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Bis(1-acetonylpyridinium) pyridinium hexaiodobismuth(III)

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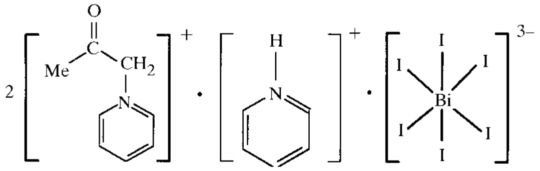
The crystal structure of the title complex, $(C_8H_{10}N)_2(C_5H_6N)[BiI_6]$, contains discrete $[BiI_6]^{3-}$ anions, and $(HNC_5H_5)^+$ and $(CH_3COCH_2NC_5H_5)^+$ cations separated by normal van der Waals contacts. The $[BiI_6]^{3-}$ anion has the Bi atom on an inversion centre. The $(HNC_5H_5)^+$ cation also lies about an inversion centre and is disordered. The $(CH_3COCH_2NC_5H_5)^+$ cation lies in a general position.

Comment

In our systematic investigation of the hybrid Mo(W) main-group metal clusters, we have synthesized successfully the hybrid cluster $[Mo_3(BiI_3)S_4(OAc)(dtp)_3(py)]$ (Lu *et al.*, 1997) from the reaction of the trimolybdenum cluster $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(\mu\text{-}OAc)(dtp)_3(py)]$ with BiI_3 [dtp = $S_2P(OC_2H_5)_2^-$ and OAc = CH_3COO^-]. When we changed the reaction conditions and used $[Mo_3S_4(dtp)_4(H_2O)]$, BiI_3, $NaOAc{\cdot}3H_2O$ and $KS_2CN(CH_2CH_2OH)_2$ as the starting materials to perform the reaction in the presence of acetone and pyridine, an unexpected complex, $[(BiI_6)(CH_3COCH_2NC_5H_5)_2(HNC_5H_5)]$, was obtained. Although there are some reports about relevant complexes such as Ag_3BiI_6 (Dzeranova *et al.*, 1985) and Cs_3BiI_6 (Dzeranova *et al.*, 1984), their crystal structures have not been reported.

In the structure of the title complex, (I), the Bi center exhibits an octahedral geometry with approximate O_h symmetry. A Bi—I distance of *ca* 3.08 Å is comparable with that in BiI_3 (3.10 Å; Wells, 1975), which has an octahedral layer structure. Obviously, the formation of $[BiI_6]^{3-}$ should be through the reaction of BiI_3 with I^-. To meet the requirements of the electrovalent balance of the molecule, $[CH_3COCH_2NC_5H_5]$ must be a cation. The ^1H NMR spectrum in DMSO-d_6 of this complex shows the signals of CH_2 and CH_3 at δ 5.66 and 2.28 p.p.m., respectively, for $[CH_3COCH_2NC_5H_5]^+$ and reveals two types of pyridine groups in a 1:2 ratio for $(HNC_5H_5)^+$ and $(CH_3COCH_2NC_5H_5)^+$, respectively. It seems that this novel cation $[CH_3COCH_2NC_5H_5]^+$ resulted from the stepwise reaction of acetone, halogen(I_2) and pyridine. But the reaction details are not yet known.



(I)

Experimental

For the preparation of (I), $[Mo_3S_4(dtp)_4(H_2O)]$ (0.1 g), $KS_2CN(CH_2CH_2OH)_2$ (0.1 g), $Na(OAc){\cdot}3H_2O$ (0.03 g) and 0.1 ml pyridine were dissolved in 10 ml dichloromethane, then stirred for 10 min. BiI_3 (0.1 g) in 8 ml acetone was added in the resulting solution. The mixture was stirred for 1 h and filtered, then evaporated in air. After two weeks, red crystals were obtained. The metal elements of the complex were proved to be Bi by ICP–AES analysis.

Crystal data

$(C_8H_{10}NO)_2(C_5H_6N)[BiI_6]$
M_r = 1322.83
Monoclinic, $P2_1/n$
a = 10.675 (2) Å
b = 11.083 (2) Å
c = 15.195 (3) Å
β = 108.19 (3)°
V = 1707.9 (6) Å^3
Z = 2
D_x = 2.572 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20 reflections
θ = 7.95–12.94°
μ = 10.605 mm^{-1}
T = 293 (2) K
Prism, red
0.13 × 0.13 × 0.10 mm

Data collection

Rigaku AFC-5R diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.261, $T_{\max}$ = 0.346
3358 measured reflections
3358 independent reflections
2264 reflections with $I > 2\sigma(I)$
$\theta_{\max}$ = 26.0°
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 13$
$l = -18 \rightarrow 17$
3 standard reflections every 300 reflections frequency: 120 min intensity decay: 3.4%

Refinement

Refinement on F^2
$R(F)$ = 0.036
$wR(F^2)$ = 0.091
S = 1.039
3358 reflections
151 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.94 e Å^{-3}
$\Delta\rho_{\min}$ = −1.00 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Bi1—I2	3.0772 (9)	Bi1—I1	3.0871 (8)
Bi1—I3	3.0850 (9)		
I2—Bi1—I3	88.50 (3)	I3—Bi1—I1	90.91 (3)
I2—Bi1—I1	88.82 (3)		

The three crystallographically independent positions (C9, C10 and C11) in a centrosymmetric six-membered ring of the $(HNC_5H_5)^+$

cation exist a statistical distribution of C and N with an occupancy of 1.028 of a C atom (*i.e.* $\frac{5}{6}$C + $\frac{1}{6}$N). All calculations were performed using the *SHELXTL* (Sheldrick, 1995) program package. The distance between the deepest hole and theI3 atom is 0.92 Å, so this hole can be referred to as the ghost of the I3 atom.

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