Collection des données

Diffractomètre Syntex $P2_1$
Balayage ω–2θ
Correction d'absorption: aucune
2114 réflexions mesurées
2114 réflexions indépendantes
1095 réflexions observées $[I > 4\sigma(I)]$

$\theta_{\max} = 27{,}5°$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 12$
3 réflexions de référence mesurées toutes les 60 réflexions
variation d'intensité: 1%

Affinement

Affinement basé sur les F
$R = 0{,}05$
$wR = 0{,}04$
$S = 1{,}47$
1095 réflexions
124 paramètres
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0{,}034$

$\Delta\rho_{\max} = 0{,}46$ e Å^{-3}
$\Delta\rho_{\min} = -0{,}48$ e Å^{-3}
Correction d'extinction: aucune
Facteurs de diffusion des *International Tables for X-ray Crystallography* (1974, Tome IV)

Tableau 1. *Coordonnées atomiques et facteurs d'agitation thermique isotrope équivalents* (Å^2)

$$U_{\text{éq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\text{éq}}$
Cu	1	0	1	0,0265 (8)
N(1)	1,1282 (6)	0,0753 (6)	0,8086 (5)	0,032 (3)
N(2)	1,3876 (6)	0,1798 (7)	0,6268 (5)	0,038 (3)
N(3)	1,4543 (6)	0,1906 (6)	0,8678 (5)	0,026 (3)
N(4)	1,2390 (6)	0,1356 (7)	1,0958 (5)	0,038 (3)
N(5)	1,5709 (6)	0,2887 (6)	1,1109 (5)	0,034 (3)
C(1)	1,3126 (7)	0,1453 (7)	0,7675 (6)	0,026 (4)
C(2)	1,4161 (7)	0,2051 (8)	1,0286 (7)	0,028 (4)
C(3)	1,1084 (8)	0,7182 (9)	0,4044 (7)	0,035 (4)
C(51)	1,7611 (8)	0,3951 (8)	1,0409 (7)	0,042 (4)
C(52)	1,5534 (8)	0,2936 (8)	1,2778 (7)	0,041 (4)
O(1)	1,2048 (5)	0,6012 (6)	0,4027 (5)	0,053 (4)
O(2)	0,9236 (5)	0,6936 (6)	0,4841 (5)	0,052 (3)
O(3)	1,1740 (5)	0,8495 (6)	0,3423 (5)	0,043 (3)

Tableau 2. *Paramètres géométriques* (Å, °)

Cu—N(1)	1,920 (4)	N(5)—C(2)	1,342 (6)
Cu—N(4)	1,931 (4)	N(5)—C(52)	1,448 (7)
N(1)—C(1)	1,282 (6)	N(5)—C(51)	1,476 (6)
N(2)—C(1)	1,323 (6)	C(3)—O(3)	1,221 (6)
N(3)—C(1)	1,392 (6)	C(3)—O(1)	1,270 (6)
N(3)—C(2)	1,364 (6)	C(3)—O(2)	1,339 (6)
N(4)—C(2)	1,305 (6)		
N(1)—Cu—N(4)	88,9 (2)	N(1)—C(1)—N(3)	122,7 (5)
C(1)—N(1)—Cu	128,8 (4)	N(2)—C(1)—N(3)	113,4 (4)
C(2)—N(3)—C(1)	125,7 (4)	N(4)—C(2)—N(5)	122,6 (5)
C(2)—N(4)—Cu	129,6 (4)	N(4)—C(2)—N(3)	121,1 (5)
C(2)—N(5)—C(52)	121,3 (4)	N(5)—C(2)—N(3)	116,3 (5)
C(2)—N(5)—C(51)	121,7 (5)	O(3)—C(3)—O(1)	124,7 (6)
C(52)—N(5)—C(51)	116,7 (4)	O(3)—C(3)—O(2)	119,6 (6)
N(1)—C(1)—N(2)	123,9 (5)	O(1)—C(3)—O(2)	115,7 (6)

D	H	A	$D\cdots A$	D—H$\cdots A$
N(1)	H(1*A*)	O(3$^{\text{i}}$)	3,061 (6)	154
N(2)	H(2*A*)	O(1$^{\text{ii}}$)	2,893 (5)	158
N(3)	H(3*A*)	O(3$^{\text{ii}}$)	2,908 (5)	159
O(2)		O(1$^{\text{i}}$)	2,593 (6)	

Codes de symétrie: (i) $2 - x, 1 - y, 1 - z$; (ii) $3 - x, 1 - y, 1 - z$.

