Acta Cryst. (1993). C**49**, 1467–1469

Structure of μ-1,2-Bis(dicyclohexylphosphino)ethane-bis{[1,2-bis(dicyclohexylphosphino)ethane]gold(I)} Bis(dicyanoaurate)

T. Mark McCleskey

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA

Lawrence M. Henling† and Kathleen A. Flanagan

The Beckman Institute, Mail Code 139-74, California Institute of Technology, Pasadena, California 91125, USA

Harry B. Gray

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA

(*Received* 22 *January* 1992; *accepted* 15 *January* 1993)

Abstract

The compound $[(Au\{(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2\})_2\{\mu\text{-}(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2\}]^{2+}\ [Au(CN)_2]_2^{2-}$ luminesces strongly (λ_{max} = 508 nm) in acetonitrile at room temperature. Both gold(I) atoms are in trigonal planar environments, bound to one chelating bis(dicyclohexylphosphino)ethane (dcpe), and linked to one another by one bridging dcpe. The bridging unit is stretched with an Au···Au distance of 7.0501 Å; clearly no Au-Au interaction is present.

Comment

Only a few gold dimer compounds have been reported to luminesce in solution (Che, Kwong, Poon & Yam, 1990; Che, Wong, Lai & Kwong, 1989; Khan, Fackler, King, Wang & Wang, 1989; King, Wang, Khan & Fackler, 1989). In all of these cases a significant Au-Au interaction exists. There has been some ambiguity in the assignment of the emission as coming from a $d\sigma^*$ to $p\sigma$ or a $d\delta^*$ to $p\sigma$ transition. The title compound, $[Au_2(dcpe)_3]^{2+}[Au(CN)_2]_2^{2-}$, was synthesized to explore the role of the Au-Au interaction; it luminesces at 508 nm in CH_3CN at room temperature.

Each approximately trigonal-planar Au atom in the cation is coordinated to the two P atoms of one bidentate dcpe and to a single P atom of the bridging dcpe. A center of symmetry relates the two halves of the complex. For the non-bridging ligand, the Au—P distances are 2.422 (2) and 2.440 (2) Å forming an angle of 87.4 (1)°. The other Au—P distance is 2.318 (1) Å and the surrounding angles are 135.3 (1) and 136.9 (1)°. The Au···Au separation is 7.0501 Å, indicating no Au-Au interaction. The emission is logically assigned to a p_z to d_{xy}, $d_{x^2-y^2}$ transition in the AuP_3 unit.

Two dicyanoaurate anions, with the gold atoms on centers of symmetry, balance the charge. The remaining distances and angles are normal.

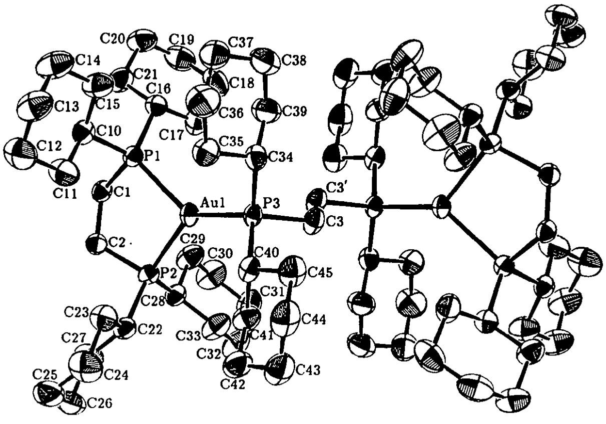


Fig. 1. An *ORTEP* view of the dication with 50% probability ellipsoids showing the numbering system. H atoms are not shown.

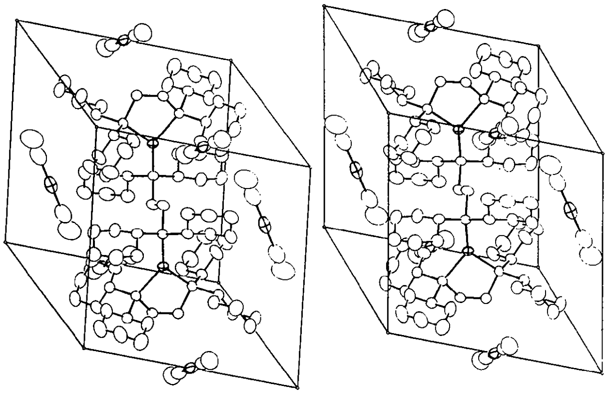


Fig. 2. An *ORTEP* stereo-illustration of the unit cell; atoms are drawn at the 50% probability level with H atoms omitted.

