HOMOTRINUCLEAR Fe_3^{III} μ – OXO SALICYLATE CLUSTER. SYNTHESIS, STRUCTURE AND PROPERTIES

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Abstract. A reaction of iron and barium nitrate with ammonium salicylate in the mixture of solvents (MeOH, THF, DMAA) gave the new homotrinuclear complex [hexa-μ-salicylato-($O,O^{,}$)-μ_3-oxo(diaqua)(salicylato)triiron(III)] di(dimethylacetamide)(methanol)sesqui(tetrahydrofuran)·2.6-hydrate, $[Fe_3O(SalH)_7(H_2O)_2](DMAA)_2(MeOH)(THF)_{1.5}(H_2O)_{2.6}$ (1). Single-crystal X-ray study has demonstrated that the titled complex $\{Fe_3O\}$ belongs to the well-known group of μ_3-oxo homotrinuclear carboxylates. The IR, Mössbauer spectra, thermal behaviour of the complex were studied.

Keywords: carboxy-cluster, Iron(III), salicylate, IR, Mössbauer, TG data.

Introduction

Nowadays a great scientific interest to the *nd* elements' clusters is demonstrated [1-2]. This interest is due to the architecture (design changes) of their chemical bonds, molecular and self-assembly in the crystal [3], the optical properties [4], the catalyst [5], magnetic and single molecule magnet (SMMs) [6], as well as their use as building blocks in 1D, 2D, 3D, MOFs systems [7], and precursors to obtain nanomaterials [8]. In our Laboratory of Bioinorganic Chemistry and Nanocomposites (LCBANC) the various polydentate ligands were synthesized and studied [9-13]. There are quite extensive known complexes (clusters) obtained with mono- or polycarboxylic acids in the scientific literature. However publications of clusters with salicylic acid as a ligand are scarce. In recent years we have synthesized and studied the homo- and heteronuclear complexes of copper and iron with this acid [14-16]. In continuation of our studies the synthesis and some spectral Infrared (IR), Mössbauer (MS) and thermogravimetric (TG) data of the trinuclear iron (III) carboxy-cluster $[Fe_3^{III}O(SalH)_7(H_2O)_2](DMAA)_2(CH_3OH)(THF)_{1.5}(H_2O)_{2.6}$ (**1**) are presented in this article.

Results and discussion

X-Ray crystallography

Single-crystal X-ray study has demonstrated that compound (**1**) with composition $[Fe_3^{III}O(SalH)_7(H_2O)_2](DMAA)_2(CH_3OH)(THF)_{1.5}(H_2O)_{2.6}$, where SalH denotes monodeprotonated salicylic acid, DMAA= dimethylacetamide, THF= tetrahydrofuran is a member of the large family of "basic carboxylates" containing a central planar $[M_3(\mu_3\text{-}O)]^{7+}$ core and the carboxylato ligands, which are situated above and below this plane. Three Fe^{3+} ions occupy the vertexes of isosceles triangle; Fe···Fe distances equal 3.3338(8), 3.2961(7), and 3.3019(6)A. The structural parameters are typical of "basic carboxylates", Figure 1. Six $\eta^1{:}\eta^1{:}\mu_2$ $SalH^-$ ligands bridge the metal atoms. One terminal monodentate $SalH^-$ ligand and two water molecules in the apical positions complete octahedral coordination of the iron atoms. The distances between the Fe atoms and the donor atoms of the $SalH^-$ bridging ligands are in the ranges 1.999(2)–2.020(2) Å for Fe1, 1.988(3)–2.036(2) Å for Fe2, and 1.974(3)–2.026(2) Å for Fe3, the shortest Fe-O bonds in the cluster being the Fe– μ_3-O in each case, and the longest being the ones in trans respective positions (trans effect), Table 1.

The conformation of all $SalH^-$ ligands is stabilized by intramolecular O-H···O hydrogen bonds, Table 2. The hydroxyl groups of the $SalH^-$ ligands, which bridge Fe1 and Fe3 ions, are pointed in opposite direction, while the two other pairs of these groups stick out in the same direction. The hydroxyl groups of two bridging ligands, which are close to monodentate apical ligand, participate in bifurcated H-bonds with non-coordinated O15 atom. Since the cluster moiety in the structure is neutral no counter anions are present the 3D structure of the complex in the crystal lattice is defined by direct intercluster hydrogen-bonding as well as by H-bonds involving solvent molecules, Table 2, and by π-π stacking interactions.

