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Chiral metal complexes
35*. Unusual terdentate behaviour in the crystal structure of chloro[*N*,*N*′-di(2-picolyl)-*N*-(2-pyridinecarboxamide)-1,2-diaminocyclohexane]palladium(II) perchlorate hemihydrate

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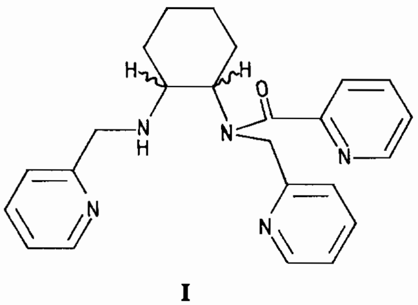
Abstract

An improved method of synthesis for the tetradentate ligand *rac*-*N*,*N*′-di(2-picolyl)-1,2-diaminocyclohexane, (*rac*-picchxn), is described. The controlled reaction of 2-pyridinecarboxylic acid with this compound results in the potentially pentadentate N_5 ligand *N*,*N*′-di(2-picolyl)-*N*-(2-pyridinecarboxamide)-1,2-diaminocyclohexane, (*rac*-picchxnam). A palladium(II) complex of this ligand was isolated and its crystal structure determined by X-ray diffraction. $[Pd(picchxnam)Cl]ClO_4 \cdot \frac{1}{2}H_2O$, $C_{24}H_{28}N_5O_{5.5}Cl_2Pd$, crystallises in the monoclinic space group *Pn* (non-standard No. 7) with $a = 12.006(2)$, $b = 8.207(2)$, $c = 13.477(2)$ Å, $\beta = 100.80(1)°$, $Z = 2$. The structure was refined to $R = 0.039$ by least-squares techniques for 2066 reflections. The ligand coordinates as a terdentate through the two picolyl pyridine-N atoms and the secondary amine-N atom. This results in a five-membered chelate ring and an unusual eight-membered ring which contains the tertiary amide nitrogen atom. The pyridinecarboxamide group does not coordinate, but is non-planar and is orientated away from the PdN_3Cl square-plane. The Pd–Cl, Pd–N(amine) and Pd–N(pyridyl) distances are 2.309(3), 2.079(7), 2.091(8) and 2.029(8) Å, respectively.

Introduction

We have reported previously [1–3] on the coordination behaviour of a number of linear N_4 diamide tetradentates containing both secondary and tertiary amide groups on reaction with palladium(II). The secondary amides have been shown to readily deprotonate on coordination with the picolinamide residues forming normal five-membered chelate rings. However, the substituted N atoms of the tertiary amide ligands in bpenMeH† and bpenMe₂ have been shown not to coordinate, thereby giving rise to complexes containing unusual eight- [1, 2] and eleven-membered [3] chelate rings, respectively.

The picchxnam ligand (I), prepared in this work, contains both a secondary amine and a tertiary amide group as well as three terminal pyridine groups, all of which contain potential N donor atoms. As was found in other analogues the tertiary amide remains uncoordinated in the palladium(II) complex reported here, thereby forcing the ligand to act as an unusual terdentate.



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*Part 34 is ref. 9.

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†Picchxn is *N*,*N*′-di(2-picolyl)-1,2-diaminocyclohexane; picchxnam is *N*,*N*′-di(2-picolyl)-*N*-(2-pyridinecarboxamide)-1,2-diaminocyclohexane; bpenMeH is *N*-methyl-*N*,*N*′-di(2-pyridinecarboxamide)-1,2-ethane; bpenMe₂ is *N*,*N*′-dimethyl-*N*,*N*′-di(2-pyridinecarboxamide)-1,2-ethane.

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Experimental

NMR spectra were recorded on a Varian XL-200 spectrometer and are reported in ppm relative to DSS, TMS or known solvent resonances used as internal calibrants.

rac-Picchxn·4HCl

The optically active forms of picchxn have been synthesised previously [4], using *N,N*-dimethylformamide as solvent for the formation of the intermediate Schiff's base. The facile method reported below gives the product in a significantly higher yield in less than 5 h.

To a stirred solution of *trans*-1,2-diaminocyclohexane (Aldrich, 5.0 g, 0.044 mol) in benzene (150 cm^3) in a 250 cm^3 round-bottom flask was added slowly, with stirring pyridine-2-carboxaldehyde (Aldrich, 9.83 g, 0.088 mol) in benzene (20 cm^3). The resulting straw-yellow solution was stirred for 15 min, during which time it turned cloudy due to the formation of the Schiff's base and consequent release of water. The benzene and water were removed on a rotary evaporator at 50 °C to leave a pale yellow solid which was triturated with 60/90 petroleum ether, filtered off, washed with a minimum amount of diethyl ether and air dried. Yield 10.3 g (80%); m.p. 132–133 °C uncorrected. NMR, DMSO-d_6, ppm: 1.48 (br, 2H); 1.74 (br, 6H); 3.48 (br, 2H); 7.40 (t, 2H); 7.84 (m, 4H); 8.24 (s, 2H); 8.54 (d, 2H).

