Crystal structure of (2,3,6,7-tetrahydro-1,3,7-trimethyl-2,6-dioxo-1*H*-purin-8-yl-κ*C*)(di-thiocarboxylato-2-κ^2*C*,*S*)-tris(trimethylphosphine-κ*P*) cobalt(I) tetrahydrofuran solvate, $C_{22}H_{44}CoN_4O_3P_3S_2$

Tingting Zheng[*, I, II], Wengang Xu[II], Junye Li[II] and Faguan Lu[II]

[I] Department of Chemistry, Capital Normal University, Beijing 100048, P. R. China
[II] School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, P. R. China

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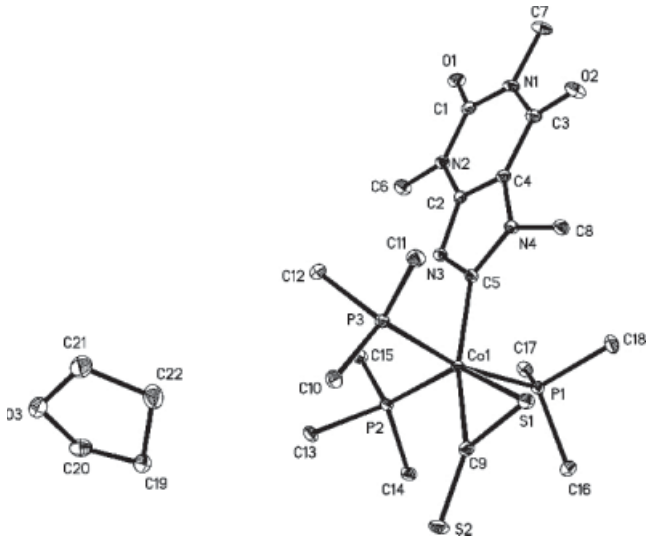

Abstract

$C_{22}H_{44}CoN_4O_3P_3S_2$, monoclinic, $P2_1/c$ (no. 14), a = 12.775(3) Å, b = 14.680(3) Å, c = 16.174(3) Å, β = 104.15(3)°, V = 2941.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.0242, $wR_{ref}(F^2)$ = 0.0640, T = 293 K.

Table 1. Data collection and handling.

Crystal:	redish-brown blocks, size 0.19×0.2×0.22 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.19 cm^{-1}
Diffractometer, scan mode:	Bruker APEX II, φ and ω
$2\theta_{max}$:	55.08°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	17015, 6663
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6090
$N(param)_{refined}$:	328
Programs:	SHELX [6]

Source of material

Standard vacuum techniques were used in manipulations of volatile and air sensitive materials. Literature procedures were followed in the preparation of methyltetrakis(tri-methylphosphane)cobalt(I) [5]. Caffeine was extracted from tea and purified by recrystallization. Other chemicals were used as purchased. A solution of caffeine 0.32 g (1.65 mmol) in 30 mL of diethyl ether was combined with a solution of $CoMe(PMe_3)_4$ 0.44 g (1.64 mmol) in 20 mL of diethyl ether at 195K. The reaction mixture was allowed to warm to ambient temperature and stirred for 16 h. Then, 0.13 g (1.70 mmol) of carbon disulfide was injected into the mixed solution. The reaction mixture stirred continuously for 10h and turned reddish-brown. After filtering, the red solid residue was extracted with the mixed solution of tetrahydrofuran and pentane (50mL). The title compound was obtained from recrystallization from the mixed solution of tetrahydrofurane and pentane at 277K yielding red-brown crystals suitable for X-ray diffraction. Yield: 0.68 g (65%).

* Correspondence author (e-mail: xli63@sdu.edu.cn)

Discussion

In the past few years, the chemistry of caffeine has been the subject of study due to its crucial performance as adenosine receptor antagonists in biological systems [1-4]. In the title compound, the cobalt atom is five-coordinated in a trigonal bipyramidal geometry. Two phosphorus atoms of two trimethyl phosphine ligands (P1, P3) occupy the axial position. The equatorial position are occupied by the third trimethyl phosphine ligand, the κ*C* caffeine and the side on coordinated S=C group of the carbon disulfide. The axial angle P3–Co1–P1 is 167.42°, indicating a distorted trigonal bipyramidal geometry. The length of the bond S1–C9 is 1.693(14) Å, which is slightly longer than the length of the bond S2–C9 1.6329(14) Å. The length of the Co1–P2 bond is a little bit shorter compared with the lengths of Co1–P1 and Co1–P3 resulting from the *trans*-effect of the sulfur atom of the carbon disulfide.

