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Note

Functionalised phosphines: structure of bis(2-aminophenyldiphenylphosphine-κ^2N,P)copper(I) perchlorate ethanol solvate

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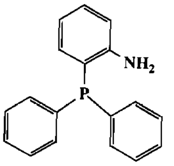
Abstract

The functionalised phosphine, 2-aminophenyldiphenylphosphine (2-PNH$_2$) reacts with [Cu(CH$_3$CN)$_4$]ClO$_4$ to yield the complex [Cu(2-PNH$_2$)$_2$]ClO$_4$·C$_2$H$_5$OH. The compound has been characterised spectroscopically and the structure determined by the X-ray method. The crystals are monoclinic with $a = 12.816(4)$, $b = 27.547(8)$, $c = 12.189(3)$ Å, $\beta = 121.33(3)^\circ$, $U = 3675.6$ Å^3, $Z = 4$, space group $C2/m$. The structure was refined to $R = 0.036$ for 2339 unique data. The copper(I) atom is in a distorted tetrahedral environment with each ligand forming a five-membered chelate ring by the binding of the amino-nitrogen and phosphorus donor atoms with Cu–P and Cu–N bond lengths of 2.258(1) and 2.177(3) Å, respectively.

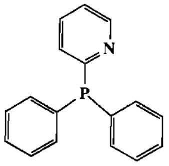
Key words: Crystal structures; Copper complexes; Functionalized-phosphine complexes

Introduction

The coordination chemistry of triphenylphosphine is extensive and has been well documented, however the chemistry of ortho-functionalised phosphines with 'soft' phosphorus and 'hard/soft' nitrogen donor ligands is much less well-known with the ligands 2-aminophenyldiphenylphosphine (I) (2-PNH$_2$) [1], and diphenyl(2-pyridyl)phosphine (II) (2-PN) [2], receiving most attention.



I
(2-PNH$_2$)



II
(2-PN)

As well as retaining many of the desirable metal-binding characteristics of phosphines, these ligands also have the additional advantage of possessing a functional group with enhanced coordination abilities due to its close proximity to the phosphine donor. Such ligands may be of interest in the design and development of new homogeneous catalytic systems catalysed by their transition metal complexes.

Studies with **II** have shown it has a propensity to bridge between adjacent metal centres (presumably because of the formation of unstable four-membered chelate rings) [3, 4] whereas **I** readily forms chelate complexes with platinum [5] and rhodium [6]. In addition, the deprotonated amido form of ligand **I** has been reported for these metal species [7, 8] and for nickel [9]. The products of reaction of **II** with [Cu(CH$_3$CN)$_4$]BF$_4$ are also known, including for example [Cu$_2$(μ-(2-PN))$_3$(CH$_3$CN)](BF$_4$)$_2$ [10], but a similar study with **I** has not been done and forms the basis of this report.

The complex [Cu(2-PNH$_2$)$_2$]ClO$_4$·C$_2$H$_5$OH has been isolated and is found to be stable against oxidation with oxygen in contrast to the 1,2-diaminoethane system. A single-crystal X-ray structural analysis reveals the copper bound to two chelated ligands in a distorted tetrahedral coordination geometry with Cu–P and Cu–N bond distances of 2.258(1) and 2.177(3) Å, respectively. This structure represents one of the few stable examples of coordination to copper by an aromatic primary amine.

Experimental

IR spectra were recorded on a BIO-RAD FTS-40 instrument on nujol mulls. Mass spectra were obtained using a Varian VG70-250S double focussing magnetic sector spectrometer by the LSIMS method. An isotope abundance calculation was performed to confirm the identity of the [Cu(PNH$_2$)$_2$]$^+$ ion. Microanalyses were performed by the Campbell Microanalytical Laboratory, University of Otago.

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Preparation of $[Cu(2\text{-}PNH_2)_2]ClO_4 \cdot C_2H_5OH$

To a solution of 2-aminophenyldiphenylphosphine [11] (0.277 g; 1 mmol) in ethanol (40 cm^3) was added $[Cu(CH_3CN)_4]ClO_4$ (0.164 g; 0.5 mmol) in CH_2Cl_2 (10 cm^3). The solution was heated under a brisk flow of nitrogen until the volume was reduced to approximately 25 cm^3. On cooling and standing at room temperature small colourless crystals were deposited. These were filtered off and washed with ethanol and diethyl ether and dried *in vacuo*. Yield 40%. *Anal.* Found: C, 59.8; H, 4.7; N, 3.7. *Calc.* for $C_{38}H_{38}ClCuN_2O_5P_2$: C, 59.8; H, 5.0; N, 3.7%.

