Lectures - Thursday, June 12

L7

There is no escape from complicated structures

PŘED KOMPLIKOVANÝMI STRUKTURAMI NENÍ ÚNIKU

M. Dušek

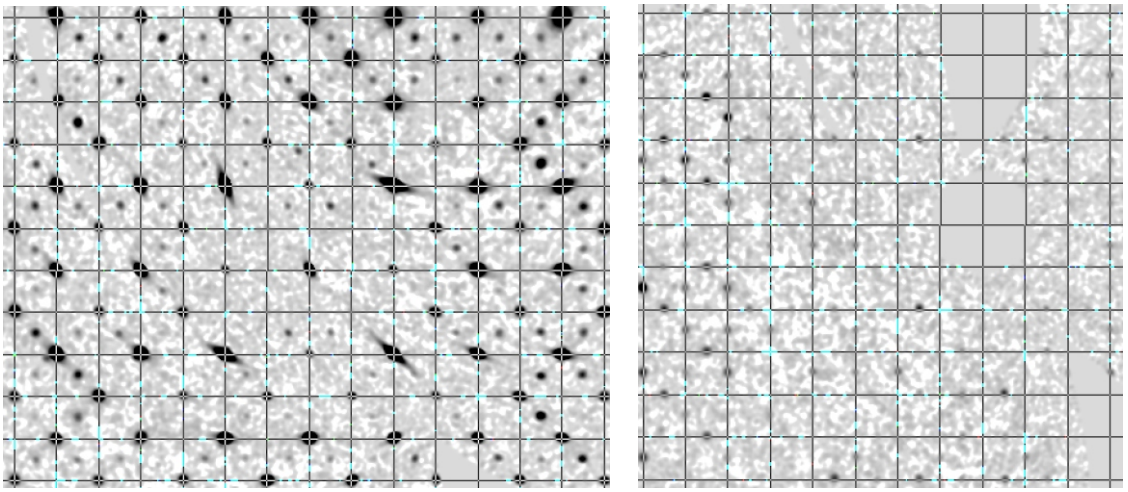
Fyzikální ústav AVČR, Na Slovance 2, 182 21 Praha 8, Česká Republika
dusek@fzu.cz

Příspěvek byl inspirován stým výročím krystalografie. U takto staré disciplíny se oprávněně předpokládá, že její metody jsou dokonale vyvinuté a její aplikace více méně rutinní. To je nepochybně pravda a lze to doložit těžko uvěřitelným počtem desítek tisíc nových krystalových struktur, které každoročně přibývají do krystalografických databází. U takto staré disciplíny se dále předpokládá, že se již nerozvíjí, protože vývoj jejích metodik byl už dokončen. Tento dosti rozšířený názor je, jako každá polopravda, velmi nebezpečný, protože vede k redukci krystalografických pracoviš na čistě servisní útvary, čímž brzdí vývoj oboru a zpětně podporuje svou vlastní pravdivost. Dopad neboli impakt zaostávání krystalografických metod by byl přitom drtivý pro řadu oborů a byl dokonce exaktně vyjádřen jako IF = 50 [1].

Existence servisních pracoviš , které řeší velké množství nejrůznějších krystalových struktur, je přitom pro rozvoj oboru stejně důležitá jako soustředěná práce úzce zaměřených specialistů. Servisní pracoviště pomáhají formulovat efektivní postupy řešení, ale současně mohou také identifikovat problémy, na které současné metody nestačí a které vzhledem k nesmírné rozmanitosti krystalových struktur nejde dobře předvídat. Pokud taková látka na sítu servisního pracoviště uvízne, je velmi důležité, jestli ještě existuje někdo, komu by mohla být předána, anebo jestli bude ve jménu efektivity a pragmatismu raději ignorována. Pokud je krystalografie oborem, který již žádný další vývoj nemá mít, tak ho jistě ani mít nebude. V této situaci však - přinejmenším v České Republice - ještě nejsme.

Přednáška vychází z patnáctileté praxe laboratoře strukturní analýzy ve Fyzikálním ústavu, tedy z období, kdy již bylo možné v této laboratoři měřit rutinně větší počty struktur. Na základě této zkušenosti a s přihlédnutím k neúplným informacím z renomovaných laboratoří na VŠCHT a PřFUK se pokusím kvantifikovat, s jakou četností se objevují komplikované struktury v situaci, kdy po nich nikdo cíleně nepátrá, což je téměř vždy případ chemická krystalografie. Na příkladech ukáži, že ačkoli badatelé běžných chemických pracoviš si nic nepřejí méně než problematické krystalové struktury, přesto tyto látky mimoděk připravují, a to ve spektru pokrývajícím veškeré možnosti moderní krystalografie. Tyto látky, pokud na to zbývá čas a kapacita, posouvají metodiku krystalografie dopředu a rozšiřují okruh problémů, které budou v budoucnu řešeny rutinně.

