

Chloride anion recognition by neutral platinum(II) and palladium(II) 5,5'-bis-amide substituted bipyridyl receptor molecules

Paul D. Beer,^{a*} Nicholas C. Fletcher,^a Michael G. B. Drew^b and Trevor J. Wear^c

^aInorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, U.K.

^bDepartment of Chemistry, University of Reading, PO Box 224, Reading RG2 6AD, U.K.

^cKodak Ltd, Headstone Drive, Harrow, Middlesex HA1 4TY, U.K.

(Received 24 May 1996; accepted 8 July 1996)

Abstract—A series of new acyclic platinum(II) and palladium(II) 5,5'-bis-amide substituted 2,2'-bipyridyl receptors have been synthesized and single-crystal structural investigations of two receptors are described. Proton NMR anion binding studies reveal that these neutral receptors recognize chloride anions in dimethyl sulfoxide solution. Copyright © 1996 Elsevier Science Ltd

Keywords: anion; recognition; platinum; palladium; bipyridyl; chloride.

The molecular recognition [1] and sensing [2] of anionic species is a rapidly expanding area of hostguest chemistry. A variety of positively charged and neutral electron-deficient abiotic receptor molecules have been synthesized and shown in some cases to selectively recognize anions [3, 4]. As part of a research programme aimed at designing new optical and electrochemical sensory reagents for anions [2], we have recently reported new classes of anion receptor that contain positively charged organometallic and coordination transition metal Lewis acidic binding sites in combination with amide N-H groups [5,6]. For example, spectral and electrochemical recognition of anions has been demonstrated by ruthenium(II) 4,4'and 5,5'-bis-disubstituted bipyridyl derivatives [7,8]. In an effort to investigate the effect of charge of the Lewis acidic centre upon the anion recognition process, we describe here the preparation and anion complexation ability of new neutral platinum(II) and palladium(II) bipyridyl receptors.

RESULTS AND DISCUSSION

Anion receptor syntheses

The preparation of the 5,5'-bis-amide substituted 2,2'-bipyridyl ligands has been described previously

(Fig. 1) [8]. Attempts were made to coordinate the ligands L^1 , L^2 , L^3 and L^4 to platinum(II) using $K_2[PtCl_4]$ (Scheme 1). The literature procedures for the preparation of such complexes are usually made in water [9]. However, all the ligands demonstrated an extreme hydrophobicity. Consequently, ligand L^1 was dissolved in methanol (using the preparation of Pt(phen)Cl₂ as a precedent [10]), to which was added the platinum precursor $K_2[PtCl_4]$ in aqueous acetonitrile, with stirring for several hours. The product $Pt(L^1)Cl_2$ was isolated following removal of the solvent and recrystallized from methanol as a yellow solid in 70% yield. Ligands L²⁻⁴ proved insoluble in methanol, so warm DMSO was used as the reaction solvent. After several hours of heating with $K_2[PtCl_4]$ the solvent was removed by vacuum distillation, and the products $Pt(L^{2-4})Cl_2$ were obtained as yellow solids.

The analogous palladium complexes $Pd(L^{1,3,4})Cl_2$ were prepared similarly using $K_2[PdCl_4]$ in good yields as yellow-brown solids. Unfortunately, extreme insolubility problems with the palladium complex product of L^2 prevented its characterization.

It is noteworthy that with the platinum complexes the addition of water caused a dramatic colour change from yellow to bright red. This colour change has also been observed under extreme conditions with Pt(bipy)Cl₂, and typically is derived from refluxing [Pt(bi-

^{*} Author to whom correspondence should be addressed.



Fig. 1. 5,5'-Bis-amide-substituted bipyridyl ligands.



py)(NH₃)₂]²⁺ in hydrochloric acid to give the red form [11,12]. There is substantial evidence that the yellow and red complexes are monomeric structures and so it has been postulated that the colour change is due to differing spatial arrangements in the crystal structure. Since the amide functionalized complexes readily change colour on the addition of water, this could be attributed to hydrogen bonding to water by the complexes, forcing the crystal structure to rearrange in some manner. Unfortunately, the poor solubility of the complexes prevented a solution investigation into this phenomenon using electronic spectroscopy.

