$a = 11.6819\,(14)$ Å
$b = 15.2304\,(16)$ Å
$c = 16.349\,(2)$ Å
$\beta = 107.548\,(10)°$
$V = 2773.5\,(6)$ Å^3
$Z = 2$
$D_x = 1.620$ Mg m^{-3}
D_m not measured

$\mu = 1.162$ mm^{-1}
$T = 173\,(2)$ K
Prism
$0.34 \times 0.32 \times 0.12$ mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction:
  ψ scans (*XEMP*; Siemens 1994*a*)
  $T_{\min} = 0.741$, $T_{\max} = 0.870$
5061 measured reflections
4869 independent reflections
3161 reflections with
  $I > 2\sigma(I)$

$R_{\rm int} = 0.029$
$\theta_{\max} = 24.99°$
$h = -13 \rightarrow 13$
$k = -18 \rightarrow 1$
$l = -19 \rightarrow 0$
3 standard reflections
  every 247 reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.073$
$S = 0.863$
4869 reflections
325 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.432$ e Å^{-3}
$\Delta\rho_{\min} = -0.393$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ag—P1^{i}	2.4017 (11)	Ag···O1	2.959 (3)
Ag—P2	2.4060 (11)	P1—C1	1.839 (4)
Ag···Ag^{i}	2.9532 (7)	P2—C1	1.835 (4)
P1^{i}—Ag—P2	170.72 (4)	C11—P1—Ag^{i}	111.39 (13)
P1^{i}—Ag···Ag^{i}	92.62 (3)	C1—P1—Ag^{i}	112.34 (13)
P2—Ag···Ag^{i}	88.81 (3)	C31—P2—C41	106.68 (18)
P1^{i}—Ag···O1	108.07 (7)	C31—P2—C1	105.32 (19)
P2—Ag···O1	81.11 (7)	C41—P2—C1	105.03 (17)
Ag^{i}···Ag—O1	72.95 (7)	C31—P2—Ag	114.98 (13)
C21—P1—C11	105.39 (19)	C41—P2—Ag	112.33 (13)
C21—P1—C1	106.19 (18)	C1—P2—Ag	111.75 (13)
C11—P1—C1	105.20 (18)	P2—C1—P1	111.5 (2)
C21—P1—Ag^{i}	115.55 (14)		
C1—P2—P1^{i}—C1^{i}	51.7 (2)	Ag—P2—P1—Ag^{i}	−8.92 (4)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994*b*). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1371). Services for accessing these data are described at the back of the journal.

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Tetrakis(acetonitrile-*N*)copper(I) Tetrafluoroborate

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Abstract

The title compound, $[Cu(H_3CCN)_4]BF_4$, is isomorphous with the analogous compounds $[M(H_3CCN)_4]ClO_4$ (M = Cu, Ag). It contains three independent formula units. A large spread of values of chemically equivalent dimensions is observed, notably in the cations, which display tetrahedral coordination at copper, with Cu—N

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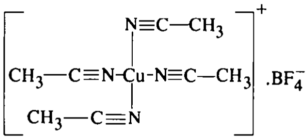
1.964 (6)–2.028 (6) Å (average 1.993 Å) and N—Cu—N 105.4 (2)–113.4 (2)° (average 109.4°).

Comment

The cation $[Cu(H_3CCN)_4]^+$ has been suggested as a model for the coordination of copper in some flavoenzymes (Hemmerich & Sigwart, 1963). The effect of γ radiation from a ^{60}Co source on the perchlorate salt is to form distorted tetrahedral Cu^{2+} centres whose electron spin resonance and light absorption spectra are similar to those of oxidoreductases containing copper (Gould & Ehrenberg, 1968). We present here the structural determination of the salt $[Cu(H_3CCN)_4]BF_4$, (I). Other salts of the same cation have already been structurally characterized: the hexafluorophosphate acetonitrile solvate (Black, Levason & Webster, 1995), the perchlorate (Csöregh, Kierkegaard & Norrestam, 1975) and a salt with a complex chlorotungsten anion (Neuhaus & Dehnicke, 1993). The hexafluorophosphate adopts a unit cell with similar dimensions to the current structure, but in $P2_12_12_1$. The perchlorate salt is isomorphous with the current structure and also with the analogous silver compound $[Ag(H_3CCN)_4]ClO_4$ (Jones & Bembenek, 1993). Curiously, all these compounds crystallize with three independent formula units.



