

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: AB1203). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Copper Disordered Hexakis(phenylethynyl)pentaargentate(I) Cluster

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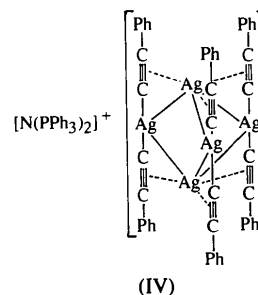
Abstract

The X-ray single-crystal structure determination of an anionic cluster, $[\text{Ag}_{4.46}\text{Cu}_{0.54}(\text{C}_8\text{H}_5)_6]^-$, with bis(triphenylphosphine)iminium counterions, $[\text{N}(\text{C}_{18}\text{H}_{15}\text{P})_2]^+$, prepared from the reaction of $[\text{Cu}(\text{C}\equiv\text{CPh})_2]^-$ and $[\{\text{Ag}(\text{C}\equiv\text{CPh})\}_n]^-$ in a 1:4 mole ratio, revealed a trigonal bipyramidal arrangement of Ag_5 with positional disorder, with copper substituting silver in some equatorial positions making the ratio of metal atoms 8.3 Ag:1 Cu. Each equatorial metal atom is σ bonded to the alkynyl ligands in an almost linear fashion. Ag atoms in apical positions are asymmetrically π bonded, with varying degrees of strength, to three alkyne ligands each.

Comment

We have recently reported the syntheses and structures of the pentanuclear clusters $[\text{Au}_3\text{Cu}_2(\text{C}\equiv\text{CPh})_6]^-$, (I) (Abu-Salah, Al-Ohaly & Knobler, 1985), and $[\text{Au}_3\text{Ag}_2(\text{C}\equiv\text{CPh})_6]^-$, (II) (Mazhar-Ul-Haque, Horne & Abu-Salah, 1992). The structures of both clus-

ters comprise trigonal bipyramids of metal atoms, with Au atoms occupying equatorial positions and Cu or Ag atoms in apical positions. We have also reported the syntheses and characterization of the homonuclear $[\text{Ag}_5(\text{C}\equiv\text{CPh})_6]^-$ and the heteronuclear $[\text{Ag}_4\text{Cu}(\text{C}\equiv\text{CPh})_6]^-$ anionic clusters (Abu-Salah, Al-Ohaly & Mutter, 1990). We assigned the Cu atom in the latter cluster an equatorial position with the four Ag atoms in two environments, namely two equatorial and two apical. X-ray single-crystal structure determination of the same silver–copper cluster compound, (IV), showed that copper is not present in the 4:1 ratio, but in a lower one of 8.3:1, which has also been shown by recent elemental analyses.



The crystal structure of the pentanuclear anionic cluster compound is shown in Figs. 1 and 2. The metal atoms have a trigonal bipyramidal arrangement. The equatorial positions were found to be disordered between Ag and Cu atoms in the ratio 4.6:1. Thus, the total Ag:Cu ratio in the crystal is 8.3:1. This ratio is in full agreement with the chemical analysis. Since the Ag atoms are predominant and the presence of the Cu atom, which has shorter $\text{Cu}\cdots\text{C}$ bond length than $\text{Ag}\cdots\text{C}$, does not have an obvious effect on the displacement parameters of the C atoms bonded to the metal atoms, the anionic cluster will be described as $[\text{Ag}_5(\text{C}\equiv\text{CPh})_6]^-$.

The present anionic cluster, (IV), is generally similar to that found in (I) and (II), except it has higher symmetry. The Ag(1) atom lies on the twofold axis, which passes through the midpoints of $\text{Ag}(2)\cdots\text{Ag}(2a)$ and $\text{Ag}(3)\cdots\text{Ag}(3a)$. The non-bonding metal–metal distances are $\text{Ag}(1)\cdots\text{Ag}(2)$ 3.945 (1), $\text{Ag}(2)\cdots\text{Ag}(2a)$ 3.893 (1) Å and axial $\text{Ag}(3)\cdots\text{Ag}(3a)$ 3.783 (1) Å. The latter distance is equal to the axial $\text{Ag}\cdots\text{Ag}$ distance in (II). On the other hand, the distances of Ag(3) to the equatorial atoms, Ag(1), Ag(2) and Ag(2a) are 3.024 (1), 2.903 (1) and 2.934 (1) Å, respectively, indicating substantial metal–metal bonding.

