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

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

	x	y	z	U_{eq}
Ni	0	0.63340 (6)	0.02252 (6)	0.02670 (14)
O1	0.2444 (4)	0.6394 (3)	0.3011 (3)	0.0662 (10)
N1	0.1442 (6)	0.6147 (4)	0.1284 (4)	0.0386 (11)
N2	0.1493 (5)	0.6418 (4)	−0.0873 (3)	0.0318 (10)
N3	0	1.2000 (6)	−0.1284 (5)	0.067 (2)
C1	0.1378 (5)	0.6460 (5)	0.2371 (3)	0.0456 (10)
C2	0.2816 (4)	0.5796 (5)	0.0782 (4)	0.0492 (11)
C3	0.2856 (4)	0.6737 (5)	−0.0299 (4)	0.0472 (11)
C4	0.1339 (4)	0.7518 (5)	−0.1857 (3)	0.0432 (9)
C5	0	0.7172 (9)	−0.2505 (6)	0.051 (2)
C6	0	0.7012 (7)	0.2877 (5)	0.045 (2)
C7	0	0.8929 (6)	0.3001 (5)	0.053 (2)
C8	0	0.9841 (6)	0.1907 (4)	0.0448 (13)
C9	0.1252 (4)	1.0244 (4)	0.1380 (3)	0.0449 (9)
C10	0.1266 (4)	1.0999 (4)	0.0327 (5)	0.0495 (10)
C11	0	1.1372 (6)	−0.0198 (5)	0.0470 (13)

Table 2. *Selected geometric parameters* (Å, °)

Ni—N1^i	1.862 (5)	C2—C3	1.501 (5)
Ni—N2^i	1.925 (5)	C6—C7	1.561 (7)
O1—C1	1.263 (5)	C7—C8	1.502 (7)
N1—C1	1.325 (6)	C8—C9	1.375 (5)
N1—C2	1.454 (7)	C9—C10	1.401 (7)
N2—C3	1.479 (6)	C10—C11	1.381 (5)
N3—C11	1.394 (7)		
N1^i—Ni—N1	93.6 (3)	N1—C1—C6	119.5 (5)
N1^i—Ni—N2^i	86.24 (10)	N1—C2—C3	106.2 (4)
C1—N1—Ni	128.2 (4)	N2—C4—C5	112.2 (4)
C2—N1—Ni	112.6 (4)	C1^i—C6—C7	109.6 (3)
C4—N2—Ni	119.4 (3)	C8—C7—C6	114.1 (4)
O1—C1—N1	123.4 (5)	C9—C8—C7	121.0 (2)
O1—C1—C6	117.1 (4)	C10—C11—N3	120.2 (3)

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

Data collection: Siemens *P3* software. Cell refinement: Siemens *P3* software. Data reduction: *XDISK* (Siemens, 1991). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1990). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1076). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 623–625

Tetrakis(acetonitrile-*N*)copper(I) Hexafluorophosphate(V) Acetonitrile Solvate

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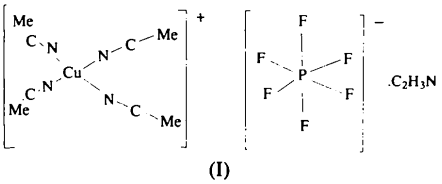
(*Received* 28 *June* 1994; *accepted* 2 *November* 1994)

Abstract

The chemical species in the asymmetric unit of the title complex, $[Cu(C_2H_3N)_4]PF_6.C_2H_3N$, consist of tetrahedral $[Cu(CH_3CN)_4]^+$ cations [Cu—N 1.968 (6)–2.030 (6) Å], $[PF_6]^-$ anions and acetonitrile solvate molecules.

Comment

As part of a study of Cu^I complexes with Group 15 and Group 16 donors, we have been studying $[Cu\{PhSe(CH_2)_nSePh\}_2]^+$ cations. Multinuclear NMR studies show that these exist in solution in acetonitrile as the Se-bonded complexes, with no evidence for substitution by the solvent. Colourless crystals, grown from the mixture by vapour diffusion of diethyl ether, formed over several days but turned white after a few seconds exposure to air. The crystals have been subjected to X-ray examination and shown to be those of the acetonitrile adduct $[Cu(CH_3CN)_4]PF_6.MeCN$, (I).