Les intensités ont été corrigées des facteurs de Lorentz et de polarisation. La structure a été résolue à l'aide des méthodes directes (*MULTAN*88; Debaerdemaeker *et al.*, 1988). L'affinement des paramètres x, y, z, β_{ij} pour les atomes non hydrogènes, B_{iso} pour les atomes d'hydrogène, a été effectué à l'aide du programme *ORXFLS* (Busing, 1971). Les coordonnées de l'atome d'hydrogène appartenant à l'ion hydrogénocarbonate n'ont pu être déterminées. Les dessins de la structure ont été obtenus à l'aide du programme *ORTEP*II (Johnson, 1976). Les angles dièdres ont été calculés à l'aide du programme *BEST PLANES* (Ito & Sugawara, 1983).

Les listes des facteurs de structure, des facteurs d'agitation thermique anisotrope, des coordonnées des atomes d'hydrogène, des distances et angles des atomes d'hydrogène, des plans moyens et des angles de torsion ont été déposées au dépôt d'archives de l'UICr (Référence: DU1088). On peut en obtenir des copies en s'adressant à: The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

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(Nitrito-*O*,*O*′)bis(triphenylphosphine)-copper(I), $(PPh_3)_2Cu(NO_2\text{-}O,O')$

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Abstract

Symmetric binding of nitrite *via* both O atoms to Cu$^{\text{I}}$ [Cu—O = 2.191 (4) Å] was observed. The copper coordination geometry is significantly distorted from tetrahedral, as evidenced by the angles P—Cu—P [127.75 (7)°] and O—Cu—O [56.7 (2)°].

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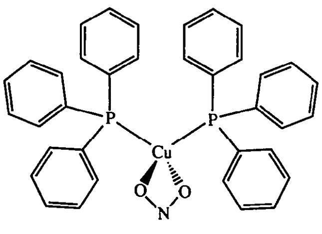
Comment

The crystal structure determination of the title compound, $(PPh_3)_2Cu(NO_2\text{-}O,O')$, (I), was undertaken as part of our work on synthetic modeling of the interactions of nitrogen oxides with copper sites in biological and heterogeneous catalytic systems (Ruggiero *et al.*, 1993; Tolman, Carrier, Ruggiero, Antholine & Whittaker, 1993; Halfen, Mahapatra, Olmstead & Tolman, 1994; Halfen & Tolman, 1994). In particular, we have been interested in defining the structural features of $Cu^I\text{–}(NO_2^-)$ adducts because such species have been implicated as possible intermediates in denitrification reactions catalyzed by copper nitrite reductases (Hulse, Averill & Tiedje, 1989; Jackson, Tiedje & Averill, 1991).



(I)

The X-ray crystal structure determination of the title compound revealed that the overall geometry (Fig. 1) is closely analogous to that of its precursor, $(PPh_3)_2Cu(NO_3\text{-}O,O')$ (Messmer & Palenik, 1969). Particularly noteworthy features (with comparable data for the nitrate precursor given in square brackets) are the molecular twofold rotational axis through Cu1 and N3, the symmetrical nitrito-*O*,*O'* coordination with a Cu—O distance of 2.191 (4) Å, a wide P—Cu—P angle of 127.75 (7)° [131.2 (1)°], and an O—Cu—O bite angle of 56.7 (2)° [57.5 (3)°]. The Cu—O bond length is significantly longer than the $Cu^I\text{—}O_{nitrite}$ distance in the only other copper(I) complex known to contain such a bond, $[(^iPr_3TACN)_2Cu_2(\mu\text{-}NO_2\text{-}N{:}O)]PF_6$ [Cu—O = 1.968 (2) Å; $^iPr_3TACN$ = 1,4,7-triisopropyl-1,4,7-triazacyclononane] (Halfen, Mahapatra, Olmstead & Tolman, 1994), suggesting that the $Cu^I\text{–}(NO_2^-)$ interaction in the title complex is rather weak.