These bond lengths are less than or equal to the $\text{Ag}\cdots\text{Ag}$ bond of 3.033 Å found in polymeric $[\text{Ag}_2(\text{C}\equiv\text{CPh})_2(\text{PMe}_3)_2]$, (III) (Corfield & Shearer, 1966). Each Ag atom at an equatorial position is end-on σ -bonded to two ethynyl atoms in a nearly linear fashion; the $\text{C}(81)\text{—Ag}(1)\text{—C}(81a)$ and $\text{C}(82)\text{—}$

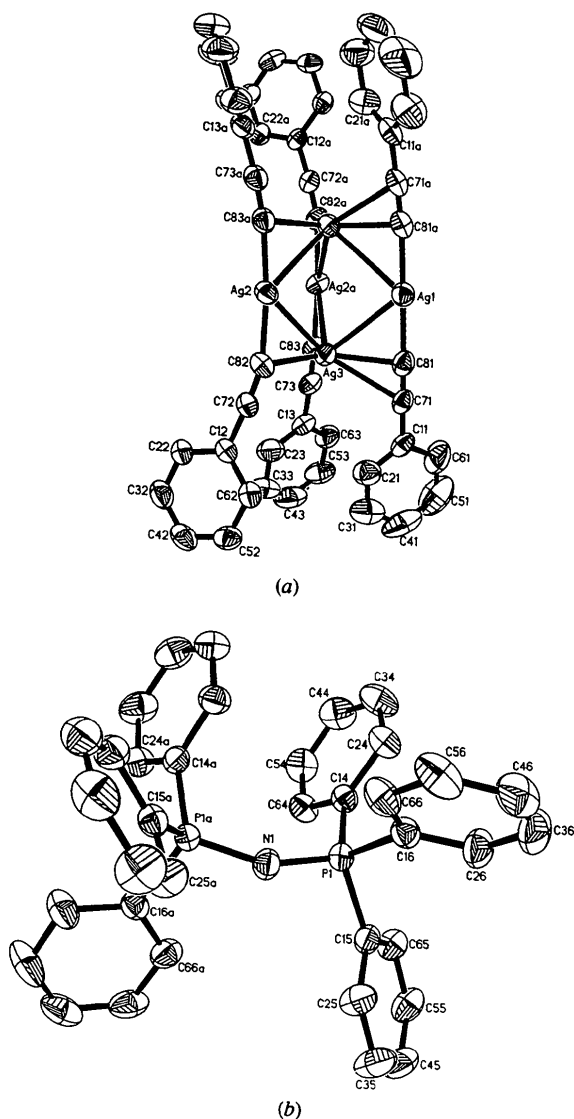


Fig. 1. The molecular structure of (a) the $[Ag_5(C\equiv CPh)_6]^-$ anionic cluster and (b) the $[N\{P(C_6H_5)_3\}_2]^+$ cation, showing the labelling of the non-H atoms. Displacement ellipsoids are drawn at the 50% probability level.

$Ag(2)-C(83a)$ angles are $178.9(2)$ and $174.2(2)^\circ$, respectively. The $Ag-C$ bond lengths are equal within experimental error; $Ag(1)-C(81)$ $2.027(5)$, $Ag(2)-C(82)$ $2.037(4)$ and $Ag(2)-C(83a)$ $2.037(5)$, average $2.034(3)$ Å. The above $Ag-C$ bonds are statistically equal to the $Ag-C$ bond of $2.04(1)$ Å found in (III). The axial Ag atoms are within β -bonding distance of the ethynyl group, the $Ag-C$ distances range from $2.274(4)$ to $2.362(4)$ Å for the C atoms at β -positions and from $2.665(4)$ to $2.905(4)$ Å for C atoms at α -positions to the phenyl group. Such bonds have been described as asymmetrical π bonds, as in (I), (II) and (III). However, there are two types of asymmetrical

