Crystal structure of bis(3,5-dimethylpyrazole)-*N*,*N*′-μ-[1,3-bis(diphenylphosphino)propane]-*P*,*P*′-digold(I)] diperchlorate, $C_{37}H_{42}N_4P_2Au_2Cl_2O_8$

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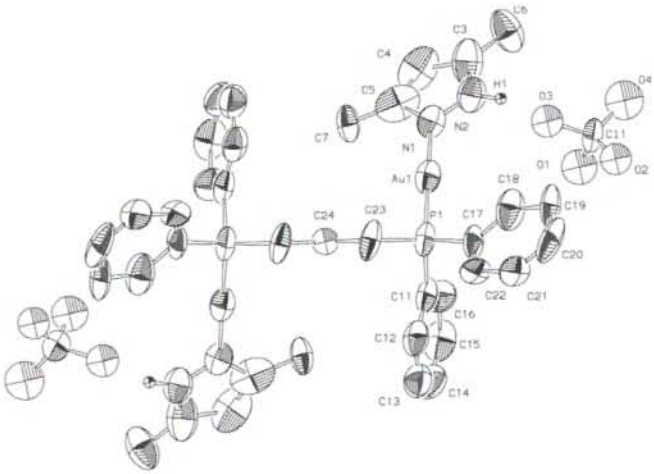
Received March 10, 1999, CCDC-No. 1267/142



Abstract

$C_{37}H_{42}Au_2Cl_2N_4O_8P_2$, monoclinic, *C*12/*c*1 (No. 15), *a* = 22.598(3) Å, *b* = 11.626(1) Å, *c* = 18.539(2) Å, β = 116.37(1)°, *V* = 4363.9 Å^3, *Z* = 4, $R_{gt}(F)$ = 0.061, *wR*(*F*) = 0.077, *T* = 293 K.

Source of material

The synthesis of the title compound was carried out by the reaction of [dpppAu$_2$](ClO$_4$)$_2$ (dppp = 3-bis(diphenylphosphine)propane) and 3,5-dimethyl pyrazole in THF solution. The precipitate obtained was extracted by hot chloroform to give the analytical sample [1]. Single crystals suitable for X-ray diffraction analysis were obtained by crystallization from CH_2Cl_2/hexane.

Discussion

A large number of dinuclear bis(phosphines)digold(I) derivatives are known. In these complexes the ligands opposite to the coordinated P atom can be alogenides [2-5] or anionic species containing N [6,7], C [8], O [9], or S [10, 11] as donor atoms. Their structures show that intra or intermolecular gold-gold interactions might be present. These weak bonding forces, whose activation depends on electronic and/or steric factors, are responsible of the structural features in the solid state.

The structure of [μ-dpppAu$_2$(pzH)$_2$]$^{2+}$(ClO$_4$)$_2$ (dppp = 3-bis(diphenylphosphine)propane) (**I**) consists of two centrosymmetric units with gold atoms in a linear coordination (P–Au–N =177.97(2)°). This angle is larger than those found in related compounds [2-4] where attractive intermolecular gold-gold interactions are present, while in (**I**) neither intra- nor intermolecular gold-gold interactions occur. Generally complexes of the type [μ-dpppAu$_2$L$_2$] assume an *anti* conformation, as, in fact (**I**), that has a torsion angle Au–P–P–Au of 89.2(2)°. The *anti* conformations bring the metal atoms too far to give intramolecular interactions, that can even be absent in a cationic polymer in *syn* conformation [12]. Thus the number of methylene groups of the bis(phosphine) ligands plays an important role in the occurrence of attractive intramolecular forces. In the case of (**I**), their absence, even in the intermolecular mode, should be attributed to packing factors, since the bulky 3,5- dimethylpyrazole does not prevent gold-gold short contacts [1]. The bond distances Au–P of 2.233(5) Å and Au–N of 2.05(2) Å are similar to those found in the related dicationic complexes [μ-dppmAu$_2$(pzH)$_2$]$^{2+}$ and [μ-dppeAu$_2$(pzH)$_2$]$^{2+}$ [1] and in neutral compounds as [Au$_2$(μ-HX)(μ-dmpe)] [6]. The perchlorate anions are bound to the N–H of the pyrazole rings by hydrogen bonds.

Table 1. Data collection and handling.

