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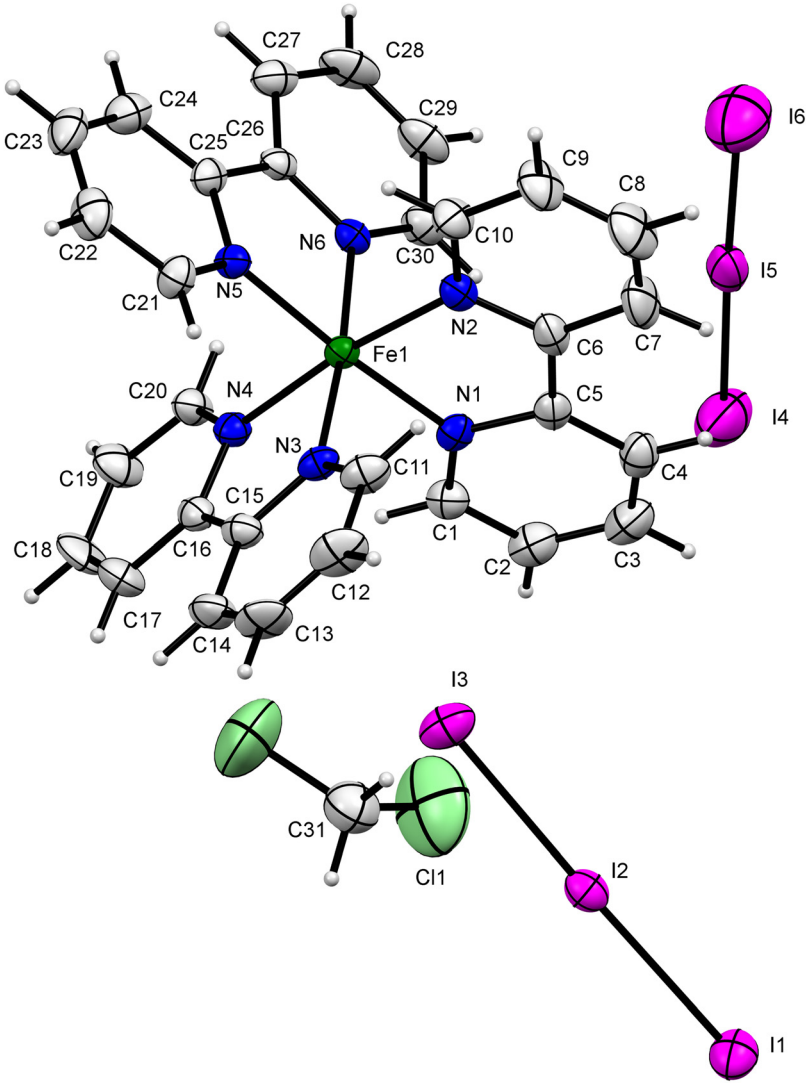
Crystal structure of tris(2,2′-bipyridine-κ^2*N*,*N*′) iron(II) triiodide – dichloromethane (2/1), $C_{61}H_{50}Cl_2Fe_2I_{12}N_{12}$



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Abstract

$C_{61}H_{50}Cl_2Fe_2I_{12}N_{12}$, orthorhombic, *Pbcn* (no. 60), a = 13.0247(4) Å, b = 17.0204(5) Å, c = 34.1475(9) Å, β = 90, V = 7570.0(4) Å^3, Z = 4, $R_{gt}(F)$ = 0.0694, $wR_{ref}(F^2)$ = 0.1605, T = 293(2) K.

CCDC no.: 2247456.

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

Table 1: Data collection and handling.