1. http://www.iucr.org/home/leading-article/2010/2010-07-12.



a) b)

Figure 1. Příklad problematické kubické látky se satelitními reflexemi. (a) rekonstrukce roviny hk0 z obrázků plošného detektoru; (b) rekonstrukce roviny hk1/2.

L8

DISORDERS: PROBLEMS OR NEW INFORMATION IN CHEMICAL CRYSTALLOGRAPHY?

J. Moncoľ

Institute of Inorganic Chemistry, Technology and Materials,
Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislave,
Radlinského 9, SK-81237 Bratislava, Slovenská Republika
jan.moncol@stuba.sk

The last decades is characterized rapid development of single-crystal crystallography. This progress can be assigned markedly expand of diffractometers with area detectors and installation of microfocused X-Ray sources. The massive expand of single-crystal structural analysis is related also with progress of software. The software progress determinate also requirement of solving crystal structures containing disorders. The quanta of disordered crystal structures correspond with growth average numbers of atoms in determined crystal structures. The most popular software for chemical crystallography is SHELX in various versions [1], which can be used in more graphical interfaces and software package, for example WINGX [2], XSEED [3], OLEX2 [4], ShelXle [5] and PLATON/SYSTEM-S [6]. The software package OLEX2 [4] can be also used for determination of crystal structure with its programs Olex2.solve and Olex2.refine. The instructions of program Olex2.refine are familiar SHELXL, but program contains also individual directions. Second usefully software package for chemical crystallography with independent utility for refinement of crystal structure is CRYSTALS [7]. However, alternative software package for determination of crystal structure of standard, modulated and magnetic samples is JANA-2006 [8]. All these programs allow determination of disorders with alternative approach of constrains, restrains and rigid-body modeling. The strategy of refinement of variable disorders have been documented relative adequately for the two most popular programs for chemical crystallography SHELXL [9,10] and CRYSTALS [10,12].

The disorder can describe as a violation of the crystal symmetry and translation. The content of the asymmetric units in disordered structures is not identical, but it is identical on average. The disorders can be decided to more groups.

Substitutional disorders are indentified if a crystallographic position is occupied by more than one type of atom for example in minerals and ionic crystals. The problems of substitutional disorder can be solved by similar strategy in both main programs for chemical crystallography SHELXL and CRYSTALS. The relative rare examples of substitutional disorders are crystal structures containing more than one chemical different molecules in same place. On the Figure 1 is drawn example of substitutional disorders containing alternative toluene and benzoic acid molecules in same place of cell.

Positional disorders represent fact that an atom might be found in more than one position. They can be defined as rotational disorder, pseudorotational disorder and whole molecule disorder. Rotation disorder is presented if a group with rotational freedom might be found in two or more different rotatmers. A typical example of rotation disorder is the *terc*-butyl group (See Figure 2). Typical example of pseudorotational disorder is tetrahydrofurene, where saturated cycles might also be found in two conformations next to each other. On the Figure 3 is shown infrequent example of pseudorotational disorder of metalocycles in crystal structure of iron(III) Schiff-base complex. Whole molecule disorder is most often localised for co-crystallised solvents, but it can be observed in crystal structures of coordination compound, where ligands lie around special positions. On the Figure 4 is drawn example of whole molecule disorder of bridging *N*-methylnicotinamide ligand in copper(II) complex around special position of inversion centre. Second example of whole molecule disorder is caffeine ligand, which lies on 4-fold rotoinversion axes in copper(II) complex (See Figure 5).

The disordered groups of structures can be exist as static disorder or dynamic disorder. The rotation disorders can modeled in discrete positions using programs for chemical crystallography, but program CRYSTALS pro-

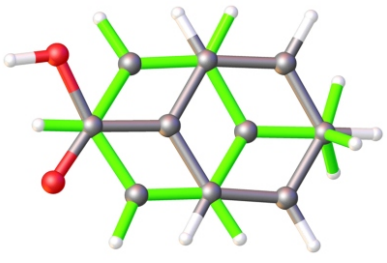


Figure 1. Substitute disorder containing toluene and benzoic acid.

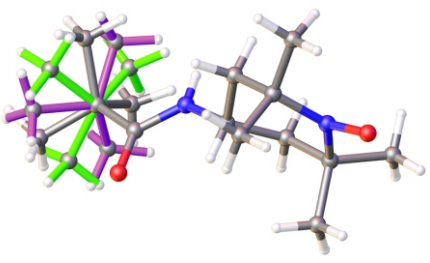


Figure 2. Rotating disorder of *terc*-butyl group in three positions.