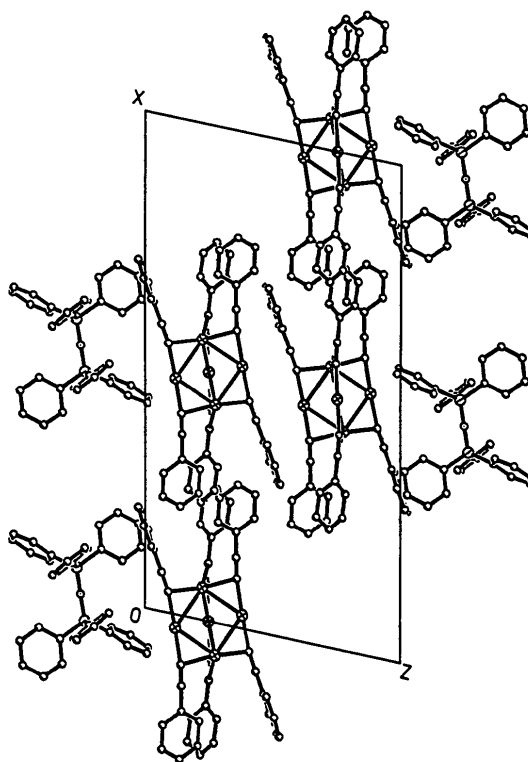


Fig. 2. Packing diagram viewed down the b axis.

π bonding in the present cluster. The first type involves $Ag(3)-[C(81),C(71)]$; the $Ag(3)-C(81)$ and $Ag(3)-C(71)$ distances are $2.362(4)$ and $2.665(4)$ Å, respectively, and the $Ag(3)-C(81)-C(71)$ angle is $90.6(3)^\circ$. The second type involves $Ag(3)-[C(82),C(72)]$ and $Ag(3)-[C(83),C(73)]$; the $Ag(3)-C(82)$, $Ag(3)-C(83)$, $Ag(3)-C(72)$ and $Ag(3)-C(73)$ distances are $2.274(4)$, $2.343(4)$, $2.905(3)$ and $2.898(4)$ Å, respectively, and the $Ag(3)-C(82)-C(72)$ and $Ag(3)-C(83)-C(73)$ angles are $109.4(3)$ and $105.2(3)^\circ$, respectively. The second type of π -interaction may be better described as a weakly asymmetrical π bond.

The $C\equiv C$ bond lengths are equal within experimental error [average $1.205(3)$ Å]. The average value is statistically equal to the uncoordinated acetylene distance of $1.204(2)$ Å (Kennard *et al.*, 1972) and the $C\equiv C$ bond of $1.208(18)$ Å found in (III). The structural parameters of the $[N\{P(C_6H_5)_3\}_2]^+$ cation are normal.

Experimental

The complex was prepared by addition of silver phenylacetylide (0.418 g, 2 mmol) to $[N\{P(C_6H_5)_3\}_2][Cu(C_2Ph)_2]$ (0.402 g, 0.5 mmol) in acetone (25 cm^3). Stirring for 1 h, filtration and addition of hexane to the filtrate afforded the complex. Elemental analysis for $C_{84}H_{60}Ag_{4.46}Cu_{0.54}NP_2$: calculated C 60.72, H 3.61, N 0.84, Ag 29.02, Cu 2.05%; found C 60.65, H 3.61, N 0.88, Ag 29.00, Cu 1.95%.