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

Atom	Site	x	y	z	U_{iso}
H(20A)	4*e*	0.3600	0.9239	–0.0067	0.028
H(20B)	4*e*	0.3423	1.0278	0.0076	0.028
H(20C)	4*e*	0.2522	0.9572	0.0132	0.028
H(14A)	4*e*	0.6855	1.0888	0.3431	0.028
H(14B)	4*e*	0.6112	1.1600	0.2842	0.028
H(14C)	4*e*	0.6378	1.0670	0.2463	0.028
H(12A)	4*e*	0.0745	1.1460	0.0337	0.032
H(12B)	4*e*	0.1822	1.1124	0.0137	0.032
H(12C)	4*e*	0.1823	1.1992	0.0701	0.032
H(10A)	4*e*	0.1036	0.9273	0.1657	0.028
H(10B)	4*e*	0.1366	0.9320	0.0786	0.028
H(10C)	4*e*	0.0301	0.9793	0.0883	0.028
H(11A)	4*e*	0.0173	1.1286	0.1708	0.032
H(11B)	4*e*	0.1153	1.1796	0.2299	0.032
H(11C)	4*e*	0.0821	1.0827	0.2554	0.032
H(15A)	4*e*	0.5821	1.0986	0.4579	0.029
H(15B)	4*e*	0.4615	1.0713	0.4500	0.029
H(15C)	4*e*	0.4889	1.1639	0.4119	0.029
H(13A)	4*e*	0.5602	0.8952	0.3111	0.028
H(13B)	4*e*	0.4983	0.9034	0.3833	0.028
H(13C)	4*e*	0.6187	0.9354	0.4002	0.028
H(17A)	4*e*	0.0115	0.8097	0.5409	0.038
H(17B)	4*e*	0.0661	0.8963	0.5898	0.038
H(17C)	4*e*	0.1206	0.8006	0.6104	0.038

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(18A)	4*e*	0.1619	0.7164	0.2822	0.034
H(18B)	4*e*	0.2132	0.6577	0.3630	0.034
H(18C)	4*e*	0.2870	0.7186	0.3211	0.034
H(22A)	4*e*	0.2757	1.1581	0.3692	0.026
H(22B)	4*e*	0.2882	1.1252	0.4633	0.026
H(22C)	4*e*	0.1731	1.1335	0.4015	0.026
H(19A)	4*e*	0.2825	0.8276	0.1501	0.028
H(19B)	4*e*	0.3982	0.8151	0.2100	0.028
H(19C)	4*e*	0.3786	0.7977	0.1118	0.028
H(21A)	4*e*	0.5728	0.9249	0.1867	0.028

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(21B)	4*e*	0.5537	1.0029	0.1185	0.028
H(21C)	4*e*	0.5346	0.9011	0.0895	0.028
H(32A)	4*e*	0.7627	0.9303	0.1404	0.032
H(32B)	4*e*	0.8738	0.9833	0.1578	0.032
H(31A)	4*e*	0.8454	0.7930	0.1735	0.032
H(31B)	4*e*	0.9270	0.8408	0.1283	0.032
H(33A)	4*e*	0.9884	0.9329	0.3473	0.042
H(33B)	4*e*	0.9159	0.8487	0.3566	0.042
H(34A)	4*e*	0.8395	1.0061	0.2871	0.045
H(34B)	4*e*	0.7703	0.9162	0.2809	0.045