Crystal:	colourless prism, size 0.2 × 0.2 × 0.35 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	1493.00 cm^{-1}
Diffractometer:	Rigaku AFC5R, ω/2θ
$2\theta_{max}$:	124.06°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3848, 3440
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 3\ \sigma(I_{obs})$, 1921
$N(param)_{refined}$:	226
Program:	TEXSAN [13]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
C(24)	4*e*	1.0	0.072(2)	1/4	0.070(6)
O(1)	8*f*	0.643(2)	0.183(3)	0.191(2)	0.13(1)
O(2)	8*f*	0.666(1)	0.348(2)	0.255(2)	0.101(8)
O(3)	8*f*	0.567(2)	0.314(3)	0.158(2)	0.10(1)
O(4)	8*f*	0.612(2)	0.210(4)	0.291(3)	0.15(1)
H(1)	8*f*	0.9971	0.2921	-0.0904	0.12

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Au(1)	8*f*	0.97818(4)	0.20511(7)	0.05825(5)	0.0854(6)	0.0808(6)	0.0757(5)	0.0034(5)	0.0144(4)	0.0099(5)
P(1)	8*f*	0.9154(2)	0.0821(4)	0.0864(3)	0.076(3)	0.076(3)	0.053(3)	0.008(2)	–0.002(2)	–0.008(2)
N(1)	8*f*	1.0335(8)	0.323(1)	0.032(1)	0.09(1)	0.07(1)	0.09(1)	–0.005(8)	0.03(1)	–0.006(9)
N(2)	8*f*	1.0264(9)	0.338(2)	–0.044(1)	0.10(1)	0.09(1)	0.09(1)	–0.01(1)	0.03(1)	–0.01(1)
C(3)	8*f*	1.065(2)	0.423(2)	–0.050(2)	0.16(3)	0.10(2)	0.11(2)	–0.01(2)	0.02(2)	–0.02(2)
C(4)	8*f*	1.100(1)	0.454(2)	0.034(2)	0.14(2)	0.06(1)	0.20(3)	–0.04(1)	0.03(2)	–0.02(2)
C(5)	8*f*	1.082(1)	0.394(2)	0.081(2)	0.13(2)	0.05(1)	0.23(4)	–0.02(1)	0.08(2)	–0.04(2)
C(6)	8*f*	1.062(2)	0.460(2)	–0.126(2)	0.20(4)	0.11(2)	0.09(2)	–0.05(2)	0.07(2)	–0.02(2)
C(7)	8*f*	1.103(1)	0.398(2)	0.169(2)	0.12(2)	0.08(2)	0.06(2)	–0.02(2)	0.01(2)	–0.02(1)
C(11)	8*f*	0.854(1)	0.156(2)	0.104(1)	0.07(1)	0.08(1)	0.06(1)	0.00(1)	0.00(1)	–0.01(1)
C(12)	8*f*	0.818(1)	0.101(2)	0.139(1)	0.09(2)	0.08(1)	0.08(1)	0.04(1)	0.01(1)	0.01(1)
C(13)	8*f*	0.771(1)	0.152(3)	0.151(1)	0.09(2)	0.15(2)	0.09(2)	0.00(2)	0.02(1)	0.03(2)
C(14)	8*f*	0.759(1)	0.267(2)	0.132(2)	0.09(2)	0.12(2)	0.12(2)	0.03(2)	0.03(1)	0.03(2)
C(15)	8*f*	0.793(1)	0.328(2)	0.100(2)	0.13(2)	0.07(1)	0.12(2)	0.03(1)	0.02(2)	–0.01(1)
C(16)	8*f*	0.841(1)	0.269(2)	0.084(1)	0.09(2)	0.09(2)	0.12(2)	0.03(1)	0.04(1)	0.03(1)
C(17)	8*f*	0.871(1)	–0.026(2)	0.008(1)	0.08(1)	0.11(2)	0.05(1)	0.02(1)	0.00(1)	–0.04(1)
C(18)	8*f*	0.873(1)	–0.006(2)	–0.065(1)	0.12(2)	0.09(2)	0.10(2)	0.02(1)	0.01(1)	–0.03(1)
C(19)	8*f*	0.842(2)	–0.074(3)	–0.131(2)	0.12(2)	0.10(2)	0.06(2)	–0.01(2)	–0.01(2)	–0.04(2)
C(20)	8*f*	0.806(1)	–0.162(3)	–0.118(2)	0.08(2)	0.14(2)	0.12(2)	0.02(1)	–0.03(1)	–0.08(2)
C(21)	8*f*	0.805(1)	–0.185(3)	–0.048(2)	0.09(2)	0.10(2)	0.10(2)	–0.06(2)	0.04(2)	–0.06(2)
C(22)	8*f*	0.839(1)	–0.115(2)	0.015(2)	0.08(2)	0.09(2)	0.10(2)	–0.06(2)	0.05(2)	–0.04(2)
C(23)	8*f*	0.9622(9)	–0.001(1)	0.176(1)	0.09(1)	0.05(1)	0.07(1)	0.02(1)	–0.02(1)	–0.01(1)
Cl(1)	8*f*	0.6210(3)	0.2602(7)	0.2261(4)	0.082(4)	0.191(6)	0.090(4)	0.012(4)	0.029(3)	–0.006(4)

Acknowledgments. The authors are grateful to C.N.R. (Roma) and University of Camerino for financial support.

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