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Synthesis, structural and thermal characterization of a novel 3D Fe^{III} Complex

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ABSTRACT

Crystal structure and thermal stability of the hydrated crystals of the Glycine (the basic amino acid) and ammonium ferrous sulphate compound, Ammonium hexaaqua ferrate(iii) sulphate have been reported here. The title compound crystallized in the space group $P2_1/c$ with $Z = 2$ and unit cell dimensions $a = 6.2383(10) \text{ \AA}$, $b = 12.6076(19) \text{ \AA}$, $c = 9.2652(13) \text{ \AA}$. In the title compound, $\text{FeH}_{12}\text{O}_6 \cdot 2(\text{O}_4\text{S}) \cdot 2(\text{H}_4\text{N})$, the Fe^{III} atom exists in a octahedral coordination environment. Each $\text{Fe}(\text{H}_2\text{O})_6$ complex anion is surrounded by four sulphate anion acceptor groups and four ammonium cation donor groups. The ions are held together by $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds into a layer network. Thermal behaviour of crystals has been investigated by TG/DTA analysis.

Keywords : Crystal growth, iron(iii) complex, thermogravimetric analysis, X-ray diffraction.

INTRODUCTION

The rational design and syntheses of novel coordination compounds have achieved considerable progress in the field of crystal engineering, owing to their potential applications as gas storage, luminescence [1], magnetism [2] and dielectrics. Iron(III) sulphate is used in dyeing as a mordant, and as a coagulant for industrial wastes. It is also used in pigments, and in pickling baths for aluminum and steel [3]. Medically it is used as an astringent and styptic [4]. Fe^{III} aquacomplexes as effective photocatalysts for the degradation of pesticides in homogenous aqueous solutions (5).

The characterizations of Fe^{III} complex, as a metal-organic compound have been reported [6-9]. Herein, we report the synthesis and crystal structure of a novel Fe^{III} complex, as an inorganic compound, based on Glycine and ammonium ferrous sulphate which resulted in the formation of the title compound, FeH₁₂O₆.2(O₄S).2(H₄N), was identified by single X-ray diffraction.

MATERIALS AND METHODS

Experimental

All reagents used in the synthesis were of analytical grade. The crystal determination was performed on a Bruker APEX II CCD area detector diffractometer equipped with graphite-monochromatized MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). TG/DTA analysis was carried out with the help of an instrument NETZSCH STA 409 C/CD using alumina crucible as a reference in the temperature range between 30°C and 1000°C with a heating rate of 10°C/min in protected nitrogen atmosphere.

Synthesis of the complex

Glycine and ammonium ferrous sulphate is weighed in equimolar ratio (1:1) and stirred continuously in 50ml deionized water at room temperature. The solution is stirred continuously for one hour to produce a homogeneous solution. Then the mixture is filtered by using whattmann filter paper. Single crystals of the title compound suitable for X-ray diffraction were obtained after 25 days by slow evaporation of aqueous solution.

Table 1 : Crystallographic data

Chemical formula	FeH ₁₂ O ₆ .2(O ₄ S).2(H ₄ N)
Molecular weight	392.17
System	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 6.2383(10) Å, b = 12.6076(19) Å, c = 9.2652(13) Å $\alpha = 90^\circ$, $\beta = 106.524^\circ$, $\gamma = 90^\circ$
Cell volume, Z	698.61(18) (Å ³), 2
Density(calculated)	1.864 g/cm ³
Absorption coefficient (μ)	1.45 mm ⁻¹
Diffractometer	Bruker APEXII CCD area detector diffractometer
Radiation	Mo K α ($\lambda = 0.71073 \text{ \AA}$)
θ range (degree)	2.8 to 28.4
Range of h,k,l	-6 \leq h \leq 8, -16 \leq k \leq 16, -12 \leq l \leq 12
Reflections measured	6726
Independent reflections	1740
Final R indices [I > 2 σ (I)]	R1 = 0.0214, wR2 = 0.0611
R indices (all data)	R1 = 0.0225, wR2 = 0.0604
Data/restraints/parameters	1740/9/129