Structural studies

Pt(L²)Cl₂. Crystals of complex Pt(L²)Cl₂ suitable for X-ray structural analysis were obtained as yellow needles by dissolving in warm DMSO and subsequent slow evaporation over 9 months. The structure is shown in Fig. 2, together with the atomic numbering scheme. The platinum complex has crystallographic C_2 symmetry and there is a DMSO solvent molecule per complex, with a hydrogen bond between the amide nitrogen atom N(12) and the oxygen atom in the solvent DMSO [N(12)…O(1S) (-x, -y, 1-z) 2.838



Fig. 2. Thermal motion ellipsoid plot of $Pt(L^2)Cl_2$, with ellipsoids drawn at the 30% probability level.

Å]. The bond lengths and angles for the bipyridyl platinum fragments are in good agreement with those for Pt(bipy)Cl₂ (both the red and yellow forms) [12] (Table 1). It was observed that the bond distances between the platinum centre and the ligated atoms were slightly smaller than with Pt(bipy)Cl₂ [12]. This is probably due to the electron-withdrawing effect of the new amide functionalized ligand, causing better $d-\pi^*$ back bonding, and consequently shorter bond lengths are observed and the reduced electron density on the platinum centre facilitates stronger bonding to the chloride ligands.

The molecules are planar and stack in a staggered array of overlapping units, as shown in Fig. 3a and b. The structure does not, however, demonstrate the configuration of either the yellow or the red isomorph of $Pt(bipy)Cl_2$, with the Pt—Pt distance being comparatively much larger (6.695 Å) [12]. The individual units lie in line with each other as in the red form, but the two platinum atoms do not sit directly over each other. It is presumed that on the addition of water, a rearrangement can occur which brings the two platinum centres closer together, by virtue of a change in the hydrogen bonding arrangement, giving the distinct colour change observed.

 $Pd(L^1)Cl_2$. Crystals of complex $Pd(L^1)Cl_2$ suitable for X-ray structure analysis were obtained as yellow needles by dissolving in warm DMSO and subsequent

| Parameter | Pt(L ²)Cl ₂ | Yellow forms of Pt(bipy)Cl ₂ | Red forms of Pt(bipy)Cl ₂ |
|--------------------------|------------------------------------|---|--------------------------------------|
| Pt(1)—N(1) | 1.94(2) | 2.006(10) | 2.001(6) |
| | | 2.011(10) | |
| Pt(1)Cl(1) | 2.248(7) | 2.281(4) | |
| | | 2.300(3) | |
| N(1)—Pt(1)—N(1)#1 | 79.3(9) | | 80(1) |
| N(1) - Pt(1) - Cl(1) | 96.1(5) | 94.3(3) | 96(1) |
| N(1) - Pt(1) - Cl(1) + 1 | 175.1(5) | 175.9(3) | 184ª |
| | | 174.7(3) | |
| Cl(1) - Pt(1) - Cl(1) #1 | 88.6(4) | 89.1(1) | 88(1) |
| Inter Pt-Pt | 6.965 | 4.435 | 3.45 |
| | | | |

Table 1. Dimensions (Å) and angles (°) in the metal coordination spheres for Pt(L²)Cl₂, yellow and red forms of Pt(bipy)Cl₂ [12]

^aCalculated value.



Fig. 3. PLUTON straw plots of the structure of $Pt(L^2)Cl_2$, illustrating the linear array of the complexes.

slow evaporation over 6 months. The structure is shown in Fig. 4, together with the atomic numbering scheme. The units themselves indicate that the bond lengths and distances are similar to those of Pd(bipy)Cl₂ [13], with changes in the metal-to-ligand bond distances again associated with the additional electron-withdrawing nature of the amide groups (Table 2).

These planar molecules also pack closely in a linear stack (Fig. 5a, b); however, in this case the packing is more similar to the literature (compare the Pd—Pd distances in Table 2) [13], where the packing is isomorphic with the yellow form of Pt(bipy)Cl₂. There is no solvent in this structure and two types of hydrogen bond link the individual units together in a twodimensional lattice. One is formed between an amide



Fig. 4. Thermal motion ellipsoid plot of $Pd(L^1)Cl_2$, with ellipsoids drawn at the 50% probability level.

