The Preparation and Coordination Chemistry of 2,6-Diacetylpyridine Bis(6-chloro-2-pyridylhydrazone)

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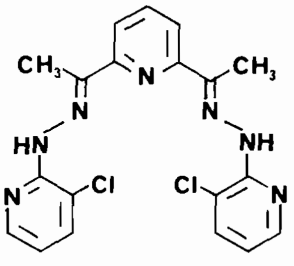
Abstract

The condensation of 2,6-diacetylpyridine with 6-chloro-2-hydrazinopyridine in the presence of acid results in the formation of the novel pentadentate ligand 2,6-diacetylpyridine bis(6-chloro-2-pyridylhydrazone). The ligand is planar, and forms complexes with a wide range of transition and non-transition metal ions. A number of geometries appear to be adopted, although a number of pentagonal bipyramidal complexes were characterised.

Introduction

There has been much interest in the past decade in complexes of multidentate ligands which impose 'uncommon' geometries or coordination numbers upon metal ions [1]. Five-coordinate complexes have attracted particular attention, and numerous pentadentate ligands have been designed [2]. Ligands incorporating imine-type nitrogen donor atoms have been shown to be of interest [3]. Early examples of this type of ligand include 2,6-diacetylpyridine bis(semicarbazone) (dapscH_2), 2,6-diacetylpyridine bis(benzoylhydrazone) (dapbhH_2) and 2,6-diacetylpyridine bis(2-pyridylhydrazone) (dapphH_2) [4]. Over the past few years we have investigated the preparation and coordination chemistry of macrocyclic ligands closely related to dapphH_2 [5], and recently became interested in the properties of sterically hindered open chain analogues. In this paper, we report the preparation of the novel, potentially pentadentate, ligand 2,6-diacetylpyridine bis(6-chloro-2-pyridylhydrazone) (L), and describe some aspects of its coordination chemistry.



L

Experimental

6-Chloro-2-hydrazinopyridine

2,6-Dichloropyridine (5.0 g, 33.8 mmol) was added to hydrazine hydrate (25 cm^3), and the suspension heated to reflux under a dinitrogen atmosphere for 4 h, after which time a clear solution had been obtained. This was allowed to cool overnight, when 6-chloro-2-hydrazinopyridine was obtained as off-white crystals (4.0 g, 82%). *Anal.* Found: C, 41.4; H, 4.0; N, 29.4. Calc. for $C_5H_6N_3Cl$: C, 41.8; H, 4.2; N, 29.3% (M^+, m/z 143, 145; ^1H NMR, $CDCl_3$, 7.5, 1H, dd, 7.4 Hz, 8.3 Hz; 6.7, 1H, dd, 8.3 Hz, 0.8 Hz; 6.7, 1H, dd, 7.4 Hz, 0.7 Hz; 6.3, 1H, bs; 3.5, 2H, bs).

2,6-Diacetylpyridine Bis(6-chloro-2-pyridylhydrazone) (L)

2,6-Diacetylpyridine (0.336 g, 2 mmol) and 6-chloro-2-hydrazinopyridine (0.574 g, 4 mmol) were heated to reflux in methanol (100 cm^3) containing concentrated hydrochloric acid (3 drops) for 2 h, after which time an intense orange solution had been obtained. Treatment with ammonium hexafluorophosphate (1.0 g), followed by concentration *in vacuo* gave well formed orange crystals of $[H_2L][PF_6]_2$ (0.874 g, 78%). *Anal.* Found: C, 40.6; H, 3.3; N, 18.0. Calc. for $C_{19}H_{17}N_7Cl_2$: C, 40.7; H, 3.2; N, 17.6%. (M^+, 413, 415, 417; ^1H NMR, CD_3SOCD_3, 8.1, 2H, d, 7.8 Hz; 7.9, 1H, t, 7.5 Hz; 7.7, 2H, t, 7.9 Hz; 7.32, 2H, d, 7.9 Hz; 6.9, 2H, d, 7.5 Hz; 6.3, 2H, bs; IR, 3278, 1610, 1591, 1510, 1431, 838 and 556 cm^{-1}).