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}
C(14)	4*e*	0.3287(1)	0.9672(1)	0.02470(8)	0.0219(7)	0.0212(7)	0.0136(6)	0.0003(6)	0.0065(5)	–0.0006(5)
Co(1)	4*e*	0.34995(1)	1.05922(1)	0.22394(1)	0.01265(9)	0.01058(9)	0.01090(9)	–0.00039(6)	0.00424(7)	0.00068(6)
P(1)	4*e*	0.17799(3)	1.06903(2)	0.15114(2)	0.0138(2)	0.0153(2)	0.0129(2)	0.0010(1)	0.0036(1)	–0.0006(1)
P(3)	4*e*	0.50614(3)	1.04512(2)	0.32109(2)	0.0138(2)	0.0142(2)	0.0129(2)	–0.0006(1)	0.0037(1)	0.0007(1)
S(2)	4*e*	0.45462(3)	1.18520(2)	0.08753(2)	0.0319(2)	0.0173(2)	0.0221(2)	–0.0032(1)	0.0160(2)	0.0026(1)
S(1)	4*e*	0.35584(3)	1.21562(2)	0.24044(2)	0.0225(2)	0.0118(2)	0.0177(2)	–0.0008(1)	0.0078(1)	–0.0006(1)
P(2)	4*e*	0.38856(3)	0.95320(2)	0.13868(2)	0.0150(2)	0.0126(2)	0.0130(2)	–0.0001(1)	0.0059(1)	–0.0001(1)
O(1)	4*e*	0.12160(8)	0.70114(7)	0.46925(7)	0.0236(5)	0.0206(5)	0.0238(5)	–0.0043(4)	0.0083(4)	0.0071(4)
N(4)	4*e*	0.25423(9)	1.02432(8)	0.37838(7)	0.0160(5)	0.0141(5)	0.0129(5)	–0.0005(4)	0.0057(4)	0.0002(4)
N(3)	4*e*	0.27656(9)	0.89958(8)	0.30541(7)	0.0154(5)	0.0140(5)	0.0155(5)	–0.0007(4)	0.0059(4)	0.0021(4)
O(2)	4*e*	0.15269(9)	1.00607(7)	0.53388(7)	0.0327(6)	0.0266(6)	0.0200(5)	–0.0044(5)	0.0148(4)	–0.0037(4)
N(1)	4*e*	0.13916(9)	0.85313(8)	0.50057(7)	0.0178(6)	0.0226(6)	0.0134(5)	–0.0036(5)	0.0071(4)	0.0032(4)
C(5)	4*e*	0.2895(1)	0.99183(9)	0.30958(8)	0.0120(6)	0.0161(6)	0.0124(6)	0.0004(5)	0.0034(5)	0.0004(5)
C(2)	4*e*	0.2327(1)	0.87684(9)	0.37025(8)	0.0131(6)	0.0151(6)	0.0143(6)	0.0005(5)	0.0029(5)	0.0028(5)
C(10)	4*e*	0.6241(1)	1.0963(1)	0.29568(9)	0.0152(6)	0.0194(7)	0.0216(7)	–0.0028(5)	0.0055(5)	–0.0009(5)
N(2)	4*e*	0.20430(9)	0.78989(8)	0.38882(7)	0.0181(5)	0.0149(5)	0.0170(6)	–0.0014(4)	0.0070(4)	0.0023(4)
C(3)	4*e*	0.1691(1)	0.94455(9)	0.48767(9)	0.0154(6)	0.0217(7)	0.0134(6)	–0.0025(5)	0.0040(5)	0.0014(5)
C(9)	4*e*	0.3992(1)	1.15725(9)	0.16484(9)	0.0162(6)	0.0140(6)	0.0160(6)	0.0002(5)	0.0038(5)	0.0014(5)
C(16)	4*e*	0.1511(1)	1.1401(1)	0.05588(9)	0.0214(7)	0.0240(7)	0.0173(7)	0.0044(6)	0.0028(6)	0.0041(6)
C(17)	4*e*	0.1032(1)	0.9645(1)	0.11690(9)	0.0158(6)	0.0222(7)	0.0189(7)	–0.0031(5)	0.0044(5)	–0.0034(5)
C(1)	4*e*	0.1531(1)	0.7765(1)	0.45337(9)	0.0134(6)	0.0217(7)	0.0155(6)	–0.0015(5)	0.0021(5)	0.0055(5)
C(18)	4*e*	0.0875(1)	1.1211(1)	0.20860(9)	0.0184(7)	0.0263(7)	0.0200(7)	0.0046(6)	0.0053(6)	–0.0050(6)