This solid was dissolved in absolute ethanol (150 cm^3) and transferred to a 250 cm^3 Parr low-pressure hydrogenation vessel. To this solution was added 10% palladium on charcoal catalyst (*c.* 0.5 g) and the mixture was hydrogenated at 3 atm. until hydrogen uptake had ceased (*c.* 2 h). The reaction mixture was filtered through a celite pad to remove the catalyst and concentrated hydrochloric acid (17 cm^3) was added. Removal of the solvent left an off-white crystalline solid which was collected at the pump, washed with absolute ethanol (2×25 cm^3 portions) and acetone (50 cm^3) and then air dried. Yield 14.60 g (94%); m.p. 215–216 °C decomp. uncorr. NMR, DMSO-d_6, ppm: 1.08 (br m, 4H); 1.64 (br d, 2H); 2.02 (br d, 2H); 2.58 (br, 2H); 3.80 (q, 4H); 7.25 (t, 2H); 7.46 (d, 2H); 7.74 (t, 2H); 8.48 (d, 2H).

rac-Picchxnam

A sample of *rac*-picchxn·4HCl (5.0 g, 0.011 mol) was dissolved in aqueous NaOH (2 M, 150 cm^3) and the free tetraamine was extracted into dichloromethane, the extract dried with anhydrous Na_2SO_4, and the solvent removed at reduced pressure to leave a pale yellow oil (3.3 g, 0.011 mol). This oil was dissolved in pyridine (20 cm^3) and was added to a solution containing 2-pyridinecarboxylic acid (1.35 g, 0.011 mol) and triphenylphosphite (3.41 g, 0.011 mol) in pyridine, and the mixture was heated on a steam-bath for 5 h following a method previously described [5]. The volume of the reaction solution was reduced on a rotary evaporator, and water (150 cm^3) was added to azeotropically remove most of the remaining pyridine. The resulting oil was dissolved in chloroform (150 cm^3) and the extracts washed with saturated $NaHCO_3$ solution (3×50 cm^3), water (3×50 cm^3), dried with Na_2SO_4, and the solvent removed. The crude ligand was further purified by loading onto a column of neutral alumina (3×25 cm), washing with $CHCl_3$ and eluting with MeOH/$CHCl_3$ (1:3). The entire eluted yellow–orange band was collected and the solvent removed to leave the crude ligand as a dark yellow–orange oil. Yield 3.49 g.

[Pd(picchxnam)Cl]ClO$_4$·½H$_2$O

A sample of the crude ligand prepared above (1.0 g) was dissolved in acetone (10 cm^3) to which water (20 cm^3) was added and the solution was then heated. To this hot solution was added dropwise, with stirring, a solution of K_2PdCl_4 (0.813 g, 25 mmol) in water (20 cm^3). When the addition was complete the solution was heated on a steam-bath to remove the acetone and then was filtered through a small pad of celite under suction. Saturated $NaClO_4$ solution (2 cm^3) was added, whereby a pale yellow crystalline solid immediately precipitated. On cooling, this product was collected at the pump, washed with a minimum amount of ice-cold water and air dried. Yield 0.27 g. NMR, DMSO-d_6, ppm: 0.90 (br s, 1H); 1.62 (br m, 7H); 2.14 (br d, 1H); 4.24 (dd, 1H); 5.00 (m, 2H); 5.21 (dd, 2H); 7.42 (d, 1H); 7.66 (m, 4H); 7.92 (m, 2H); 8.13 (t, 1H); 8.24 (t, 1H); 8.66 (d, 1H); 8.86 (d, 1H); 9.08 (d, 1H).

A sample of the product was recrystallised from nitrobenzene to yield crystals suitable for the structure determination reported below.

Crystal and molecular structure of [Pd(picchxnam)Cl]ClO$_4$·½H$_2$O

Crystal data

$C_{24}H_{28}N_5O_{5.5}Cl_2Pd$, $M_r = 651.8$, monoclinic, $a = 12.006(2)$, $b = 8.207(2)$, $c = 13.477(2)$ Å, $\beta = 100.80(1)°$, $U = 1304.4$ Å^3, $Z = 2$, $D_m = 1.65$ (by flotation), $D_c = 1.659$ g cm^{-3}, $F(000) = 662$, μ(Mo Kα) = 9.53 cm^{-1}, space group *Pn* (non-standard No. 7).