Crystal:	Black block
Size:	0.72 × 0.29 × 0.15 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	5.39 mm^{-1}
Diffractometer, scan mode:	Xcalibur, ω
θ_{max}, completeness:	26.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	56,694, 7815, 0.051
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6480
$N(param)_{refined}$:	402
Programs:	CrysAlis^{Pro} [1], Olex2 [2], Shelx [3, 4]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.3331 (7)	0.5111 (6)	0.3596 (3)	0.047 (2)
H1	0.311819	0.528952	0.335156	0.057*
C2	0.4356 (8)	0.5134 (6)	0.3686 (4)	0.060 (3)
H2	0.482634	0.533029	0.350643	0.073*
C3	0.4680 (9)	0.4870 (7)	0.4037 (4)	0.068 (3)
H3	0.537244	0.488624	0.410223	0.081*
C4	0.3980 (8)	0.4579 (6)	0.4294 (3)	0.054 (2)
H4	0.419702	0.439063	0.453619	0.064*
C5	0.2956 (7)	0.4562 (5)	0.4200 (3)	0.043 (2)
C6	0.2127 (8)	0.4306 (5)	0.4449 (3)	0.046 (2)
C7	0.2272 (11)	0.3969 (7)	0.4821 (3)	0.072 (3)
H7	0.293131	0.389876	0.491942	0.086*
C8	0.1462 (12)	0.3752 (8)	0.5031 (3)	0.081 (4)
H8	0.156477	0.350440	0.527072	0.098*
C9	0.0489 (10)	0.3880 (7)	0.4906 (3)	0.068 (3)
H9	−0.007682	0.374256	0.505729	0.082*
C10	0.0375 (8)	0.4230 (6)	0.4536 (3)	0.052 (2)
H10	−0.028358	0.432876	0.444290	0.062*
C11	0.1099 (8)	0.3105 (6)	0.3720 (3)	0.055 (2)
H11	0.108070	0.309636	0.399242	0.066*
C12	0.1074 (9)	0.2399 (6)	0.3518 (4)	0.070 (3)
H12	0.104567	0.192488	0.365250	0.084*
C13	0.1092 (10)	0.2411 (6)	0.3127 (4)	0.070 (3)
H13	0.106777	0.194000	0.298897	0.084*
C14	0.1145 (8)	0.3109 (7)	0.2924 (3)	0.059 (3)
H14	0.116415	0.311893	0.265195	0.071*
C15	0.1169 (7)	0.3801 (5)	0.3142 (3)	0.044 (2)
C16	0.1236 (6)	0.4584 (6)	0.2968 (3)	0.041 (2)
C17	0.1326 (9)	0.4731 (7)	0.2571 (3)	0.061 (3)
H17	0.135524	0.431461	0.239561	0.073*
C18	0.1373 (10)	0.5490 (7)	0.2436 (3)	0.068 (3)
H18	0.143214	0.558910	0.216868	0.082*
C19	0.1330 (10)	0.6110 (7)	0.2702 (3)	0.066 (3)
H19	0.136088	0.663062	0.262059	0.079*
C20	0.1241 (8)	0.5912 (5)	0.3091 (3)	0.045 (2)
H20	0.120228	0.632005	0.327124	0.054*
C21	−0.1048 (7)	0.4392 (6)	0.3625 (3)	0.049 (2)
H21	−0.081288	0.388414	0.358053	0.059*
C22	−0.2084 (8)	0.4557 (8)	0.3564 (3)	0.064 (3)
H22	−0.252542	0.417051	0.347045	0.077*
C23	−0.2439 (8)	0.5293 (8)	0.3644 (3)	0.063 (3)
H23	−0.313024	0.541409	0.361078	0.076*
C24	−0.1752 (8)	0.5860 (7)	0.3776 (3)	0.059 (3)
H24	−0.198229	0.636597	0.382834	0.071*
C25	−0.0747 (7)	0.5679 (5)	0.3829 (2)	0.042 (2)
C26	0.0031 (7)	0.6218 (5)	0.3976 (2)	0.0375 (18)
C27	−0.0191 (9)	0.6968 (6)	0.4114 (3)	0.053 (2)
H27	−0.085126	0.717115	0.409243	0.064*
C28	0.0578 (11)	0.7405 (6)	0.4281 (3)	0.069 (3)
H28	0.044940	0.790726	0.437663	0.083*
C29	0.1518 (10)	0.7091 (6)	0.4304 (3)	0.061 (3)
H29	0.204705	0.737545	0.442006	0.074*
C30	0.1710 (8)	0.6351 (6)	0.4159 (3)	0.053 (2)
H30	0.237305	0.614976	0.417354	0.063*
C31	0.500000	0.4784 (13)	0.250000	0.089 (6)
H31A[a]	0.478277	0.444905	0.271435	0.106*
H31B[a]	0.521724	0.444904	0.228566	0.106*
Cl1	0.4034 (5)	0.5325 (5)	0.2358 (3)	0.203 (4)
Fe1	0.11257 (9)	0.48480 (7)	0.37793 (3)	0.0328 (3)
I1	0.81878 (6)	0.23650 (5)	0.31024 (2)	0.0692 (2)
I2	0.60101 (6)	0.27721 (4)	0.31379 (2)	0.05317 (19)
I3	0.38621 (6)	0.31501 (5)	0.31996 (3)	0.0726 (2)
I4	0.60213 (9)	0.70436 (8)	0.42937 (4)	0.1127 (4)
I5	0.44135 (7)	0.65181 (5)	0.48069 (2)	0.0738 (3)
I6	0.28363 (11)	0.59529 (11)	0.53402 (5)	0.1374 (5)
N1	0.2632 (5)	0.4843 (4)	0.3845 (2)	0.0385 (15)
N2	0.1173 (6)	0.4426 (4)	0.4313 (2)	0.0404 (16)
N3	0.1149 (5)	0.3791 (4)	0.3537 (2)	0.0398 (16)
N4	0.1206 (5)	0.5176 (4)	0.3228 (2)	0.0387 (16)
N5	−0.0379 (5)	0.4938 (4)	0.37451 (19)	0.0361 (15)
N6	0.0980 (5)	0.5919 (4)	0.39992 (19)	0.0353 (15)