Crystal data

[N(C₁₈H₁₅P)₂][Ag_{4.46}Cu_{0.54}-
(C₈H₅)₆]M_r = 1660.79

Monoclinic

C2/c

a = 28.058 (6) Å

b = 17.315 (2) Å

c = 14.962 (1) Å

β = 101.36 (1)°

V = 7127 (2) Å³

Z = 4

D_x = 1.548 Mg m⁻³

Data collection

Siemens P4 four-circle
diffractometer

ω scans

Absorption correction:

ψ scan

T_{min} = 0.600, T_{max} =
0.796

7031 measured reflections

5980 independent reflections

4708 observed reflections

[I > 2σ(I)]

Refinement

Refinement on F²

R(F) = 0.032

wR(F²) = 0.082

S = 1.021

5967 reflections

420 parameters

w = 1/[σ²(F_o²) + (0.0393P)²
+ 7.14P]where P = (F_o² + 2F_c²)/3

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25
reflections

θ = 17.34–17.55°

μ = 1.452 mm⁻¹

T = 293 K

Plate

0.80 × 0.60 × 0.32 mm

Pale yellow

R_{int} = 0.0138θ_{max} = 25°

h = -1 → 33

k = -1 → 20

l = -17 → 17

3 standard reflections
monitored every 97
reflections

intensity decay: none

(Δ/σ)_{max} < 0.001Δρ_{max} = 0.412 e Å⁻³Δρ_{min} = -0.367 e Å⁻³

Extinction correction: none

Atomic scattering factors
from *International Tables*
for *Crystallography* (1992,
Vol. C)

C(13)	0.1879 (2)	0.3579 (3)	0.3549 (3)	0.083 (1)
C(23)	0.2007 (2)	0.4009 (4)	0.2854 (4)	0.124 (2)
C(33)	0.2500 (3)	0.4200 (5)	0.2911 (6)	0.158 (3)
C(43)	0.2841 (3)	0.3971 (5)	0.3625 (7)	0.158 (3)
C(53)	0.2717 (2)	0.3563 (4)	0.4303 (5)	0.136 (2)
C(63)	0.2240 (2)	0.3364 (3)	0.4272 (4)	0.107 (2)
N(1)	0	0.1843 (2)	-1/4	0.058 (1)
P(1)	-0.0513 (1)	0.2083 (1)	-0.2336 (1)	0.046 (1)
C(14)	-0.0577 (1)	0.3103 (2)	-0.2170 (2)	0.050 (1)
C(24)	-0.0918 (1)	0.3543 (2)	-0.2760 (2)	0.068 (1)
C(34)	-0.0918 (2)	0.4339 (2)	-0.2646 (3)	0.089 (1)
C(44)	-0.0589 (2)	0.4688 (2)	-0.1980 (3)	0.087 (1)
C(54)	-0.0256 (2)	0.4257 (2)	-0.1391 (3)	0.077 (1)
C(64)	-0.0249 (1)	0.3466 (2)	-0.1479 (2)	0.061 (1)
C(15)	-0.0633 (1)	0.1574 (2)	-0.1352 (2)	0.054 (1)
C(25)	-0.0528 (2)	0.0792 (2)	-0.1291 (3)	0.077 (1)
C(35)	-0.0599 (2)	0.0380 (2)	-0.0551 (3)	0.098 (1)
C(45)	-0.0775 (2)	0.0731 (3)	0.0140 (3)	0.089 (1)
C(55)	-0.0886 (2)	0.1502 (2)	0.0085 (2)	0.078 (1)
C(65)	-0.0816 (1)	0.1930 (2)	-0.0661 (2)	0.064 (1)
C(16)	-0.0966 (1)	0.1758 (2)	-0.3291 (2)	0.053 (1)
C(26)	-0.1441 (1)	0.1627 (3)	-0.3201 (3)	0.082 (1)
C(36)	-0.1773 (2)	0.1337 (3)	-0.3937 (3)	0.107 (2)
C(46)	-0.1638 (2)	0.1185 (2)	-0.4740 (3)	0.095 (1)
C(56)	-0.1176 (2)	0.1326 (2)	-0.4847 (3)	0.087 (1)
C(66)	-0.0833 (1)	0.1611 (2)	-0.4117 (2)	0.069 (1)

† Partial occupancy (see text).

