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КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE OF INDIUM(III) SCHIFF BASE COMPLEX

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The title compound [In($C_{22}H_{30}N_4O_4$)]Cl (I) bis[(N-salicylidene-N′-(2-hydroxyethyl)ethyleneediamine)indium(III) chloride is prepared, and its crystal structure is determined by single crystal X-ray diffraction at room temperature. The complex crystallizes in the monoclinic space group $P2_1/n$, $a = 9.9704(6)$, $b = 24.9554(15)$, $c = 10.5707(6)$ Å, $\beta = 116.46(2)°$, $V = 2354.6(2)$, $Z = 4$. The X-ray analysis reveals that the In^{III} ion is surrounded by four nitrogen and two oxygen atoms from two ligands leading to a distorted octahedral geometry. The molecule has the form of tongs at a junction point with the metal. Five membered rings adopt envelope conformation. In the crystal structure, the molecules are linked via N—H...Cl, O—H...O, O—H...Cl, and C—H...Cl intermolecular interactions. The structure is further stabilized by C—H...π (arene) interactions.

Keywords: crystal structure, Schiff base, metal complex, X-ray diffraction, hydrogen bonding.

Introduction. Schiff-base ligands are commonly used as complexing agents [1]. These ligands synthesized by the condensation of N-(2-hydroxyethyl)ethylenediamine) and salicylaldehyde have strong coordination abilities to various metal ions. We have previously reported [2] a chromium(III) nitrate complex with Schiff-base L, where L is N-salicylidene-N′-(2-hydroxyethyl)ethylenediamine. The literature is available with metal complexes of similar type structures [3, 4], but there are relatively few reports published on indium(III) complexes with these ligands. In continuation of our ongoing structural studies on metal Schiff-base complexes, herein, we report the single crystal structure of bis[(N-salicylidene-N′-(2-hydroxyethyl)ethylenediamine)indium(III) chloride [I] (Fig. 1).

Experimental. Equipments and Measurements. Elemental analyses for C, H, and N were obtained using an American PE2400 II CHNS/O elemental analyzer. Infrared spectra were recorded on a Nicolet 5DXB spectrophotometer using KBr discs in the 4000—400 cm^{-1} region. Single crystal structure data were collected on Smart Apex CCD with graphite-monochromated MoK_α ($\lambda = 0.71073$ Å) radiation at 296(2) K.

Synthesis of the title complex. The complex was prepared by dissolving equimolar (2 mmol) salicylaldehyde and N-(2-hydroxyethyl)ethylenediamine) in methanol. After stirring for 10 min a yellow color solution was obtained. To this solution $InCl_3$ (2 mmol) was added, and the mixture was stirred for about 30 min. Upon slow evaporation, pale yellow crystals were obtained at room temperature. Anal. Calcd. for $C_{22}H_{30}N_4O_4InCl$ (%): C 46.82, H 5.32, N 9.93. Found: C 46.20, H 5.38, N 9.46.

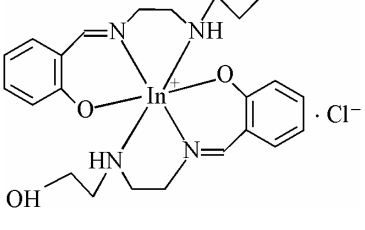

Fig. 1. Schematic diagram of the molecule (I)

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Table 1

Crystal and Experimental Data

CCDC No.	767454
Empirical formula	$[InC_{22}H_{30}N_4O_4]Cl$
Formula weight	564.78
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions, Å	$a = 9.9704(6)$, $b = 24.9554(15)$, $c = 10.5707(6)$
V, Å^3	2354.6(2)
Z	4
D_{cal}, g/cm^3	1.593
μ, mm^{-1}	1.153
Radiation (MoK_α), Å	0.71073
$F(000)$	1152
θ range for data collection, deg.	2.34—25.73
Reflections collected	22493
Independent reflections	4142
No. of reflections $[I > 2\sigma(I)]$	3735
No. of parameters	305
Final R indices R / wR	0.0271 / 0.0631
Goodness of fit on F^2	1.038
Refinement method	Full-matrix least-squares on F^2
Measurement	Bruker SMART CCD
Program system	SAINT
Structure determination / refinement	SHELXS97 / SHELXL97
Molecular graphics	ORTEP-3 and PLATON

Spectroscopic characterization of I. The IR spectra of the ligand (Schiff base) and the In complex were recorded separately. The characteristic bands of the Schiff base appeared at 1632 and 1538 cm^{-1} ($\gamma_{C=N}$ stretching) have slightly shifted to 1620 and 1525 cm^{-1}. This may be ascribed to complexation of the metal to the ligand. The bands due to the $\gamma(NH_2)$ stretching of coordinated ethelynediamine (3251 and 3160 cm^{-1}) were also present. The two sharp peaks in the region 735—790 cm^{-1} may be assigned to the C—H bending vibration.

Structure Determination and Refinement. Diffraction data were measured at room temperature with a Bruker SMART CCD area detector [5]. Preliminary lattice parameters and orientation matrix were obtained from three sets of frames. The intensity data were collected using graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å).

Integration and scaling of the intensity data were accomplished using SAINT [5]. The structure was solved by direct methods and refined by a full matrix least-squares procedure based on F^2 [6]. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were included in the calculated positions in the riding model approximation. The details of the data collection and refinement are summarized in Table 1. The geometry and molecular graphics were computed using PARST [7], ORTEP-3 [8], and PLATON [9] programs.

