$V = 1612.3$ (2) Å^3
$Z = 4$
$D_x = 1.471$ Mg m^{-3}

Prism
$0.20 \times 0.15 \times 0.10$ mm
Green

Data collection

Nicolet *R*3 diffractometer
$\theta/2\theta$ scans
Absorption correction:
  Ψ method
  $T_{\min} = 0.75$, $T_{\max} = 0.87$
1343 measured reflections
1343 observed reflections
  $[F > \sigma(F)]$

$\theta_{\max} = 33.18°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 20$
1 standard reflection
  frequency: 60 min
  intensity variation:
    negligible

Refinement

Refinement on *F*
Final $R = 0.048$
$wR = 0.045$
$S = 1.11$
1106 reflections
109 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F)]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.435$ e Å^{-3}
$\Delta\rho_{\min} = -0.453$ e Å^{-3}
Atomic scattering factors
  from *International Tables for X-ray Crystallography*
  (1974, Vol. IV)

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

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

	x	*y*	*z*	$U_{\rm eq}$
Ni1	0.0575 (1)	0.4838 (1)	0.2500	0.032 (1)
O1	0.1042 (4)	0.3182 (4)	0.3062 (2)	0.043 (2)
O2	0.3011 (6)	0.5773 (5)	0.2500	0.045 (3)
N1	−0.0382 (6)	0.6167 (5)	0.3119 (2)	0.053 (3)
C1	0.0514 (8)	0.3055 (6)	0.3567 (3)	0.054 (4)
C2	0.0850 (7)	0.1683 (6)	0.3877 (2)	0.053 (4)
C3	0.0305 (8)	0.1488 (6)	0.4406 (3)	0.056 (4)
C4	−0.0626 (8)	0.2636 (6)	0.4674 (2)	0.052 (4)
C5	−0.0959 (7)	0.3974 (6)	0.4411 (3)	0.051 (4)
C6	−0.0417 (7)	0.4226 (6)	0.3867 (3)	0.051 (4)
C7	−0.0717 (8)	0.5693 (6)	0.3625 (3)	0.055 (4)
C8	−0.0680 (7)	0.7824 (6)	0.3023 (3)	0.055 (3)
C9	−0.1671 (10)	0.8136 (9)	0.2500	0.055 (5)

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

Ni1—O1	2.030 (4)	C4—C5	1.369 (8)
Ni1—O2	2.015 (5)	C5—C6	1.392 (9)
Ni1—N1	2.034 (5)	C6—C1	1.448 (8)
O1—C1	1.286 (7)	C6—C7	1.444 (8)
C1—C2	1.450 (7)	C7—N1	1.313 (8)
C2—C3	1.352 (9)	N1—C8	1.505 (7)
C3—C4	1.395 (8)	C8—C9	1.491 (7)
O1—Ni1—O2	98.0 (1)	C1—C6—C5	119.8 (5)
O1—Ni1—N1	89.5 (2)	C7—C6—C1	121.4 (5)
O1—Ni1—O1*A*	83.8 (2)	C7—C6—C5	118.7 (5)
O2—Ni1—N1	94.9 (2)	N1—C7—C6	129.3 (5)
N1—Ni1—N1*A*	94.4 (3)	C7—N1—Ni1	124.3 (4)
Ni1—O1—C1	130.0 (3)	C8—N1—Ni1	120.3 (4)
O1—C1—C6	124.0 (5)	C8—N1—C7	115.3 (5)
O1—C1—C2	120.5 (5)	C9—C8—N1	112.8 (5)
C6—C1—C2	115.5 (5)	C8—C9—C8*A*	115.4 (7)

2 g of the title complex was warmed in 80 ml 96.5% ethanol until completely dissolved. When this solution was left to cool, diamagnetic needle-shaped crystals began to precipitate, but as slow cooling continued, green paramagnetic prismatic crystals were obtained (48 h).

The phase problem was solved by direct methods using *SHELXS*86 (Sheldrick, 1986). All calculations were performed on a NOVA 3/12 computer using *SHELXTL* (Sheldrick, 1983).