Crystallographic data collection and structure determination

Single-crystal data (0.25 \times 0.22 \times 0.19 mm³) were collected at 293 K on a Bruker Apex II CCD area detector diffractometer [10] equipped with graphite-monochromated MoK α radiation. The structure was solved using direct methods and successive Fourier difference synthesis (SHELXS-97) [11], and refined using the full-matrix least-squares method on F² with anisotropic

thermal parameters for all nonhydrogen atoms (SHELXL-97) [11]. Molecular graphics done by ORTEP 3 [12] and that of molecular packing with Mercury [13]. Software used to prepare cif material is SHELXL-97 [14] and PLATON [15]. The final agreement factor values are $R1 = 0.021$, $wR2=0.061$, $w = 1/[\sigma^2(F_o)^2 + (0.0348P)^2 + 0.2411P]$ where $P = (F_o^2 + 2F_c^2)/3$. A summary of the crystallographic data is given in Table 1.

Crystallographic data for the structural analysis has CSD-number : 423075, Further details of the crystal structure investigation(s) may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax:(+49)7247-808-666; e-mail:crysdata@fiz-karlsruhe.de).

RESULTS AND DISCUSSION

Structural Characterization

Structural characterization involves powder XRD and single XRD.

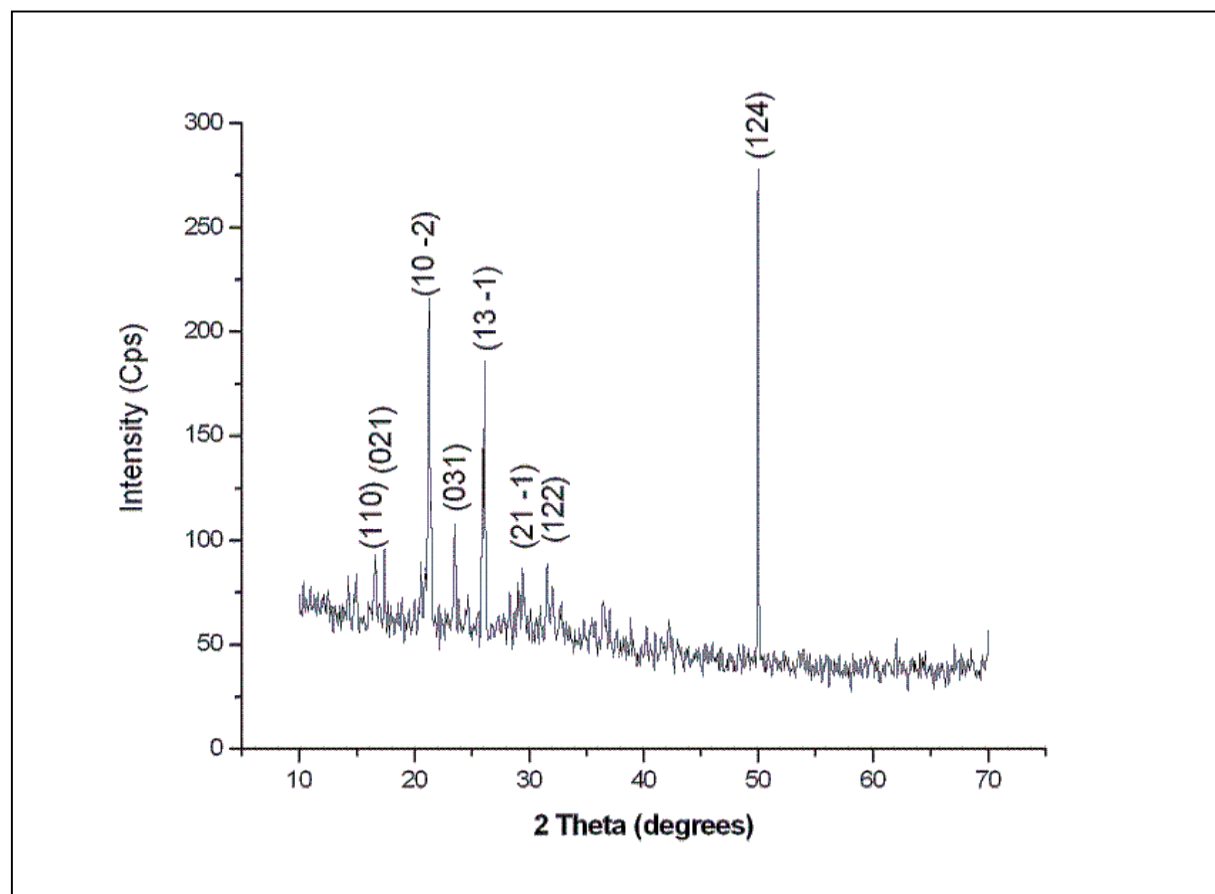


Fig. 1 : Powder XRD of Fe^{III} complex.

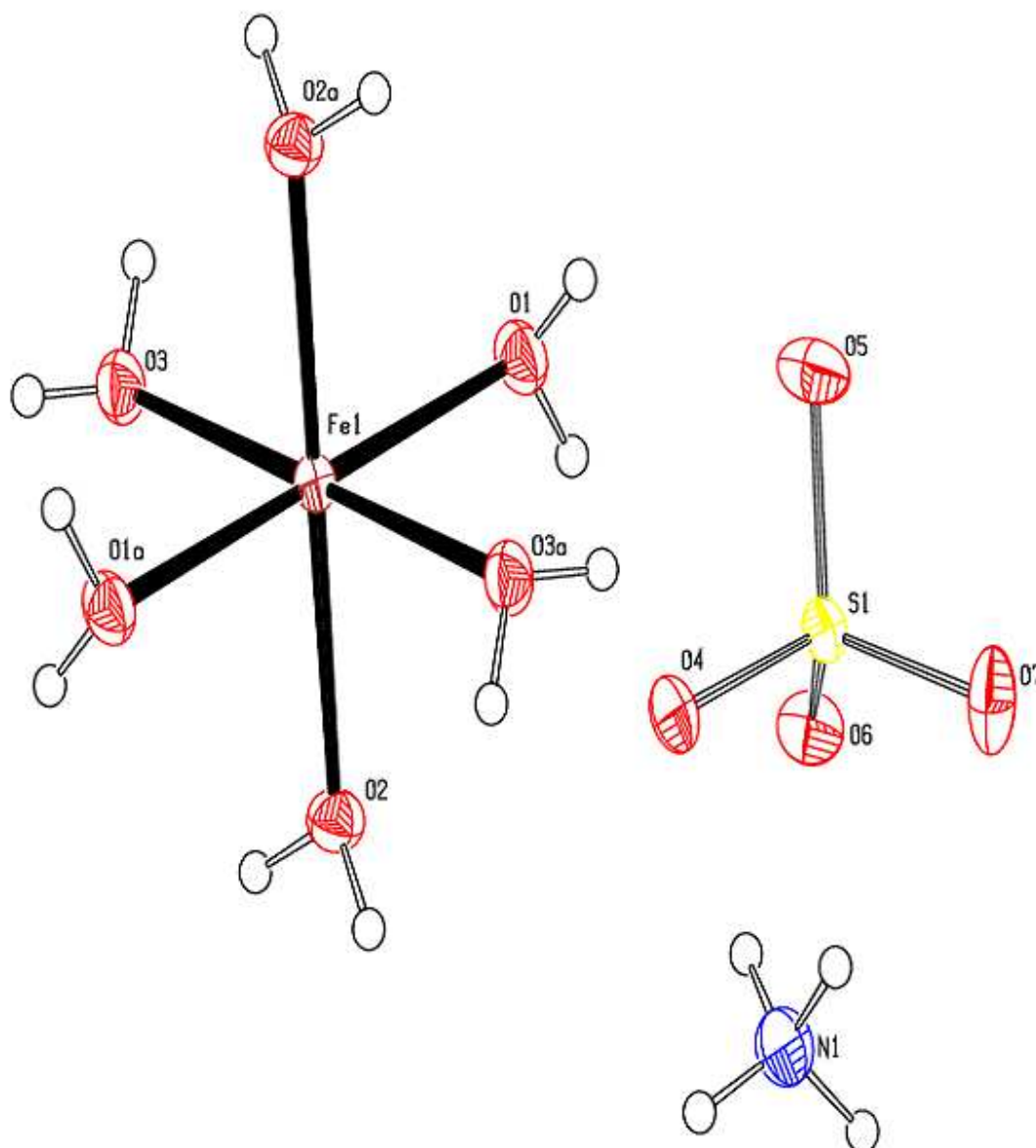


Fig. 2 : ORTEP diagram of Fe^{III} complex.