(I)

The cations almost have the expected tetrahedral geometry with N—Cu—N angles in the range 102.7 (3)–114.0 (3)° (see Table 2), and with nearly linear Cu—N—C [168.0 (6)–177.4 (6)°] and N—C—C [176.5 (8)–

179.2 (8)°] angles (see Fig. 1). There is no experimental difference between the free (solvate) and coordinated acetonitrile geometries. The $[PF_6]^-$ anions are unexceptional [P—F 1.532 (7)–1.601 (5) Å]. The H atoms were not apparent in the electron density maps and thus were not included in the model. The crystal chosen had the absolute configuration reported (wR = 0.0678 compared with wR = 0.0755 for the enantiomorph). The cation has been characterized previously (Neuhaus & Dehnicke, 1993; Pohl, Lotz, Saak & Haase, 1989), most pertinantly as the perchlorate salt (Csöregh, Kierkegaard & Norrestam, 1975), which shows a similar geometry to the present example. The perchlorate salt adopts a unit cell with similar cell dimensions and the same unusual value of Z (*i.e.* 12), but without the solvate molecule and with a different space group. A packing diagram for the title salt is shown in Fig. 2.

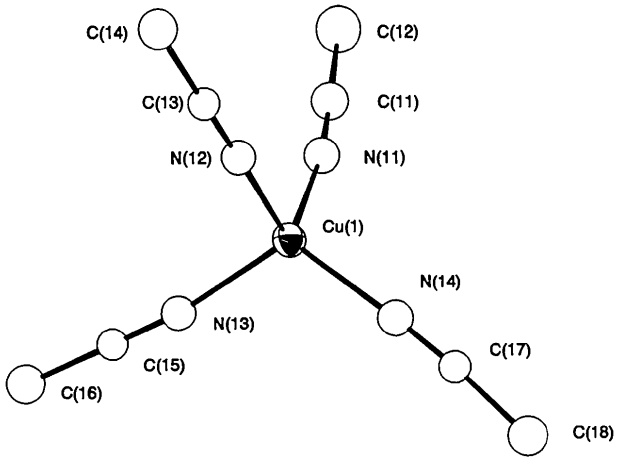


Fig. 1. View of one $[Cu(CH_3CN)_4]^+$ cation showing the atom-labelling scheme. The displacement ellipsoids are drawn at the 50% probability level.

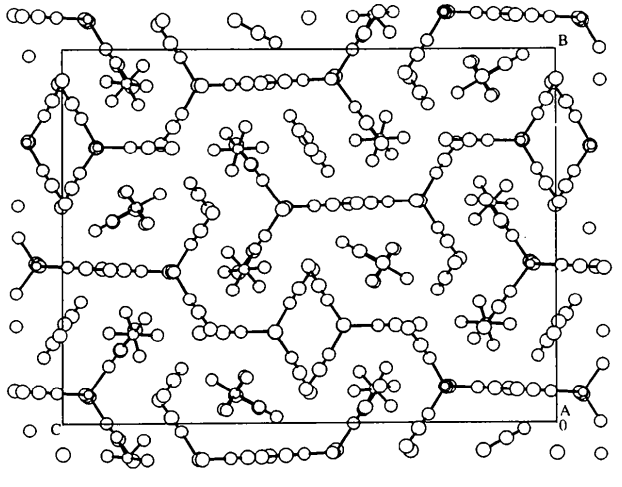


Fig. 2. View of the unit cell looking down **a**.

Experimental

Crystal data

$[Cu(C_2H_3N)_4]PF_6.C_2H_3N$
M_r = 413.77
Orthorhombic
$P2_12_12_1$
a = 8.563 (3) Å
b = 21.871 (1) Å
c = 27.728 (11) Å
V = 5192.9 (2.7) Å^3
Z = 12
D_x = 1.587 Mg m^{-3}
D_m = 1.59 Mg m^{-3}
D_m measured by flotation
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 250 reflections
μ = 1.38 mm^{-1}
T = 150 K
Air-sensitive needle
0.20 × 0.12 × 0.08 mm
Colourless

Data collection

Enraf–Nonius FAST area detector diffractometer
ω scans
Absorption correction: none
21 901 measured reflections
8033 independent reflections
5927 observed reflections [$F > 4\sigma(F)$]
R_{int} = 0.049
θ_{max} = 25.1°
$h = -7 \rightarrow 9$
$k = -24 \rightarrow 24$
$l = -23 \rightarrow 30$
No standard reflections (not applicable for FAST data collection)

Refinement

Refinement on F
R = 0.0539
wR = 0.0678
S = 1.09
5914 reflections
397 parameters
H atoms not located
$w = 1/[\sigma^2(F) + 0.0015F^2]$
$(\Delta/\sigma)_{max}$ = 0.2
$\Delta\rho_{max}$ = 1.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.94 e Å^{-3}
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976) for C, H, N, P and F atoms and from *International Tables for X-ray Crystallography* (1974, Vol. IV) for Cu atoms

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

U_{iso} for C and N; $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for other atoms.

