Rui Duan, Yu Guojun, Hui Tian, Man Wang and Qiong Wu*

Crystal structure of [2,2′-{azanediy}bis[(propane-3,1-diyl)(azanylylidene)methylylidene]]bis(3,5-dichlorophenolato)- $\kappa^2\text{O},\text{O}'$ -isothiocyanato- κN -iron(III), $\text{C}_{21}\text{H}_{19}\text{Cl}_4\text{FeN}_4\text{O}_2\text{S}$

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Abstract

$\text{C}_{21}\text{H}_{19}\text{Cl}_4\text{FeN}_4\text{O}_2\text{S}$, monoclinic, $P2_1/c$ (no. 14), $a = 16.304(2)$ Å, $b = 11.1675(15)$ Å, $c = 14.1041(16)$ Å, $\beta = 109.322(4)^\circ$, $V = 2423.3(5)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0802$, $wR_{\text{ref}}(F^2) = 0.1769$, $T = 150.0$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

*Corresponding author: Qiong Wu, Department of Chemical Science and Technology, Kunming University, Kunming, Yunnan 65200, P. R. China, E-mail: wuqiongkm@163.com. <https://orcid.org/0000-0001-7931-6750>

Rui Duan, Yu Guojun, Hui Tian and Man Wang, Department of Chemical Science and Technology, Kunming University, Kunming, Yunnan 65200, P. R. China

Table 1: Data collection and handling.

Crystal:	Red block
Size:	$0.20 \times 0.16 \times 0.12$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	1.18 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	25.0° , 97%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	16,085, 4167, 0.092
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3042
$N(\text{param})_{\text{refined}}$:	298
Programs:	CrysAlis ^{PRO} [1], Olex2 [2], SHELX [3, 4]

Source of material

A sample of 0.191 g of the powdered 3,5-dichlorosalicylaldehyde (1 mmol) was placed in a conical flask containing 50 ml ethanol, then 0.131 g 3,3′-diaminodipropylamine 0.5 mmol was added, and the mixture was stirred at room temperature for 12 h. Then 0.20 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.5 mmol) was added to the above mixture under stirring and the solution was gradually turned into purple-black. The obtained filtrate was kept undisturbed for two weeks. Black crystal suitable for single crystal diffraction analysis appeared at the bottom of the container.

Experimental details

The structure was solved with the Olex2 program [2] as an interface together with the SHELXT and SHELXL programs [3, 4]. All H atoms were placed in geometrically idealized positions and refined using a riding model, with C–H = 0.98 (methylene), 0.95 Å (benzene), and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ for H atoms.

Comment

The introduction of multidentate Schiff-base ligands that can both chelate and bridge metal ions, representing a promising route for the isolation of novel metallic complexes. So far, a number of complexes with unexpected