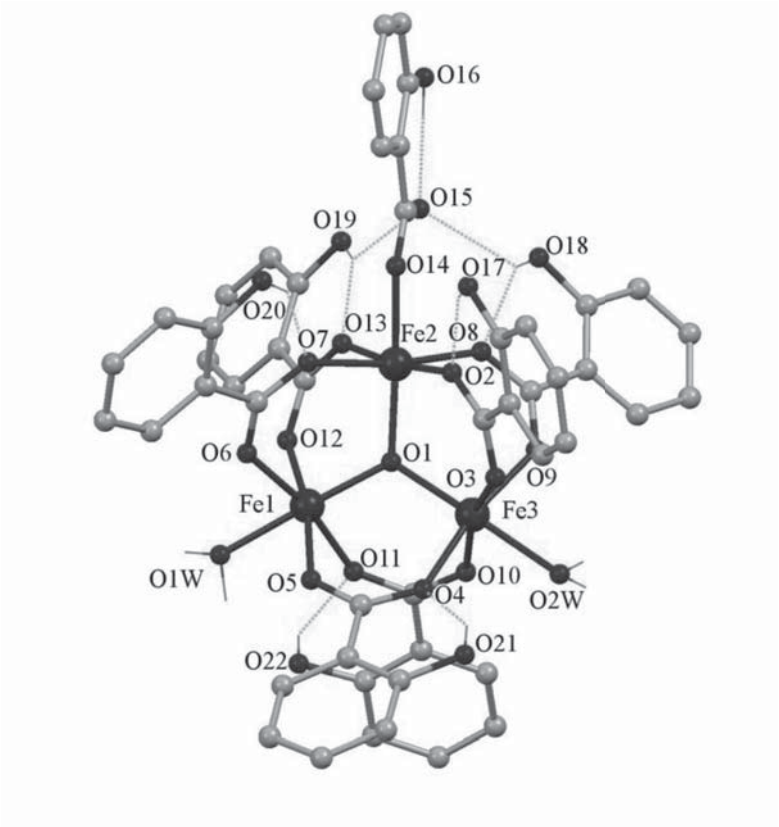


Figure 1. Molecular structure of $[Fe_3O(SalH)_7(H_2O)_2]$ cluster.
The hydrogen atoms on carbon atoms are not presented for clarity.

Table 1.

Selected bond lengths and bond angles in coordination sphere of each metal atom.

Bond	d, Å	Bond	d, Å	Bond	d, Å
Fe1-O1	1.906(2)	Fe2-O1	1.926(2)	Fe3-O1	1.902(2)
Fe1-O6	1.999(2)	Fe2-O14	1.988(3)	Fe3-O9	1.974(3)
Fe1-O12	2.003(2)	Fe2-O8	2.021(2)	Fe3-O10	1.996(3)
Fe1-O11	2.015(3)	Fe2-O13	2.031(2)	Fe3-O3	2.009(3)
Fe1-O5	2.020(2)	Fe2-O2	2.036(2)	Fe3-O4	2.026(2)
Fe1-O1*w*	2.045(3)	Fe2-O7	2.037(2)	Fe3-O2*w*	2.076(2)
Angle	***ω***, deg	***Angle***	***ω***, deg	***Angle***	***ω***, deg
O1-Fe1-O6	96.28(9)	O1-Fe2-O14	170.69(10)	O1-Fe3-O9	95.98(9)
O1-Fe1-O12	93.92(9)	O1-Fe2-O8	95.21(9)	O1-Fe3-O10	97.78(10)
O6-Fe1-O12	91.32(10)	O14-Fe2-O8	91.76(10)	O9-Fe3-O10	91.82(12)
O1-Fe1-O11	93.79(9)	O1-Fe2-O13	94.32(9)	O1-Fe3-O3	96.54(10)
O6-Fe1-O11	169.31(10)	O14-Fe2-O13	92.28(10)	O9-Fe3-O3	91.74(12)
O12-Fe1-O11	91.57(11)	O8-Fe2-O13	86.28(10)	O10-Fe3-O3	164.79(10)
O1-Fe1-O5	9648(9)	O1-Fe2-O2	92.34(9)	O1-Fe3-O4	94.14(9)
O6-Fe1-O5	87.15(11)	O14-Fe2-O2	81.26(10)	O9-Fe3-O4	169.46(10)
O12-Fe1-O5	169.60(10)	O8-Fe2-O2	91.82(10)	O10-Fe3-O4	89.69(11)
O11-Fe1-O5	88.15(11)	O13-Fe2-O2	173.22(10)	O3-Fe3-O4	84.20(11)
O1-Fe1-O1*w*	176.38(9)	O1-Fe2-O7	92.64(9)	O1-Fe3-O2*w*	178.61(9)
O6-Fe1-O1*w*	87.14(10)	O14-Fe2-O7	80.61(10)	O9-Fe3-O2*w*	85.38(10)
O12-Fe1-O1*w*	84.78(10)	O8-Fe2-O7	171.97(10)	O10-Fe3-O2*w*	82.41(10)
O11-Fe1-O1*w*	82.88(10)	O13-Fe2-O7	91.49(10)	O3-Fe3-O2*w*	83.15(10)
O5-Fe1-O1*w*	84.87(10)	O2-Fe2-O7	89.50(10)	O4-Fe3-O2*w*	84.48(10)