	x	y	z	U_{iso}/U_{eq}
Cu1	0.5062 (1)	0.40481 (4)	0.77393 (3)	0.0250 (5)
Cu2	−0.0215 (1)	0.25693 (4)	0.42823 (3)	0.0252 (5)
Cu3	−0.0143 (1)	0.42195 (4)	1.05264 (3)	0.0273 (5)
P1	0.0147 (3)	0.0797 (1)	0.6509 (1)	0.0259 (12)
P2	0.0206 (3)	0.2367 (1)	0.8563 (1)	0.0279 (12)
P3	−0.0315 (2)	0.4110 (1)	0.6316 (1)	0.0280 (12)
F11	0.1414 (6)	0.0343 (3)	0.6679 (3)	0.109 (6)
F12	−0.1169 (5)	0.0365 (3)	0.6734 (2)	0.058 (4)
F13	0.1454 (6)	0.1212 (3)	0.6270 (3)	0.072 (5)
F14	0.0222 (12)	0.1161 (4)	0.6980 (3)	0.140 (7)
F15	0.0040 (10)	0.0428 (4)	0.6014 (2)	0.115 (6)
F16	−0.1162 (6)	0.1243 (3)	0.6314 (3)	0.089 (5)
F21	0.1494 (5)	0.2786 (2)	0.8326 (2)	0.051 (4)
F22	−0.1095 (6)	0.1959 (3)	0.8814 (2)	0.067 (4)
F23	−0.0679 (8)	0.2341 (4)	0.8077 (2)	0.121 (6)
F24	0.1102 (7)	0.2405 (4)	0.9056 (2)	0.108 (6)
F25	0.1202 (8)	0.1790 (3)	0.8440 (4)	0.112 (6)
F26	−0.0755 (7)	0.2962 (3)	0.8714 (3)	0.087 (5)
F31	0.0629 (5)	0.3552 (2)	0.6548 (2)	0.049 (3)
F32	−0.1598 (7)	0.4040 (4)	0.6714 (3)	0.109 (6)
F33	−0.1310 (5)	0.4660 (2)	0.6091 (2)	0.045 (3)
F34	−0.1311 (10)	0.3651 (3)	0.6012 (3)	0.121 (7)
F35	0.0575 (7)	0.4567 (3)	0.6645 (3)	0.089 (5)

F36	0.0853 (8)	0.4159 (4)	0.5900 (2)	0.120 (6)
N11	0.5954 (7)	0.4787 (3)	0.7401 (2)	0.0272 (16)
N12	0.6023 (7)	0.3304 (3)	0.7427 (2)	0.0247 (15)
N13	0.5998 (7)	0.4074 (3)	0.8401 (2)	0.0254 (15)
N14	0.2764 (7)	0.4047 (3)	0.7738 (2)	0.0274 (16)
N21	0.2115 (7)	0.2599 (3)	0.4306 (2)	0.0262 (15)
N22	−0.1078 (7)	0.2576 (3)	0.3612 (2)	0.0249 (15)
N23	−0.1203 (7)	0.3269 (3)	0.4636 (2)	0.0256 (16)
N24	−0.1054 (7)	0.1811 (3)	0.4606 (2)	0.0231 (15)
N31	0.0353 (7)	0.4987 (3)	1.0890 (2)	0.0322 (17)
N32	0.0941 (6)	0.4183 (3)	0.9891 (2)	0.0263 (15)
N33	0.0265 (7)	0.3475 (3)	1.0937 (2)	0.0353 (17)
N34	−0.2503 (7)	0.4213 (3)	1.0457 (2)	0.0281 (16)
C11	0.6631 (9)	0.5155 (4)	0.7206 (3)	0.0290 (20)
C12	0.7538 (10)	0.5630 (4)	0.6957 (3)	0.0428 (25)
C13	0.6771 (8)	0.2958 (3)	0.7251 (3)	0.0220 (18)
C14	0.7784 (9)	0.2496 (4)	0.7007 (3)	0.0322 (20)
C15	0.6681 (8)	0.4099 (4)	0.8745 (3)	0.0211 (17)
C16	0.7599 (8)	0.4130 (4)	0.9192 (3)	0.0316 (21)
C17	0.1437 (8)	0.4053 (4)	0.7762 (3)	0.0227 (18)
C18	−0.0287 (9)	0.4047 (4)	0.7825 (3)	0.0335 (20)
C21	0.3424 (8)	0.2595 (3)	0.4311 (3)	0.0231 (18)
C22	0.5136 (9)	0.2576 (3)	0.4312 (2)	0.0291 (18)
C23	−0.1697 (8)	0.2588 (4)	0.3252 (3)	0.0230 (17)
C24	−0.2475 (9)	0.2605 (4)	0.2773 (3)	0.0405 (23)
C25	−0.1855 (8)	0.3668 (4)	0.4804 (3)	0.0242 (18)
C26	−0.2686 (9)	0.4192 (4)	0.5010 (3)	0.0343 (22)
C27	−0.1599 (8)	0.1413 (3)	0.4794 (3)	0.0211 (18)
C28	−0.2334 (9)	0.0901 (4)	0.5068 (3)	0.0364 (22)
C31	0.0442 (8)	0.5406 (4)	1.1130 (3)	0.0301 (20)
C32	0.0554 (9)	0.5972 (4)	1.1427 (3)	0.0372 (22)
C33	0.1478 (8)	0.4148 (3)	0.9520 (3)	0.0239 (18)
C34	0.2148 (9)	0.4106 (4)	0.9032 (3)	0.0328 (21)
C35	0.0260 (9)	0.3055 (3)	1.1170 (3)	0.0267 (18)
C36	0.0310 (9)	0.2510 (4)	1.1470 (3)	0.0369 (21)
C37	−0.3771 (9)	0.4240 (4)	1.0491 (3)	0.0310 (21)
C38	−0.5554 (9)	0.4282 (4)	1.0533 (3)	0.0321 (20)
N41*S*	0.0115 (8)	0.4833 (3)	0.4332 (2)	0.0423 (18)
N42*S*	0.0609 (8)	0.3543 (3)	0.2408 (3)	0.0425 (20)
N43*S*	0.4704 (9)	0.3241 (3)	0.9621 (3)	0.0489 (20)
C41*S*	0.0102 (9)	0.4585 (4)	0.3977 (3)	0.0334 (19)
C42*S*	0.0136 (10)	0.4264 (4)	0.3509 (3)	0.0413 (21)
C43*S*	0.1529 (9)	0.3849 (4)	0.2249 (3)	0.0359 (22)
C44*S*	0.2782 (11)	0.4258 (5)	0.2047 (4)	0.0548 (28)
C45*S*	0.4032 (9)	0.2863 (4)	0.9804 (3)	0.0370 (22)
C46*S*	0.3225 (11)	0.2345 (5)	1.0051 (4)	0.0588 (29)