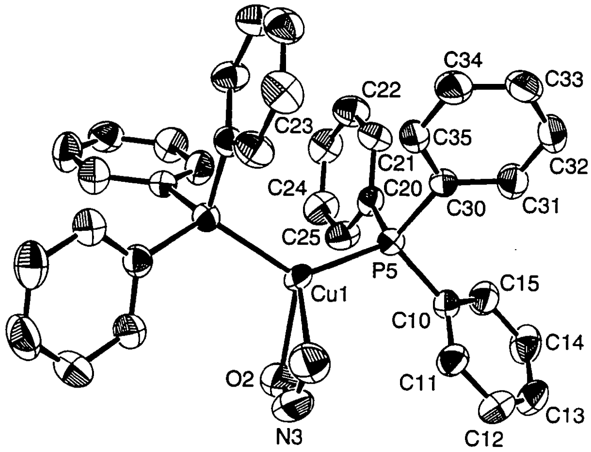


Fig. 1. *ORTEP* (Johnson, 1965) representation of the complex with H atoms omitted (50% probability ellipsoids).

Experimental

The title complex was prepared by adding $NaNO_2$ in MeOH to a solution of $(PPh_3)_2Cu(NO_3\text{-}O,O')$ (Messmer & Palenik, 1969) in refluxing CH_3CN. The resulting white precipitate was crystallized by diffusion of Et_2O into a CH_2Cl_2 solution.

Crystal data

$[Cu(NO_2)(C_{18}H_{15}P)_2]$
$M_r = 634.13$
Monoclinic
$C2/c$
$a = 24.443\ (9)$ Å
$b = 9.102\ (2)$ Å
$c = 15.356\ (5)$ Å
$\beta = 116.01\ (3)°$
$V = 3070\ (4)$ Å^3
$Z = 4$
$D_x = 1.372\ (2)$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 12\text{–}24°$
$\mu = 0.846$ mm^{-1}
$T = 297$ K
Prism
0.55 × 0.45 × 0.35 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: empirical (three ψ scans)
$T_{min} = 0.89$, $T_{max} = 1.00$
4009 measured reflections
3919 independent reflections
2457 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.093$
$\theta_{max} = 28°$
$h = 0 \rightarrow 32$
$k = 0 \rightarrow 12$
$l = -20 \rightarrow 20$
3 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on I
$R = 0.063$
$wR = 0.060$
$S = 1.72$
2457 reflections
191 parameters
H-atom parameters not refined
$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 0.90$ e Å^{-3}
$\Delta\rho_{min} = -0.63$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

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

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cu1	1/2	0.40179 (8)	1/4	2.96 (3)
P5	0.40863 (5)	0.5103 (1)	0.19711 (8)	2.64 (4)
O2	0.4993 (2)	0.1900 (4)	0.3172 (3)	5.4 (2)
N3	1/2	0.1147 (7)	1/4	5.9 (3)

C10	0.3452 (2)	0.3880 (5)	0.1767 (3)	3.0 (2)
C11	0.3470 (2)	0.2478 (5)	0.1438 (4)	3.8 (2)
C12	0.2984 (2)	0.1524 (6)	0.1228 (4)	4.9 (2)
C13	0.2486 (2)	0.1957 (6)	0.1351 (4)	5.2 (3)
C14	0.2463 (2)	0.3337 (7)	0.1684 (4)	4.6 (2)
C15	0.2944 (2)	0.4304 (5)	0.1890 (3)	3.9 (2)
C20	0.4090 (2)	0.6416 (5)	0.2867 (3)	2.9 (2)
C21	0.4099 (2)	0.7926 (5)	0.2749 (3)	3.7 (2)
C22	0.4187 (2)	0.8864 (5)	0.3506 (4)	4.3 (2)
C23	0.4265 (2)	0.8321 (6)	0.4382 (4)	4.3 (2)
C24	0.4253 (2)	0.6819 (6)	0.4514 (4)	4.4 (2)
C25	0.4169 (2)	0.5888 (5)	0.3759 (3)	4.0 (2)
C30	0.3826 (2)	0.6170 (4)	0.0856 (3)	2.8 (2)
C31	0.3216 (2)	0.6289 (5)	0.0202 (3)	3.9 (2)
C32	0.3050 (2)	0.7111 (6)	−0.0640 (4)	4.5 (2)
C33	0.3475 (2)	0.7825 (5)	−0.0825 (3)	4.1 (2)
C34	0.4079 (2)	0.7709 (5)	−0.0189 (4)	4.2 (2)
C35	0.4249 (2)	0.6886 (5)	0.0645 (3)	3.7 (2)