C(11)	4*e*	0.5101(1)	1.1014(1)	0.42216(9)	0.0196(7)	0.0242(7)	0.0140(6)	–0.0001(6)	0.0030(5)	–0.0029(5)
C(12)	4*e*	0.5512(1)	0.93131(9)	0.35835(9)	0.0204(7)	0.0187(7)	0.0171(7)	0.0027(5)	0.0038(5)	0.0037(5)
C(4)	4*e*	0.2174(1)	0.95061(9)	0.41744(9)	0.0142(6)	0.0168(6)	0.0134(6)	–0.0012(5)	0.0034(5)	0.0025(5)
C(7)	4*e*	0.0792(1)	0.8387(1)	0.5661(1)	0.0278(8)	0.0324(8)	0.0190(7)	–0.0072(6)	0.0138(6)	0.0024(6)
C(6)	4*e*	0.2177(1)	0.7142(1)	0.3341(1)	0.0310(8)	0.0157(7)	0.0254(8)	–0.0020(6)	0.0134(6)	–0.0002(6)
C(8)	4*e*	0.2472(1)	1.11829(9)	0.40539(9)	0.0216(7)	0.0162(6)	0.0160(6)	0.0010(5)	0.0076(5)	–0.0010(5)
C(15)	4*e*	0.3584(1)	0.83438(9)	0.15451(9)	0.0243(7)	0.0137(6)	0.0214(7)	0.0001(5)	0.0105(6)	–0.0004(5)
C(13)	4*e*	0.5291(1)	0.9445(1)	0.13266(9)	0.0178(7)	0.0211(7)	0.0191(7)	0.0013(5)	0.0090(5)	–0.0011(5)
O(3)	4*e*	0.97518(9)	0.84238(8)	0.25436(7)	0.0274(6)	0.0371(6)	0.0271(6)	0.0089(5)	0.0058(5)	0.0050(5)
C(19)	4*e*	0.8355(1)	0.9333(1)	0.1764(1)	0.0193(7)	0.0367(9)	0.0236(8)	0.0031(6)	0.0044(6)	0.0057(6)
C(20)	4*e*	0.8945(1)	0.8440(1)	0.1765(1)	0.0334(8)	0.0244(8)	0.0221(8)	–0.0060(6)	0.0065(6)	–0.0001(6)
C(21)	4*e*	0.9343(1)	0.8909(1)	0.3162(1)	0.0317(9)	0.048(1)	0.0218(8)	0.0065(8)	0.0019(7)	–0.0008(7)
C(22)	4*e*	0.8351(2)	0.9426(1)	0.2699(1)	0.0294(9)	0.057(1)	0.0259(9)	0.0112(8)	0.0047(7)	–0.0057(8)

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References

1. Daly, J. W.: Adenosine receptors: Targets for future drugs. J. Med. Chem. **25** (1982) 197-207.
2. Jacobson, K. A.; Shi, D.; Gallo-Rodriguez, C.: Effect of trifluoromethyl - and other substituents on activity of xanthines at adenosine receptors. J. Med. Chem. **36** (1993)2639-2644.
3. Shamim, M. T.; Ukens, D.; Padgett, W. L.; Daly, J. W.: Effects of 8-cycloalkyl substituents on the activity of mono-, di-, and trisubstituted alkylxanthines with substitution at the 1-, 3-, and 7-positions. J. Med. Chem. **32** (1989) 1231-1237.
4. Jacobson, K. A.; van Galen, P. J. M.; Williams, M.: perspective, adenosine receptors:pharmacology,structure activity relationships and therapeutic potential. J. Med. Chem. **35** (1992) 407-422.
5. Klein, H.-F.; Karsch, H. H.: Methylkobaltverbindungen mit nicht chelatisierenden Liganden, I. Methyltetrakis(trimethylphosphin)cobalt und seine Derivate. Chem. Ber. **108** (1975) 944-955.
6. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.