Table 2.

Hydrogen bond distances (Å) and angles (°).

D–H···A	d(D–H)	d(H···A)	d(D···A)	(DHA)	Symmetry transformation for acceptor
O17-H17···O2	0.84	1.87	2.590(4)	143.4	*x, y, z*
O19-H19A···O13	0.84	1.96	2.672(4)	142.0	*x, y, z*
O19-H19A···O15	0.84	2.19	2.736(5)	123.0	*x, y, z*
O18-H18A···O8	0.84	1.98	2.651(3)	135.7	*x, y, z*
O18-H18A···O15	0.84	2.30	2.862(4)	124.6	*x, y, z*
O22-H22···O11	0.84	1.85	2.561(4)	142.2	*x, y, z*
O22-H22···O1*w*	0.84	2.64	3.360(4)	145.0	*x, y, z*
O21-H21A···O4	0.84	1.81	2.546(4)	144.5	*x, y, z*
O20-H20A···O7	0.84	1.87	2.592(4)	143.9	*x, y, z*
O16-H16···O15	0.84	1.84	2.570(5)	144.5	*x, y, z*
O1*w*-H1*w*1···O5*w*1	0.91	2.06	2.647(7)	120.6	*x, y*-1, *z*
O1*w*-H2*w*1···O22	0.92	2.71	3.360(4)	128.8	*x, y, z*
O2*w*-H1*w*2···O3*w*	0.86	1.81	2.668(5)	175.8	-*x*+1, -*y*+1, -*z*+2

Infrared spectra

The studied compound has an IR spectrum with numerous absorption bands (Fig. 2). However there are some bands which are characteristic for specific groups: medium intensity and broad absorption band with maximum at 3238 cm^{-1} was assigned to ν(OH) of water molecules and salicylate anions, including the ones forming the hydrogen bonds; 3064 and 2976 cm^{-1} – to $\nu_{as,s}$ (CH, benzene ring of salicylic ion, $SalH^-$, Sal^{2-}); 2879 and 2838 cm^{-1} – to $\nu_{as,s}$ (CH, methyl groups of DMAA, methanol); 1585 and 1457 cm^{-1} – to $\nu_{as,s}$(COO) for bridging bidentate fashion; 1618 cm^{-1} - to ν(CO) of monodentate $SalH^-$ anion, DMAA, δ(H_2O); intensive absorption band at 1389 cm^{-1} - to bending bands, δ, of CH_3 or CH_3-CH_3-C bending. The rest bands in the limits 1400-650 cm^{-1} may be assigned to fingerprint region of this complex [17-19].