Experimental

Crystal data

$[Au_2(C_{26}H_{48}P_2)_3][Au(CN)_2]_2$
M_r = 2159.78
Triclinic
$P\bar{1}$
a = 12.184 (5) Å
b = 12.616 (4) Å
c = 15.243 (4) Å

D_x = 1.68 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 15–16.5°
μ = 6.987 mm^{-1}

---

† Contribution No. 8797.

$\alpha = 99.07\ (2)°$
$\beta = 91.12\ (3)°$
$\gamma = 112.24\ (3)°$
$V = 2133.6\ (12)$ Å^3
$Z = 1$

$T = 298$ K
Prism
$0.22 \times 0.16 \times 0.08$ mm
Colorless

Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: by integration from crystal shape
$T_{\min} = 0.38$, $T_{\max} = 0.59$
15196 measured reflections
7486 independent reflections

7486 observed reflections [all reflections used]
$\theta_{\max} = 25°$
$h = -14 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -18 \rightarrow 18$
3 standard reflections frequency: 167 min intensity variation: 0.2%

Refinement

Refinement on F^2
Final $R = 0.0424$
$wR = 0.0045$
$S = 1.45$
7486 reflections
437 parameters
H-atom parameters not refined

$(\Delta/\sigma)_{\max} = 0.04$
$\Delta\rho_{\max} = 2.7$ e Å^{-3}
$\Delta\rho_{\min} = -0.45$ e Å^{-3}
Extinction correction: Becker & Coppens (1974) type 1 isotropic
Extinction coefficient: $0.174\ (11) \times 10^{-6}$

Weights were taken as $1/\sigma^2(F_o^2)$; variances $[\sigma^2(F_o^2)]$ derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data by propagation of error plus another additional term, $(0.014\langle I\rangle)^2$. Goodness of fit for merging data was 1.02; R_{merge} for duplicates, 0.027. Dispersion corrections and atomic scattering factors were taken from Cromer & Waber (1974). The final R for $F_o^2 > 3\sigma$ was 0.0301; the final wR, 0.0030.

Data collection: Enraf-Nonius CAD-4 software version 5.0 (Schagen, Straver, van Meurs & Williams, 1989). Cell refinement: Enraf-Nonius CAD-4 software version 5.0. Data reduction: *CRYM* (Duchamp, 1964). Program(s) used to solve structure: *CRYM*. Program(s) used to refine structure: *CRYM*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *CRYM*.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\text{eq}} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Au1	0.17347 (2)	0.02897 (2)	0.19685 (2)	0.0330 (1)
P1	0.2098 (1)	0.1597 (1)	0.3400 (1)	0.0349 (3)
P2	0.1320 (1)	−0.1287 (1)	0.2797 (1)	0.0354 (3)
C1	0.1612 (5)	0.0605 (5)	0.4215 (4)	0.037 (1)
C2	0.1780 (5)	−0.0544 (5)	0.3962 (4)	0.039 (1)
P3	0.1920 (1)	0.0465 (1)	0.0482 (1)	0.0325 (3)
C3	0.0520 (5)	−0.0039 (5)	−0.0239 (4)	0.044 (2)
C10	0.3647 (5)	0.2553 (5)	0.3832 (4)	0.041 (1)
C11	0.4485 (6)	0.1930 (6)	0.3592 (5)	0.064 (2)
C12	0.5779 (6)	0.2689 (7)	0.3928 (6)	0.080 (3)
C13	0.6186 (6)	0.3818 (6)	0.3602 (6)	0.073 (2)
C14	0.5391 (7)	0.4460 (6)	0.3835 (6)	0.074 (2)
C15	0.4091 (6)	0.3712 (5)	0.3501 (5)	0.061 (2)
C16	0.1203 (5)	0.2496 (5)	0.3598 (4)	0.042 (1)
C17	−0.0091 (6)	0.1797 (6)	0.3224 (4)	0.054 (2)
C18	−0.0856 (6)	0.2511 (7)	0.3350 (6)	0.068 (2)
C19	−0.0774 (7)	0.3067 (7)	0.4318 (6)	0.071 (2)
C20	0.0505 (6)	0.3780 (6)	0.4685 (5)	0.065 (2)
C21	0.1269 (6)	0.3059 (6)	0.4572 (4)	0.054 (2)
C22	0.2201 (5)	−0.2201 (5)	0.2607 (4)	0.042 (1)
C23	0.3494 (5)	−0.1486 (5)	0.2465 (5)	0.054 (2)
C24	0.4194 (6)	−0.2257 (7)	0.2250 (6)	0.072 (2)
C25	0.4151 (6)	−0.2969 (6)	0.2965 (6)	0.070 (2)
C26	0.2884 (7)	−0.3690 (6)	0.3109 (5)	0.069 (2)
C27	0.2154 (6)	−0.2949 (6)	0.3317 (5)	0.059 (2)
C28	−0.0221 (5)	−0.2308 (5)	0.2808 (4)	0.041 (1)
C29	−0.1060 (6)	−0.1708 (6)	0.3084 (5)	0.058 (2)
C30	−0.2342 (6)	−0.2571 (7)	0.3081 (6)	0.073 (2)
C31	−0.2778 (6)	−0.3376 (7)	0.2191 (5)	0.074 (2)
C32	−0.1952 (6)	−0.3983 (6)	0.1921 (5)	0.073 (2)
C33	−0.0686 (6)	−0.3112 (6)	0.1907 (5)	0.066 (2)
C34	0.2765 (5)	0.1970 (5)	0.0316 (4)	0.041 (1)
C35	0.4011 (5)	0.2414 (5)	0.0802 (5)	0.056 (2)
C36	0.4752 (7)	0.3673 (7)	0.0751 (6)	0.081 (3)
C37	0.4099 (7)	0.4451 (6)	0.1063 (5)	0.075 (2)
C38	0.2917 (7)	0.4035 (6)	0.0538 (5)	0.072 (2)
C39	0.2141 (6)	0.2781 (6)	0.0621 (5)	0.061 (2)
C40	0.2729 (5)	−0.0386 (5)	−0.0078 (4)	0.037 (1)
C41	0.2131 (6)	−0.1676 (5)	0.0000 (4)	0.051 (2)
C42	0.2896 (6)	−0.2330 (6)	−0.0373 (5)	0.062 (2)
C43	0.3098 (7)	−0.2216 (7)	−0.1335 (5)	0.069 (2)
C44	0.3656 (6)	−0.0954 (7)	−0.1447 (5)	0.067 (2)
C45	0.2920 (6)	−0.0271 (6)	−0.1056 (4)	0.058 (2)
Au2	0.000	−0.500	0.000	0.0726 (1)
C4	0.0203 (9)	−0.5557 (8)	0.1096 (7)	0.093 (3)
N1	0.0333 (9)	−0.5851 (9)	0.1737 (7)	0.147 (4)
Au3	0.500	0.000	0.500	0.0773 (1)
C5	0.6236 (9)	−0.0053 (8)	0.4175 (7)	0.090 (3)
N2	0.6932 (9)	−0.0091 (8)	0.3712 (7)	0.118 (3)

