$2C_4H_{12}P^+.Br_{10}Cu_4^{2-}$

Fig. 1. Stereoscopic illustration of the stacking of $Cu_4Br_{10}^{2-}$ anions in $(Me_4P)_2Cu_4Br_{10}$.

This study extends the crystal chemistry of compounds in the series $(Me_4PcX)_n(MX_2)_m$, where Pc = N, P, As or Sb; M = divalent metal ion, and X = Cl, Br or I (Pressprich, Bond & Willett, 1991). For an $n{:}m$ ratio of 2:1, the Cu^{2+} salts assume the β-K_2SO_4 structure for Pc = N, X = Cl (Clay, Murray-Rust & Murray-Rust, 1975), Pc = N, X = Br (Hasebe, Mashiyama & Gesi, 1985), Pc = P, X = Cl (Pressprich, Bond, Willett & White, 1989) and Pc = P, X = Br (Madariaga, Alberdi & Zúñiga, 1990). The first three all exhibit incommensurate phases. For $n{:}m$ = 1:1, only $(Me_4N)CuCl_3$ is known (Weenk & Spek, 1976; Willett, Bond, Haije, Soonieus & Maaskant, 1988) and is notable for the existence of phases manifesting a cooperative, dynamic Jahn–Teller effect (Willett *et al.*, 1988; Haije & Maaskant, 1988) and one-dimensional ferromagnetic behavior at low tempera-

ture (Landee & Willett, 1979). For $n{:}m$ = 1:2, the above-cited $(Me_4N)_2Cu_4Cl_{10}$ salt is found, while $(Me_4P)Cu_2Cl_5$ assumes a structure with a complex two-dimensional Cu/Cl framework (Haije, Dobbelaar & Maaskant, 1986).

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Structure of Dicarbonyl(η^4-1,5-cyclooctadiene)(triphenylphosphine)ruthenium

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Abstract. [Ru(η^4-C_8H_{12})(CO)$_2${P(C_6H_5)$_3$}], M_r = 527·57, monoclinic, $P2_1/n$, a = 9·130 (6), b = 16·638 (13), c = 16·163 (14) Å, β = 99·2 (1)°, V = 2423 (8) Å^3, Z = 4, D_m = 1·43, D_x = 1·45 g cm^{-3}, Mo $K\alpha$ radiation, λ = 0·71069 Å, μ = 7·227 cm^{-1}, $F(000)$ = 1080, T = 295 K. R = 0·066 for 1867 reflections with $I > 3\sigma(I)$ in the $\pm h$, $+k$, $\pm l$ quadrant. The Ru atom is coordinated by seven atoms, six C atoms, and one P atom, located at distances varying from 1·8 to 2·3 Å. Some of the C atoms belonging to the cyclooctadiene molecule exhibit important anisotropic displacement coefficients.

Table 1. *Crystal data and refinement parameters*

Formula	$C_{28}H_{27}O_2PRu$
Molecular weight	527·57
Crystal dimensions (mm)	0·5 × 0·4 × 0·2
Diffractometer	Syntex $P2_1$
Lattice constants	From 25 reflections within $20 \leq 2\theta \leq 25°$
Absorption correction	No
Scan type	$\theta/2\theta$
Scan width (°)	2·0–2·3
Scan speed (° min^{-1})	Variable (2–10)
2θ limits (°)	2·5–45
Reflections collected	7194
h,k,l range	± 9, + 17, ± 17
Non-equivalent reflections	3185 [1867 with $I > 3\sigma(I)$]
Standard reflections	006, 301, 080 (every 297 measurements); no decay observed
Internal agreement	0·049
No. of variables*	200
Solution method	Patterson synthesis
Refinement method	Least squares based on Fs
H atoms	Not included
(Shift/e.s.d.)$_{max}$	0·19 for Ru; 0·04 for all other atoms
R	0·066
wR	0·060
w	$1/\sigma(F)^2$
S	3·1
$|\Delta\rho|_{max}$	0·9 e Å^{-3}
System of programs	XRAY72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972)
f'(Ru), f''(Ru)	International Tables for X-ray Crystallography (1974, Vol. IV)

* H atoms omitted from refinement; C11–C28 refined isotropically.