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Preparation of Metal Complexes

Method 1

$[H_2L][PF_6]_2$ (0.1 mmol) and the appropriate metal acetate or chloride (0.1 mmol) were heated to reflux in methanol (25 cm^3) until all solids had dissolved, and no further colour changes had occurred (1–2 h). The solution so obtained was treated with ammonium hexafluorophosphate and concentrated to give the metal complexes in 70–80% yield.

Method 2

2,6-Diacetylpyridine (0.1 mmol), metal acetate or chloride (0.1 mmol) and 6-chloro-2-hydrazinopyridine (0.2 mmol) were heated to reflux in methanol (25 cm^3) containing concentrated hydrochloric acid (1 drop) for 1 h, after which period the solution was treated with ammonium hexafluorophosphate. The orange solution was concentrated *in vacuo*, to give the metal complexes as crystalline solids.

Results and Discussion

The reaction of 2,6-dichloropyridine with hydrazine hydrate leads to the formation of the monosubstituted derivative, 6-chloro-2-hydrazinopyridine in high yield. The product was fully characterised on the basis of its spectroscopic properties, which are otherwise unremarkable. Even after prolonged reaction times, no evidence for the formation of 2,6-bis(hydrazino)pyridine was obtained in this reaction. In contrast, the bis(hydrazino) compound was the major product when 2,6-dibromopyridine was reacted with hydrazine hydrate. It is interesting to note, that the replacement of the hydrazine by the better nucleophile, methylhydrazine, resulted in the formation of bis(methylhydrazino) compounds from both 2,6-dichloro and 2,6-dibromopyridine [6].

The condensation of 6-chloro-2-hydrazinopyridine with 2,6-diacetylpyridine occurs smoothly in the presence of acid to yield the orange bis(hydrazone) salt, $[H_2L][PF_6]_2$. The spectroscopic properties of the bis(hydrazone) are fully in accord with the proposed structure. The ^1H NMR spectrum indicates a highly symmetrical, C_{2v}, structure in solution. We have also determined the crystal and molecular structure of the cation in the solid state, and shown it to possess the near planar ***transoid*** arrangement shown in Scheme 1 [7].

Metal complexes of the new pentadentate ligand could be prepared by the reaction of the performed ligand with a metal salt, or by a template condensation of 2,6-diacetylpyridine with 2-chloro-6-hydrazinopyridine in the presence of a metal ion. The same products were obtained in each case.

