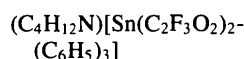


yielded large (>1 cm) colorless crystals of the title ammonium stannate.

Crystal data



$M_r = 650.18$

Orthorhombic

Pbca

$a = 16.700(1) \text{ \AA}$

$b = 17.781(1) \text{ \AA}$

$c = 19.708(1) \text{ \AA}$

$V = 5852.1(6) \text{ \AA}^3$

$Z = 8$

$D_x = 1.476 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 12\text{--}13^\circ$

$\mu = 0.941 \text{ mm}^{-1}$

$T = 298(2) \text{ K}$

Block

$0.50 \times 0.50 \times 0.50 \text{ mm}$

Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer

ω scans

Absorption correction:

ψ scan (North, Phillips & Mathews, 1968)

$T_{\min} = 0.550$, $T_{\max} = 0.625$

5134 measured reflections

5134 independent reflections

3195 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 25^\circ$

$h = -19 \rightarrow 0$

$k = -21 \rightarrow 0$

$l = -23 \rightarrow 0$

3 standard reflections

frequency: 60 min

intensity decay: none

Refinement

Refinement on F^2

$R(F) = 0.0509$

$wR(F^2) = 0.1310$

$S = 0.990$

5134 reflections

307 parameters

H atoms: $U(\text{H}) = 1.5U_{\text{eq}}(\text{C})$

$w = 1/[\sigma^2(F_o^2) + (0.0717P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.572 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.481 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Sn1—C1	2.152 (3)	Sn1—O1	2.255 (4)
Sn1—C7	2.131 (3)	Sn1—O3	2.219 (3)
Sn1—C13	2.137 (3)		
C1—Sn1—C7	118.7 (2)	C7—Sn1—O1	88.9 (1)
C1—Sn1—C13	111.9 (1)	C7—Sn1—O3	90.6 (1)
C1—Sn1—O1	87.4 (1)	C13—Sn1—O1	90.7 (1)
C1—Sn1—O3	88.6 (1)	C13—Sn1—O3	93.4 (2)
C7—Sn1—C13	129.3 (2)	O1—Sn1—O3	175.1 (1)

The CF_3 and $(\text{CH}_3)_4\text{N}$ groups are disordered but the disorder could not be resolved. The disorder affected the phenyl rings which had to be refined as rigid hexagons.

Data collection: *CAD-4 VAX/PC* (Enraf–Nonius, 1988). Cell refinement: *CAD-4 VAX/PC*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *DIRDIF94* (Beurskens *et al.*, 1994). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976) in *SHELXTL/PC* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL93*.

The authors thank the University of Malaya (F102/96 and F677/96) for supporting this work.

Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: SK1049). 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. (1997). **C53**, 213–215

A Pteridin-6-yl Alkene-1,2-dithiolate Complex of Cobalt

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Abstract

The crystal structure of the title compound, $(\eta^5\text{-cyclopentadienyl})[6\text{-(1,2-dimercaptoethen-1-yl)-2-(N,N'-dimethylaminomethylideneamino-3-methylpteridin-4(3H)-$

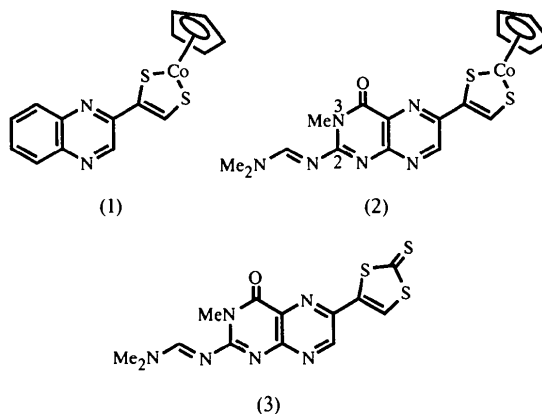
onato(2-)-S,S']cobalt(III) monohydrate, [Co(C₅H₅)-(C₁₂H₁₂N₆OS₂)]·H₂O, shows the sulfur/cobalt-containing ring, the pteridine ring system and the pteridine-2-amino protecting group to be coplanar.