Table 2. *Atomic coordinates and equivalent displacement parameters* ($Å^2$); *e.s.d.'s are given in parentheses*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}/U_{iso}*
Ru	0·1408 (1)	0·11677 (6)	0·41712 (6)	0·0409 (5)
O(1)	−0·1889 (9)	0·1357 (5)	0·4154 (5)	0·048 (4)
O(2)	0·2487 (9)	0·0548 (5)	0·5941 (6)	0·056 (4)
C(1)	−0·058 (1)	0·1299 (7)	0·4131 (7)	0·034 (5)
C(2)	0·209 (1)	0·0771 (7)	0·5276 (8)	0·032 (5)
C(3)	0·247 (1)	0·1534 (8)	0·3094 (7)	0·039 (5)
C(4)	0·168 (1)	0·118 (1)	0·2250 (7)	0·058 (6)
C(5)	0·103 (1)	0·0341 (9)	0·2336 (8)	0·058 (6)
C(6)	0·058 (1)	0·0184 (7)	0·3210 (9)	0·045 (6)
C(7)	0·153 (2)	−0·0180 (7)	0·3866 (9)	0·053 (6)
C(8)	0·310 (2)	−0·0415 (8)	0·3841 (9)	0·065 (7)
C(9)	0·401 (1)	0·0243 (9)	0·349 (1)	0·069 (7)
C(10)	0·351 (1)	0·1100 (9)	0·3667 (7)	0·042 (5)
P	0·1822 (3)	0·2480 (2)	0·4618 (2)	0·024 (1)
C(11)	0·071 (1)	0·3260 (7)	0·4010 (7)	0·030 (3)
C(12)	0·075 (1)	0·4062 (7)	0·4288 (7)	0·040 (4)
C(13)	−0·011 (1)	0·4653 (8)	0·3813 (8)	0·048 (4)
C(14)	−0·101 (1)	0·4417 (8)	0·3065 (8)	0·043 (4)
C(15)	−0·107 (1)	0·3627 (7)	0·2785 (7)	0·045 (4)
C(16)	−0·017 (1)	0·3030 (7)	0·3268 (8)	0·036 (3)
C(17)	0·152 (1)	0·2707 (6)	0·5698 (6)	0·024 (3)
C(18)	0·239 (1)	0·3261 (7)	0·6191 (7)	0·032 (3)
C(19)	0·215 (1)	0·3405 (7)	0·7026 (8)	0·042 (3)
C(20)	0·100 (1)	0·2988 (7)	0·7314 (8)	0·040 (4)
C(21)	0·014 (1)	0·2445 (8)	0·6831 (8)	0·046 (4)
C(22)	0·036 (1)	0·2304 (7)	0·5990 (7)	0·035 (3)
C(23)	0·374 (1)	0·2831 (7)	0·4644 (7)	0·029 (3)
C(24)	0·408 (1)	0·3379 (7)	0·4069 (8)	0·043 (4)
C(25)	0·564 (1)	0·3565 (8)	0·4087 (8)	0·062 (4)
C(26)	0·669 (1)	0·3238 (8)	0·4692 (9)	0·055 (4)
C(27)	0·635 (1)	0·2684 (8)	0·5254 (8)	0·050 (4)
C(28)	0·481 (1)	0·2462 (7)	0·5234 (7)	0·040 (3)

* Isotropic temperature factor for atoms C(11)–C(28).

Experimental. The title complex was obtained by irradiation (Philips HPK 125, Pyrex vessel) of a solution of $Ru(CO)_4PPh_3$ (2 mmol) (Whymann, 1973) and 1,5-cyclooctadiene (40 mmol) in anhydrous degassed THF (100 ml) for 15 h at 248 K under argon. Chromatography on degassed silica using hexane/ethyl acetate (4:1), followed by crystallization from hexane/ether at 248 K yielded yellow microcrystals (57·3%). D_m measured by flotation in an aqueous solution of ZnI_2. Table 1 lists the relevant data for the structure refinement. Atomic and displacement parameters are listed in Table 2. The molecular structure is shown in Fig. 1 and selected bond lengths and angles are presented in Table 3.*

Related literature. $M(CO)_3(\eta^4$-1,3-diene) complexes (M = Fe, Ru, Os) have a square pyramidal structure and an IR set of CO bands consistent with point symmetry m (C_s). Their intramolecular rearrangements can usually be blocked on the ^{13}C NMR time scale with activation energies of 28–50 kJ mol^{-1}. $M(CO)_3(\eta^4$-1,5-cyclooctadiene) complexes (M = Fe, Ru) seem to belong to the same structural type, as shown by the X-ray analysis of $Fe(CO)_3(\eta^4$-1,5-cyclooctadiene) (Grevels, Jacke, Klotzbücher, Krüger, Seevogel & Tsay, 1987). The latter compound is highly fluxional with CO site exchanges taking place on the picosecond time scale. No other geometries have been observed in equilibrium with the ground-state structure in any of these systems.

* Lists of structure factors and anisotropic displacement coefficients have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54078 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
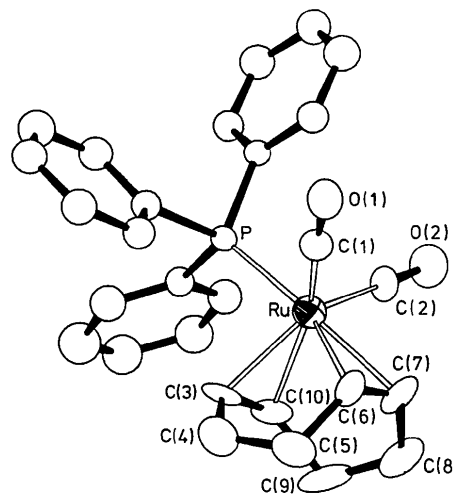

Fig. 1. Molecular structure of $Ru(CO)_2(\eta^4$-1,5-cyclooctadiene)PPh$_3$.