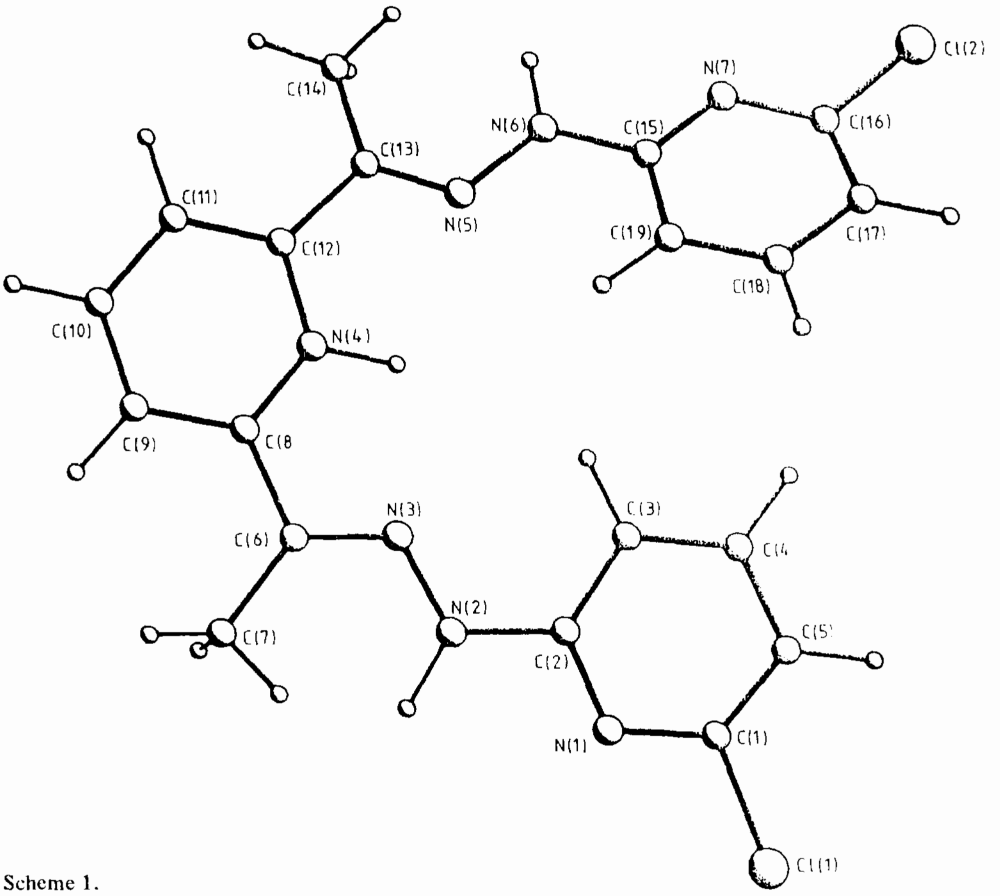
TABLE I. Analytical Data

Compound	Found (Calculated) (%)		
	C	H	N
$[FeLCl(MeOH)][PF_6]$	35.3 (35.2)	3.2 (3.1)	14.3 (14.4)
$[CoL(H_2O)_2][PF_6]_2$	28.3 (28.3)	2.7 (2.7)	12.2 (12.2)
$[NiL(OH)(H_2O)][PF_6]$	35.1 (34.9)	2.9 (3.0)	15.3 (15.0)
$[CuLCl(H_2O)][PF_6]$	34.1 (33.7)	2.8 (2.8)	14.3 (14.5)
$[CuL(H_2O)_2]$-$[PF_6]\cdot H_2O$	33.7 (33.7)	2.9 (3.4)	14.1 (14.4)
$[ZnL][PF_6]_2$	29.7 (29.6)	2.3 (2.2)	12.7 (12.7)
$[\{ZnL\}_2]$	47.9 (47.8)	3.3 (3.1)	20.5 (20.5)
$[PdL]\cdot 2H_2O$	41.5 (41.2)	3.7 (3.7)	17.5 (17.6)
$[\{AgL\}_2][PF_6]_2$	34.5 (34.2)	2.6 (2.6)	14.7 (14.7)
$[HL][AuCl_4]$	29.2 (29.0)	3.1 (2.8)	12.5 (12.5)
$[UO_2L][PF_6]_2\cdot H_2O$	22.9 (23.0)	2.0 (1.7)	9.8 (9.8)
$[SnMe_2L][PF_6]_2\cdot 2H_2O$	28.3 (18.3)	2.7 (3.0)	11.0 (11.0)
$[CdLCl][PF_6]$	32.4 (32.3)	2.7 (2.4)	13.8 (13.9)

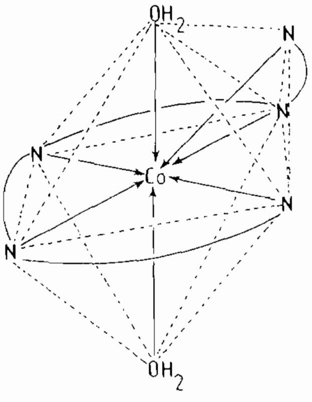
Complexes of the new pentadentate ligand were obtained with iron(II), cobalt(II), nickel(II), copper(II), copper(I) and zinc(II). Analytical data for the complexes obtained are given in Table I. No complexes were isolated from attempted template reactions in the presence of, or reactions of the free ligand with, oxovanadium(V), chromium(III) or manganese(II). This is not unexpected for vanadium(V) or chromium(III), where pentagonal planar or pentagonal bipyramidal complexes are extremely uncommon [8, 9]. In the case of manganese(II), five and seven coordinate geometries about the metal are rather more common, but generally occur in macrocyclic complexes, in which the ligand forces the geometry on the cation.