Table 2. Dimensions (Å) and angles (°) in the metal coordination spheres for $Pd(L^1)Cl_2$, yellow and red forms of $Pd(bipy)Cl_2$ [13]

| Parameter | $Pd(L^{1})Cl_{2}$ | Pd(bipy)Cl ₂ |
|--------------------------|-------------------|-------------------------|
| Pd(1)—N(12) | 2.002(12) | 2.03(1) |
| Pd(1) - N(1) | 2.028(10) | 2.03(1) |
| Pd(1)Cl(1) | 2.261(4) | 2.317(3) |
| Pd(1)—Cl(2) | 2.271(4) | 2.277(3) |
| N(12) - Pd(1) - N(1) | 81.2(4) | 80.5(4) |
| N(12) - Pd(1) - Cl(1) | 175.6(3) | 175.0(3) |
| N(1) - Pd(1) - Cl(1) | 94.4(3) | 95.3(3) |
| N(12) - Pd(1) - Cl(2) | 94.6(3) | 94.4(4) |
| N(1) - Pd(1) - Cl(2) | 175.8(3) | 174.5(3) |
| Cl(1)— $Pd(1)$ — $Cl(2)$ | 89.8(2) | 89.9(1) |
| Closest inter Pd-Pd | 4.9148 | 4.587 |

nitrogen [N(23)] atom and an adjacent chloride [Cl(2)] ligand lying in the plane [N(23)—Cl(2) (0.5-x,-y,0.5+z) 3.321 Å]. The other is formed from the amide nitrogen [N(33)] atom and an amide oxygen [O(22)] atom in the molecule directly above the stack [N(33)—O(32) (0.5+x, y, 0.5-z) 2.907 Å]. In order to achieve this hydrogen bond, there are two differences in the conformation of the ligand in the palladium complex relative to the platinum complex, where both carbonyl groups are positioned on the same side as each other and on the same side as the metal atom. By contrast, in the palladium complex, while one carbonyl group is on the metal side, the other is rotated around to point away from the metal so that it can participate in hydrogen bonding. In addition, this atom is severely twisted out of the plane of the pyridine ring to which it is attached, thus the C(11)-C(10)-C(31)-N(33) torsion angle is 37.1° compared to the more expected angle for C(2)-C(3)-C(21)-N(23) of -2.1° (Table 3).

Proton NMR anion coordination studies

The addition of tetrabutylammonium chloride to DMSO- d_6 solutions of the neutral platinum and palladium(II) bipyridyl receptors resulted in significant downfield perturbations of the 4,4'-bipyridyl and especially the amide protons (Table 4). Typically, an amide proton shift of $\Delta \delta = 0.1$ ppm was observed after the addition of two equivalents of the chloride salt. As noted previously, these results suggest that favourable amide CONH---Cl⁻ hydrogen bonding is a crucial contributing factor to the overall anion complexation process. Disappointingly, precipitation problems with the $ML^{2,3}$ Cl₂ (M = Pt, Pd) receptors precluded complete titration curves being obtained. However, stability constants for 1:1 receptor: chloride anion stoichiometry were determined from the titration data of the other receptors using the least squares curve fitting program EQNMR [14], and the results are summarized in Table 4. Within experimental error all four neutral platinum(II) and palladium(II) receptors complex the chloride anion with similar magnitudes of stability constant, suggesting neither the nature of the metal nor the alkyl or aryl





Fig. 5. PLUTON straw plot of the structure of $Pd(L^1)Cl_2$, illustrating the two-dimensional array of the molecules, held together by intermolecular hydrogen bonding.

substituent greatly influences the strength of halide anion binding. Interestingly, charged ruthenium(II) 5,5'-bis-amide-substituted 2,2'-bipyridyl receptor analogues [8] exhibited only slightly larger magnitudes of

Table 3. Selected torsion angles (°) in $Pt(L^2)Cl_2$ and $Pd(bipy)Cl_2$ [13]

| $Pt(L^2)Cl_2$ | |
|------------------------------------|--------|
| C(2) - C(3) - C(11) - N(12) | 163.3 |
| C(3)-C(11)-N(12)-C(14) | 171.7 |
| C(11) - N(12) - C(14) - C(15) | 104.1 |
| N(12)-C(14)-C(15)-C(16) | 173.9 |
| C(14) - C(15) - C(16) - C(17) | 72.4 |
| Pd(bipy)Cl ₂ | |
| C(2)-C(3)-C(21)-N(23) | -2.1 |
| C(3) - C(21) - N(23) - C(24) | 177.0 |
| C(21) - N(23) - C(24) - C(25) | - 75.9 |
| N(23)-C(24)-C(25)-C(26) | -70.6 |
| C(24) - C(25) - C(26) - C(27) | 164.4 |
| C(11)-C(10)-C(31)-N(33) | 37.1 |
| C(10)-C(31)-N(33)-C(34) | -172.9 |
| C(31) - N(33) - C(34) - C(35) | 134.4 |
| N(33)C(34)C(35)C(36) | -60.5 |
| C(34)— $C(35)$ — $C(36)$ — $C(37)$ | 172.8 |
| | |

stability constant with chloride in DMSO, of typical value 45 dm³ mol⁻¹, implying that the charged or neutral character of the transition metal bipyridyl coordinated Lewis acid centre is not critical to the inclusive thermodynamic stability of anion binding in these systems.