Unit cell parameters initially were determined from precession photographs using Mo Kα radiation. Accurate cell parameters were obtained from a least-squares fit to diffractometer data. The crystal used for data collection had dimensions 0.34 × 0.50 × 0.56 mm. Intensities were collected at −90 °C on a Nicolet-XRD P3 four-circle diffractometer [6] in the range $4° < 2\theta < 50°$ using Mo Kα radiation. Reflections were corrected for Lorentz, polarisation and (empirically) absorption effects [6]. With respect to the latter, the maximum and minimum transmission factors were 0.646 and 0.564, respectively. Of the 2441 reflections measured, 2066 gave counts for which $I > 3\sigma(I)$, and these were used for the structure determination.

Structure determination

The structure, solved by the heavy-atom method, was refined by full-matrix least-squares calculations in which $\Sigma w\Delta^2$ was minimised. The weight applied to each reflection was based on counting statistics. A difference map phased on the cation showed two positions for the chlorine atom of the perchlorate ion which were of approximately equal density and c. 0.8 Å apart. Six peaks were identifiable as oxygen atoms, of which two (Oa, Ob) were bonded to both disordered chlorine atoms. Thus the anion was included with full occupancy for these two oxygen atoms, and with half occupancy both at the two chlorine positions and at the four positions attributable to the remaining oxygen atoms. The map also showed a peak corresponding to a lattice water molecule, the height of which was in accord with the hemihydrate formulation. Further difference maps were used to locate the approximate positions of the hydrogen atoms, other than those of O(w), and their positions were optimised assuming C–H and N–H to be 1.0 Å and appropriate bonding geometries. The refinement was terminated when the maximum change in any parameter was $< 0.1\sigma$. Final values for R and R' $[= (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{1/2}]$ were 0.039 and 0.032, respectively. A final difference map showed no density $> |0.6|$ e Å^{-3}. All calculations were carried out on a FACOM M340S computer using programs written by F.S.S. Neutral atom scattering factors, with corrections being applied for anomalous dispersion, were taken from ref. 7.

The final non-hydrogen atomic parameters are given in Table 1.

Results and discussion

The synthesis of the ligand using triphenylphosphite in pyridine as a coupling system for the formation of tertiary amides [5] presents the inherent problem of subsequent removal of these high boiling point species during product isolation. Purification by distilling the ligand was not possible since these high molecular weight amine/amide products decompose on heating, even at reduced pressures.

TABLE 1. Final atomic coordinates (fractional $\times 10^4$) for non-hydrogen atoms of $[Pd(picchxnam)Cl]ClO_4 \cdot \frac{1}{2}H_2O$ with e.s.d.s in parentheses

	x	*y*	*z*
Pd	2500	344.8(8)	2500
Cl	1759(2)	2943(3)	2267(2)
N(11)	1025(7)	−713(10)	2825(6)
N(21)	3936(7)	1085(10)	2043(7)
N(1)	3085(6)	−2036(9)	2722(7)
C(11)	−22(9)	−45(14)	2654(8)
C(12)	−970(8)	−940(16)	2735(8)
C(13)	−827(9)	−2516(14)	3047(8)
C(14)	235(9)	−3200(12)	3262(8)
C(15)	1143(9)	−2272(12)	3133(8)
C(16)	2355(9)	−2943(12)	3379(8)
C(1)	4330(8)	−2221(11)	3093(7)
C(2)	4741(8)	−1430(11)	4138(7)
C(3)	6053(9)	−1536(12)	4423(8)
C(4)	6449(9)	−3302(13)	4401(9)
C(5)	5997(9)	−4106(12)	3382(9)
C(6)	4693(8)	−4001(10)	3135(7)
C(21)	3939(9)	966(13)	1044(7)
C(22)	4896(10)	1158(15)	675(8)
C(23)	5890(10)	1491(13)	1329(9)
C(24)	5913(9)	1640(12)	2340(8)
C(25)	4918(9)	1410(11)	2675(7)
C(26)	4860(8)	1670(11)	3800(7)
N(2)	4322(6)	293(9)	4242(5)
C(O3)	3617(8)	542(11)	4914(7)
O(3)	3137(6)	−570(8)	5263(5)
N(31)	4319(7)	3198(10)	5576(6)
C(31)	4138(9)	4616(14)	5953(8)
C(32)	3035(11)	5226(12)	5983(8)
C(33)	2120(9)	4265(14)	5634(9)
C(34)	2311(8)	2742(12)	5271(8)
C(35)	3422(9)	2299(12)	5249(8)
Cl(1)	8702(7)	3090(10)	4891(7)
Cl(2)	8775(7)	3019(10)	4278(9)
O(a)	8131(13)	1864(18)	4295(9)
O(b)	8783(12)	4490(16)	4743(14)
O(1c)	9525(15)	2620(20)	5579(14)
O(1d)	7743(24)	3101(28)	5347(17)
O(2c)	9795(12)	2437(23)	4357(15)
O(2d)	8462(21)	3562(25)	3251(21)
O(w)	6713(12)	2813(19)	5954(9)