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} */U _{eq}
Fe1	0.68685 (7)	0.16998 (11)	0.38499 (8)	0.0288 (3)
Cl1	0.97872 (13)	0.27064 (18)	0.45449 (15)	0.0336 (5)
Cl2	0.88176 (14)	0.70500 (18)	0.28935 (16)	0.0364 (5)
Cl3	0.68504 (15)	0.5748 (2)	0.47682 (17)	0.0439 (6)
Cl4	0.96799 (14)	0.5130 (2)	0.80399 (16)	0.0372 (5)
S1	0.41465 (14)	0.1760 (2)	0.42112 (18)	0.0459 (6)
O1	0.7954 (3)	0.2115 (5)	0.3599 (4)	0.0283 (13)
O2	0.6895 (3)	0.3138 (5)	0.4630 (4)	0.0314 (13)
N1	0.6265 (4)	0.2661 (7)	0.2511 (5)	0.0336 (17)
N2	0.6763 (4)	0.0139 (6)	0.2881 (5)	0.0340 (17)
H2	0.7164	0.0265	0.2551	0.041*
N3	0.7697 (4)	0.0874 (6)	0.5188 (5)	0.0266 (15)
N4	0.5740 (5)	0.1154 (7)	0.4038 (5)	0.0406 (19)
C00M	0.5070 (5)	0.1392 (7)	0.4120 (6)	0.0301 (19)
C1	0.7479 (5)	0.4028 (7)	0.2838 (6)	0.0291 (19)
C2	0.8123 (5)	0.3220 (7)	0.3432 (6)	0.0264 (18)
C3	0.8980 (5)	0.3675 (7)	0.3837 (6)	0.0280 (18)
C4	0.9194 (5)	0.4828 (7)	0.3689 (6)	0.0291 (19)
H4	0.9772	0.5111	0.3984	0.035*
C5	0.8541 (5)	0.5580 (7)	0.3093 (6)	0.0299 (19)
C6	0.7705 (6)	0.5211 (8)	0.2690 (6)	0.033 (2)
H6	0.7272	0.5752	0.2308	0.039*
C7	0.6609 (5)	0.3594 (8)	0.2286 (6)	0.034 (2)
H7	0.6274	0.4040	0.1716	0.040*
C8	0.5449 (5)	0.2205 (9)	0.1791 (7)	0.044 (2)
H8A	0.5206	0.2799	0.1250	0.053*
H8B	0.5018	0.2070	0.2137	0.053*
C9	0.5631 (6)	0.1027 (9)	0.1342 (7)	0.046 (2)
H9A	0.5100	0.0792	0.0789	0.056*
H9B	0.6094	0.1171	0.1046	0.056*
C10	0.5904 (6)	−0.0011 (9)	0.2068 (6)	0.042 (2)
H10A	0.5452	−0.0136	0.2385	0.050*
H10B	0.5927	−0.0744	0.1682	0.050*
C11	0.7015 (6)	−0.1031 (8)	0.3424 (7)	0.041 (2)
H11A	0.7064	−0.1645	0.2939	0.049*
H11B	0.6545	−0.1284	0.3680	0.049*
C12	0.7865 (5)	−0.0986 (7)	0.4297 (6)	0.034 (2)
H12A	0.8089	−0.1813	0.4450	0.041*
H12B	0.8294	−0.0528	0.4085	0.041*
C13	0.7805 (6)	−0.0429 (7)	0.5255 (6)	0.033 (2)
H13A	0.7306	−0.0786	0.5407	0.040*
H13B	0.8339	−0.0623	0.5819	0.040*
C14	0.8191 (5)	0.1512 (7)	0.5922 (6)	0.0265 (18)
H14	0.8595	0.1088	0.6460	0.032*
C15	0.8191 (5)	0.2810 (7)	0.6011 (5)	0.0241 (17)
C16	0.8850 (5)	0.3316 (8)	0.6824 (6)	0.0290 (19)
H16	0.9282	0.2812	0.7259	0.035*
C17	0.8881 (5)	0.4510 (7)	0.6998 (6)	0.0284 (18)
C18	0.8274 (5)	0.5294 (8)	0.6359 (6)	0.032 (2)
H18	0.8316	0.6134	0.6471	0.039*
C19	0.7613 (5)	0.4811 (7)	0.5560 (6)	0.0290 (18)
C20	0.7547 (5)	0.3548 (7)	0.5363 (6)	0.0273 (18)

geometries and properties have been synthesized *via* the combination of different multidentate Schiff-base ligands and 3d/4f metal ions. However, related research on halogenated multidentate ligands is still at an early stage. As a part of our current research interest on the exploration of the regulating effect of Schiff base ligands on transition metal complexes [5–8], we report herein a new iron complex constructed by a halogenated multidentate ligand.

The asymmetric unit of the title structure consist of a mononuclear complex with the Fe(III) center showing octahedral coordination by three nitrogen atoms and two oxygen atoms from halogenated ligand L2-, and one nitrogen atom from the SCN- ligand. The bond lengths distributions for Fe–O and Fe–N are in the range of 1.939(5) and 2.187(7) Å. The average bond length of Fe–N is slight longer than that of Fe–O. The bond angles of the Fe(III) centers range from 84.3(2)° to 175.8(2)°. These values match with the previously reported Fe(III) Schiff-base compounds [9]. Intermolecular interaction analysis shows that, beside the neighboring monomers create C–H... π interactions, the substituted chlorine atoms formed halogen bonding play an important part in linking the neighboring molecules to form one-dimensional helical supramolecular chain (Cl2...Cl1ⁱ, D...A = 3.419(12) Å, Cl4... Cl2ⁱⁱ, D...A = 3.427(3) Å symmetry code: (i): 2–x, 1–y, 1–z; x, 3/2–y, 1/2+z; Cl4...Cl2ⁱⁱ, D...A = 3.785(3) Å; symmetry code: (ii): x, 1/2–y, 1/2+z).

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