Table 2. Selected geometric parameters (Å, °)

Ag(1)—Ag(3)	3.0239 (6)	C(82)—C(72)	1.206 (5)
Ag(2)—Ag(3)	2.9031 (6)	C(72)—C(12)	1.440 (5)
Ag(2)—Ag(3 ¹)	2.9337 (5)	C(12)—C(22)	1.377 (5)
Ag(1)—C(81)	2.027 (5)	C(22)—C(32)	1.362 (6)
Ag(2)—C(82)	2.037 (4)	C(32)—C(42)	1.363 (7)
Ag(2)—C(83 ¹)	2.037 (5)	C(42)—C(52)	1.361 (6)
Ag(3)—C(81)	2.362 (4)	C(52)—C(62)	1.384 (6)
Ag(3)—C(82)	2.274 (4)	C(62)—C(12)	1.390 (5)
Ag(3)—C(83)	2.343 (4)	C(83)—C(73)	1.199 (6)
Ag(3)—C(71)	2.665 (4)	C(73)—C(13)	1.440 (6)
Ag(3)—C(72)	2.905 (4)	C(13)—C(23)	1.383 (7)
Ag(3)—C(73)	2.898 (4)	C(23)—C(33)	1.409 (9)
C(81)—C(71)	1.209 (6)	C(33)—C(43)	1.346 (9)
C(71)—C(11)	1.434 (6)	C(43)—C(53)	1.336 (10)
C(11)—C(21)	1.354 (7)	C(53)—C(63)	1.376 (8)
C(21)—C(31)	1.351 (8)	C(63)—C(13)	1.380 (6)
C(31)—C(41)	1.315 (11)	N(1)—P(1)	1.565 (1)
C(41)—C(51)	1.370 (12)	P(1)—C(14)	1.799 (3)
C(51)—C(61)	1.379 (11)	P(1)—C(15)	1.802 (3)
C(61)—C(11)	1.365 (7)	P(1)—C(16)	1.805 (3)
Ag(3)—Ag(1)—Ag(3 ¹)	77.45 (2)	C(31)—C(41)—C(51)	118.7 (9)
Ag(1)—Ag(3)—Ag(2 ¹)	82.92 (1)	C(41)—C(51)—C(61)	119.6 (9)
Ag(2)—Ag(3)—Ag(2 ¹)	83.67 (2)	C(51)—C(61)—C(11)	121.0 (8)
C(81)—Ag(1)—C(81 ¹)	178.2 (9)	Ag(2)—C(82)—C(72)	163.5 (4)
C(81)—Ag(1)—Ag(3)	51.2 (1)	Ag(3)—C(82)—C(72)	109.4 (3)
C(81)—Ag(1)—Ag(3 ¹)	127.7 (1)	Ag(2)—C(82)—Ag(3)	84.5 (1)
C(83)—Ag(2)—C(82 ¹)	174.2 (2)	C(82)—C(72)—C(12)	175.0 (4)
C(83 ^{1<td>133.3 (1)</td><td>C(72)—C(12)—C(22)</td><td>119.5 (4)</td>}	133.3 (1)	C(72)—C(12)—C(22)	119.5 (4)
C(82)—Ag(2)—Ag(3)	51.2 (1)	C(72)—C(12)—C(62)	122.1 (3)
C(83 ¹¹)	52.5 (1)	C(22)—C(12)—C(62)	118.4 (4)
C(82)—Ag(2)—Ag(3 ¹)	131.9 (1)	C(32)—C(22)—C(12)	121.0 (4)
C(82)—Ag(3)—C(83)	118.7 (2)	C(22)—C(32)—C(42)	120.6 (5)
C(82)—Ag(3)—C(81)	127.5 (1)	C(52)—C(42)—C(32)	119.8 (4)
C(83)—Ag(3)—C(81)	112.8 (2)	C(42)—C(52)—C(62)	120.5 (4)
C(82)—Ag(3)—C(71)	126.3 (1)	C(52)—C(62)—C(12)	119.7 (4)
C(83)—Ag(3)—C(71)	101.9 (1)	Ag(2 ¹)—C(83)—C(73)	170.9 (4)
C(82)—Ag(3)—Ag(2)	44.3 (1)	Ag(3)—C(83)—C(73)	105.2 (3)
C(83)—Ag(3)—Ag(2)	115.2 (1)	Ag(2 ¹)—C(83)—Ag(3)	83.8 (2)
C(81)—Ag(3)—Ag(2)	118.8 (1)	C(83)—C(73)—C(13)	175.8 (4)