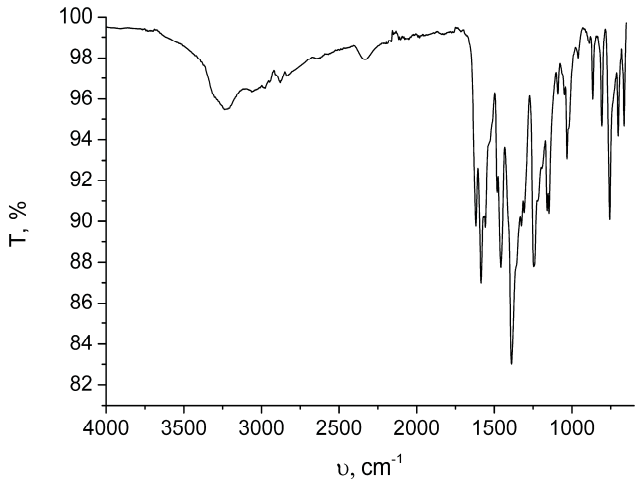


Figure 2. IR spectrum of investigated complex.

Thermogravimetric analysis

The thermo-gravimetric curves of {Fe_3O} complex are presented in Fig. 3. They demonstrate that the complex (**1**) is thermo unstable. The thermolysis process is beginning at 25 °C and involves many steps. The DTG and TG curves suggest the first process at 25–100 °C is endothermic and corresponds to weight loss of ~3%. It seems to be highly probable that the observed change is attributable to elimination of crystalized water molecules (2.6H_2O). Subsequent exothermic processes at 100–280 (I), 280–320 (II), 320-380 (III) and 380–440 (IV) °C are due to the elimination of all solvent molecules and destruction of remaining organic ligands (Table 3). The final thermolysis product consists of ~12% of the initial weight and corresponds to the iron oxide, Fe_2O_3 (calculated: 10.36 %). Schematically, the decomposition of complex may be presented by the following:

$$[Fe_3O(SalH)_7(H_2O)_2]\cdot(DMAA)_2(MeOH)(THF)_{1.5}(H_2O)_{2.6} \xrightarrow[-2.6(H_2O)]{I}$$

$$[Fe_3O(SalH)_7(H_2O)_2]\cdot(DMAA)_2(MeOH)(THF)_{1.5} \xrightarrow[-1.5(THF)-(MeOH)-2(DMAA)-2.5(SalH)]{II}$$

$$[Fe_3O(SalH)_{4.5}] \xrightarrow[-0.5(SalH)]{III} [Fe_3O(SalH)_4] \xrightarrow[-2(SalH)]{IV} [Fe_3O(SalH)_2] \xrightarrow[-2(SalH)]{V} [Fe_2O_3]$$

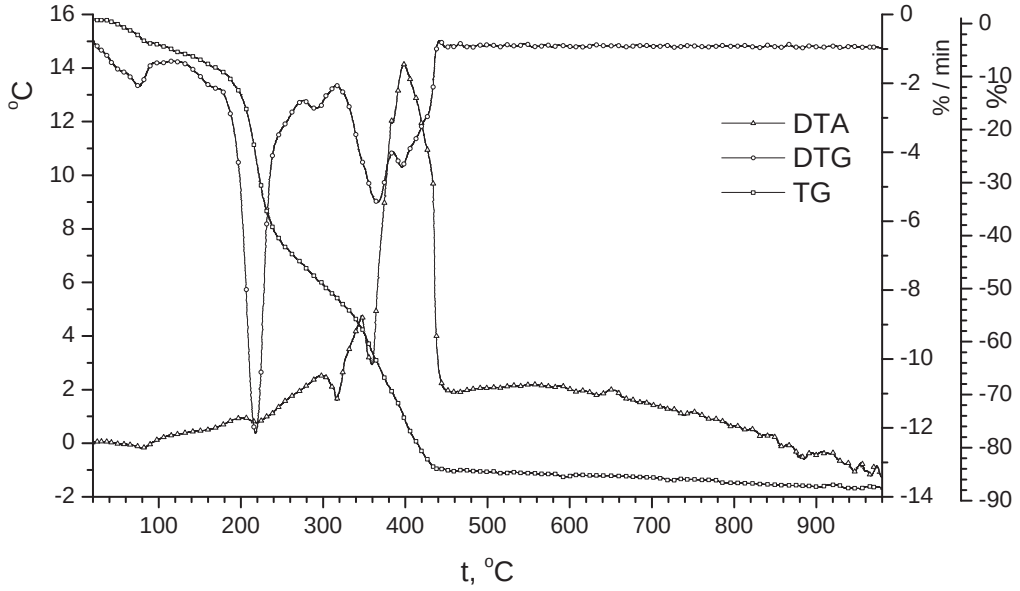


Figure 3. Termogravimetry curves, TG, DTG, and DTA of investigated complex.