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71310 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1026]

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The First Dinuclear Cobalt–Rhenium Cluster Compound: Hexacarbonylbis(μ-dicyclohexylphosphanido)cobaltrhenium

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Abstract

The title compound [hexacarbonyl-1κ^4C,2κ^2C-bis(μ-dicyclohexylphosphido-1:2κ^2P)cobaltrhenium(*Co*—*Re*) 0.5-methanol solvate] belongs to a type of edge-linked tetrahedron-octahedron coordination complex. The molecule has local C_{2v} symmetry with ecliptic conformation of the carbonyl ligands at both metal centres, and a Co—Re single-bond length of 2.786 (1) Å.

Comment

In the course of our work on phosphanido-bridged homo- and heteronuclear metal-atom cluster compounds (Haupt, Balsaa & Flörke, 1988; Haupt, Heinekamp & Flörke, 1989; Flörke & Haupt, 1993) we isolated the title compound with a Co—Re bond symmetrically bridged by two dicyclohexylphosphanido groups.

The cobalt atom has distorted tetrahedral coordination from two carbonyl ligands and the bridging P atoms. These bridging atoms and four of the carbonyl groups give rise to a distorted octahedral coordination at the rhenium metal. The central $CoReP_2$ ring is nearly planar; the maximum deviation from the best plane is 0.02 Å with a dihedral angle of 2.2°. With respect to the different metal atomic radii, the ring may be regarded as regular. It shows two equal *M*—P bond lengths for Co [2.111 (1) and 2.116 (1) Å] as well as for Re [2.541 (1) and 2.544 (1) Å]. The enclosed ring angles at both P atoms are acute [72.8 (1) and 72.9 (1)°] and the P—*M*—P angles reflect the distorted coordination polyhedron of each metal atom [121.3 (1) and 92.9 (1)° for Co and Re, respectively]. The most interesting structural feature is the Co—Re single bond which meets the requirement of 18 valence electrons for each metal atom and has a length of 2.786 (1) Å.

We have established on the basis of the Cambridge Structural Database (CSD; Allen *et al.*, 1979) that the only other cobalt-rhenium cluster reported so far is $[Co_2Re(\mu_3\text{-}CC_6H_4Me_4)(CO)_{10}]$ (Jeffery, Lewis, Lewis & Stone, 1985), with Co—Re bond lengths of 2.686 (1) and 2.720 (1) Å. This triangular cluster has distinctly different bonding and bridging patterns, so direct comparison of the heteronuclear bond lengths from both structures is not possible.

However, if we refer to the homonuclear single-bond lengths in the phosphanido-bridged cluster compounds $(C_5H_5)_2Co_2(\mu\text{-}PPh_2)_2$ [2.56 (1) Å (Coleman & Dahl, 1967)], $(CO)_4(C_5H_5)Co_2(\mu\text{-}PMe_2)$ [2.593 (3) Å (Keller & Vahrenkamp, 1978)] and $[(CO)_8Re_2(\mu\text{-}PPh_2)]^-$ [3.062 (1) Å (Haupt, Heinekamp & Flörke, 1989)], a combination of the increments gives a 'calculated' Co—Re single-bond length of 2.81 Å. Although this rough approach neglects the influence of different ligands and different numbers of bridging groups in the compounds considered, it should come close to a reasonable value for a phosphanido-bridged Co—Re single bond. Our measured length of 2.786 (1) Å is fairly close to this estimation.

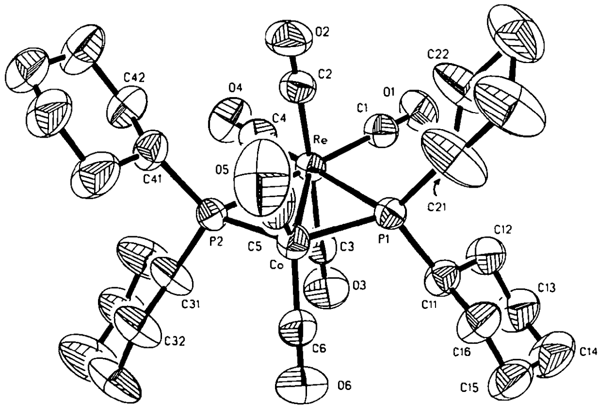

Fig. 1. Molecular structure showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