Table 2. *Geometric parameters* (Å, °)

Au1—P1	2.440 (2)	P2—C22	1.847 (6)
Au1—P2	2.422 (2)	P2—C28	1.833 (6)
Au1—P3	2.318 (1)	P3—C3	1.846 (6)
P1—C1	1.849 (6)	P3—C34	1.846 (6)
P1—C10	1.851 (6)	P3—C40	1.844 (6)
P1—C16	1.846 (6)	C1—C2	1.531 (8)
P2—C2	1.839 (6)	C3—C3$^{\text{i}}$	1.502 (8)
P1—Au1—P2	87.4 (1)	C2—P2—C22	103.6 (3)
P1—Au1—P3	136.9 (1)	C2—P2—C28	104.9 (3)
P2—Au1—P3	135.3 (1)	C22—P2—C28	105.4 (3)
Au1—P1—C1	103.9 (2)	Au1—P3—C3	116.4 (2)
Au1—P1—C16	118.0 (2)	Au1—P3—C34	113.6 (2)
Au1—P1—C10	119.2 (2)	Au1—P3—C40	112.3 (2)
C1—P1—C10	103.3 (3)	C3—P3—C34	105.2 (3)
C1—P1—C16	103.5 (3)	C3—P3—C40	103.5 (3)
C10—P1—C16	106.6 (3)	C34—P3—C40	104.7 (3)
Au1—P2—C2	103.9 (2)	P1—C1—C2	114.8 (4)
Au1—P2—C22	117.8 (2)	P2—C2—C1	116.0 (4)
Au1—P2—C28	119.4 (2)	P3—C3—C3$^{\text{i}}$	114.3 (4)

Symmetry code: (i) $-x, -y, -z$.

The material was synthesized by adding three-quarters of an equivalent of the chelating phosphine ligand to 50 ml of argon-purged MeOH containing 150 mg of AuCN, which was prepared according to a literature procedure (Chadwick & Sharpe, 1966). After 1 h of stirring, the solvent was evaporated to 10 ml under reduced pressure. The white precipitate was collected by vacuum filtration; crystals for X-ray diffraction were grown by recrystallization from MeOH.