CONCLUSIONS

New acyclic neutral platinum(II) and palladium(II) 5,5'-bis-amide-substituted 2,2'-bipyridyl receptors have been prepared and the single-crystal structures of two receptors determined. Proton NMR chloride anion binding studies in deuteriated DMSO solution reveal that these neutral receptors complex the halide anion via favourable amide CO--NH---Cl⁻ hydrogen bonding interactions. Stability constant evaluations suggest the strength of halide anion binding is largely independent of the nature of the d^8 metal or the alkyl/aryl amide-linked substituent.

EXPERIMENTAL

Instrumentation

NMR spectra were recorded on a Bruker AM300 instrument using the solvent deuterium signal as an





^{*a*} Errors estimated to be $\leq 10\%$.

internal reference. Mass spectrometry was performed by the analytical services at Kodak Ltd, Harrow. Elemental analyses were performed at the Inorganic Chemistry Laboratory, University of Oxford. Unless stated to the contrary, commercial grade chemicals were used without further purification.

The preparation of the ligands have been described previously [8].

Synthesis

Platinum(II) (5,5'-bis(methoxyethylamido)-2,2'*bipyridine*) *dichloride* (PtL¹Cl₂), Ligand L¹ (36 mg, 0.101 mmol) was dissolved in methanol (20 cm³) with gentle heating, to which was added $K_2[PtCl_4]$ (47 mg, 0.114 mmol) in 50% aqueous acetonitrile (20 cm³). The reaction mixture was stirred for 4.5 h and filtered. The solvent was removed from the filtrate giving a yellow residue, and the product was isolated after recrystallization from methanol. Yield 44 mg, 70%. ¹H NMR (DMSO) : δ 3.29 (4H, m, NHCH₂CH₂), 3.32 (6H, s, OCH₃), 3.50 (4H, m, CH₂CH₂O), 8.75 (2H, d, J = 8.4 Hz, bipyCH⁴), 8.79 (2H, d, J = 8.5 Hz, bipyCH3), 9.15 (2H, bt, NH), 9.88 (2H, s, bipy CH6). Found: C, 34.9; H, 3.7; N, 7.7. Calc. for C₁₈H₂₂N₄ O₄Cl₂Pt: C, 34.6; H, 3.6; N, 8.0%. FAB-MS: [MH]⁺ 625, [M-Cl]⁺ 589.

Platinum(II) (5,5'-bis(butylamido)-2,2'-bipyridine)dichloride (PtL²Cl₂). Ligand L² (46 mg, 0.130 mmol) and K₂[PtCl₄] (85 mg, 0.205 mmol) were mixed in DMSO (20 cm³) and heated at 60°C for 1 h. Following additional stirring for 22 h at room temperature, the solvent was removed at reduced pressure at approx. 60°C to give a yellow solid. The residue was ground up, stirred in water (50 cm³) for 2 h, filtered and dried *in vacuo*, giving a red solid which went yellow on drying. Yield 51 mg, 63%. ¹H NMR (DMSO) : δ 0.91 (6H, t, J = 7.2 Hz, CH₂CH₃), 1.33 (4H, m, CH₂CH₂CH₃), 1.54 (4H, m, CH₂CH₂CH₂), 2.37 (4H, m, NHCH₂CH₂), 8.75 (4H, s, bipyCH³ and bipyCH⁴), 9.01 (2H, t, J = 5.3 Hz, NH), 9.87 (2H, d, J = 2.0 Hz, bipyCH⁶). Found : C, 37.8 ; H, 4.1 ; N, 8.3. Calc. for C₂₀H₂₆N₄O₂Cl₂Pt · 2H₂O : C, 38.7 ; H, 4.2 ; N, 9.0%. FAB-MS : [MH]⁺ 620, [M-Cl]⁺ 579.