C(81)—Ag(3)—Ag(2 ¹)	108.1 (1)	C(73)—C(13)—C(63)	120.4 (5)
C(82)—Ag(3)—Ag(1)	116.3 (1)	C(73)—C(13)—C(23)	121.1 (4)
C(83)—Ag(3)—Ag(1)	115.1 (1)	C(63)—C(13)—C(23)	118.4 (5)
C(81)—Ag(3)—Ag(1)	42.0 (1)	C(13)—C(23)—C(33)	118.6 (6)
C(71)—C(81)—Ag(1)	172.7 (4)	C(43)—C(33)—C(23)	121.0 (7)
Ag(3)—C(81)—C(71)	90.6 (3)	C(53)—C(43)—C(33)	120.6 (7)
Ag(1)—C(81)—Ag(3)	86.8 (2)	C(43)—C(53)—C(63)	120.2 (7)
C(81)—C(71)—C(11)	177.2 (4)	C(53)—C(63)—C(13)	121.2 (6)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	x	y	z	U _{eq}
Ag(1)†	0	0.1260 (1)	1/4	0.080 (1)
Cu(1)†	0	0.1260 (1)	1/4	0.080 (1)
Ag(2)†	-0.0266 (1)	0.3242 (1)	0.1196 (1)	0.075 (1)
Cu(2)†	-0.0266 (1)	0.3242 (1)	0.1196 (1)	0.075 (1)
Ag(3)	0.0634 (1)	0.2623 (1)	0.2246 (1)	0.074 (1)
C(81)	0.0714 (2)	0.1271 (2)	0.2429 (3)	0.082 (1)
C(71)	0.1148 (2)	0.1318 (2)	0.2480 (3)	0.076 (1)
C(11)	0.1666 (2)	0.1370 (2)	0.2588 (3)	0.080 (1)
C(21)	0.1887 (2)	0.1917 (4)	0.2166 (4)	0.112 (2)
C(31)	0.2375 (3)	0.1978 (5)	0.2288 (5)	0.148 (2)
C(41)	0.2664 (3)	0.1493 (7)	0.2814 (8)	0.186 (5)
C(51)	0.2463 (4)	0.0971 (6)	0.3319 (8)	0.208 (5)
C(61)	0.1964 (3)	0.0897 (4)	0.3180 (5)	0.153 (3)
C(82)	0.0416 (2)	0.3291 (2)	0.0920 (3)	0.077 (1)
C(72)	0.0777 (1)	0.3495 (2)	0.0660 (2)	0.068 (1)
C(12)	0.1191 (1)	0.3805 (2)	0.0347 (2)	0.064 (1)
C(22)	0.1229 (2)	0.4591 (2)	0.0240 (3)	0.081 (1)
C(32)	0.1614 (2)	0.4904 (3)	-0.0059 (3)	0.101 (1)
C(42)	0.1971 (2)	0.4442 (3)	-0.0265 (3)	0.103 (2)
C(52)	0.1942 (2)	0.3663 (3)	-0.0171 (3)	0.091 (1)
C(62)	0.1554 (2)	0.3335 (2)	0.0133 (3)	0.076 (1)
C(83)	0.0958 (2)	0.3303 (2)	0.3581 (3)	0.082 (1)
C(73)	0.1378 (2)	0.3403 (2)	0.3555 (3)	0.080 (1)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

C(71)—C(11)—C(21)	122.5 (4)	P(1 ^b)—N(1)—P(1)	149.2 (3)
C(71)—C(11)—C(61)	120.9 (5)	N(1)—P(1)—C(14)	113.7 (2)
C(21)—C(11)—C(61)	116.5 (6)	N(1)—P(1)—C(15)	108.9 (1)
C(31)—C(21)—C(11)	122.4 (6)	N(1)—P(1)—C(16)	108.6 (1)
C(41)—C(31)—C(21)	121.3 (9)		

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $-x, y, -\frac{1}{2} - z$.