Comment

Recently, X-ray structure determinations of aldehyde oxidase from *Desulfovibrio gigas* (Romão, Archer, Moura, Moura, LeGall, Eng, Schneider, Hof & Huber, 1995), of DMSO reductase from *Rhodobacter sphaeroides* (Schindelin, Kisker, Hilton, Rajagopalan & Rees, 1996) and of the tungstopterin enzyme ferredoxin aldehyde oxidoreductase from *Pyrococcus furiosus* (Chan, Mukund, Kletzin, Adams & Rees, 1995) have clarified earlier suggestions based on degradative work (Johnson, Wuebbens & Rajagopalan, 1989) for the structure of Moco, the ubiquitous cofactor of the oxomolybdo enzymes.

We have been examining compounds which serve as models for the structure and mode of action of Moco (Collison, Garner & Joule, 1996). In particular, we are interested in the interaction between the molybdenum centre and the pteridine unit and have reported electrochemical experiments (Armstrong, Austerberry, Birks, Beddoes, Helliwell, Joule & Garner, 1993) on a quinoxaline cobalt complex, (1) (Armstrong, Austerberry, Beddoes, Helliwell, Joule & Garner, 1993), which demonstrated co-operativity between the metal centre and the heterocycle, and thus strongly suggests that comparable interactions are involved in the mode of action of these enzymes. In addition to synthesizing simpler model substances having pyridines as surrogates for the pteridine unit (Austerberry, 1992), we have now succeeded in preparing a cobalt complex, (2), which has a complete pteridine unit, albeit carrying an unnatural *N*-3-methyl substituent and a dimethylaminomethylidene as blocking substituent on the 2-amino group.

The title complex, (2), could be prepared by the reaction of the pteridin-6-yl-1,3-dithiole-2-thione (3) with (cyclooctadiene)(cyclopentadienyl)carbonylcobalt(I) in refluxing toluene and crystallized from MeCN/Cl(CH₂)₂Cl with water of crystallization (m.p. > 593 K). Full details of the organic synthesis of (3) and of electrochemical investigations on (2) will be described elsewhere.



The crystal structure of (2) shows, as expected, that the two rings of the pteridine system are planar. In contrast to the analogous quinoxaline complex (1) (Armstrong, Austerberry, Beddoes, Helliwell, Joule & Garner, 1993), in which the cobalt-containing ring and the quinoxaline ring make an angle of 10° with one another, in the present structure, the cobalt-containing ring and the pteridine system are completely coplanar. The 2-amino blocking substituent is clearly also fully conjugated with the system, being coplanar with the pteridine unit.

Experimental

The title compound was recrystallized from an acetonitrile/1,2-dichloroethane solution.

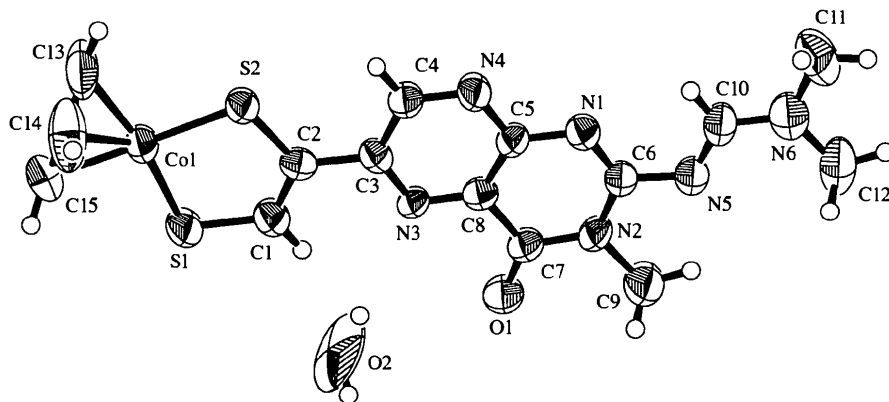


Fig. 1. ORTEP (Johnson, 1965) drawing of the title molecule, with ellipsoids at the 50% probability level, showing the atomic numbering system.