$$\left[\begin{array}{c} N{\equiv}C{-}CH_3 \\ | \\ CH_3{-}C{\equiv}N{-}Cu{-}N{\equiv}C{-}CH_3 \\ | \\ CH_3{-}C{\equiv}N \end{array}\right]^+ .BF_4^-$$

(I)

The formula unit of the current structure (I) is shown in Fig. 1. There is a considerable spread of chemically equivalent dimensions, notably at the Cu atoms (values in Å or °, average values in brackets): Cu—N 1.964 (6)–2.028 (6) (1.993), N—C 1.107 (6)–1.140 (7) (1.123), C—C 1.416 (10)–1.493 (9) (1.466), N—Cu—N 105.4 (2)–113.4 (2) (109.4), C—N—Cu 169.9 (5)–179.0 (7) (174.2) and N—C—C 176.3 (7)–179.6 (6) (178.3).

These values for the Cu—N bonds are slightly shorter than those in the hexafluorophosphate, which was also measured at low temperature; 1.968 (6)–2.030 (6) (2.006) Å.

Experimental

Crystals were obtained by slow diffusion of diisopropyl ether into a dichloromethane solution of $[Cu(H_3CCN)_4]BF_4$.

Crystal data

$[Cu(C_2H_3N)_4]BF_4$
$M_r = 314.57$
Orthorhombic
$Pna2_1$
$a = 23.882\ (4)$ Å
$b = 8.3285\ (12)$ Å
$c = 20.338\ (3)$ Å
$V = 4045.2\ (11)$ Å^3
$Z = 12$
$D_x = 1.550$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 64 reflections
$\theta = 5.0$–$12.5°$
$\mu = 1.652$ mm^{-1}
$T = 173\ (2)$ K
Tablet
0.50 × 0.35 × 0.20 mm
Colourless

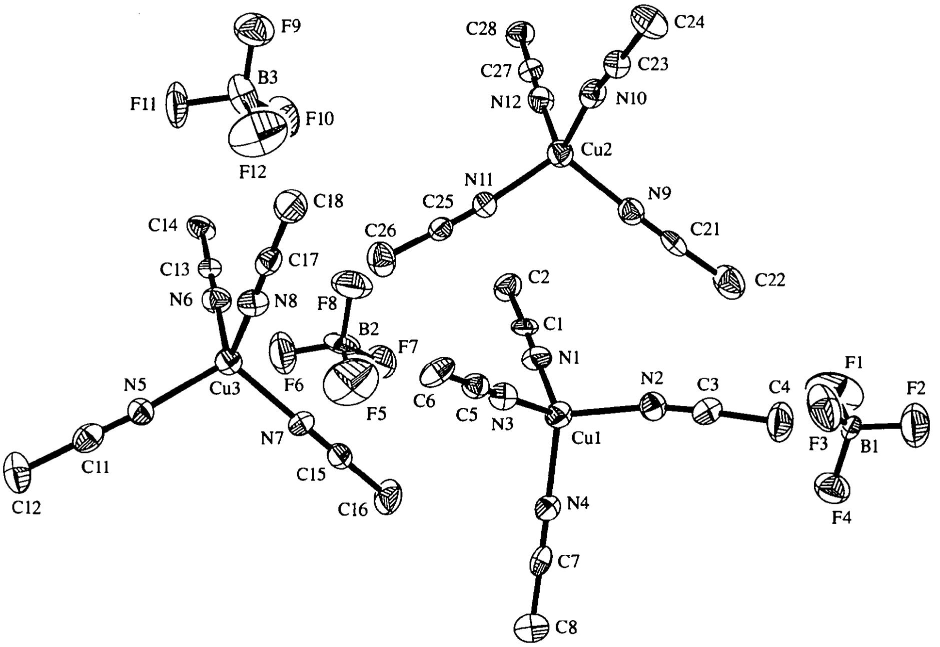


Fig. 1. The asymmetric unit of the title compound in the crystal. Ellipsoids represent 50% probability levels.