Table 3.

Thermogravimetric data for $[Fe_3O(SalH)_7(H_2O)_2]\cdot(DMAA)_2(MeOH)(THF)_{1.5}(H_2O)_{2.6}$ complex.

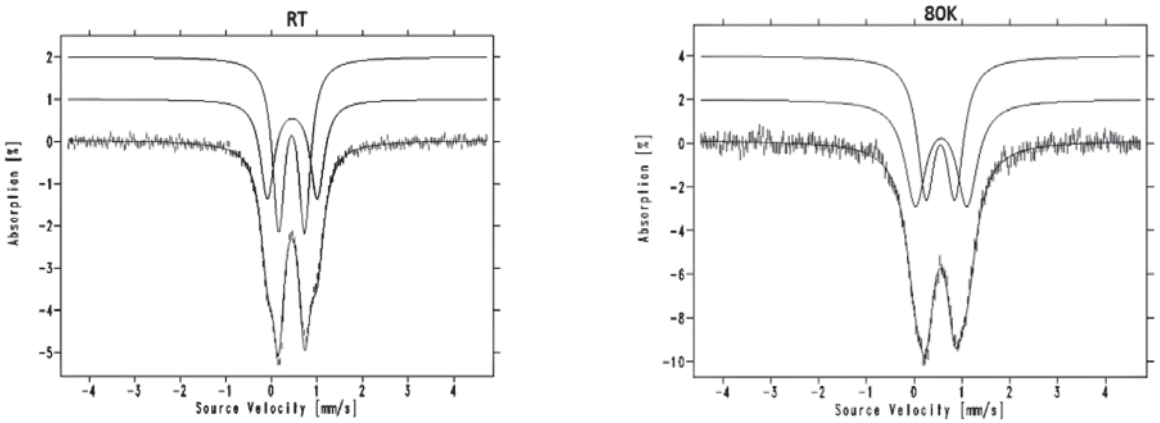
Nr. process	Effect	T, ^{0}C			Weight loss. found, %
		onset	maxim	end	
I	endo	25	70	100	3
II	exo	100	220	280	42
III	exo	280	290	320	7
IV	exo	320	360	380	17
V	exo	380	395	440	15

Mössbauer spectra

The Mössbauer spectra of the investigated complex at 300 and 80 K are presented in Fig. 4. It's clear observed that both spectra consist of more than one subspectrum. The best fit was obtained when each spectrum was approximated by 2 doublets. The parameters of subspectrums are presented in Table 4. The values of isomer shift and quadrupol splitting correspond to iron(III) in the high spin state (S=5/2) [20].

Taking into consideration the molecular structure of this complex it was expected that the relative area of one

subspectrum will be two times larger than another one. In reality the relative areas of these subspectrums are not so different. Only at RT the relative area of doublet I is ~ 40 % and we may suppose that doublet I corresponds to iron atom which is coordinated with monodentate $SalH^-$ anion. But at the 80 K this parameter practically is the same as for doublet II. This fact may be explained if suppose that the Debye-Weller factor, f', for iron containing Fe-H_2O or Fe-$SalH^-$ bonds in {Fe_3O} fragment.



(a) (b)

Figure 4. Mossbauer spectra of $[Fe_3O(SalH)_7(H_2O)_2]\cdot(DMAA)_2(MeOH)(THF)_{1.5}(H_2O)_{2.6}$ at: a-RT and b-80K.

Table 4.

Parameters of the Mössbauer spectra of $[Fe_3O(SalH)_7(H_2O)_2]\cdot(DMAA)_2(MeOH)(THF)_{1.5}(H_2O)_{2.6}$ cluster.

T,K	mm/s				
	δ_{Fe}	ΔE_Q	$\Gamma_L=\Gamma_R$	S_{rel}	
RT	0.459	1.094	0.363	0.42	Doublet I
	0.444	0.569	0.318	0.62	Doublet II
80	0.545	0.602	0.433	0.56	Doublet II
	0.564	1.078	0.329	0.53	Doublet I

δ_{Fe} - isomer schift relative to alpha-Fe at RT;
ΔE_Q – quadrupole splitting;
Γ_L,Γ_R – the line width;
S_{rel} – relative area ob subspectrum;
RT – room temperature.