Crystal data

[Co(C₅H₅)(C₁₂H₁₂N₆OS₂)]·
H₂O
M_r = 462.43
Monoclinic
C2/m
a = 21.334 (6) Å
b = 6.985 (2) Å
c = 17.100 (6) Å
β = 123.45 (2)°
V = 2126 (1) Å³
Z = 4
D_x = 1.444 Mg m⁻³
D_m not measured

Mo Kα radiation
λ = 0.7107 Å
Cell parameters from 19
reflections
θ = 7.8–13.9°
μ = 1.028 mm⁻¹
T = 295.2 K
Tabular
0.20 × 0.20 × 0.01 mm
Green

Data collection

Rigaku AFC-5R diffractometer
ω–2θ scans
Absorption correction:
ψ scans (North, Phillips
& Mathews, 1968)
T_{min} = 0.852, T_{max} = 1.000
2126 measured reflections
2064 independent reflections

1295 reflections with
I > 3σ(I)
R_{int} = 0.02865
θ_{max} = 25.05°
h = 0 → 25
k = 0 → 8
l = –20 → 17
3 standard reflections
every 150 reflections
intensity decay: 1.55%

Refinement

Refinement on F²
R = 0.0657
wR = 0.0787
S = 3.332
1295 reflections
166 parameters
H atoms not refined
w = 1/[σ²(F_o)
+ 0.00002|F_o|²]

(Δ/σ)_{max} = 0.0360
Δρ_{max} = 0.93 e Å⁻³
Δρ_{min} = –0.34 e Å⁻³
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Co1—S1	2.103 (4)	N4—C4	1.34 (1)
Co1—S2	2.114 (4)	N4—C5	1.33 (1)
Co1—C13	2.06 (2)	N5—C6	1.36 (1)
Co1—C14	2.01 (1)	N5—C10	1.30 (2)
Co1—C15	2.012 (9)	N6—C10	1.32 (2)
S1—C1	1.70 (1)	N6—C11	1.45 (2)
S2—C2	1.72 (1)	N6—C12	1.48 (2)
O1—C7	1.22 (1)	C1—C2	1.35 (2)
N1—C5	1.36 (1)	C2—C3	1.51 (2)
N1—C6	1.30 (1)	C3—C4	1.41 (2)
N2—C6	1.37 (1)	C5—C8	1.38 (2)
N2—C7	1.37 (1)	C7—C8	1.48 (2)
N2—C9	1.50 (2)	C13—C14	1.37 (2)
N3—C3	1.30 (1)	C14—C15	1.38 (1)
N3—C8	1.31 (1)		
S1—Co1—S2	91.7 (2)	Co1—S2—C2	104.5 (4)
Co1—S1—C1	105.0 (5)		

The H atoms were placed in idealized positions (C—H 0.95 Å) at the beginning of each least-squares cycle and assigned isotropic displacement parameters 20% greater than the equivalent U value of the atoms to which they were

bonded. The water molecule was assigned 0.5 site occupancy. Parallel solution and refinement in space group C2 were carried out. Both matrix-dampening and partial-shift strategies were adopted to overcome the inherent ill-conditioning. The resultant bond lengths were unreasonable and the displacement ellipsoids misshapen. In spite of the larger number of refined parameters, the R and wR factors were significantly higher than the C2/m structure and the goodness-of-fit parameter was worse. Attempts were made in space group C2/m to resolve the C9 and C11 atoms, which show considerable elongation of ellipsoids in the b direction, into two disordered positions, but were unsuccessful. Thus, the results given here for C2/m appear to be the best achievable from this difficult very thin crystal despite some rather large U₂₂ values.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR92* (Altomare, Casciarano, Giacovazzo & Guagliardi, 1993). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

The authors thank the SERC (UK) for funds for the purchase of the Rigaku AFC-5R diffractometer.

Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: HA1172). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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