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction:
ψ scans (*XEMP*; Siemens, 1994*a*)
$T_{\min} = 0.590$, $T_{\max} = 0.719$
7131 measured reflections
7110 independent reflections
4835 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.007$
$\theta_{\max} = 25°$
$h = -28 \rightarrow 28$
$k = -9 \rightarrow 0$
$l = -24 \rightarrow 24$
3 standard reflections every 247 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.091$
$S = 0.931$
7110 reflections
500 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.117$

$\Delta\rho_{\max} = 0.476$ e Å^{-3}
$\Delta\rho_{\min} = -0.439$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.597 (19)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—N1	1.973 (6)	Cu2—N11	1.999 (5)
Cu1—N2	2.000 (6)	Cu2—N12	1.972 (6)
Cu1—N3	2.026 (5)	Cu3—N5	1.964 (6)
Cu1—N4	2.013 (5)	Cu3—N6	2.011 (5)
Cu2—N9	1.983 (5)	Cu3—N7	1.977 (4)
Cu2—N10	2.028 (6)	Cu3—N8	1.976 (6)
N1—Cu1—N2	112.5 (3)	N10—Cu2—N12	108.0 (2)
N1—Cu1—N3	112.3 (2)	N9—Cu2—N10	105.6 (2)
N1—Cu1—N4	109.9 (3)	N10—Cu2—N11	107.96 (19)
N2—Cu1—N3	106.7 (2)	N5—Cu3—N8	112.31 (17)
N2—Cu1—N4	105.4 (2)	N5—Cu3—N7	110.8 (3)
N3—Cu1—N4	109.8 (2)	N7—Cu3—N8	112.2 (3)
N9—Cu2—N12	110.7 (2)	N5—Cu3—N6	107.2 (3)
N11—Cu2—N12	113.4 (2)	N6—Cu3—N8	107.4 (3)
N9—Cu2—N11	110.8 (2)	N6—Cu3—N7	106.63 (19)

Methyl groups were refined as rigid groups allowed to rotate but not tip. However, slow convergence of some methyl parameters may indicate rotational disorder. The origin was fixed by the method of Flack & Schwarzenbach (1988). The structure was refined as a racemic twin with components 0.60 and 0.40 (2).

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994*b*). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1379). Services for accessing these data are described at the back of the journal.

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[*N*,*N*′-(1,1,2,2-Tetramethylethylene)bis(3,5-di-*tert*-butylsalicylideneiminato)]cobalt(II)†

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Abstract

Dimerization of the molecule of the title compound, $[Co(C_{36}H_{54}N_2O_2)]$, an efficient dioxygen carrier, is prevented by the methyl and *tert*-butyl substituents. The square-planar complex is bisected by a crystallographic mirror plane, with disorder of the $-CMe_2-CMe_2-$ region. Molecular dimensions [Co—O 1.846 (2) and Co—N 1.850 (2) Å] are very similar to those of the related 3-*tert*-butylsalicylidenato complex.

Comment

Transition metal Schiff base complexes are of interest in catalysis (Jacobsen *et al.*, 1991) and in small-molecule

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† Systematic name: {4,4′,6,6′-tetra-*tert*-butyl-2,2′-[1,1,2,2-tetramethylethanediylbis(nitrilomethylidyne)]diphenolato-*O*,*N*,*N*′,*O*′}cobalt(II).