The purple complex, $[FeLCl][PF_6]$, was obtained as a mono methanolate from the reaction of $[H_2L][PF_6]_2$ with iron(II) chloride in methanol. The compound is probably a pentagonal bipyramidal species, with the axial sites occupied by a methanol molecule and chloride ion.

The dark brown complex $[CoL(H_2O)_2][PF_6]_2$ was obtained by either of the two methods described above. The infrared spectrum of the complex exhibited stretching frequencies at 3351 and 3372 cm^{-1} attributed to the secondary NH groups, and also bands at 3613 and 3545 cm^{-1} due to the coordinated water molecules. There is a single imine stretching mode at 1606 cm^{-1}. This doubling of the NH and OH modes suggests that a distorted geometry is adopted, rather than a regular pentagonal bipyramid. We suggest that the complex may adopt a capped octahedral geometry (Scheme 2), with the quasi-helical geometry forced upon the metal by the bulky chloro substituents on the terminal pyridyl rings. The complex was paramagnetic, with a magnetic moment of 4.67 BM, as expected for a d^7 cobalt(II) ion in a



Scheme 1.



Scheme 2.

pseudo-octahedral field. This value may be compared with values of 4.47 BM for [Co(dapphH$_2$)I]I [10] and 5.25 BM for [Co(dapphH$_2$)(H$_2$O)$_2$]Cl$_2$ [11]. The cyclic voltammogram of acetonitrile solutions of the complex exhibited a reversible oxidation to the cobalt(III) complex at $E_{1/2}$ = 0.00 V (*vs* Ag$^+$, MeCN, Ag). No reduction waves, either reversible or irreversible, could be detected, even at rapid scan rates. This same cobalt(III) species could be obtained by aerial oxidation of methanol solutions of [CoL(H$_2$O)$_2$][PF$_6$]$_2$ in the presence of activated charcoal. The infrared spectrum of the isolated yellow cobalt(III) complex showed a single imino stretch and no NH modes. This suggests that the secondary NH groups have become deprotonated. This was supported by microanalysis of the product, which suggested a formulation [Co(L–2H)(MeCN)$_2$][PF$_6$]. The complex was diamagnetic, as expected for a low spin d^6 ion. The ability of cobalt(III) to stabilise deprotonated amido functionalities in potentially pentadentate ligands has been noted previously [12].

The very dark brown nickel(II) complex is readily obtained from aqueous methanolic solution. Microanalysis of the solid material indicated a formulation, [NiL(H$_2$O)OH][PF$_6$] or [Ni(L–H)(H$_2$O)$_2$][PF$_6$]. The infrared spectrum does not exhibit any absorptions in the 3000–3300 cm^{-1} region, which is not completely compatible with either of the above formulations. The magnetic moment of the complex was determined to be 3.39 BM, which is relatively high for a pseudo-octahedral nickel(II) centre. It is possible that this is due to a large amount of spin-orbit coupling to the ground state, as expected for such a low symmetry ligand.