Experimental

Crystal data

$[CoRe(C_{12}H_{22}P)_2(CO)_6]$.-
$0.5(CH_3OH)$
$M_r = 823.7$
Triclinic
$P\bar{1}$
$a = 10.452\ (3)$ Å
$b = 11.664\ (4)$ Å
$c = 15.641\ (4)$ Å
$\alpha = 94.37\ (2)°$
$\beta = 89.75\ (2)°$
$\gamma = 111.87\ (2)°$
$V = 1763.8\ (8)$ Å^3

$Z = 2$
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 7\text{-}16°$
$\mu = 4.07\ \text{mm}^{-1}$
$T = 293$ K
Prism
0.50 × 0.34 × 0.28 mm
Red

Data collection

Siemens *R3m/V* diffractometer
$\omega\text{-}2\theta$ scans
Absorption correction: empirical *via* ψ scans
$T_{\min} = 0.690$, $T_{\max} = 0.894$
15189 measured reflections
8161 independent reflections
6813 observed reflections
$[F > 4\sigma(F)]$

$R_{\rm int} = 0.022$
$\theta_{\max} = 27.5°$
$h = -13 \rightarrow 13$
$k = -15 \rightarrow 15$
$l = -21 \rightarrow 21$
4 standard reflections
monitored every 400 reflections
intensity variation: none

Refinement

Refinement on F
Final $R = 0.038$
$wR = 0.034$
$S = 1.583$
6813 reflections
379 parameters
H-atom parameters not refined

Calculated weights
$w = 1/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.95$ e Å^{-3}
$\Delta\rho_{\min} = -0.80$ e Å^{-3}
Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1990)

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

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

	x	y	z	$U_{\rm eq}$
Re	0.2227 (1)	−0.0032 (1)	0.1460 (1)	0.042 (1)
Co	0.2347 (1)	0.1392 (1)	0.2992 (1)	0.046 (1)
P1	0.3589 (1)	0.2221 (1)	0.1970 (1)	0.044 (1)
P2	0.1068 (2)	−0.0511 (1)	0.2891 (1)	0.046 (1)
C1	0.3087 (6)	0.0299 (6)	0.0346 (4)	0.057 (4)
O1	0.3569 (5)	0.0449 (5)	−0.0308 (3)	0.079 (3)
C2	0.0662 (6)	0.0396 (6)	0.1118 (4)	0.056 (4)
O2	−0.0268 (5)	0.0626 (5)	0.0927 (3)	0.087 (4)
C3	0.3789 (7)	−0.0423 (6)	0.1896 (4)	0.063 (4)
O3	0.4690 (5)	−0.0639 (5)	0.2137 (4)	0.109 (4)
C4	0.1264 (7)	−0.1761 (6)	0.1055 (4)	0.062 (4)
O4	0.0725 (5)	−0.2773 (4)	0.0804 (3)	0.082 (4)
C5	0.1174 (8)	0.2127 (6)	0.3180 (5)	0.074 (5)
O5	0.0439 (7)	0.2631 (6)	0.3357 (5)	0.132 (5)
C6	0.3598 (7)	0.1483 (7)	0.3744 (4)	0.067 (4)
O6	0.4420 (6)	0.1602 (6)	0.4263 (4)	0.113 (5)
C11	0.5479 (6)	0.2618 (6)	0.2073 (4)	0.056 (4)
C12	0.6243 (6)	0.2560 (7)	0.1253 (4)	0.069 (4)
C13	0.7736 (7)	0.2760 (8)	0.1443 (5)	0.087 (6)
C14	0.8445 (8)	0.3902 (9)	0.2000 (6)	0.095 (7)