Table 3. *Relevant bond distances* (Å) *and angles* (°);
e.s.d.'s are given in parentheses

Ru—C(1)	1·818 (12)	C(1)—O(1)	1·206 (14)
Ru—C(2)	1·913 (13)	C(2)—O(2)	1·139 (15)
Ru—C(3)	2·208 (13)	C(3)—C(4)	1·551 (16)
Ru—C(6)	2·299 (13)	C(4)—C(5)	1·532 (21)
Ru—C(7)	2·302 (13)	C(5)—C(6)	1·555 (20)
Ru—C(10)	2·204 (12)	C(6)—C(7)	1·395 (18)
Ru—P	2·313 (4)	C(7)—C(8)	1·495 (21)
Ru—M(1)	2·089	C(8)—C(9)	1·536 (22)
Ru—M(2)	2·192	C(9)—C(10)	1·538 (21)
		C(10)—C(3)	1·416 (16)
C(1)—Ru—C(2)	104·5 (5)	Ru—C(1)—O(1)	176 (1)
C(1)—Ru—P	90·5 (4)	Ru—C(2)—O(2)	179 (1)
C(2)—Ru—P	91·3 (4)	C(3)—C(4)—C(5)	113 (1)
M(1)—Ru—P	89·1	C(4)—C(5)—C(6)	113 (1)
M(2)—Ru—P	170·3	C(5)—C(6)—C(7)	123 (1)
M(1)—Ru—C(1)	138·4	C(6)—C(7)—C(8)	125 (1)
M(1)—Ru—C(2)	117·3	C(7)—C(8)—C(9)	114 (1)
M(2)—Ru—C(1)	91·2	C(8)—C(9)—C(10)	113 (1)
M(2)—Ru—C(2)	97·8	C(9)—C(10)—C(3)	123 (1)
M(1)—Ru—M(2)	83·3	C(10)—C(3)—C(4)	123 (1)

$M(1)$ and $M(2)$ are the mid-points of C(3)—C(10) and C(6)—C(7), respectively.

This is not so for $Ru(CO)_2(\eta^4\text{-}1,5\text{-cyclooctadiene})$-PPh$_3$, which is the object of the present structural analysis.

The coordination polyhedron about ruthenium is best described by the atoms C(1), C(2) and P, and the mid-points of the two C=C double bonds of the diene, which define a distorted trigonal bipyramid. The bidentate ligand occupies an axial and an equa-

torial site, the tertiary phosphine occupies an axial site. The C(3)—C(10) ring is practically in the equatorial plane (deviation 4°) and the two double bonds are almost parallel to each other. There is no obvious reason why the two CO bond lengths are significantly different. This is reflected in the observation of two IR bands [$\nu(CO)$ 1975 and 1920 cm^{-1}] for crystals ground in Nujol.

d^8 metal diene complexes show a wide variety of fluxional behaviours on the IR time scale: Fe(CO)$_3$-(η^4-1,3-diene) complexes are rigid, whereas the present complex exhibits two observable stereoisomers whose interconversion is slow, and Fe(CO)$_3$-(η^4-1,5-cyclooctadiene) is stereochemically non-rigid on the IR time scale.

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Structure of Pentaaqua(glycine)nickel(II) Sulfate Monohydrate

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Abstract. $[Ni(C_2H_5NO_2)(H_2O)_5]SO_4.H_2O$, $M_r = 337\cdot9$, monoclinic, $P2_1/c$, $a = 5\cdot726$ (1), $b = 12\cdot302$ (2), $c = 17\cdot010$ (2) Å, $\beta = 97\cdot92$ (1)°, $V = 1187$ (1) Å^3, $Z = 4$, $D_m = 1\cdot88$ (2), $D_x = 1\cdot890$ (1) Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0\cdot71073$ Å, $\mu = 1\cdot83$ mm^{-1}, $F(000) = 704$, $T = 291$ K, $R = 0\cdot026$, 1938 unique observed reflections. The structure consists of $[Ni(H_3^+NCH_2COO^-)(H_2O)_5]^{2+}$ cations, sulfate anions and water molecules. The coordination around Ni is distorted octahedral with bonds to one glycine O atom and five water molecules. This is probably the first case of monodentate oxygen coordination by the glycine zwitterion. The structure is stabilized by a system of hydrogen bonds involving water–water, water–O(sulf.), water–O(Gly), O(sulf.)–N(Gly) and N(Gly)–O(Gly) interactions.

Experimental. The study of the title compound was undertaken as part of an investigation of nickel sulfate–glycine–water and nickel sulfate–triglycine sulfate–water systems, respectively. These systems are interesting within the bioinorganic chemistry framework and because of the possible formation of compounds with ferroelectric properties. The compound was prepared by evaporation of a dilute aqueous solution of glycine and nickel sulfate in 2:1 molar ratio. The crude green product was dissolved in water and the solution was allowed to stand in air for a few days. Green crystals obtained were stable in air and to X-rays. Density was determined by flota-

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