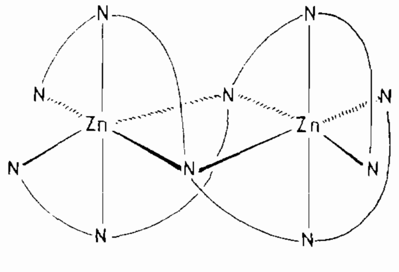
The deep purple copper complex, $[CuLCl(H_2O)][PF_6]$, is readily prepared by the reaction of copper(II) chloride with either the preformed ligand, or with 2,6-diacetylpyridine and 6-chloro-2-hydrazinopyridine. The magnetic moment of the complex was determined to be 1.51 BM, which is considerably below the expected spin-only value of 1.73 BM. This suggests a considerable spin-exchange interaction between adjacent centres. It is well known that one of the curious features of the magnetic behaviour of copper(II) is the large number of complexes in which spin-exchange occurs between the copper atoms, even in systems which would be expected to be magnetically dilute. The effect of the stereochemistry about the metal atom has been shown to have relatively little effect on the observed magnetic moment [13]. We propose the complex is a pentagonal bipyramid, with the pentadentate ligand occupying the equatorial sites, and the chloride and water ligands in the axial positions. The ESR spectrum is in accord with this formulation. The spectrum exhibits the expected ordering of g values $g_\perp > g_\parallel \simeq 2$, with precise values of $g_\perp = 2.202$, $g_\parallel = 2.046$, $A_\parallel = 123.3$ G. These parameters correspond closely with those reported for the structurally characterised pentagonal bipyramidal copper(II) complex with the bis-Schiff base derived from 2,6-diacetylpyridine and diethylenetriamine ($g_\parallel = 2.03$, $g_\perp = 2.20$, $A_\parallel = 132$ G) [14], and are consistent with a $(d_{z^2})^1(d_{x^2-y^2})^2$ ground state.

Cyclic voltammetric studies of acetonitrile solutions of the complex revealed a reversible reduction wave centred at $E_{1/2} = +0.008$ V (*vs.* Ag^+, MeCN, Ag), corresponding to reduction to a copper(I) complex. The reversibility of the reduction wave at all scan speeds investigated strongly suggests that there are no major structural changes associated with the reduction. It is tempting to propose the formation of a pentagonal bipyramidal copper(I) complex, although further studies are required to establish this formulation. The copper(I) complex $[CuL(H_2O)_2][PF_6]\cdot H_2O$ was isolated from the reaction of $[Cu(MeCN)_4][PF_6]$ with $[H_2L][PF_6]_2$ in aqueous acetonitrile, and exhibited an identical cyclic voltammogram to the previously described copper(II) complex. On the basis of these observations, combined with the ESR spectra, we propose pentagonal bipyramidal solution species $[CuL(MeCN)_2]^{n+}$.

The zinc complexes are also of some interest. The reaction of zinc acetate or zinc chloride with either 2,6-diacetylpyridine and 6-chloro-2-hydrazinopyridine or $[H_2L][PF_6]_2$ gives the yellow product $[ZnL][PF_6]_2$. Treatment of the complex with sodium hydroxide solution leads to the formation of an intensely purple solution. This colour change could be followed by electronic spectroscopy. The yellow solution of the zinc complex exhibits absorption maxima at 48 310 and 30 120 cm^{-1}, whereas the purple solution shows maxima at 49 750, 29 410, 35 970 and 23 585 cm^{-1}. The colour change is fully reversible upon the addition of acid. Concentration of the purple solution *in vacuo* results in the deposition of a purple solid, soluble in both polar and non-polar solvents. Microanalysis of the purple solid indicated a stoichiometry $[Zn(L-2H)]$, and the infrared spectrum showed two imine stretches at 1606 and 1585 cm^{-1}, and no NH stretches in the 3000–3500 cm^{-1} region. The mass spectrum of the complex exhibited peaks due to a parent ion at $m/z = 952-964$; the relative intensities were exactly those expected for $[\{Zn(L-2H)\}_2]$. The mass spectrum also exhibited peaks at $m/z = 476-482$, corresponding to the monomer $[ZnL]$. We propose that the complex is dimeric with an octahedral geometry about each zinc ion (Scheme 3). This is fully in accord with the crystallographically determined structure of the complex $[\{Zn(dapph)\}_2]$, which is formed by the reaction of base with $[ZnL]Cl_2$ [15]. The deprotonated ligand in the dpph complex is not planar, but is twisted about the C—C bond between the central pyridine ring and the side chain. We have already shown that this same non-planarity is seen in the dimeric complex $[\{AgL\}_2][PF_6]_2$ [16].

