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Crystal structure of tetrakis(acetonitrile)silver(I) tetrafluoroborate, $[Ag(C_2H_3N)_4][BF_4]$

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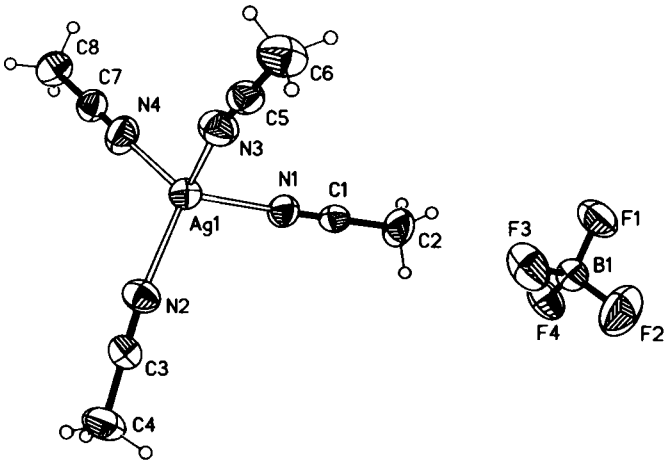

Abstract
$C_8H_{12}AgBF_4N_4$, orthorhombic, $Pna2_1$ (no. 33), $a = 24.249(5)$ Å, $b = 8.608(2)$ Å, $c = 20.640(4)$ Å, $V = 4308.3$ Å^3, $Z = 12$, $R_{gt}(F) = 0.022$, $wR_{ref}(F^2) = 0.055$, $T = 178$ K.

Source of material
The title complex was formed during the reaction of 2-cyano-6-methoxybenzothiazole with silver(I) tetrafluoroborate in a mixture of tetrahydrofuran and acetonitrile in the ratio of 3:1. On cooling the reaction mixture to 5 °C, colorless plate-shaped crystals were formed.

Discussion
Tetrakis(acetonitrile)silver(I) tetrafluoroborate can successfully be used as precursor for the synthesis of many hetero-metallic transition metal complexes which possess novel properties, for example, in material sciences. In addition, it can be applied in the synthesis of further silver(I) species comprising acetonitrile and tetrafluoroborate, respectively [1-3]. The structure of tetrakis-(acetonitrile)silver(I) perchlorate has been determined at 240 K by Nilsson and Oskarsson [4] and re-determined by Jones and Bembenek [5] at 173 K in order to obtain more reliable dimensions. The crystallographic results of both groups showed large variations regarding Ag—N interatomic bond distances and N–Ag–N angles in the three independent $[Ag(CH_3CN)_4]$ cations. Isotypic tetrakis(acetonitrile)copper(I) tetrafluoroborate [6] and perchlorate [7] compounds are described.
The title complex is composed of discrete $[Ag(CH_3CN)_4]^+$ and BF_4^- ions. The asymmetric unit comprises three $[Ag(CH_3CN)_4]^+$ moieties and three BF_4^- anions. As in the case of the respective silver(I) perchlorate complex there is a considerable range of equivalent dimensions in the tetrafluoroborate species regarding the interatomic bond distances Ag—N: 2.229(3) Å – 2.316 Å, N—C: 1.117(4) Å – 1.142(4) Å, C—C: 1.436(5) Å – 1.449(4) Å and the N–Ag–N angles: 104.2(1)° – 115.8(1)°, Ag–N–C: 165.4(3)° – 178.9(3)°, N–C–C: 178.4(4)° – 179.6(4)°. It seems that the silver–nitrogen bonds are rather weak and hence, the title complex eliminates acetonitrile by abstracting the crystals from the solution. It possesses almost the same crystallographic data as the silver(I) perchlorate species (vide supra) indicating that the tetra-fluoroborate anion is located at the same position as the perchlorate in the crystal lattice, probably, because both perchlorate and tetrafluoroborate have comparable ionic radii. Although the crystal structure analysis indicates no interaction between the tetrafluoroborate ion and the silver cation, the B—F bond distances are between 1.350(5) Å – 1.406(5) Å. Therefore the cationic and the anionic building blocks exhibit a slightly distorted tetrahedral geometry.

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Table 1. Data collection and handling.