Powder XRD

In order to confirm the structure of the grown crystal, powder X-ray diffraction was recorded at a wavelength of radiation $\lambda=1.540598 \text{ \AA}$ (Cu) using reflection scan mode. The powder X-ray diffraction pattern of the grown crystal is shown in Fig. 1. The well defined Bragg's peaks at specific 2θ angles show the high crystallinity. The sharp peaks found in spectra shows good crystallinity of the grown crystals.

Single XRD

The three dimensional structure of the title compound, $\text{FeH}_{12}\text{O}_6 \cdot 2(\text{O}_4\text{S}) \cdot 2(\text{H}_4\text{N})$, is built up from $\text{Fe}(\text{H}_2\text{O})_6$ octahedra, SO_4 square planar and NH_4 forms tetrahedra (Fig. 2). The $\text{Fe}(\text{H}_2\text{O})_6$ octahedra is highly distorted as indicated by the Fe–O bond distance ranging from 2.0940 (10) to

2.1435 (10) Å close to that 2.098 (3) to 2.137 (3) Å, predicted by Becker [16] for octahedral ferrate ions [17].

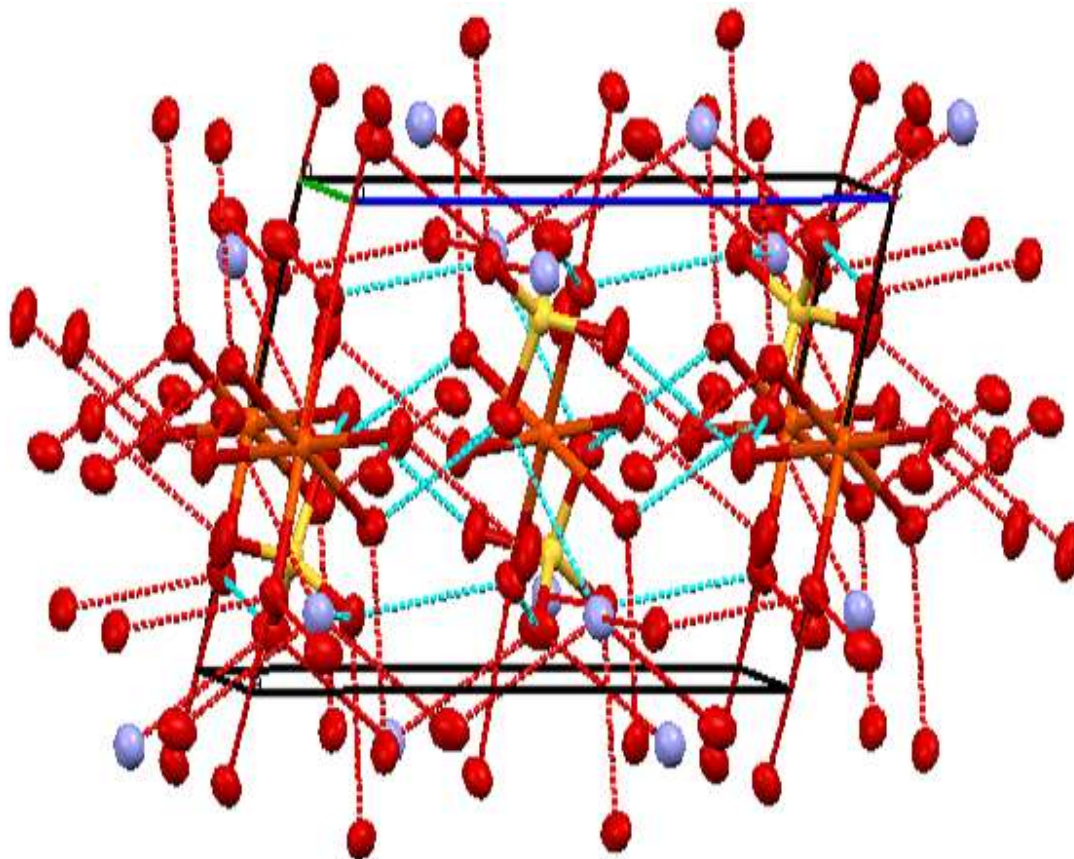


Fig. 3 : The molecular packing viewed down the a axis by N—H...O and O—H...O hydrogen bonds. H atoms have been omitted for clarity.

Each $\text{Fe}(\text{H}_2\text{O})_6$ complex anion is surrounded by four sulphate anion acceptor groups and four ammonium cation donor groups [18]. The O—Fe—O bond angles indicate little distortion from a regular octahedron (spread of values $180.0(1)$ – $88.95(5)^\circ$) [19]. The anions and cations are held together by N—H...O hydrogen bonds forming a three dimensional network involving all H atoms. The title compound consists of one NH_4 ion, one SO_4 ion and a hexa aqua-iron with the Fe^{III} ion in a slightly distorted octahedral coordination environment. The crystal structure is stabilized by N—H...O and O—H...O hydrogen bonds viewed along the a axis (Fig. 3) [20].

Thermal Characterization

Fig. 4. shows the TG/DTA curve which explains the decomposition and percentage of weight loss at various temperatures. In TGA result, the initial weight loss (26%) between 80°C and 160°C is due to loss of water. Calculation of total amount of water corresponding to this loss yields five and half moles of water. The second weight loss (26.5%) between 160°C to 450°C is due to decomposition of sulphate molecule and remaining half mole of water molecule. In the last stage, the weight loss (27%) between 580°C to 680°C is due to decomposition of remaining sulphate and ammonium molecules.