This work was supported by National Science Foundation Grant CHE 89-22067.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71098 (44 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1004]

References

Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* **A30**, 129–147.
Chadwick, B. M. & Sharpe, A. G. (1966). *Adv. Inorg. Chem. Radiochem.* **8**, 156–157.
Che, C. M., Kwong, H. C., Poon, C. K. & Yam, V. W. W. (1990). *J. Chem. Soc. Dalton Trans.* pp. 3215–3219.
Che, C. M., Wong, W. T., Lai, T. F. & Kwong, H. L. (1989). *J. Chem. Soc. Chem. Commun.* pp. 243–244.
Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 99–101. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Duchamp, D. J. (1964). Am. Crystallogr. Assoc. Meet., Bozeman, Montana, Abstract B-14, pp. 29–30.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-3974. 3rd revision. Oak Ridge National Laboratory, Tennessee, USA.
Khan, N. I., Fackler, J. P. Jr, King, C., Wang, J. C. & Wang, S. (1989). *Inorg. Chem.* **27**, 1672–1673.
King, C., Wang, J. C., Khan, N. I. & Fackler, J. P. Jr (1989). *Inorg. Chem.* **28**, 2145–2149.
Schagen, J. D., Straver, L., van Meurs, F. & Williams, G. (1989). *CAD-4 Manual.* Version 5. Enraf-Nonius, Delft, The Netherlands.

Acta Cryst. (1993). C**49**, 1469–1473

Dimeric Copper(II) Triphenylacetate Adducts with 4-Picoline

MICHINARI YAMANAKA AND SHIGERU OHBA*

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi, Kohoku-ku, Yokohama 223, Japan

TADASHI TOKII

Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga 840, Japan

C. FREDERICK JURY AND OMAR W. STEWARD

Department of Chemistry, Duquesne University, Pittsburgh, PA 15282, USA

MICHINOBU KATO

13–30, Takatorikita 4, Asaminami-ku, Hiroshima, 731-01, Japan

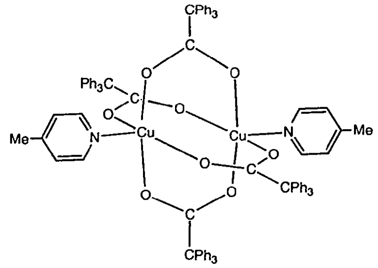
(*Received* 9 *October* 1992; *accepted* 2 *February* 1993)

Abstract

The crystal structure of tetrakis(μ-triphenylacetato-O:O')-bis[(4-methylpyridine-N)copper(II)] ditoluene solvate (I), $[Cu(Ph_3CCOO)_2(4\text{-pic})]_2.2C_7H_8$ (4-pic = 4-picoline), at 120 K, and the analogous $[Cu(Ph_3CCOO)_2(4\text{-pic})]_2.2C_6H_6$ (II) at 290 K were determined by single-crystal X-ray diffraction. The crystal structures of (I) and (II) are essentially identical, and the coordination geometry around the Cu atoms is distorted toward trigonal bipyramidal. The Cu···Cu distances are 2.793 (2) and 2.835 (4) Å in (I) and (II), respectively.

Comment

The electron spin resonance (ESR) spectrum of the title complex, $[Cu(Ph_3CCOO)_2(4\text{-pic})]_2$, shows a marked change over the temperature range 133 to 310 K (Jury, 1989). The spectral change can be explained by assuming an interconversion of two conformers of the complex. In order to prove the assumption, X-ray intensity data of a crystal of (II), grown from a benzene solution, were collected at room temperature. The structural determination of (II) was unsuccessful because of the poor experimental resolution. The complex was recrystallized from toluene and intensity measurements of a crystal of (I) were carried out at 120 K. The structure of (I) was solved and as a result of this the structure of (II) could be analyzed with reference to the solved structure of (I). The crystal structures of (I) and (II) are essentially the same except for the accommodation of the solvent molecules (Fig. 1). There is no disorder of the 4-picoline ligands. The crystals did not show X-ray diffraction after efflorescence. In conclusion, the origin of the temperature-dependent ESR spectrum of $[Cu(Ph_3CCOO)_2(4\text{-pic})]_2$ was not resolved by the present studies.



$[Cu(Ph_3CCOO)_2(4\text{-pic})]_2$

The coordination geometry around the Cu atoms is distorted trigonal bipyramidal (TBP) (Fig. 2). The TBP structure of the dimeric copper(II) carboxylates has been observed for a number of copper(II) trichloroacetates (Uekusa *et al.*, 1992, and references therein), $[Cu(Ph_3CCOO)_2(py)]_2.C_6H_6$ (III) (Steward *et al.*, 1991) and $[Cu(PhMe_2CCOO)_2(2,6\text{-lutidine})]_2.C_6H_6$ (Fujita *et al.*, 1993). The distortion of the metal coordination sphere in the dimeric systems from square pyramidal (SP) to trigonal bipyrmidal (TBP) decreases the $-2J$ value and there is a good linear correlation between the $-2J$ value and the Cu···Cu distance (Uekusa *et al.*, 1992).

Acta Crystallographica Section C
ISSN 0108-2701 © 1993