is unfortunate because a study of the influence of the overall charge upon catalysis of nitrile hydration would be valuable. Analogous complexes in which the two imine groups have been reduced to amines (for example by BH_4^-) could prove interesting in this regard.

Experimental

N.m.r. spectra were recorded with a JEOL FX-100 or FX-90Q spectrometer, i.r. spectra as KBr disks on a JASCO A302 spectrophotometer. Elemental analyses were performed by the Microanalytical Service, University of Queensland, St. Lucia, and AMDEL, the Australian Microanalytical Service, Melbourne, Victoria.

Mononuclear Complex (**2**) *and* $[Pd_2LCl]Cl{\cdot}H_2O{\cdot}0.5CH_3OH$.—A solution of 2-(*N*,*N*-dimethylcarbamoylthio)-5-methylisophthaldehyde (**I**) (0.0994 g, 0.396 mmol) and 2-(2-aminoethyl)pyridine (0.1986 g, 1.68 mmol) in methanol (2 cm^3) was held at the boiling point for 15 min and then added to a solution of $PdCl_2$ (0.1406 g, 0.793 mmol) and KCl (0.1310 g, 1.76 mmol) in boiling water (2 cm^3). The pale orange flocculent precipitate which formed initially redissolved after heating for a few minutes at the boiling point to produce a clear orange solution which yielded the orange crystalline mononuclear complex (**2**) on cooling. The crystals were collected, washed with methanol, and dried in vacuum at 80 °C. Yield 0.1543 g (Found: C, 44.9; H, 3.5; Cl, 8.4; N, 6.5. $C_{16}H_{15}ClN_2OPdS$ requires C, 45.2; H, 3.6; Cl, 8.3; N, 6.6%). I.r.: ν(C=O) 1 672 cm^{-1}. N.m.r. $[(CD_3)_2SO]$: ^{1}H, δ 2.28 (3 H, s, aryl CH_3), 3.49 (2 H, br m, CH_2), 3.84 (2 H, br m, CH_2), 7.5—9.0 (7 H, m, aryl H + imine H), and 10.64 (1 H, s, CHO). ^{13}C, δ 19.13 (C^1), 57.11 (C^{10}), 122.50, 124.01 ($C^{12,14}$), 130.24, 132.03, 133.38, 139.40, 141.62 ($C^{2-7,13}$), 152.02 (C^{15}), 158.79 (C^{11}), 163.56 (C^8), and 190.27 (C^{16}); C^9 obscured by solvent peak. Further (**2**) together with single crystals of $[Pd_2LCl_2]Cl{\cdot}H_2O{\cdot}0.5CH_3OH$ separated from the filtrate over a period of several days and an individual crystal of the latter was hand-picked for the crystallographic study.

$[Pd_2L(CH_3CO_2)_2]PF_6$.—A solution of 2-(2-*aminoethyl*)-pyridine (0.0354 g, 0.29 mmol) and compound (**I**) (0.0262 g, 0.10 mmol) in dichloromethane (2 cm^3) was heated at the boiling point for 15 min and was then added at room temperature to a solution of palladium(II) acetate (0.0512 g, 0.23 mmol) and tetrabutylammonium hexafluorophosphate (0.0758 g, 0.20 mmol) in dichloromethane (2 cm^3). The solvent was removed under vacuum at room temperature and the residue was dissolved in methanol (2 cm^3). Yellow rosettes of $[Pd_2L(CH_3CO_2)_2]PF_6$ crystallized from the solution after 3—4 d at −25 °C. The solid was collected and washed with diethyl ether. Yield 0.018 g (20%) (Found: C, 37.0; H, 3.4; N, 6.2. $C_{27}H_{29}F_6N_4O_4PPdS{\cdot}H_2O$ requires C, 36.8; H, 3.6; N, 6.4%). N.m.r. $[(CD_3)_2SO]$: ^{1}H, δ 1.86 (6 H, s, CH_3CO_2), 2.34 (3 H, s, aryl CH_3), 3.88 (4 H, br m, CH_2), resonance due to other CH_2 group obscured by H_2O peak at 3.58, and 7.4—8.5 (12 H, m, aryl H + imine H); ^{13}C, δ 19.89 (C^1), 56.29 (C^8), 123.85, 125.42($C^{10,12}$), 126.23 (C^5), 132.41 (C^4), 136.58 (C^2), 140.75, 140.97 ($C^{3,11}$), 149.13 (C^{13}), 158.36 (C^9), 167.95 (C^6), 23.57 (acetate CH_3), and 176.07 (acetate CO_2); solvent peak obscures C^7 signal.