Experimental

The reaction was performed following the synthesis procedure described by us [16] but using 1.25 g $Ba(NO_3)_2$ instead of the $CoCl_2\cdot 6H_2O$. The dark red single crystals as rectangular prisms precipitated after 3 days. Yeld 0.92 g (49 % relative to the iron salt). The results of elemental analysis, %: Found: C, 49.47; H, 5.53; N, 2.20. Calculated for $C_{64}H_{78.2}Fe_3N_2O_{31.1}$: C, 49.89; H, 5.11; N, 1.81.

IR spectrum(ν, cm^{-1}): 3238.5 sh, 3063.6 vw, 2976.1 vw, 2878.9 vw, 2878.9 vw, 1618.0 m, 1585.3 s, 1557.7 w, 1481.4 s, 1457.2 s, 1388.6 vs, 1324.8 w, 1307.2 w, 1245.7 s, 1194.4 vw, 1090.8 s, 1048.7 s, 1032.0 s, 960.35 w, 887.86 vw, 865.77 s, 807.23 s, 756.48 vs, 702.40 s, 664.15 s (vs= very strong, s= strong, m= medium, w=weak, vw= very weak and sh=shoulder).

The complex was analyzed for C, H, and N by the elemental analysis group of the Institute of Chemistry of the Academy of Sciences of Moldova.

X-ray diffraction analysis X-Ray data were collected at 200 K temperature on a *Xcalibur E* diffractometer equipped with an EOS CCD area detector and a graphite monochromator utilizing Mo*K*a radiation. Final unit cell dimensions were obtained and refined on an entire dataset. All calculations to solve and refine the structure were carried out with the program SHELX97 [21]. Lorentz and polarization effects and absorption corrections were applied for diffracted reflections. The C–bound H atoms were placed in calculated positions and were treated using a riding model approximation with Uiso(H)=1.2Ueq(C). Crystal data and details on the structure refinement are given in Table 5. *CCDC 975526* contains the supplementary crystallographic data.

Table 5.

Crystallographic parameters and the data collection statistics for complex {Fe_3O}.

Parameter	Value
Empirical formula	$C_{64}H_{78.2}N_2O_{31.1}Fe_3$
Formula weight, *M*	1540.64
Temperature (K)	200
Crystal system	triclinic
Space group	*P*-1
Z	2
a (Å)	15.3001(8)
b (Å)	15.643(2)
c (Å)	18.0709(9)
α (°)	94.253(7)
β (°)	105.700(5)
γ (°)	117.134(9)
V, (Å^3)	3605.5(6)
D_{calc} (g cm^{-3})	1.419
μ(mm^{-1})	0.683
F(000)	1606
Refinement method	Full-matrix least-squares on F^2
θ Range for data collection(°)	1.56 - 26.00
Limiting indices	-18≤*h*≤17
	-19≤*k*≤19
	-22≤*l*≤22
Reflections collected	29738
Reflections with[*I*>2σ(*I*)]	14180
Data/restraints/ parameters	14180 / 9 / 888
Goodness-of-fit on F^2	1.003
R_1, wR_2[*I*>2σ(*I*)]	*R*1 = 0.0572, *wR*2 = 0.1682
R_1, wR_2(all data)	*R*1 = 0.0742, *wR*2 = 0.1809
Largest difference in peak and hole (e Å^{-3})	1.219 and -0.556

IR spectra were recorded on a Specord M75 spectrometer in the 650–4000 cm^{-1} range and a Perkin-Elmer 100 FT-IR spectrometer.

Integrated *thermal analysis* was carried out on a Paulik–Paulik–Erdey derivatograph in air with Al_2O_3 as a reference. The recording conditions were 1/5 (DTG), 1/10 (DTA), and 100/100 (TG), T_{max} = 1000 C, heating rate 5 °C/min, a sample weight 50 mg.

Mössbauer spectra were acquired using a conventional spectrometer in the constant-acceleration mode (MS4, Edina, USA) equipped with a ^{57}Co source (3.7 GBq) in a rhodium matrix. Isomer shifts are quoted relative to alpha-Fe at room temperature. The sample was measured at room temperature and 80 K. The spectra were fitted using the WMOSS Mössbauer Fitting Program.

Acknowledgments

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