Crystal:	colorless block, size 0.3 × 0.3 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	14.35 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD 1k, ω
$2\theta_{max}$:	52.9°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	49085, 9646
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 8408
$N(param)_{refined}$:	500
Programs:	SHELXS-97 [8], SHELXL-97 [9]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2A)	4a	0.1325	0.5464	0.6146	0.093
H(2B)	4a	0.1557	0.4146	0.5672	0.093
H(2C)	4a	0.0944	0.4018	0.5955	0.093
H(4A)	4a	0.1696	0.5586	0.2068	0.091
H(4B)	4a	0.1158	0.4924	0.1715	0.091
H(4C)	4a	0.1469	0.3895	0.2247	0.091
H(6A)	4a	–0.1416	0.4621	0.4804	0.098
H(6B)	4a	–0.1434	0.3903	0.4089	0.098
H(6C)	4a	–0.1719	0.5544	0.4232	0.098
H(8A)	4a	0.0773	1.3142	0.4172	0.082
H(8B)	4a	0.0166	1.3065	0.4475	0.082
H(8C)	4a	0.0245	1.3204	0.3707	0.082
H(10A)	4a	0.2809	0.0679	0.2991	0.102
H(10B)	4a	0.3043	0.2417	0.3014	0.102
H(10C)	4a	0.3397	0.1070	0.2678	0.102
H(12A)	4a	0.3187	0.0700	–0.1250	0.100

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(12B)	4a	0.3262	0.2537	−0.1332	0.100
H(12C)	4a	0.2707	0.1716	−0.1573	0.100
H(14A)	4a	0.1753	0.9013	0.0816	0.077
H(14B)	4a	0.2271	0.9032	0.0335	0.077
H(14C)	4a	0.2366	0.9044	0.1102	0.077
H(16A)	4a	0.0036	0.2813	0.0694	0.100
H(16B)	4a	0.0094	0.1100	0.0988	0.100
H(16C)	4a	0.0134	0.1365	0.0222	0.100
H(18A)	4a	0.3512	0.6194	0.3922	0.091
H(18B)	4a	0.3788	0.5309	0.4522	0.091

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(18C)	4a	0.3241	0.4627	0.4194	0.091
H(20A)	4a	0.4710	−0.3388	0.1936	0.075
H(20B)	4a	0.4161	−0.3462	0.2365	0.075
H(20C)	4a	0.4751	−0.3426	0.2710	0.075
H(22A)	4a	0.6297	0.6110	0.2347	0.083
H(22B)	4a	0.6625	0.4568	0.2149	0.083
H(22C)	4a	0.6500	0.4928	0.2895	0.083
H(24A)	4a	0.3899	0.5749	0.0432	0.099
H(24B)	4a	0.3310	0.5707	0.0781	0.099
H(24C)	4a	0.3478	0.4362	0.0283	0.099