The reactions of $[H_2L][PF_6]_2$ with a range of other transition and non-transition metal ions was also investigated. In general the products of these reactions were not fully characterised.

Reaction with cadmium(II) chloride resulted in the formation of the pale yellow complex $[CdLCl][PF_6]$. It seems likely that this complex exhibits some distorted six-coordinate geometry. Treatment with base led to the formation of dark coloured solutions, but no solid materials could be isolated from these. In contrast, no complexes could be isolated from the interaction of $[H_2L][PF_6]_2$ with mercury(II) acetate or mercury(II) chloride. This probably represents the preference of mercury(II) for low-coordination numbers.

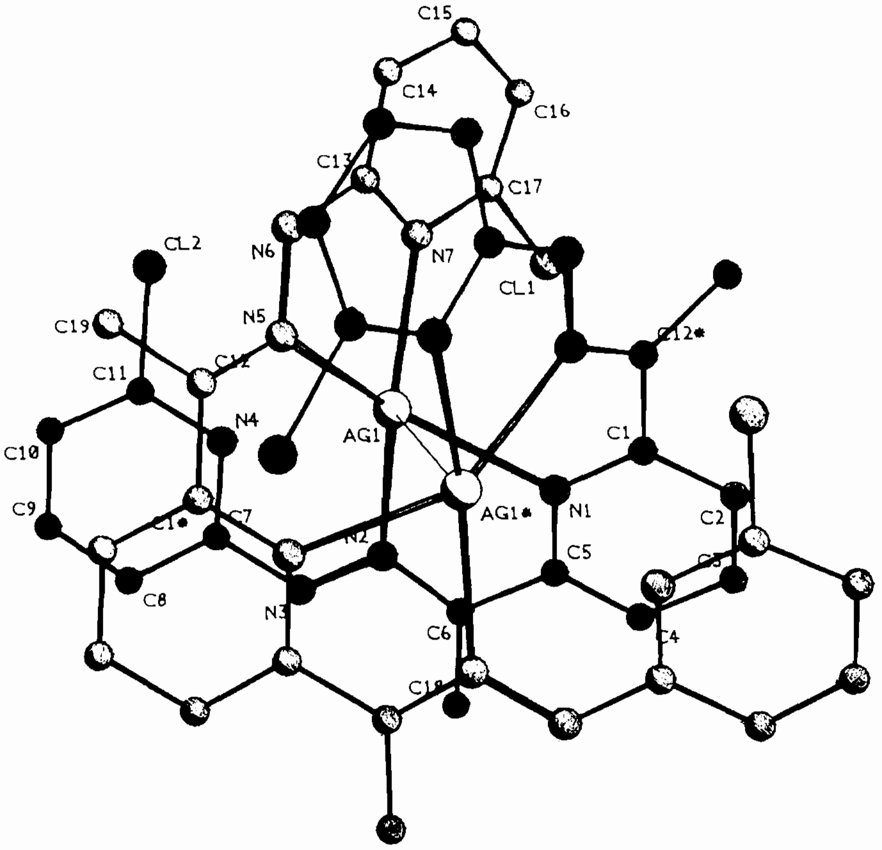


Scheme 3.