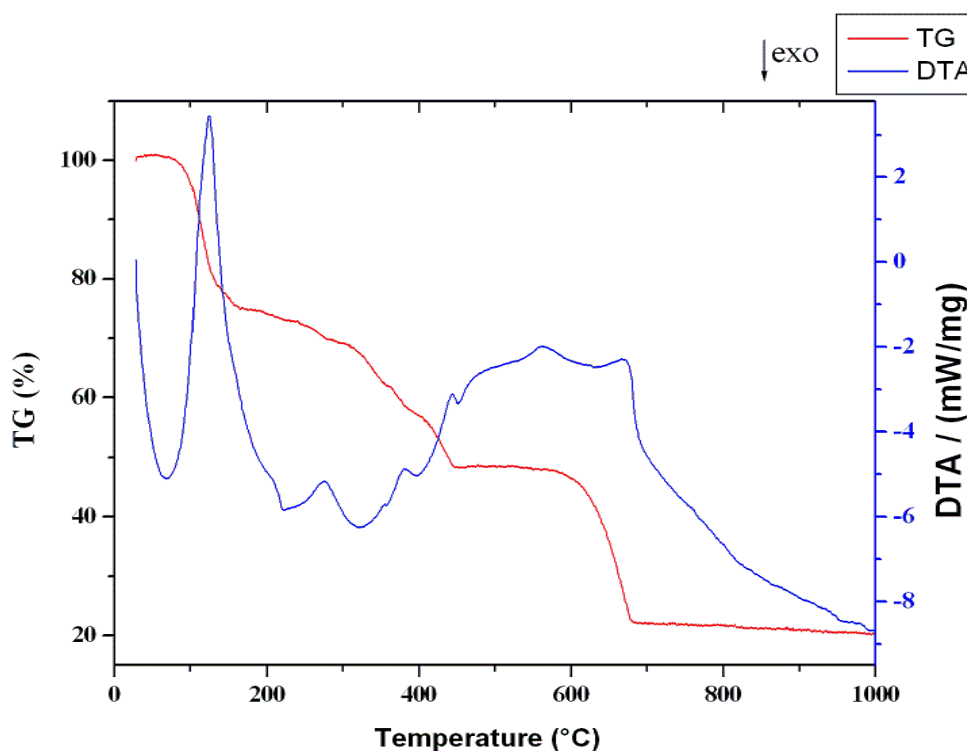


Fig. 4 : TG-DTA spectrum of Fe^{III} complex

In DTA result, the initial endotherm lying below 200°C coincides with initial weight loss in TGA. Therefore it is due to desorption of five and half moles of water. The minor endotherm just above 200°C is due to desorption of half mole of water and one mole of sulphate. The endotherm with a maximum of 563.8°C is due to decomposition of sulphate. It is followed by another endotherm close to 662°C due to decomposition of the residue obtained by the previous decomposition.

CONCLUSION

Fe^{III} complex single crystal was grown by slow evaporation technique. X-ray diffraction studies confirm the crystallinity and shows that the complex crystal is monoclinic. Crystal molecular structure of Ammonium hexaaqua ferrate(iii) sulphate has been determined using the direct method. The Differential thermal analysis together with thermogravimetric analysis reveal that the material is stable upto 80°C. These results are interesting not only for new structure type but also indicates the relationship between the structure and property. We are presently exploring this complex in nano sized form and studying the relationship between nano sized crystal and single crystal.

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REFERENCES

- [1] Zhao, B., Gao, H. L., Chen, X. Y., Cheng, P., Shi, W., Liao, D. Z., Yan, S. P. and Jiang, Z. H. *Chem. Eur. J.*, **2006**, 12, 149.
- [2] Bao-Qing Ma., Da-Shun Zhang., Song Gao., Tian-Zhu Jin., Chun-Hua Yan. and Guan-Xian Xu. *Angew. Chem. Int. Ed.*, **2000**, 39, 3644.
- [3] Ferric sulfate, The Columbia Encyclopedia. **2007**, Sixth Edition, Retrieved November.