Platinum(II) (5,5'-bis(3,4-dimethoxyphenylamido)-2,2'-bipyridine) dichloride (PtL³Cl₂). Using ligand L³, an analogous synthetic procedure was used as in the preparation of Pt(L²)Cl₂. Yield 78%. ¹H NMR (DMSO) : δ 3.76 (6H, s, OCH₃), 3.78 (6H, s, OCH₃), 6.98 (2H, d, J = 9.3 Hz, ArCH⁵), 7.33 (2H, d, J = 8.2 Hz, ArCH⁶), 7.45 (2H, s, ArCH²), 8.84 (2H, d, J = 9.8 Hz, bipyCH⁶), 8.94 (2H, d, J = 7.8 Hz, bipyCH³), 9.96 (2H, s, bipyCH⁶), 10.68 (2H, s, NH). Found : C, 42.2; H, 3.1; N, 6.8. Calc. for C₂₈H₂₆N₄O₆Cl₂Pt: C, 43.1; H, 3.4; N, 7.2%. FAB-MS: [MH]⁺ 780, [M-Cl]⁺ 744.

Platinum(II) (5,5'-bis(4-hydroxyphenylamido)-2,2'bipyridine) dichloride (PdL⁴Cl₂). Using ligand L⁴, an analogous synthetic procedure was used as in the preparation of Pt(L¹)Cl₂. Yield 68%. ¹H NMR (DMSO) : δ 6.78 (4H, d, J = 8.3 Hz, PhCH²), 7.55 (4H, d, J = 8.2 Hz, PhCH³), 8.82 (2H, d, J = 8.2 Hz, bipyCH⁴), 8.92 (2H, d, J = 8.0 Hz, bipyCH³), 9.41 (2H, s, bipyCH⁶), 9.92 (2H, s, OH), 10.59 (2H, s, NH). Found : C, 39.5; H, 2.8; N, 6.9. Calc. for C₂₄H₁₈N₄O₄Cl₂Pt · 2H₂O : C, 39.6; H, 3.0; N, 7.7%.

Palladium(II) (5,5'-bis(methoxyethylamido)-2,2'-bipyridine) dichloride (PdL¹Cl₂). Using ligand L¹, an analogous synthetic procedure was used as in the preparation of Pt(L¹)Cl₂. Yield 89%. ¹H NMR (DMSO) :

δ 3.28 (4H, m, NHCH₂CH₂), 3.34 (6H, s, OCH₃), 3.49 (4H, m, CH₂CH₂O), 8.74 (2H, d, J = 8.4 Hz, bipyCH⁴), 8.76 (2H, d, J = 8.4 Hz, bipyCH³), 9.12 (2H, bt, NH), 9.50 (2H, s, bipyCH⁶). Found : C, 40.2 ; H, 3.8 ; N, 10.5. Calc. for C₁₈H₂₂N₄O₄Cl₂Pd : C, 40.4 ; H, 4.1 ; N, 10.5%. FAB-MS : [MH]⁺ 535, [M-Cl]⁺ 501, [MH-2Cl]⁺ 460.

Palladium(II) (5,5'-bis(3,4-dimethoxyphenylamido)-2,2'-bipyridine) dichloride (PdL²Cl₂). Using ligand L³, an analogous synthetic procedure was used as in the preparation of Pt(L²)Cl₂, giving a brown solid. Yield 68%. ¹H NMR (DMSO) : δ 3.77 (6H, s, OCH₃), 3.79 (6H, s, OCH₃), 7.00 (2H, bd, ArCH⁵), 7.35 (2H, bd, Hz, ArCH⁶), 7.47 (2H, s, ArCH²), 8.8–8.9 (4H, m, bipyCH⁴ and bipyCH³), 9.62 (2H, s, bipyCH⁶), 10.68 (2H, s, NH). Found : C, 44.7; H, 3.4; N, 7.1. Calc. for C₂₈H₂₆N₄O₆Cl₂Pd : C, 48.6; H, 3.8; N, 8.1%.