Crystal structure of bis(2-aminophenyldiphenylphosphine-κ²N,P)copper(I) perchlorate·ethanol

Crystal data

Crystals suitable for data collection were grown by the slow evaporation of a dichloromethane/ethanol solution. $C_{38}H_{38}ClCuN_2O_5P_2$, $M=763.6$, CAD4 diffractometer, graphite-monochromated Mo Kα radiation. Cell parameters were determined from the setting angles of 16 reflections ($10.0 \leqslant \theta \leqslant 16.2°$): $a=12.816(4)$, $b=27.547(8)$, $c=12.189(3)$ Å, $\beta=121.33(3)°$, $U=3675.6$ $Å^3$; monoclinic, space group $C2/m$, $Z=4$, $D_c=1.38$ g cm^{-3}, μ(Mo Kα)$=8.0$ cm^{-1}, $F(000)=1580$.

Data collection and processing

A total of 3464 data was collected using the $\omega/2\theta$ scan technique ($\theta_{max}=25°$; $+h$, $+k$, $\pm l$) and a variable scan angle of $(0.8+0.34 \tan \theta)°$. A variable horizontal aperture of $(1.2+0.8 \tan \theta)$ was calculated; the vertical aperture was fixed at 4 mm. The scan speed varied from 0.87 to 8.24°/min with the maximum scan time set at 90 s. The intensities of the three standard reflections monitored during the data collection showed a variation of $\leqslant 1.7\%$. No absorption corrections were applied. The number of unique data measured was 3148 (merging $R=0.012$, based on intensity) [12].

Structure analysis and refinement

The structure was solved by Patterson and Fourier methods and refined by a full-matrix least-squares method [13]. The final refinement cycle converged to values of 0.036 and 0.041 for R and R_w, respectively, for the 253 variables and 2339 data for which $F^2 > 3\sigma(F^2)$. The function minimised was $\Sigma w(|F_o|-|F_c|)^2$ with the weight, w, defined as $0.970/(\sigma^2(F_o)+0.00107F_o^2)$. Phenyl ring H atoms were in calculated sites (C–H, 0.96 Å). The two amino H were located on a difference electron density map. Isotropic thermal parameters were assumed for all phenyl ring H; anisotropic thermal motion was assumed for all non-H atoms. The chlorine and two oxygens of the perchlorate anion as well as the carbon and oxygen atoms of the ethanol solvate lie in the mirror plane. Some disorder was observed for the former and two sites of occupancy 0.6 and 0.4 were noted for it. Atomic scattering factors were taken from the tabulations of Cromer and Mann [14], anomalous dispersion corrections were by Cromer and Liberman [15]. The numbering system used is shown in Fig. 1, final atomic coordinates for the non-hydrogen atoms are given in Table 1, selected bond distances and angles in Table 2. See also 'Supplementary material'.

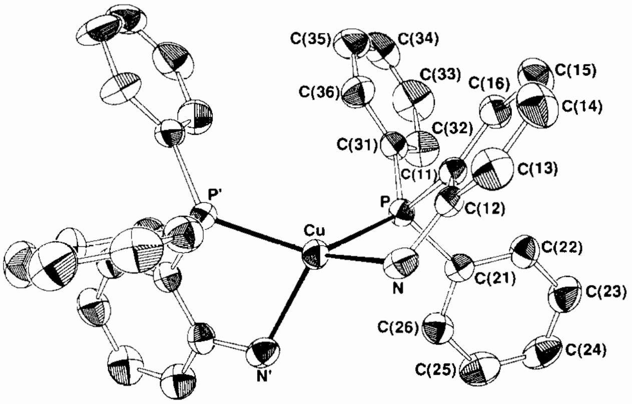

Fig. 1. Thermal ellipsoid diagram for $[Cu(2\text{-}PNH_2)_2]ClO_4 \cdot EtOH$ drawn at the 50% probability level [16].

TABLE 1. Fractional atomic coordinates for $[Cu(2\text{-}PNH_2)_2]ClO_4 \cdot EtOH$ with e.s.d.s in parentheses

Atom	*x/a*	*y/b*	*z/c*
Cu	0.0000	0.12783(2)	0.0000
Cl	0.7935(1)	0.0000	0.1901(2)
P	−0.18106(7)	0.16165(3)	−0.14405(7)
O(1)	0.8354(5)	0.0000	0.1019(6)
O(2)	0.6635(6)	0.0000	0.1269(7)
O(31)	0.8047(8)	0.0490(2)	0.2197(9)
O(32)	0.8676(14)	0.0178(4)	0.311(1)
O	−0.2008(4)	0.0000	−0.1738(4)
C(1)	−0.3121(7)	0.0000	−0.2938(8)
C(2)	−0.2957(7)	0.0000	−0.4011(8)
N	−0.0368(3)	0.0834(1)	−0.1641(3)
C(11)	−0.1666(3)	0.1518(1)	−0.2838(3)
C(12)	−0.0956(3)	0.1128(1)	−0.2783(3)
C(13)	−0.0799(3)	0.1038(1)	−0.3811(4)
C(14)	−0.1322(4)	0.1337(2)	−0.4864(4)
C(15)	−0.2013(3)	0.1733(2)	−0.4920(4)
C(16)	−0.2199(3)	0.1822(1)	−0.3927(3)
C(21)	−0.3229(3)	0.1300(1)	−0.1886(3)
C(22)	−0.4240(3)	0.1315(1)	−0.3117(3)
C(23)	−0.5291(3)	0.1059(2)	−0.3428(4)
C(24)	−0.5348(4)	0.0791(1)	−0.2519(4)
C(25)	−0.4351(4)	0.0771(1)	−0.1301(4)
C(26)	−0.3281(3)	0.1020(1)	−0.0972(3)
C(31)	−0.2196(3)	0.2260(1)	−0.1577(3)
C(32)	−0.3307(4)	0.2433(1)	−0.1813(4)
C(33)	−0.3526(5)	0.2932(2)	−0.1932(5)
C(34)	−0.2661(5)	0.3251(1)	−0.1802(4)
C(35)	−0.1550(5)	0.3085(1)	−0.1538(4)
C(36)	−0.1316(4)	0.2587(1)	−0.1429(4)