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ag(1)	4a	0.03805(1)	0.71676(3)	0.39249(1)	0.0510(1)	0.0445(1)	0.0415(1)	0.00755(9)	0.0035(1)	0.0011(1)
N(1)	4a	0.0857(1)	0.6248(3)	0.4819(1)	0.050(1)	0.047(1)	0.039(1)	0.007(1)	−0.005(1)	0.001(1)
C(1)	4a	0.1022(1)	0.5589(3)	0.5248(1)	0.040(1)	0.037(1)	0.038(1)	0.003(1)	0.002(1)	−0.005(1)
C(2)	4a	0.1229(2)	0.4736(4)	0.5800(2)	0.091(2)	0.056(2)	0.039(2)	0.017(2)	−0.012(2)	0.004(2)
N(2)	4a	0.0763(1)	0.6157(3)	0.3021(1)	0.044(1)	0.059(2)	0.040(1)	−0.001(1)	0.000(1)	−0.008(1)
C(3)	4a	0.1024(1)	0.5621(3)	0.2623(1)	0.042(1)	0.042(1)	0.037(1)	−0.008(1)	0.001(1)	−0.003(1)
C(4)	4a	0.1364(2)	0.4953(4)	0.2123(2)	0.070(2)	0.059(2)	0.053(2)	−0.002(2)	0.021(2)	−0.013(2)
N(3)	4a	−0.0494(1)	0.6267(3)	0.4067(1)	0.044(1)	0.068(2)	0.051(2)	0.002(1)	0.004(1)	−0.001(1)
C(5)	4a	−0.0898(1)	0.5648(3)	0.4186(1)	0.048(2)	0.047(2)	0.039(1)	0.006(1)	−0.001(1)	−0.007(1)
C(6)	4a	−0.1408(2)	0.4866(4)	0.4340(2)	0.059(2)	0.060(2)	0.079(2)	−0.012(2)	0.014(2)	−0.012(2)
N(4)	4a	0.0407(1)	0.9772(3)	0.4008(2)	0.073(2)	0.042(1)	0.057(2)	0.005(1)	−0.005(1)	0.005(1)
C(7)	4a	0.0405(1)	1.1082(4)	0.4055(1)	0.049(2)	0.043(2)	0.042(2)	0.003(1)	−0.005(1)	0.001(1)
C(8)	4a	0.0397(2)	1.2758(4)	0.4107(2)	0.064(2)	0.038(2)	0.062(3)	−0.002(1)	−0.002(2)	−0.010(1)
Ag(2)	4a	0.216343(9)	0.30482(3)	0.07845(1)	0.0546(1)	0.0398(1)	0.0529(1)	0.00036(9)	0.0098(1)	−0.0009(1)
N(5)	4a	0.2559(1)	0.2036(3)	0.1664(2)	0.071(2)	0.051(2)	0.056(2)	−0.005(1)	−0.008(1)	0.002(1)
C(9)	4a	0.2761(1)	0.1789(4)	0.2147(2)	0.039(2)	0.049(2)	0.058(2)	−0.011(1)	0.006(1)	−0.012(1)
C(10)	4a	0.3023(2)	0.1463(5)	0.2756(2)	0.051(2)	0.102(3)	0.050(2)	−0.008(2)	−0.007(2)	−0.014(2)
N(6)	4a	0.2562(1)	0.2126(3)	−0.0129(2)	0.067(2)	0.051(2)	0.059(2)	−0.003(1)	0.024(1)	−0.006(1)
C(11)	4a	0.2755(1)	0.1944(4)	−0.0614(2)	0.041(2)	0.049(2)	0.044(2)	0.004(1)	0.008(1)	0.002(1)
C(12)	4a	0.2997(2)	0.1705(6)	−0.1242(2)	0.057(2)	0.103(3)	0.040(2)	0.015(2)	0.009(1)	0.007(2)
N(7)	4a	0.21549(9)	0.5655(3)	0.0768(2)	0.057(1)	0.035(1)	0.045(1)	−0.0010(9)	0.002(1)	−0.002(1)
C(13)	4a	0.2142(1)	0.6969(3)	0.0755(2)	0.039(1)	0.038(2)	0.033(1)	0.001(1)	−0.003(1)	−0.004(1)
C(14)	4a	0.2132(1)	0.8650(3)	0.0752(2)	0.068(2)	0.036(1)	0.051(2)	−0.000(1)	−0.006(2)	0.001(2)
N(8)	4a	0.12694(9)	0.2181(3)	0.0741(2)	0.047(1)	0.053(1)	0.065(2)	−0.003(1)	0.005(1)	−0.004(1)
C(15)	4a	0.0812(1)	0.2020(3)	0.0703(1)	0.045(1)	0.051(2)	0.039(1)	0.005(1)	0.006(1)	0.003(1)
C(16)	4a	0.0221(1)	0.1807(5)	0.0647(2)	0.040(1)	0.106(3)	0.054(2)	0.004(2)	−0.005(2)	0.015(2)
Ag(3)	4a	0.456291(9)	0.25321(3)	0.23977(2)	0.0527(1)	0.0394(1)	0.0518(1)	−0.00260(9)	0.0033(1)	−0.0015(1)