The structure was solved by direct method and refined by full-matrix least-squares techniques to $R = 0.074$ using an Ag₄Cu metal-atom model, with Cu on the twofold axis, non-H atoms anisotropic, H atoms constrained to ride on the appropriate C atoms at a distance of 0.95 Å, fixed isotropic displacement parameters for H atoms in the cation and a common refinable isotropic displacement parameter for H atoms of each phenyl group in the anion. The ΔF map showed a peak of 3.39 e Å⁻³ at a distance of 0.43 Å from the Cu atoms. This, and the metal-carbon bond lengths being equal, dictated replacing the Cu with an Ag atom (Ag₅ model). Refinement produced a much lower R factor of 0.037 and a featureless ΔF map. The presence of Cu atoms in the elemental analysis and the improvement of the R factor indicate possible positional disorder in some Ag-atom positions. Refinement of the site-occupation factors (s.o.f.'s) of the metal atoms using the Ag₅ model confirms the presence of the positional disorder in the equatorial positions to the same extent, s.o.f.'s equal to 0.922 and 0.458 ($0.458 \times 2 = 0.916$) for atoms at general and special positions, respectively. Both Ag and Cu atoms were then included at each of the equatorial positions, given the same refinable displacement parameters and the sum of their s.o.f.'s tied to be equal to 1 for atoms at general positions and 0.5 for atoms at the special position. Final refinement produced $R = 0.032$ and s.o.f.'s of 0.821 (4) and 0.179 (4) for Ag and Cu atoms at general positions, respectively.

Data collection: XSCANS2.00a (Siemens, 1993). Cell refinement: XSCANS2.00a. Data reduction: XSCANS2.00a. Program(s) used to solve structure: SHELXTL/PC (Sheldrick, 1991). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC. Software used to prepare material for publication: SHELXL93.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: JZ1005). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis[hydrotris(1-pyrazolyl-N²)borato]zinc(II)

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Abstract

The crystal structure of the title compound, [Zn(C₉H₁₀BN₆)₂], has been determined. The Zn^{II} ion is coordinated by six N atoms, one from each of the six pyrazole rings. The coordination geometry about the Zn^{II} ion is distorted octahedral. The average Zn—N distance is 2.155 (11) Å and the average intraligand N—Zn—N bond angle is 85.6 (4)°, with average interligand N—Zn—N bond angles of 94 (2) and 177.2 (7)°.

Comment

A wide variety of [HB(pz)₃]⁻ (pz is pyrazolyl) and [HB(pz*)₃]⁻ (pz* is substituted pyrazolyl) complexes have been reported for transition metals and main group elements (Trofimenko, 1993). Recently, pyrazolylborate derivatives have played an important role in the synthesis of the model metalloenzyme complex, carbonic anhydrase (Loony, Han, McNeill & Parkin, 1993; Alsfasser, Ruf, Trofimenko & Vahrenkamp, 1993). Tetrahedral geometry is preferred for sterically bulky tris(pyrazolyl) derivatives. On the other hand, octahedral geometry is preferred for the less sterically hindered tris(pyrazolyl)borates. [HB(pz)₃]⁻ forms stable [M{HB(pz)₃}₂]-type complexes with divalent metal ions. Though the synthesis and characterization of [Zn{HB(pz)₃}₂], (I), have already been carried out (Trofimenko, 1967), the crystal structure of this complex has not yet been reported.