TABLE 2. Selected bond lengths (Å) and angles (°) for $[Cu(2\text{-}PNH_2)_2]ClO_4\cdot EtOH$ with e.s.d.s in parentheses

Cu–P	2.258(1)	Cu–N	2.177(3)	N–C(12)	1.437(4)
N–H(1)	0.82(4)	N–H(2)	0.86(4)		
P–Cu–N	82.7(1)	P–Cu–P′	131.3(1)	P–Cu–N′	126.2(1)
N–Cu–N′	111.7(2)	Cu–N–C(12)	109.1(2)	Cu–N–H(1)	104(2)
Cu–N–H(2)	120(3)	C(12)–N–H(1)	111(2)	C(12)–N–H(2)	108(2)
H(1)–N–H(2)	105(3)				

Results and discussion

The ligand 2-PNH_2 readily reacts with $[Cu(CH_3CN)_4]ClO_4$ in a molar ratio of 2:1 to yield $[Cu(2\text{-}PNH_2)_2]ClO_4\cdot C_2H_5OH$. Evidence that the amine N was coordinated was obtained from the IR spectrum where a band was observed at 3303 cm^{-1}. This was identified as due to an N–H stretching mode and may be compared with the bands at 3413 and 3329 cm^{-1} in the free ligand. Bands at 1117 and 625 cm^{-1} were consistent with ionic perchlorate. Mass spectral data obtained by the method of liquid secondary ion mass spectrometry using *m*-nitrobenzyl alcohol as the matrix gave a *m/z* peak at 617 consistent with the $[^{63}Cu(2\text{-}PNH_2)_2]^+$ cation. The complex was stable in the solid state and relatively stable in solution towards oxygen, unlike the 1,2-diaminoethane/copper(I) system. Thus the presence of the phosphine moiety confers a relative stabilising effect on the oxidation of both the copper and the amine.

Molecular structure of bis(2-aminophenyldiphenylphosphine-κ^2N,P)copper(I) perchlorate·ethanol

The copper atom lies on a crystallographic two-fold axis and hence overall the molecule possesses C_2 symmetry. The metal adopts a distorted tetrahedral coordination geometry with each ligand forming a five-membered chelate ring by the binding of the nitrogen and phosphorus donor atoms. The phosphorus atom lies at a distance of 2.258(1) Å from the copper, a length which is in the range of bond lengths observed (2.246(3)–2.295(3) Å) for a series of tetrahedral bis-triphenylphosphine complexes [17–20]. The amino nitrogen has a copper–nitrogen bond length of 2.177(3) Å, but this distance is outside the range observed (2.117(5)–2.148(5) Å) for the tetrahedral copper(I) compounds $[Cu(DEED)_2]^+$ and $[Cu(DEED)I]_2$ (DEED≡*N,N′*-diethylethylenediamine) [21]. It is however similar to that found in $[Cu(DIED)I]_2$ at 2.17 Å (av.) (DIED≡*N,N′*-di-isopropylethylenediamine) [21]. The smallest angle at the copper atom (82.7(1)°) is observed for the P–Cu–N angle within the chelate ring but this lies within the range of P–M–N angles observed for a series of amino and amido complexes of 2-PNH_2 (81.9–86.4°) [5–9]. It deviates significantly from idealised tetrahedral geometry but is merely the result of the steric constraints imposed on the metal centre by the formation of the five-membered chelate ring. The largest angle found at the copper atom is P–Cu–P′ which has a value of 131.3(1)°. This angle is greater than that observed for a range of tetrahedral bis-triphenylphosphine copper(I) compounds (115.85(9)–127.6(1)°) [17–20] and is probably the result of the metal centre attempting to accommodate the two chelating 2-PNH_2 ligands in an approximately tetrahedral geometry. This effect is further shown by the angle between the two planes containing the atoms Cu,P,N and Cu,P′,N′, respectively which is observed at 83.9°, a value significantly less than the 90° expected for a regular tetrahedron. The two amino protons, H(1) and H(2), were located on a difference electron-density map and the angles which they subtend at the nitrogen atom (105(3)–120(3)°) confirm the primary nature of the amino N.

Supplementary material

Additional material for the structure, available from the Cambridge Crystallographic Data Centre, comprises H atom parameters, thermal parameters, and a complete listing of bond lengths and angles.

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