Hence the ligand was used in a crude form after chromatographic treatment.

The reaction of 2-pyridinecarboxylic acid with one equivalent of the picchxn ligand could result in a statistical mixture of three possible species, namely mono- and disubstituted forms of picchxn as well as unreacted tetraamine. There was no evidence that these different products, if present, could be separated by the chromatographic techniques employed.

Reaction with palladium(II) and subsequent precipitation with sodium perchlorate resulted in the title compound as the sole product, with its purity evidenced by NMR (Fig. 1). Hence if any other

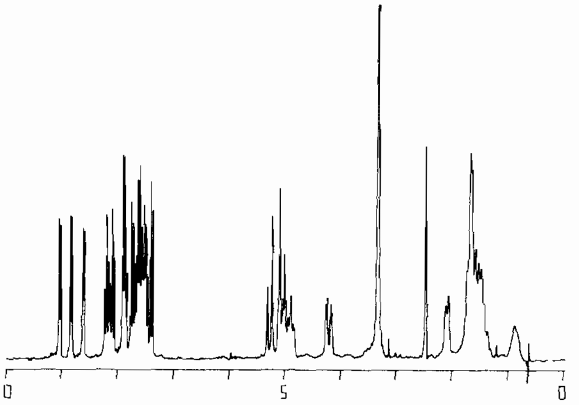

Fig. 1. ^1H NMR spectrum of the $[Pd(picchxnam)Cl]^+$ cation in DMSO-d_6.

TABLE 2. Selected molecular dimensions for the $[Pd(picchxnam)Cl]^+$ cation with e.s.d.s in parentheses

Distances (Å)			
Pd–Cl	2.309(3)	Pd–N(11)	2.091(8)
Pd–N(1)	2.079(7)	Pd–N(21)	2.029(8)
C(15)–C(16)	1.533(13)	C(25)–C(26)	1.545(12)
N(1)–C(16)	1.549(12)	N(2)–C(26)	1.481(11)
N(1)–C(1)	1.492(10)	N(2)–C(2)	1.516(11)
C(O3)–C(35)	1.542(12)	C(1)–C(2)	1.545(13)
N(2)–C(O3)	1.366(11)	C(O3)–O(3)	1.220(10)
Angles (°)			
Cl–Pd–N(1)	177.0(2)	N(11)–Pd–N(21)	171.4(4)
Cl–Pd–N(11)	95.3(2)	N(1)–Pd–N(11)	81.7(3)
Cl–Pd–N(21)	90.6(2)	N(1)–Pd–N(21)	92.4(3)
Pd–N(11)–C(11)	126.4(7)	Pd–N(21)–C(21)	116.2(7)
Pd–N(11)–C(15)	114.5(7)	Pd–N(21)–C(25)	124.1(7)
C(11)–N(11)–C(15)	118.7(9)	C(21)–N(21)–C(25)	118.7(9)
Pd–N(1)–C(16)	108.8(6)	O(3)–C(O3)–N(2)	122.7(9)
Pd–N(1)–C(1)	115.7(5)	O(3)–C(O3)–C(35)	118.5(8)
C(16)–N(1)–C(1)	113.5(7)	N(2)–C(O3)–C(35)	118.8(8)
N(1)–C(16)–C(15)	108.6(8)	C(O3)–N(2)–C(2)	117.3(7)
N(2)–C(26)–C(25)	113.1(7)	C(O3)–N(2)–C(26)	121.5(8)
N(11)–C(15)–C(16)	116.7(9)	C(2)–N(2)–C(26)	119.9(7)

