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(*E*)-2-(Thiosemicarbazonomethyl)pyridinium trichloro[(*E*)-1-(2-pyridylmethylene)thiosemicarbazonato-κ^3*N*,*N*′,*S*]indate(III) ethanol solvate

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.008 Å
R factor = 0.048
wR factor = 0.110
Data-to-parameter ratio = 16.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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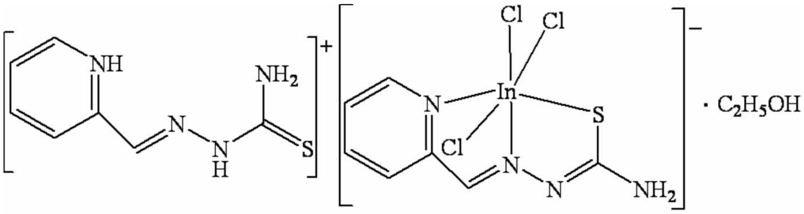
In the title compound, $(C_7H_9N_4S)[In(C_7H_7N_4S)Cl_3]\cdot C_2H_6O$, the two (*E*)-1-(2-pyridylmethylene)thiosemicarbazone (pmtcH) units show different structures; the coordinated pmtc$^-$ ligand is in the enol form but the free pmtcH$_2^+$ cation is in the keto form. The In^{III} complex assumes a distorted octahedral coordination geometry. N—H···N and N—H···Cl hydrogen bonding helps to stabilize the crystal structure.

Comment

(*E*)-1-(2-Pyridylmethylene)thiosemicarbazone (pmtcH) was recently synthesized by a reaction of pyridinecarbaldehyde and thiosemicarbazide in the laboratory, and was used to prepare the title In^{III} complex, (I). We report here the synthesis and crystal structure of (I).



(I)

The crystal structure of (I) consists of In^{III} complex anions, pmtcH$_2^+$ cations and ethanol solvent molecules. In the asymmetric unit of (I), there are two pmtc units; one coordinates as a pmtc$^-$ anion to the In^{III} ion and the other is protonated and serves as a counter-cation (Fig. 1). The C9—N2 and C2—N6 bond distances (Table 1) clearly show double-bond character for the Schiff base compound. The C1—N7 bond distance is significantly shorter than the C8—N3 bond distance, while the C1—S1 bond distance is significantly longer than C8—S2 bond distance. These facts indicate that coordinated pmtc$^-$ ligand is a deprotonated enol. The S1-containing pmtc chelates to the In^{III} ion, and three Cl$^-$ ions complete the distorted octahedral coordination geometry.

The N—H···N hydrogen bonding between complex anions and N—H···Cl hydrogen bonding between the complex anion and pmtcH$_2^+$ cation help to stabilize the crystal structure of (I). The solvent ethanol molecule links with the complex anion *via* O—H···Cl hydrogen bonding (Table 2).

Experimental

An ethanol solution (10 ml) of $InCl_3$ (29.3 mg, 0.10 mmol) was slowly diffused into a dichloromethane solution (10 ml) of (*E*)-1-(pyridin-2-ylmethylene)thiosemicarbazide (18.0 mg, 0.10 mmol). Yellow single crystals of (I) were obtained after the solution was allowed to stand at room temperature for 3 d.

Crystal data

$(C_7H_9N_4S)[In(C_7H_7N_4S)Cl_3]\cdot C_2H_6O$
$M_r = 627.71$
Triclinic, $P\overline{1}$
$a = 7.906\ (2)$ Å
$b = 12.437\ (3)$ Å
$c = 12.680\ (4)$ Å
$\alpha = 78.337\ (4)^\circ$
$\beta = 84.922\ (4)^\circ$
$\gamma = 84.130\ (4)^\circ$
$V = 1211.6\ (6)$ Å^3
$Z = 2$
$D_x = 1.721$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.51$ mm^{-1}
$T = 298\ (2)$ K
Needle, yellow
0.40 × 0.06 × 0.05 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{\min} = 0.584$, $T_{\max} = 0.928$
6388 measured reflections
4428 independent reflections
3582 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 25.5^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.110$
$S = 1.02$
4428 reflections
272 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.051P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.04$ e Å^{-3}
$\Delta\rho_{\min} = -0.79$ e Å^{-3}

Table 1
Selected bond lengths (Å).

In1—Cl1	2.6016 (14)	N2—N3	1.360 (6)
In1—Cl4	2.4130 (14)	N3—C8	1.365 (7)
In1—Cl5	2.5471 (15)	N6—C2	1.283 (6)
In1—S1	2.5189 (15)	N6—N7	1.363 (5)
In1—N5	2.277 (4)	N7—C1	1.325 (6)
In1—N6	2.256 (4)	C1—S1	1.742 (5)
N2—C9	1.271 (6)	C8—S2	1.673 (6)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···Cl5	0.82	2.49	3.281 (5)	164
N3—H3···O1$^{\rm i}$	0.86	1.96	2.810 (6)	171
N4—H4*A*···Cl1$^{\rm ii}$	0.86	2.80	3.609 (5)	158
N4—H4*B*···Cl1	0.86	2.52	3.356 (5)	163
N8—H8*A*···N7$^{\rm iii}$	0.86	2.11	2.963 (6)	172
N8—H8*B*···Cl5$^{\rm iv}$	0.86	2.62	3.408 (4)	153

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+2, -y+1, -z+2$; (iv) $x+1, y, z$.

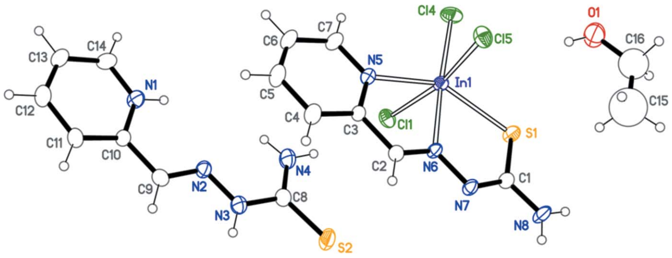


Figure 1
The molecular structure of (I) with 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

The C atoms of the ethanol solvent molecule were refined as isotropic. Methyl H atoms were placed in calculated positions with C—H = 0.96 Å and the torsion angle was refined to fit the electron density; $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$. Other H atoms were placed in calculated positions with O—H = 0.82 Å, N—H = 0.86 Å and C—H = 0.93 (aromatic) or 0.97 Å (methylene), and refined in riding mode with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C,N})$ or $1.5U_{\rm eq}({\rm O})$. The highest peak in the final difference Fourier map is 0.94 Å from atom In1.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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References

Bruker (1997). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2001). *SHELXTL*. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

m262 Fan *et al.* • $(C_7H_9N_4S)[In(C_7H_7N_4S)Cl_3]\cdot C_2H_6O$ *Acta Cryst.* (2007). E**63**, m261–m262