Palladium(II) (5,5'-bis(4-hydroxyphenylamido)-2,2'-bipyridine) dichloride (PdL⁴Cl₂). Using ligand L⁴, an analogous synthetic procedure was used as in the preparation of Pt(L²)Cl₂. Yield 67%. ¹H NMR

(DMSO):
$$\delta$$
 6.78 (4H, d, $J = 8.4$ Hz, PhCH²), 7.54
(4H, d, $J = 8.4$ Hz, PhCH³), 8.82 (2H, d, $J = 8.2$ Hz,
bipyCH⁴), 8.87 (2H, d, $J = 8.1$ Hz, bipyCH³), 9.41
(2H, s, bipyCH⁶), 9.53 (2H, s, OH), 10.57 (2H, s,
NH). Found: C, 46.0; H, 3.0; N, 8.7. Calc. for
C₂₄H₁₈N₄O₄Cl₂Pd·H₂O: C, 46.4; H, 3.2; N, 9.0%.

Crystal structure analysis

Crystal data are given in Table 5, together with refinement details. Data for both crystals were collected with Mo- K_{α} radiation using the MARresearch Image Plate System. The crystals were positioned at 75 mm from the Image Plate. Ninety-five frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program [15]. Both structures were solved using heavy atom methods with the SHELX86 program [16]. In both structures the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen

Table 5. Crystal data and structure refinement for $Pt(L^2)Cl_2$ and $Pd(L^1)Cl_2$

| Compound | $Pt(L^2)Cl_2$ | $Pd(L^1)Cl_2$ |
|---|-------------------------------|--------------------------------|
| Empirical formula | $C_{24}H_{38}Cl_2N_4O_4PtS_2$ | $C_{18}H_{22}Cl_2N_4O_4Pd$ |
| Formula weight | 1553.38 | 1071.39 |
| Temperature (K) | 293(2) | 293(2) |
| Wavelength (Å) | 0.71072 | 0.71072 |
| Crystal system | monoclinic | orthorhombic |
| Space group | C2/c | Pbca |
| Unit cell dimensions | | |
| a (Å) | 28.64(2) | 8.147(8) |
| b (Å) | 9.066(9) | 27.319(17) |
| $c(\mathbf{A})$ | 11.907(11) | 17.769(12) |
| β(°) | 103.31(1) | (90) |
| Volume (Å ³) | 3008(5) | 3955(3) |
| Z | 4 | 8 |
| Density (calculated) (Mg m^{-3}) | 1.715 | 1.799 |
| Absorption coefficient (mm^{-1}) | 5.017 | 1.243 |
| F(000) | 1544 | 2160 |
| Crystal size (mm ³) | $0.2 \times 0.3 \times 0.2$ | $0.15 \times 0.25 \times 0.25$ |
| θ range for data collection | 2.84-24.88 | 2.29-24.94 |
| Index ranges | $0 \le h \le 33$ | $0 \leq h \leq 9$ |
| - | $-9 \leq k \leq 9$ | $-32 \le k \le 32$ |
| | $-13 \leq l \leq 13$ | $-20 \le l \le 20$ |
| Reflections collected | 2604 | 11,508 |
| Independent reflections | 1723 | 3245 |
| R(int) | 0.0581 | 0.0738 |
| Data/parameters | 1723/170 | 3205/268 |
| Weighting scheme $(a, b)^a$ | 0.21, 20.56 | 0.06, 111.28 |
| Goodness-of-fit on F^2 | 1.202 | 1.179 |
| Final R indices $[I > 2\sigma(I)]$ | | |
| R_1 | 0.0872 | 0.0772 |
| R_{w2} | 0.2724 | 0.1426 |
| R indices (all data) | | |
| R_1 | 0.0996 | 0.1120 |
| R_{w2} | 0.2959 | 0.1871 |
| Largest diff. peak and hole (e $Å^{-3}$) | 1.664, -1.555 | 1.102, -0.706 |

^a Weighting scheme : $w = 1/(\sigma^2 (F_o^2) + (aP)^2 + bP)$, where $P = (F_0^2 + 2F_c^2)/3$.

atoms were included in geometric positions and were given thermal parameters equivalent to 1.2 times that of the atom to which they were bonded. Both structures were refined using SHELXL [17]. All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading. Unfortunately, in the structure refinement of Pt(L2)Cl₂, C(4) and C(5) could not be refined with positive definite thermal parameters, presumably because of some slight disorder, and were given isotropic thermal parameters. Diagrams were prepared using PLATON [18] and PLUTON [19].

Acknowledgements—We thank the EPSRC for a CASE studentship (N.C.F.) and Kodak Ltd for additional financial support. Additionally, we thank the EPSRC and the University of Reading for funds for the Image Plate System.