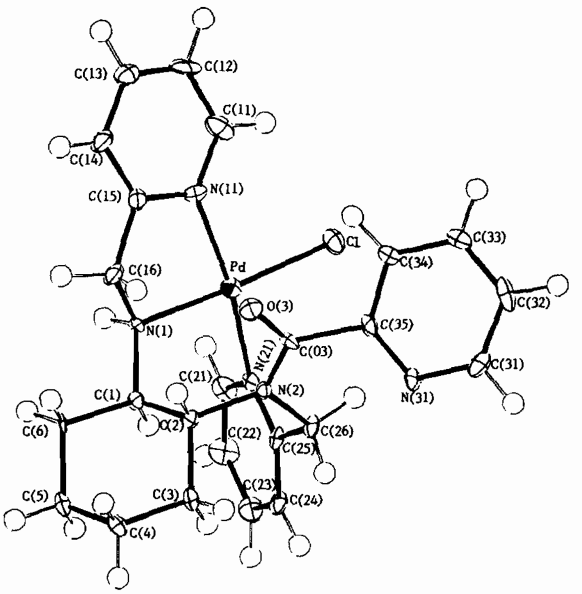

Fig. 2. Perspective drawing of the $[Pd(R,R\text{-picchxnam})Cl]^+$ cation showing the atom labelling. Thermal ellipsoids are drawn to include 35% probability.

chelate products did form they must be more soluble than the $[Pd(picchxnam)Cl]ClO_4 \cdot \frac{1}{2}H_2O$ species obtained, for which the crystal structure is reported here.

Selected molecular dimensions for the cation are given in Table 2, and Fig. 2 shows a perspective drawing [8] of the complex cation together with the atom labelling scheme. The primary molecular unit described herein relates to the cation containing the ligand in *R*,*R* configuration. Both the tertiary amide and pyridine nitrogen atoms of the picolinamide group remain uncoordinated, and hence the potentially N_5 ligand acts only as a terdentate. Steric constraints within the ion are manifest in the non-planarity of the picolinamide group. This is evidenced by the N(2)–C(O3)–C(35)–N(31) torsion angle of −51°, and by the amide N(2) atom displaying *c.* 20% pyramidal distortion.

The approximately square-planar coordination of the Pd(II) atom derives from the three nitrogen atoms of the ligand (Pd–N(11) 2.091(8), Pd–N(21) 2.029(8), Pd–N(1) 2.079(7) Å), thereby generating one five-membered and one eight-membered chelate ring, and a chloride atom (Pd–Cl 2.309(3) Å). The two nitrogen atoms of the five-membered chelate ring, the palladium and the chloride atom, are closely co-planar, with the remaining picolyl N(pyridine) atom being displaced from this plane by 0.22 Å away from the bulk of the eight-membered chelate ring. The coordination geometry observed is in accord with molecular models, which suggest that constraints imposed by a combination of the restricted flexibility of the chiral cyclohexane ring and the planarity requirements of the amide group are responsible for the form of terdentate behaviour observed.

The lattice water molecule is involved in hydrogen bonding to the coordinated amine, the free pyridyl N atom and an oxygen atom of the disordered perchlorate ion. Details of these and other close intermolecular contacts are given in Table 3.

The structural behaviour of this ligand when bound to palladium(II) is quite analogous to related N-methylated bis-picolinamide ligands reported previously [1, 3], in which the tertiary amide nitrogen atoms again were found not to coordinate. In the case of the palladium complex of the mono-alkylated

TABLE 3. Intermolecular contacts for [Pd(picchxnam)Cl]$ClO_4 \cdot \frac{1}{2}H_2O$ with e.s.d.s in parentheses

Proposed hydrogen bonding[a]			
N(1)–H(N1)···O(w^{I})	2.71(2)	O(w)···N(31)	2.84(2)
		O(w)···O(a)	3.15(2)
Intermolecular distances <3.3 Å[a]			
C(34)···O($2c^{II}$)	3.05(2)	C(15)···O(w^{I})	3.17(2)
C(11)···O($2c^{II}$)	3.11(2)	C(16)···O(w^{I})	3.22(2)
C(22)···O($1c^{I}$)	3.13(2)	N(1)···O($1d^{I}$)	3.27(2)
C(32)···O($2d^{III}$)	3.16(2)	N(11)···O(w^{I})	3.29(2)

[a] Roman numeral superscripts refer to the following equivalent positions relative to x, y, z: I: $x-\frac{1}{2}, -y, z-\frac{1}{2}$; II: $x-1, y, z$; III: $x-\frac{1}{2}, 1-y, \frac{1}{2}+z$.

ligand, $[Pd(bpenMe)Cl]^+$ [2], the molecular geometry closely parallels that observed in the present structure.

Supplementary material

Lists of anisotropic thermal parameters, complete Tables of bond lengths and angles and observed and calculated structure factors are available from F.S.S. on request.

Acknowledgements

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