[a]Occupancy: 0.5.

1 Source of materials

The precursor, $[Fe(CO)_4I_2]$ was prepared according to the literature's methods [5, 6]. The 2,2′-bipyridine was commercially available from the Aladdin Chemical Technology Co., Ltd. By following the literature's methods with modifications [7–10], the title complex was synthesized reacting the precursor with 1.5 equivalent of 2,2′-bipyridine in hexane under an inert atmosphere at room temperature. The volatiles were removed by vacuum, and residues were washed by diethyl ether. Black precipitates were crushed out from its dichloromethane solution with the addition of hexane.

2 Experimental details

Crystals of the title complex were obtained by a layer-to-layer diffusion of hexane into its dichloromethane solution.

The single crystals suitable for X-ray diffraction analysis experiment were selected and covered by silicone grease, and then mounted on a Gemini diffractometer (Xcalibur, Eos). The crystallographic data were collected on CrysAlisPro 1.171.39.46 (Rigaku Oxford Diffraction, 2018). Using Olex2 [2], the structure was solved with intrinsic phasing methods in Shelxt [3] program and refined by least squares minimization with the Shelxl package [4]. All hydrogen atoms were located by geometrical calculation. The crystallographic data in CIF file can be obtained from the Supplementary Materials or the Cambridge Structural Database with the CCDC number (2247456).

3 Comment

The precursor $[Fe(CO)_4I_2]$, first reported by Hieber and coworkers [11], is a universal reactant for the preparation of iron carbonyls and ferrous complexes. Owning to its versatile activity, the derivatives from CO-substitution or iodine-substitution have been widely reported [5–10]. For example, the reaction of amine with the precursor would probably result to the aminium salts containing a monoiron anion fac-$[Fe(CO)_3I_3]^-$ [7], the amine-coordinated complexes [8], or even the ferracyclic carbamoyl complexes [12, 13]. The ferracyclic carbamoyl complexes have been receiving arising interest for that they are structural relevant to the active site of [Fe]-hydrogenase. However, the products are highly dependence to the reaction conditions which should be carefully controlled.

Herein, the reaction of 2,2′-bipyridine with the precursor affords the title complex without carbonyls. The iron (II) is coordinated by three 2,2′-bipyridine ligands in an octahedral molecular geometry. Additionally, the forming of the triiodide anion indicates an iodine free radical-involved pathway of the reaction [8, 9]. Bond lengths and angles are in the expected ranges [14, 15].

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