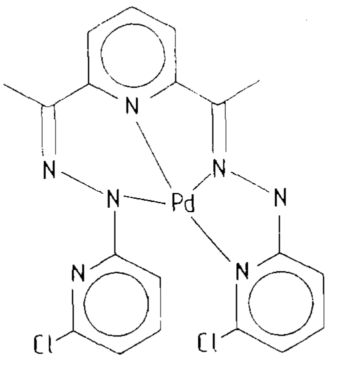
The free ligand reacted rapidly with silver(I) compounds, to give pale yellow solutions from which the dimeric complex $[\{AgL\}_2][PF_6]_2$ could be obtained upon the addition of ammonium hexafluorophosphate. The complex exhibited a single imine stretch at 1597 cm^{-1} and a single NH stretch at 3103 cm^{-1}. The ^1H NMR spectrum indicated that the complex possessed pseudo C_{2v} symmetry on the NMR timescale. In particular, a single resonance at 2.88 was observed for the methyl groups of the complex. No coupling to the silver ($I = 1/2$) nucleus was observed in the NMR spectrum. A crystal structural analysis of the complex confirmed the proposed dimeric formulation (Scheme 4) [16]. Each silver atom is bonded to both ligand molecules, and is in a very distorted tetrahedral environment, being bonded to four nitrogen atoms from the two ligands with a short Ag–N distance (236.1 pm) and a longer Ag–N interaction (272.3 pm). One of the 6-chloropyridyl groups of each ligand is not coordinated to a metal ion. The silver–silver distance is short (314 pm), although it is significantly longer than that observed in silver metal (289.9 pm).

The reaction of $[H_2L][PF_6]_2$ with either $Na[AuCl_4]$ or $H[AuCl_4]$ resulted in the formation of a copper coloured microcrystalline solid, $[HL][AuCl_4]$. The infrared spectrum exhibited absorptions at 355 cm^{-1} which may be assigned to the tetrachloroaurate counter ion. The metallic appearance suggests an unusual electronic structure, and we propose that a stacked arrangement of planar cations and anions is formed. This is in accord with the planar structure of the dication described earlier. Attempts to incorporate other metals into this system to give one-dimensional solids were unsuccessful. Treatment with nickel(II) or copper(II) salts merely resulted in the formation of the expected nickel(II) or copper(II) complexes, and the deposition of metallic gold. This is probably due to the conformational changes of the ligand associated ith coordination to the transition metal ion.

The reaction of $[H_2L][PF_6]_2$ with acetonitrile solutions of palladium(II) acetate resulted in immediate colour changes to give, initially, a deep green solution, and finally a deep purple solution. Concentration of the purple solution gave a purple solid,



Scheme 4.



Scheme 5.

which was shown by microanalysis to be of stoichiometry [Pd(L−2H)]·$2H_2O$. Although the colour suggests a similarity to the dimeric zinc complex, it does not seem likely that palladium(II) will form pseudo-octahedral complexes. No satisfactory mass spectrum could be obtained for the palladium complex. The ^1H NMR spectrum of the complex showed nine resonances in the aromatic region and two distinct methyl resonances (2.42, 2.72). This indicates an asymmetrical structure in which the two 6-chloropyridyl groups are chemically distinct. We believe that the complex is mononuclear, with a diprotonated ligand, and propose a structure of the type shown in Scheme 5. Similar structures have been proposed for the nickel(II) complex of the dianion $dpph^{2-}$ [17], and the palladium complex [Pd(paphy)Cl] (paphyH = 2-pyridinealdehyde 2-pyridylhydrazone) [18].

No complexes could be isolated from the reaction of $[H_2L][PF_6]_2$ with $K_2[PtCl_4]$ or $[Pt(cod)Cl_2]$.

The reaction of $[H_2L][PF_6]_2$ with dioxouranium(VI) acetate gave an orange solution, from which the yellow salt $[UO_2L][PF_6]_2$ could be isolated by the addition of ammonium hexafluorophosphate. The infrared spectrum of the complex exhibited a single NH stretch at 3335 cm^{-1}, a single imine stretch at 1592 cm^{-1}, and a single U=O stretching mode at 966 cm^{-1}. The fundamental frequency of the U=O stretching mode may be related to the bond length, and corresponds to a bond length of 168.1 pm. This suggests a considerable degree of back donation from the dioxouranium(VI) ion to the antibonding levels of the ligand [19]..

