X-Ray Crystal Structure of $[N(CH_2CH_2PPh_2)_3]_2Co_2$ (μ-Hg_2); the Dimeric Hg_2^{2+} Ion forms a Linear Bridge between the two Cobalt Atoms

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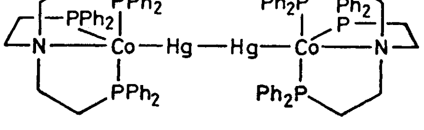
Summary The reaction of $[(np_3)CoCl]BPh_4$ {np_3 = $[N(CH_2CH_2PPh_2)_3]$} with sodium amalgam gives the tetrametallic complex $(np_3)Co(\mu$-$Hg_2)Co(np_3)$.thf (thf = tetrahydrofuran) the *X*-ray structural analysis of which shows that the Hg_2^{2+} ion linearly bridges two $Co(np_3)$ moieties.

WITHIN the past 40 years several mercury derivatives of transition metal carbonyl compounds of the general type m_2Hg, where m is a metal–carbonyl group, *e.g.*, m = $Co(CO)_4$, $Fe(CO)_2C_5H_5$, *etc.*, have been reported. These have all been formulated as Hg^{II} compounds and, generally, the fragment M–Hg–M is linear (M = Co, Fe, *etc.*).[1] However, the dimercury(I), Hg_2^{2+}, ion has not previously been found in metal-to-metal bonds and only a few complexes of this ion with O or N donor ligands have been, so far, reported.[2]



(1)

We have obtained the tetrametallic complex $(np_3)Co(\mu\text{-}Hg_2)Co(np_3)$, (**1**).thf, where np_3 is the tetradentate tripod-like ligand tris(2-diphenylphosphinoethyl)amine, $N(CH_2CH_2PPh_2)_3$ and have established the molecular structure by single-crystal *X*-ray analysis.

The complex $[(np_3)CoCl]BPh_4$[3] (1 mmol) in dry tetrahydrofuran (THF) (50 ml) was continuously stirred and treated at 50 °C under an inert atmosphere with 1% Na–Hg (*ca.* 10 mmol of Na) for 40 min. After the addition of n-butanol (50 ml) to the resultant dark red solution (which had been filtered), red-brown crystals of $(np_3)_2Co_2(\mu\text{-}Hg_2)$.thf were precipitated (yield 65%). The complex, which rapidly decomposes in air, is diamagnetic.

Crystal data: $C_{88}H_{92}Co_2Hg_2N_2OP_6$, $M = 1898{\cdot}61$, triclinic, space group $P\bar{1}$, $a = 25{\cdot}691(9)$, $b = 13{\cdot}387(5)$, $c = 13{\cdot}471(4)$ Å, $\alpha = 119{\cdot}56(8)$, $\beta = 97{\cdot}51(8)$, $\gamma = 87{\cdot}25(7)$°, $U = 3994{\cdot}48$ Å^3, $Z = 2$, $D_c = 1{\cdot}578$ g cm^{-3}, μ(Mo-K_α) = 44·0 cm^{-1}.

The crystal used was coated in paraffin to prevent air decomposition. Intensity data were collected on a Phillips computer controlled PW 1100 diffractometer using the $\omega - 2\theta$ scan technique and graphite-monochromatized Mo-K_α radiation. The structure was solved by heavy-atom techniques and refined by full-matrix least-squares methods using isotropic thermal parameters. The phenyl rings were treated as rigid groups. Refinements converged at R and R_w values of 0·067 and 0·064 for the 2687 reflections ($2\theta < 40$°) with $I > 3\sigma(I)$.†