Determination of the Molecular Structure of $[Pd_2LCl_2]Cl{\cdot}H_2O{\cdot}0.5CH_3OH$.—*Crystal data.* $C_{23}H_{23}Cl_3N_4Pd_2S{\cdot}H_2O{\cdot}0.5CH_3OH$, $M = 740.7$, monoclinic, space group *Cc* (no. 9), $a = 24.186(4)$, $b = 14.911(2)$, $c = 15.299(2)$ Å, $\beta = 104.87(1)°$, $U = 5\,333(3)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections; $\lambda_\alpha = 0.710\,69$ Å), $F(000) = 2\,936$, $D_m = 1.838(5)$ g cm^{-3}, $Z = 8$, $D_c = 1.845$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 16.9$ cm^{-1}, $T = 295(1)$ K. Crystal dimensions (distances to faces from centroid): $\pm(100)$ 0.064; $\pm(111)$ 0.143; $\pm(1\bar{1}1)$ 0.136; $(\bar{1}\bar{2}0)$ 0.114 mm.

Oscillation and Weissenberg photographs using Cu-K_α (nickel-filtered) radiation ($\lambda_\alpha = 1.5418$ Å) showed that crystals of $[Pd_2LCl_2]Cl{\cdot}H_2O{\cdot}0.5CH_3OH$ were monoclinic. Intensity data were measured for 6 578 reflections ($2.0 \leqslant 2\theta \leqslant 50.0°$) in the ω—2θ scan mode using an Enraf-Nonius CAD-4F single-crystal diffractometer equipped with graphite-monochromated Mo-K_α radiation. This resulted in 5 656 unique reflections ($R_{int} = 0.010$) after absorption correction (maximum, minimum transmission factors = 0.835, 0.619) of which 5 067 [$I \geqslant 3\sigma(I)$] were used. The intensity values of three strong reflections, monitored every 3 600 s of *X*-ray exposure time, showed no significant variation during the data collection. The intensity data were corrected for Lorentz and polarization effects. Absorption corrections were numerically evaluated to a precision of 0.5% using a Gaussian integration method;[4a,5] no correction was made for extinction.

Table 2. Fractional atomic co-ordinates for the non-hydrogen atoms of $[Pd_2LCl_2]Cl{\cdot}H_2O{\cdot}0.5CH_3OH$[a]

	Cation 1			Cation 2		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Pd(1)	0.0(−)	0.132 01(4)	0.0(−)	0.001 47(2)	0.385 74(4)	−0.020 48(4)
Pd(2)	0.120 62(2)	0.054 55(4)	−0.099 28(4)	−0.115 96(2)	0.470 78(4)	0.091 97(4)
S	0.053 5(1)	0.160 2(1)	−0.096 7(1)	−0.051 5(1)	0.362 9(1)	0.079 2(1)
Cl(1)	0.083 4(1)	0.174 3(1)	0.104 8(1)	−0.083 0(1)	0.346 0(2)	−0.123 4(1)
Cl(2)	0.091 6(1)	−0.044 8(1)	−0.005 5(2)	−0.089 1(1)	0.568 9(1)	−0.004 3(2)
N(1)	−0.071 8(2)	0.106 1(4)	−0.097 9(4)	0.073 6(3)	0.410 8(4)	0.076 9(4)
N(2)	0.143 8(2)	0.137 8(4)	−0.187 5(4)	−0.137 8(2)	0.386 8(4)	0.182 2(4)
C(1)	0.205 4(3)	0.158 8(6)	−0.174 4(6)	−0.199 5(3)	0.373 2(5)	0.180 3(6)
C(2)	0.243 8(3)	0.100 3(5)	−0.102 3(6)	−0.238 3(3)	0.426 4(5)	0.102 8(5)
C(3)	−0.122 9(3)	0.082 9(6)	−0.064 1(6)	0.123 0(3)	0.440 1(6)	0.044 0(6)
C(4)	−0.132 1(3)	0.149 5(6)	0.004 0(5)	0.135 2(3)	0.370 3(6)	−0.021 0(5)
C(5)	0.108 3(3)	0.173 0(5)	−0.255 8(5)	−0.102 8(3)	0.343 8(5)	0.243 8(5)
C(6)	−0.081 6(3)	0.117 4(5)	−0.183 0(5)	0.085 4(3)	0.392 6(5)	0.160 8(5)
C(7)	−0.069 0(4)	0.165 0(7)	−0.496 0(6)	0.082 0(4)	0.311 2(6)	0.471 0(5)
N(11)	0.184 2(3)	−0.030 7(4)	−0.116 0(5)	−0.177 4(2)	0.558 7(4)	0.113 4(4)
C(12)	0.236 4(3)	0.003 1(6)	−0.116 4(5)	−0.229 6(3)	0.524 9(5)	0.115 3(5)
C(13)	0.278 4(3)	−0.054 2(6)	−0.128 1(5)	−0.272 3(3)	0.582 1(6)	0.127 3(5)
C(14)	0.268 2(4)	−0.145 0(6)	−0.139 0(6)	−0.262 4(4)	0.672 0(6)	0.137 8(6)
C(15)	0.215 6(4)	−0.178 7(6)	−0.140 1(7)	−0.209 6(4)	0.705 5(6)	0.137 4(7)
C(16)	0.173 0(4)	−0.119 0(6)	−0.127 7(7)	−0.168 7(3)	0.646 5(5)	0.125 0(6)
N(21)	−0.039 4(2)	0.110 9(4)	0.104 8(4)	0.042 2(2)	0.397 9(4)	−0.126 8(4)
C(22)	−0.096 0(3)	0.131 4(5)	0.096 7(5)	0.098 8(3)	0.383 8(5)	−0.115 6(6)
C(23)	−0.118 2(3)	0.130 4(5)	0.170 2(6)	0.123 3(3)	0.384 1(5)	−0.188 9(5)
C(24)	−0.085 0(3)	0.107 0(5)	0.254 7(6)	0.089 3(4)	0.396 4(6)	−0.275 4(6)
C(25)	−0.028 3(4)	0.084 5(5)	0.262 7(6)	0.032 0(4)	0.412 2(6)	−0.286 9(6)
C(26)	−0.007 3(3)	0.086 5(5)	0.187 2(6)	0.010 1(3)	0.414 9(5)	−0.212 0(5)
C(31)	0.016 2(3)	0.151 4(5)	−0.209 7(5)	−0.011 0(3)	0.359 7(5)	0.192 1(5)
C(32)	0.046 5(3)	0.163 2(5)	−0.276 1(5)	−0.039 8(3)	0.344 3(5)	0.260 1(5)
C(33)	0.018 5(3)	0.168 4(5)	−0.365 9(5)	−0.009 5(3)	0.328 7(5)	0.349 3(5)
C(34)	−0.040 5(3)	0.159 0(5)	−0.395 8(5)	0.050 8(3)	0.330 7(5)	0.376 2(5)
C(35)	−0.069 7(3)	0.142 4(5)	−0.333 7(5)	0.077 8(3)	0.351 7(5)	0.308 5(5)
C(36)	−0.044 0(3)	0.139 6(5)	−0.240 3(5)	0.048 5(3)	0.365 9(5)	0.218 2(5)