Although dichlorodimethyltin(IV) would not react with methanolic solutions of $[H_2L][PF_6]_2$ directly, a smooth reaction occurred with the free ligand L, obtained by prior reaction of $[H_2L][PF_6]_2$ with triethylamine. The product of the reaction was the yellow complex $[SnMe_2L][PF_6]_2$. This complex exhibited C_{2v} symmetry on the NMR timescale. The tin-bonded methyl groups were observed at 1.67, and exhibited low-intensity satellites due to coupling to ^{119}Sn (105 Hz) and ^{117}Sn (100 Hz), typical for a *trans* diaxial arrangement of the dimethyl groups [20]. This is fully consistent with trigonal bipyramidal or pentagonal bipyramidal geometry at the metal.

In conclusion, we have demonstrated that the novel pentadentate ligand, 2,6-diacetylpyridine bis(6-chloro-2-pyridylhydrazone) is a versatile complexing agent, with a rich coordination chemistry. A variety of bonding modes may be adopted, and we are continuing structural studies of the complexes described above. One of the aims of the work was the preparation of novel macrocyclic ligands by the displacement of the chlorine substituents of the terminal pyridyl rings by nucleophilic substitution with suitable nucleophiles. In no case have we been able to achieve such a reaction.

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References

1 K. F. Purcell and J. C. Kotz, 'Inorganic Chemistry', W.B. Saunders, Philadelphia, 1977.

2 J. S. Wood, *Prog. Inorg. Chem.*, *16*, 227 (1972); B. F. Hoskins and F. D. Williams, *Coord. Chem. Rev.*, *9*, 365 (1972); C. Furliani, *Coord. Chem. Rev.*, *3*, 141 (1968).

3 L. F. Lindoy and S. E. Livingstone, *Coord. Chem. Rev.*, *2*, 173 (1967).

4 D. Wester and J. Palenik, *J. Am. Chem. Soc.*, *95*, 6505 (1973); *J. Am. Chem. Soc.*, *96*, 7565 (1974); *Inorg. Chem.*, *15*, 755 (1976); D. D. McRitchie, R. C. Palenik and G. J. Palenik, *Inorg. Chim. Acta*, *20*, L27 (1976); T. J. Gordiano, G. J. Palenik, R. C. Palenik and D. A. Sullivan, *Inorg. Chem.*, *18*, 2445 (1979).

5 E. C. Constable, F. K. Khan, J. Lewis, M. C. Liptrot and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 333 (1985); E. C. Constable, J. M. Holmes and R. C. S. McQueen, *J. Chem. Soc., Dalton Trans.*, (1986) in press, and refs. therein.

6 E. C. Constable and J. M. Holmes, *Inorg. Chim. Acta*, to be submitted.

7 E. C. Constable, J. M. Holmes and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, in press.

8 G. J. Palenik, D. W. Webster, U. Rychlewska and R. C. Palenik, *Inorg. Chem.*, *15*, 1814 (1976).

9 L.-Y. Chung, E. C. Constable, M. S. Khan, J. Lewis, P. R. Raithby and M. D. Vargas, *J. Chem. Soc., Chem. Commun.*, 1425 (1984).

10 J. D. Curry, M. A. Robinson and D. H. Busch, *Inorg. Chem.*, *6*, 1570 (1967).

11 D. Wester and G. J. Palenik, *J. Am. Chem. Soc.*, *995*, 6505 (1973).

12 C. Ansell, *Ph. D. Thesis*, Cambridge, 1982.

13 B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, *66*, 37 (1964).

14 S. M. Nelson and C. V. Knox, *J. Chem. Soc., Dalton Trans.*, 2525 (1983).

15 D. Wester and G. J. Palenik, *Inorg. Chem.*, *15*, 755 (1976).

16 E. C. Constable, J. M. Holmes and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, in press.
17 F. Lions, *Rev. Pure Appl. Chem.*, *19*, 177 (1969).
18 A. T. Casey, B. F. Hoskins and I. P. Traverso, *Aust. J. Chem.*, *37*, 739 (1984).
19 K. Nakamoto, 'Infra-red and Raman Spectra of Inorganic and Coordination Compounds', 3rd edn., Wiley, New York, 1978.
20 R. E. Poller, 'Chemistry of Organotin Compounds', Lagos Press, London, 1970.