Results and Discussion. The molecular structure of the title compound is shown in Fig. 2. The molecule has a nearly tongs shape with In1 at the junction point. It consists of an $(InL_2)^+$ cation and a chloride anion. The tridentate Schiff base ligands (L) (where L = N-salicylidene-N′-(2-hydroxyethyl)ethylenediamine) chelate the In(III) atom in the cation through four N atoms and two phenoxy O atoms to complete a distorted octahedral coordination geometry (Table 2). The In—N and In—O bond

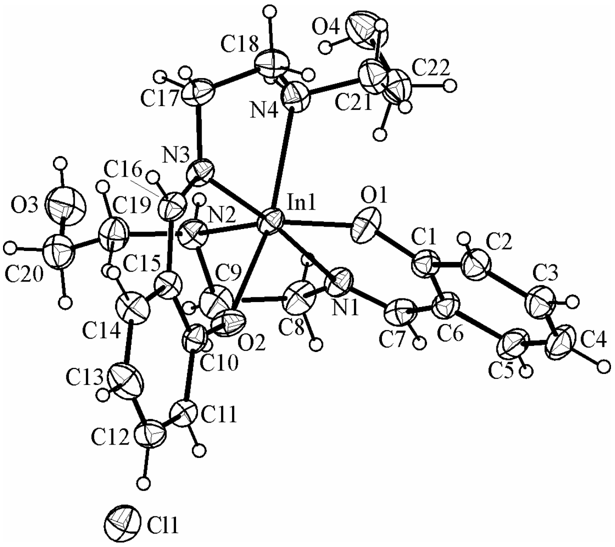

Fig. 2. ORTEP drawing of **I** showing the atom numbering scheme. Thermal ellipsoids are drawn at 30 % probability level

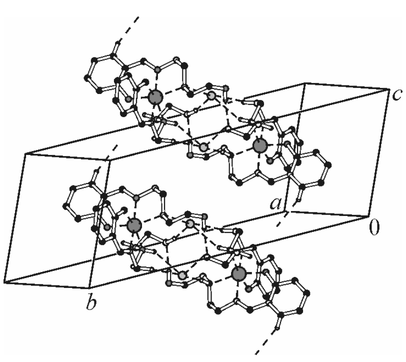

Fig. 3. Fragment of the crystal structure of **I** showing molecular chains running along the *a*-axis. For the sake of clarity, H atoms not involved in the motif shown were omitted

Table 2

Selected geometric parameters (Å, deg.)

In1—N1	2.214(2)	In1—O1	2.098(2)	N1—In1—N2	77.13(8)	O1—In1—N2	161.92(8)
In1—N2	2.275(2)	In1—O2	2.125(2)	N2—In1—N3	103.16(8)	N1—In1—O2	89.69(8)
In1—N3	2.195(2)	C7—N1	1.285(3)	N3—In1—N4	77.54(8)	O1—In1—N4	86.16(9)
In1—N4	2.325(2)	C16—N3	1.279(3)	N4—In1—N2	97.93(9)	O2—In1—N3	84.12(7)
				N1—In1—N3	173.78(8)		

lengths are normal and comparable to the literature data [10]. The C7—N1 and C16—N3 bond distances clearly show the double bond character typical of Schiff base compounds. Selected bond lengths and angles are given in Table 2. The bonds involving amine N atoms (N2 an N4) are slightly larger than those involving imine N atoms (N1 and N3), as expected. Further, the N1—In1—N2, N2—In1—N3 and N3—In1—N4 bond angles deviate from 90° by 12.48, 13.16, and 12.06° respectively. These deviations may be due to the strain created by five-membered chelate rings, viz. In1/N3/C17/C18/N4 and In1/N1/C8/C9/N2. At the metal atom, the ligands (L) are oriented almost in a meridional fashion (the dihedral angle between the least-square planes is 85.0(3)°). The conformation of the five-membered chelate rings in both ligands is that of an envelope (In1/N1/C8/C9/N2; ΔCs (C9) = 1.69 and In1/N3/C17/C18/N4; ΔCs (C18) = 12.88). With respect to the Schiff base L, the pendent hydroxyethyl groups are twisted by 41.78 and 84.95° (dihedral angles between the least-squares planes of C1—C7,N1,In1,O1,N2,C8,C9 and C19,C20,O3; C10—C15,O2,N3,In1,N4,C17,C18 and O4,C21,C22) respectively. The reason for the different values can be attributed to the notable difference in the assymetricity (ΔCs (C9) = 1.69 and ΔCs (C18) = 12.88) of the five-membered rings. In other words, the lesser the assymetricity, the smaller the twist and vice versa.

The crystal structure contains an extensive hydrogen-bond network (Fig. 3). All of the O_{hydroxy} and N_{amine} atoms in the Schiff base, along with the Cl atoms, contribute to the formation of intermolecular hydrogen bonds (Table 3). The packing is further stabilized by weak C—H...π (arene) intermolecular interactions.

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Table 3

Hydrogen bonding geometry (Å, deg.)

D—H…A	D—H	H…A	D…A	D—H…A	D—H…A	D—H	H…A	D…A	D—H…A
N2—H2N…Cl^{i}	0.81	2.43	3.225	166(3)	C5—H5…Cl^{iv}	0.93	2.81	3.711	164
O3—H30…O4^{ii}	0.82	2.04	2.857	172(4)	C17—H17B…Cl^{iii}	0.97	2.80	3.542	134
N4—H4N…Cl^{iii}	0.80	2.72	3.146	146(3)	C3—H3…Cg1^{v}	0.93	2.79	3.686	162
O4—H40…Cl^{i}	0.89	2.11	2.987	166(4)					

Symmetry code: (i) x, $-1+y$, z; (ii) $2-x$, $-y$, $1-z$; (iii) $2-x$, $1-y$, $1-z$; (iv) $1-x$, $1-y$, $-z$; (v) $-1+x$, y, z. Cg1 is the centroid of the ring C10—C15.

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