REFERENCES

- Dietrich, B., Pure Appl. Chem., 1993, 65, 1457; Pierre, J. L. and Baret, P., Bull. Soc. Chim. Fr., 1983, 367; Dietrich, B., in Inclusion Compounds, Vol. 2, ed Atwood, J. L., Davies, J. E. D. and MacNicol, D. D., Academic Press, New York, 1984, p. 337; F. P. Schmidtchen, Nachr. Chem. Tech. Lab., 1988, 36, 8.
- 2. Beer, P. D., Chem. Commun., 1996, 689.
- Hosseini, M. W., Blacker, A. J. and Lehn, J.-M., J. Am. Chem. Soc., 1900, 112, 3896 and refs therein; Schmidtchen, F. P., J. Org. Chem., 1986, 51, 5161; Beer, P. D., Wheeler, J. W., Greive, A., Moore, C. and Wear, T., J. Chem. Soc., Chem. Commun., 1992, 1225; Furuta, H., Cyr, M. and Sessler, J. L., J. Am. Chem. Soc., 1991, 113, 6677.
- Katz, H. E., Organometallics, 1987, 6, 1134; Wuerst, J. D. and Zacharie, B., J. Am. Chem. Soc., 1987, 109, 4714; Blandon, M. T., Horner, J. N. and Newcombe, M., J. Org. Chem. 1989, 54, 4626; Reetz, M. T., Niemeyer, C. M. and Harms, K., Angew. Chem., Int. Edn Engl., 1991, 30, 1472; Rudkevich, D. M., Stauthamer, W. P. R. V.,

Verboom, W., Engbersen, J. F. J., Harkema, S. and Reinhoudt, D. N., J. Am. Chem. Soc., 1992, 114, 9671.

- Beer, P. D., Hazlewood, C., Hesek, D., Hodacova, J. and Stokes, S. E., J. Chem. Soc., Dalton Trans., 1993, 1327; Beer P. D., Chen, Z., Goulden, A. J., Graydon, A. R., Stokes, S. E. and Wear, T., J. Chem. Soc., Chem. Commun. 1993, 1834; Beer, P. D., Drew, M. G. B., Graydon, A. R., Smith, D. K. and Stokes, S. E., J. Chem. Soc., Dalton Trans., 1995, 403.
- Beer, P. D., Dickson, C. A. P., Fletcher, N. C., Goulden, A. J., Grieve, A., Hodacova, J. and Wear, T. J. Chem. Soc., Chem. Commun., 1993, 828.
- Beer, P. D., Chen, Z., Goulden, A. J., Grieve, A., Hesek, D., Szemes, F. and Wear, T., J. Chem. Soc., Chem. Commun., 1994, 1269; Szemes, F. and Beer, P. D., J. Chem. Soc., Chem. Commun., 1995, 2245.
- Beer, P. D., Fletcher, N. C. and Wear, T., Polyhedron, 1996, 15, 1339.
- 9. Morgan, G. T. and Burstall, F. H., J. Chem. Soc., 1934, 965.
- 10. Palocsay, F. A. and Rund, J. V., Inorg. Chem., 1969, 8, 524.
- Textor, Von M. and Oswald, H. R., Z. Anorg. Allg. Chem., 1974, 407, 244; Bielli, E., Gidney P. M., Gillard, R. D. and Heaton, B. T., J. Chem. Soc., Dalton Trans., 1974, 2133.
- Osborn, R. S. and Rodgers, D., J. Chem. Soc., Dalton Trans., 1974, 102; Herber, R. H., Croft, M., Coyer, M. J., Bilash, B. and Sahiner, A., Inorg. Chem., 1994, 33, 2422.
- Canty, A. J., Minchin, N. J., Skelton, B. W. and White, A. H., Aust. J. Chem., 1992, 45, 423.
- 14. Hynes, M. J., J. Chem. Soc., Dalton Trans., 1993, 311.
- 15. Kabsch, W., J. Appl. Cryst. 1988, 21, 916.
- 16. Sheldrick, G. M., Acta Cryst. 1990, A46, 467.
- Sheldrick, G. M., SHELXL: Program for Crystal Structure Refinement. University of Gottingen, 1993.
- 18. Spek, A. L., Acta Cryst. 1990, A46, C34.
- 19. PLUTON: Molecular Graphics Program, Utrecht University, Utrecht, The Netherlands, 1996.