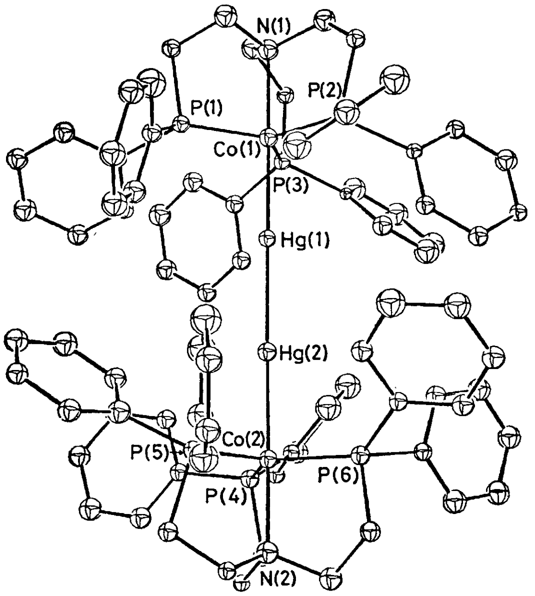


FIGURE. Perspective view of the $(np_3)Co(\mu\text{-}Hg_2)Co(np_3)$ molecule. Selected bond lengths (Å) and angles (°): Hg(1)–Hg(2) 2·651(4), Co(1)–Hg(1) 2·429(9), Co(2)–Hg(2), 2·444(9), Co(1)–P(1) 2·13(2), Co(1)–P(2), 2·11(1), Co(1)–P(3) 2·14(1), Co(1)–N(1) 2·13(4), Co(2)–P(4) 2·13(1), Co(2)–P(5) 2·16(2), Co(2)–P(6) 2.11(2), and Co(2)–N(2) 2·08(4); Co(1)–Hg(1)–Hg(2) 179·7(2), Co(2)–Hg(2)–Hg(1) 178·4(3), Hg(1)–Co(1)–N(1) 179·9(1·2), Hg(1)–Co(1)–P(1) 92·0(5), Hg(1)–Co(1)–P(2) 91·8(5), Hg(1)–Co(1)–P(3) 91·9(5), P(1)–Co(1)–P(2) 119·6(6), P(1)–Co(1)–P(3) 119·2(6), P(2)–Co(1)–P(3) 120·9(7), N(1)–Co(1)–P(1) 88·1(1·3), N(1)–Co(1)–P(2) 88·1(1·2), N(1)–Co(1)–P(3) 88·2(1·2), Hg(2)–Co(2)–N(2) 178·4(1·5), Hg(2)–Co(2)–P(4) 91·8(4), Hg(2)–Co(2)–P(5) 91·1(5), Hg(2)–Co(2)–P(6) 91·8(5), P(4)–Co(2)–P(5) 119·1(6), P(4)–Co(2)–P(6) 119·6(7), P(5)–Co(2)–P(6) 121·1(6), N(2)–Co(2)–P(4) 88·7(1·2), N(2)–Co(2)–P(5) 87·4(1·4), and N(2)–Co(2)–P(6) 89·3(1·4).

The molecular structure consists of discrete dimeric molecules of $(np_3)Co(\mu\text{-}Hg_2)Co(np_3)$ and solvated tetrahydrofuran molecules. The Figure shows a perspective view of the molecule. The four metal atoms of the Co–Hg–Hg–Co fragment are colinear; the two $Co(np_3)$ moieties are linearly attached to the dimercuric group with Co(1)–Hg(1)–Hg(2) and Hg(1)–Hg(2)–Co(2) angles of 179·7(2) and 178·4(3)°, respectively. Although the $(np_3)Co(\mu\text{-}Hg_2)Co(np_3)$ (**1**) molecule has no imposed crystallographic symmetry, corresponding bond lengths and angles in the co-ordination polyhedra of the cobalt atoms do not show significant differences. The mercury atoms are definitively di-co-ordinated; the 12 phenyl rings of the two np_3 ligands are arranged in such a way as to prevent further co-ordination. There are no contact distances between the mercury atoms and the phenyl rings shorter than 3.48 Å. The Hg–Hg bond distance of 2·651(4) Å compares well with the values reported for mercury(I) compounds, which are in the range 2·50—2·69 Å.[4] The cobalt atoms are penta-co-ordinated by the four donor atoms of the ligand np_3 and by one mercury atom with a nearly regular trigonal bipyramidal geometry; the main distortion is the displacement, 0·07 and 0·06 Å, of the cobalt atoms from the equatorial planes towards the mercury atoms which occupy axial positions. The values of the Hg–Co bond length, 2·429(9) and 2·444(9) Å, are slightly shorter than the corresponding value of 2·50 Å in $Hg[Co(CO)_4]_2$.[1b]

The tendency for the mercury of sodium amalgam to form mercury(II) derivatives of metal carbonyl compounds is known.[5] The stabilization, in the present case, of a mercury(I) derivative may be attributed to the particular conformation of the np_3 ligand. In fact, a closer approach of the $Co(np_3)$ moieties such as one would have in a $(np_3)Co(\mu\text{-}Hg)Co(np_3)$ species is probably prevented by the steric requirements of the bulky ligand. This is confirmed by the presence of some contact distances of *ca.* 3·7—3·8 Å between phenyl groups of the two $Co(np_3)$ moieties in the title compound. On the other hand the numerous phenyl groups shield the Hg_2^{2+} ion and prevent a possible disproportionation process.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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