C15	0.7702 (7)	0.3955 (8)	0.2803 (5)	0.080 (5)
C16	0.6220 (7)	0.3776 (7)	0.2601 (5)	0.072 (5)
C21	0.3424 (7)	0.3479 (6)	0.1367 (4)	0.066 (4)
C22	0.2909 (12)	0.3202 (8)	0.0493 (5)	0.115 (8)
C23	0.2763 (10)	0.4240 (7)	0.0032 (5)	0.101 (6)
C24	0.2284 (11)	0.5054 (9)	0.0555 (6)	0.136 (8)
C25	0.2913 (13)	0.5398 (8)	0.1420 (6)	0.127 (8)
C26	0.3046 (11)	0.4368 (8)	0.1882 (5)	0.113 (7)
C31	0.1508 (8)	−0.1598 (6)	0.3512 (4)	0.073 (5)
C32	0.1474 (9)	−0.1357 (7)	0.4449 (4)	0.084 (5)
C33	0.2052 (11)	−0.2138 (10)	0.4961 (5)	0.117 (8)
C34	0.1618 (13)	−0.3401 (9)	0.4656 (6)	0.137 (10)
C35	0.1645 (10)	−0.3666 (7)	0.3705 (5)	0.104 (7)
C36	0.1114 (11)	−0.2894 (7)	0.3181 (5)	0.111 (7)
C41	−0.0838 (6)	−0.0989 (6)	0.2826 (4)	0.059 (4)
C42	−0.1615 (6)	−0.2146 (6)	0.2239 (5)	0.070 (5)
C43	−0.3150 (8)	−0.2352 (8)	0.2150 (6)	0.090 (6)
C44	−0.3786 (8)	−0.2269 (9)	0.2971 (6)	0.098 (7)
C45	−0.3021 (7)	−0.1117 (9)	0.3540 (5)	0.088 (6)
C46	−0.1497 (7)	−0.0911 (9)	0.3669 (5)	0.093 (6)
C100	0.3066 (15)	0.4157 (10)	0.5198 (7)	0.052 (7)
O100	0.4146 (13)	0.4760 (13)	0.4828 (8)	0.130 (11)

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

Re—Co	2.786 (1)	Co—P1	2.111 (1)
Re—P1	2.544 (1)	Co—P2	2.116 (1)
Re—P2	2.541 (1)		
Co—Re—P1	46.4 (1)	Re—Co—P2	60.6 (1)
Co—Re—P2	46.5 (1)	P1—Co—P2	121.3 (1)
P1—Re—P2	92.9 (1)	Re—P1—Co	72.9 (1)
Re—Co—P1	60.8 (1)	Re—P2—Co	72.8 (1)

Synthesis was carried out by reaction of $Re_2(CO)_{10}$, $Co_2(CO)_8$ and $HP(C_6H_{11})_2$ (molar ratio 1:1:2) in xylene solution for 10 h at 423 K in a glass tube. Recrystallization from methanol gave red crystals.

The enclosed CH_3OH solvent molecule had a site occupation factor of 0.5. Cyclohexyl H atoms were fixed at ideal positions with common isotropic displacement parameters (U_{iso} = 0.08 Å^2). Structure solution and refinement used *SHELXTL-Plus* (Sheldrick, 1990). Other programs include *PARST* (Nardelli, 1983).

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 71340 (38 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE1031]

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Structure of Isothiocyanato(1,4,7,11-tetraazacyclotetradecane)copper(II) Thiocyanate

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Abstract

There are two independent similar copper(II) complexes in the asymmetric unit. The coordination about copper(II) in each complex forms a distorted square pyramid with the tetraamine N atoms equatorial and the N atom of the isothiocyanato group axial. The two five-membered rings are in skew forms and the two six-membered rings in chair forms. The isothiocyanato groups are almost linear. Hydrogen bonds help stabilize the crystal structure.

Comment

In the case of 3*d*-metal complexes with saturated unsubstituted macrocyclic ligands, the whole series of 12- to 16-membered tetraaza macrocycles have been investigated extensively (Hinz & Margerum, 1974; Fabbrizzi, 1979). The 14-membered tetraaza system is unique among these ligands since it exists as two isomeric forms: cyclam (1,4,8,11-tetraazacyclotetradecane) and isocyclam (1,4,7,11-tetraazacyclotetradecane). The crystal structure of $[Cu(cyclam)(ClO_4)_2]$ has been reported (Tasker & Sklar, 1975). In this paper, we determine the crystal structure of $[Cu(isocyclam)(SCN)_2]$.

(1,4,7,11-Tetraazacyclotetradecane)copper(II) perchlorate was prepared by the procedure reported by Sabatini & Fabbrizzi (1979). 1 g of the complex in 25 ml of water was treated with 0.5 g of KSCN in 10 ml of water. The resulting blue solution was evaporated to dryness. It was then dissolved in 30 ml of CH_3NO_2, filtered and evaporated to yield blue solids. Single crystals were obtained from methanol solution by slow evaporation.

A perspective view of the molecules with the numbering scheme showing displacements above and below the best planes formed by atoms N(1), N(2), N(3), N(4) and N(6), N(7), N(8), N(9) is shown in Fig. 1.

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