Table 2. *Selected geometric parameters* (Å, °)

Cu1—N11	2.019 (6)	Cu2—N23	2.006 (6)
Cu1—N12	2.018 (6)	Cu2—N24	2.019 (6)
Cu1—N13	2.004 (6)	Cu3—N31	2.004 (7)
Cu1—N14	1.968 (6)	Cu3—N32	1.994 (6)
Cu2—N21	1.997 (6)	Cu3—N33	2.017 (7)
Cu2—N22	1.999 (6)	Cu3—N34	2.030 (6)
N11—Cu1—N12	106.9 (3)	N22—Cu2—N23	107.0 (3)
N11—Cu1—N13	104.6 (3)	N22—Cu2—N24	106.7 (3)
N11—Cu1—N14	112.3 (3)	N23—Cu2—N24	105.0 (2)
N12—Cu1—N13	104.6 (3)	N31—Cu3—N32	112.3 (3)
N12—Cu1—N14	114.0 (3)	N31—Cu3—N33	110.9 (3)
N13—Cu1—N14	113.7 (3)	N31—Cu3—N34	105.3 (3)
N21—Cu2—N22	113.5 (2)	N32—Cu3—N33	112.7 (3)
N21—Cu2—N23	112.4 (2)	N32—Cu3—N34	112.2 (3)
N21—Cu2—N24	111.6 (2)	N33—Cu3—N34	102.7 (3)

The Cu-atom positions were located by direct methods (Sheldrick, 1985) and the remaining non-H atoms were found by repeated structure-factor and electron density calculations (Sheldrick, 1976).

Data collection: Enraf–Nonius software. Cell refinement: Enraf–Nonius software. Data reduction: Enraf–Nonius software. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976), *PLUTO* (Motherwell & Clegg, 1978).

We thank Professor M. B. Hursthouse and the SERC for the X-ray data collection.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: HU1132). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 625–627

μ-Aqua-bis(μ-trichloroacetato-*O*:*O*′)bis[(3-cyanopyridine)(trichloroacetato)copper(II)] Dichloroform Solvate

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(*Received* 4 *October* 1993; *accepted* 24 *May* 1994)

Abstract

The crystal structure of the title compound, $[Cu_2(C_2Cl_3O_2)_4(C_6H_4N_2)_2(H_2O)].2CHCl_3$, was determined by single-crystal X-ray diffraction. Two Cu

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