- [4] Ferric sulfate, Online medical dictionary, **2007**, Retrieved November.
- [5] Carole Catastini., Mohamed Sarakha., Gilles Mailhot, Michele Bolte. *The Science of The Total Environment*. **2002**, Vol 298, Issues 1-3, 219-228.
- [6] Ping Ping Shi, Min Min Zhao, *Acta Cryst.* **2010**, E66, m728.
- [7] Ting-Ting Wang, Ji-Min Xie, *Acta Cryst.* **2009**, E65, m1387–m1388.
- [8] Jia-Zhen Ge, Min-Min Zhao, *Acta Cryst.* **2010**, E66, m739.
- [9] Ping Ping Wang, Jiang Gong, Shi-Feng Nic, *Acta Cryst.* **2010**, E66, m1247
- [10] Bruker, APEX2 (Version 2.0-2) and SAINT. Bruker AXS Inc., Madison Wisconsin, USA **2004**.
- [11] G. M. Sheldrick A Short history of SHELX. *Acta Cryst.* **2008**, A64, 112–122.
- [12] L. J. Farrugia, ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI), *J. Appl. Cryst.* **1997**, 30, 565.
- [13] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E Pidcock, L. Rodriguez-Monge, R. Taylor, J van de Streek, P. A. Wood, Mercury CSD 2.0, *J. Appl. Cryst.* **2008**, 41, 466-470.
- [14] G. M. Sheldrick, Program for Empirical absorption correction, SADABS, version 2.03, University of Göttingen, Germany, **2002**.
- [15] A. L. Spek, *J. Appl. Cryst.* **2003**, 36, 7–13.
- [16] Eva Becker, Karl Kirchner, Kurt Mereiter, *Acta Cryst.* **2009**, E66, m702-m703.
- [17] Mourad Hidouri, Mongi Ben Amara, *Acta Cryst.* **2009**, E65, i66.
- [18] Aymen Zouaghi, Amor BenAli, Vincent Maisonneuve, Marc Leblanc, *Acta Cryst.* **2010**, E66, m702-m703.
- [19] Jia-Zhen Ge, Min-Min Zhao, *Acta Cryst.* **2010**, E66, m739.
- [20] Li-Zhuang Chen & Mei-Na Huang, *Acta Cryst.* **2010**, E66, m377.