N(9)	4a	0.4176(1)	0.3587(3)	0.3314(1)	0.049(1)	0.059(2)	0.045(1)	−0.002(1)	0.005(1)	−0.008(1)
C(17)	4a	0.3923(1)	0.4277(3)	0.3671(1)	0.044(1)	0.044(2)	0.040(1)	−0.011(1)	−0.000(1)	−0.001(1)
C(18)	4a	0.3589(2)	0.5174(4)	0.4113(2)	0.071(2)	0.053(2)	0.057(2)	−0.008(2)	0.018(2)	−0.011(1)
N(10)	4a	0.4504(1)	−0.0051(3)	0.2371(2)	0.062(2)	0.038(1)	0.066(2)	−0.000(1)	−0.013(1)	−0.001(2)
C(19)	4a	0.4517(1)	−0.1375(3)	0.2356(2)	0.041(1)	0.038(2)	0.047(2)	−0.000(1)	−0.011(1)	0.004(2)
C(20)	4a	0.4536(1)	−0.3046(3)	0.2341(2)	0.059(2)	0.031(1)	0.061(2)	−0.002(1)	−0.003(2)	−0.002(2)
N(11)	4a	0.54332(9)	0.3526(3)	0.2370(1)	0.043(1)	0.055(1)	0.052(1)	−0.002(1)	0.003(1)	−0.003(1)
C(21)	4a	0.5835(1)	0.4167(3)	0.2403(1)	0.041(1)	0.040(1)	0.042(1)	0.005(1)	0.001(1)	−0.003(1)
C(22)	4a	0.6358(1)	0.5014(4)	0.2453(2)	0.040(1)	0.054(2)	0.073(2)	−0.006(1)	−0.004(2)	0.003(2)
N(12)	4a	0.4046(1)	0.3496(3)	0.1555(1)	0.045(1)	0.045(1)	0.050(1)	0.003(1)	−0.000(1)	−0.002(1)
C(23)	4a	0.3849(1)	0.4184(3)	0.1145(1)	0.030(1)	0.035(1)	0.053(2)	0.001(1)	0.002(1)	−0.006(1)
C(24)	4a	0.3615(1)	0.5072(4)	0.0618(2)	0.061(2)	0.057(2)	0.079(3)	0.010(2)	−0.015(2)	0.006(2)
B(1)	4a	0.2064(1)	0.2162(4)	0.7352(2)	0.044(2)	0.052(2)	0.040(2)	−0.002(1)	−0.008(2)	−0.002(2)
F(1)	4a	0.1789(1)	0.2635(3)	0.7918(1)	0.080(2)	0.110(2)	0.056(1)	0.005(1)	0.018(1)	0.004(1)
F(2)	4a	0.2112(1)	0.0594(3)	0.7388(2)	0.138(2)	0.059(1)	0.148(3)	−0.004(1)	−0.001(2)	0.009(2)
F(3)	4a	0.1752(1)	0.2592(4)	0.6827(1)	0.060(1)	0.162(3)	0.056(1)	0.009(1)	−0.016(1)	0.031(1)
F(4)	4a	0.25681(8)	0.2827(3)	0.7319(1)	0.054(1)	0.102(2)	0.056(1)	−0.024(1)	0.001(1)	0.007(1)
B(2)	4a	0.2996(2)	0.7214(5)	0.9088(2)	0.046(2)	0.044(2)	0.046(2)	−0.003(2)	−0.000(1)	−0.004(1)
F(5)	4a	0.2969(1)	0.5648(3)	0.9070(2)	0.158(3)	0.045(1)	0.115(2)	0.001(1)	−0.006(2)	−0.003(1)
F(6)	4a	0.2461(1)	0.7797(3)	0.9150(1)	0.061(1)	0.120(2)	0.071(2)	0.022(1)	−0.001(1)	−0.014(1)
F(7)	4a	0.3225(1)	0.7769(3)	0.8525(1)	0.090(2)	0.095(2)	0.058(1)	−0.002(1)	0.016(1)	0.008(1)
F(8)	4a	0.3292(1)	0.7723(3)	0.9619(1)	0.082(2)	0.104(2)	0.059(1)	−0.017(1)	−0.022(1)	−0.010(1)
B(3)	4a	0.5440(2)	0.7590(5)	0.0720(3)	0.062(2)	0.061(3)	0.049(2)	0.001(2)	0.006(2)	0.008(2)
F(9)	4a	0.5700(1)	0.7038(4)	0.1282(1)	0.085(2)	0.123(2)	0.073(2)	0.001(2)	−0.020(1)	0.022(1)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
F(10)	4*a*	0.49023(9)	0.7117(3)	0.0734(2)	0.056(1)	0.138(2)	0.088(2)	−0.007(1)	0.000(1)	0.002(2)
F(11)	4*a*	0.5710(1)	0.6954(4)	0.0203(1)	0.087(2)	0.144(3)	0.079(2)	0.015(2)	0.022(1)	−0.016(2)
F(12)	4*a*	0.5481(1)	0.9140(3)	0.0709(2)	0.180(3)	0.064(2)	0.150(3)	0.004(2)	−0.004(3)	0.009(2)

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