Table 2. *Selected geometric parameters* (Å, °)

Cu1—P5	2.243 (1)	C20—C21	1.387 (6)
Cu1—O2	2.191 (4)	C20—C25	1.382 (6)
P5—C10	1.821 (4)	C21—C22	1.381 (6)
P5—C20	1.820 (4)	C22—C23	1.367 (7)
P5—C30	1.823 (4)	C23—C24	1.385 (7)
O2—N3	1.245 (5)	C24—C25	1.378 (6)
C10—C11	1.381 (6)	C30—C31	1.390 (6)
C10—C15	1.390 (6)	C30—C35	1.375 (6)
C11—C12	1.391 (6)	C31—C32	1.392 (6)
C12—C13	1.371 (7)	C32—C33	1.357 (7)
C13—C14	1.366 (8)	C33—C34	1.372 (6)
C14—C15	1.391 (6)	C34—C35	1.382 (6)
P5—Cu1—P5′	127.75 (7)	C13—C14—C15	119.9 (5)
P5—Cu1—O2	110.2 (1)	C10—C15—C14	120.7 (4)
P5—Cu1—O2′	115.4 (1)	P5—C20—C21	123.1 (4)
O2—Cu1—O2′	56.7 (2)	P5—C20—C25	118.2 (3)
Cu1—P5—C10	115.5 (2)	C21—C20—C25	118.1 (4)
Cu1—P5—C20	110.0 (1)	C20—C21—C22	120.5 (4)
Cu1—P5—C30	117.2 (1)	C21—C22—C23	120.5 (5)
C10—P5—C20	104.6 (2)	C22—C23—C24	119.9 (5)
C10—P5—C30	104.1 (2)	C23—C24—C25	119.3 (5)
C20—P5—C30	104.1 (2)	C20—C25—C24	121.7 (5)
Cu1—O2—N3	95.0 (4)	P5—C30—C31	122.8 (3)
O2—N3—O2′	113.2 (6)	P5—C30—C35	119.0 (3)
P5—C10—C11	117.8 (3)	C31—C30—C35	118.2 (4)
P5—C10—C15	123.4 (4)	C30—C31—C32	119.8 (4)
C11—C10—C15	118.7 (4)	C31—C32—C33	120.9 (4)
C10—C11—C12	120.0 (4)	C32—C33—C34	119.9 (4)
C11—C12—C13	120.6 (5)	C33—C34—C35	119.6 (4)
C12—C13—C14	120.0 (5)	C30—C35—C34	121.6 (4)

All calculations were performed using the *TEXSAN/TEXRAY* crystallographic software package (Molecular Structure Corporation, 1985). Structure solution: *MITHRIL* (Gilmore, 1984), *DIRDIF* (Beurskens, 1984).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1045). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(diphenylphosphino)methanetetradecacarbonylhexairidium Dichloromethane Solvate

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Abstract

The molecules of the title complex, μ-bis(diphenylphosphino)methane-*P*:*P′*-tetra-μ_3-carbonyl-decacarbonyl-*octahedro*-hexairidium, $[Ir_6(CO)_{14}(C_{25}H_{22}P_2)]$ are discrete monomeric units. Their coordination polyhedron is derived from that of the red $[Ir_6(CO)_{16}]$ isomer with a chelating dppm [bis(diphenylphosphino)methane] ligand replacing two equatorial terminal carbonyl groups in *cis* positions. The clusters display mirror symmetry with respect to the two P

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