Anions and solvent of crystallization[b]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cl(1A)	−0.213 8(1)	0.088 6(2)	0.495 3(2)	O(1ME)[c]	0.784 4(4)	0.022 7(6)	0.691 3(6)
Cl(2A)	−0.283 6(1)	0.168 7(2)	0.151 5(2)	C(1ME)[c]	0.778 8(11)	0.114 7(8)	0.708 0(14)
O(1W)	0.312 4(3)	0.293 6(4)	−0.166 4(5)	O(2ME)[d]	0.723 4(5)	0.126 4(6)	0.779 8(8)
O(2W)	−0.284 0(3)	0.086 5(5)	−0.043 8(6)	C(2ME)[d]	0.724 7(12)	0.035 3(9)	0.806 2(14)

[a] *x* and *z* co-ordinates of all atoms referred to those of Pd(1) of cation 1 each of which was fixed at 0.0. [b] A denotes an anion; W and ME atoms of water and methanol molecules of solvation, respectively. [c] Site occupation factor 0.535(2). [d] Site occupation factor 0.465(2).

Structure analysis and refinement. A satisfactory solution could not be obtained in the centrosymmetric space group *C*2/*c*. However, using the space group *Cc* the co-ordinates of the S, Pd, and Cl atoms were obtained using the automatic Patterson interpretation program;[6] subsequent difference maps revealed the remaining non-hydrogen atoms.[5] The structure was refined by using blocked full-matrix least-squares procedures[5] which minimize the function $\Sigma w\Delta^2$ where $\Delta = ||F_o| - |F_c||$ and w is the weight assigned to each reflection; unit weights were used throughout the refinement. Anisotropic thermal parameters were assigned to all the non-hydrogen atoms except those of the molecules of solvation for which individual isotropic thermal parameters were used. At this stage all the methylene and aromatic hydrogen atoms were clearly discernible in the difference map and all of the hydrogen atoms of the cations were included in the model at their calculated positions. A common isotropic thermal parameter was employed for each hydrogen atom type, *viz*. methyl, methylene, *etc*. At convergence the maximum residual electron density was 0.73 e Å^{-3}; final R and R' values were 0.026 and 0.027 where $R = \Sigma|\Delta|/\Sigma|F_o|$ and $R' = (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$. The parameters for the scattering factor curves for atomic C, H, N, Cl, and O were those incorporated into the SHELX 76 program,[5] while those for atomic palladium were taken from ref. 4*b*; corrections for anomalous dispersion effects were taken from ref. 4*c*. Fractional atomic co-ordinates for the non-hydrogen atoms are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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Received 21*st December* 1989; *Paper* 9/05467G