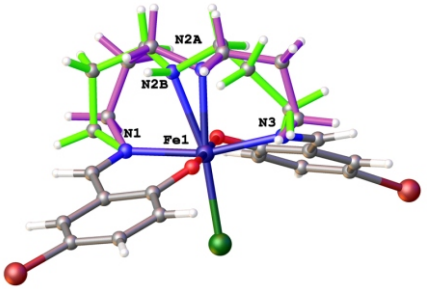


Figure 3. Pseudorotation disorder in metalocycles of iron(III) complex.

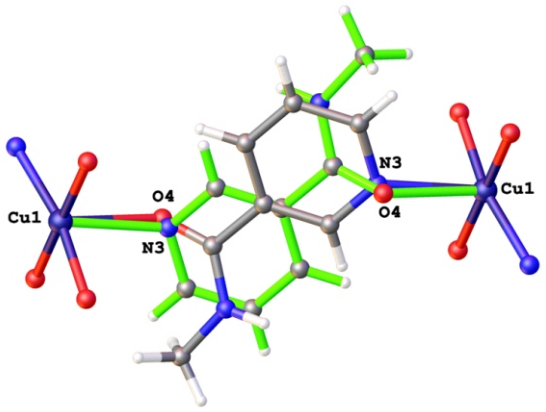


Figure 4. Disorder of bringing *N*-methylnicotinamide ligand around special.

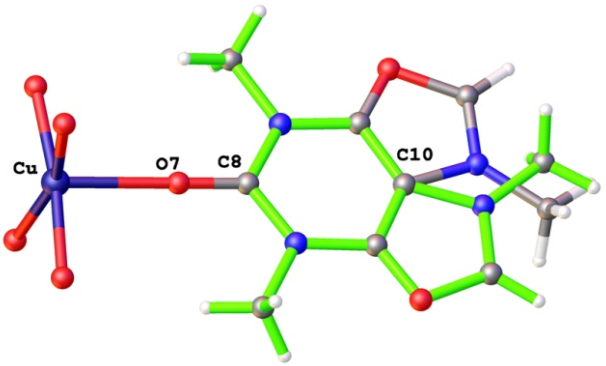


Figure 5. Disorder of caffeine ligand around special position.

poses also possibility of continual rotating model. The very usefully instructions for modeling disorders are rigid groups. For example ideal benzene ring can by modeled using instructions AFIX 66 in SHELXL, and \REGULARISE instructions HEXAGON or PHENYL in CRYSTALS. The regular angle instruction as well as instruction for regular tetrahedron and octahedron are allowed in program CRYSTALS. The disorders can be also modeled using rigid-body instructions in both programs. The rigid-body instructions can be defined using input atom coordinates from Cambridge Structural Database [13] or Idealized Molecular Geometry Library [14].

Sometimes a solvent molecule and/or small ion can be neither identified nor modeled. In such cases option SQUEEZE procedure [15] in PLATON [6] can be used. It is applied using three different ways. The older SHELXL-97 is refined only discrete model of molecule and SQUEEZE procedure is not refined. New version SHELXL-2014 (also versions 2012 and 2013) as well as CRYSTALS are refined co-operatively discrete model of molecule and SQUEEZE procedure. An alternative procedure, implemented in OLEX2, is based of bulk-solvent correction in large macromolecular structures [16].

The disorders can carry new chemical information. For example, the positional disorder of 3-pyridylmethanol ligand shows possibilities existences mononuclear molecular complex (forming hydrogen-bonding supramolecular chains) and coordination polymeric forms of copper(II) complex (See Figure 6). Second example new chemical information from disorder has been observed in crystal structure of iron(II) complex with 3,3'-(1,2,4-thiadiazole-3,5-diyl)dipyridine ligands. The both 3,3'-(1,2,4-thiadiazole-3,5-diyl)dipyridine ligands have been modeled using disorder of 1,2,4-thiadiazole rings, which allow two alternative possibilities of binding to iron atom. The crystal structure of iron(II) complex shows superposition of three regioselective isomers (See Figure 7).

In this contribution possibilities and comparisons of two the most popular program for chemical crystallography SHELXL and CRYSTALS will be shown.

1. G. M. Sheldrick, *Acta Cryst.*, **A64**, (2008), 112.
2. L. J. Farrugia, *J. Appl. Cryst.*, **45**, (2012), 849.
3. L. J. Barbour, *J. Supramol. Chem.*, **1**, (2001), 189.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.*, **42**, (2009), 339.
5. C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Cryst.*, **44**, (2011), 1281.
6. A. L. Spek, *Acta Cryst.*, **D65**, (2009), 148.

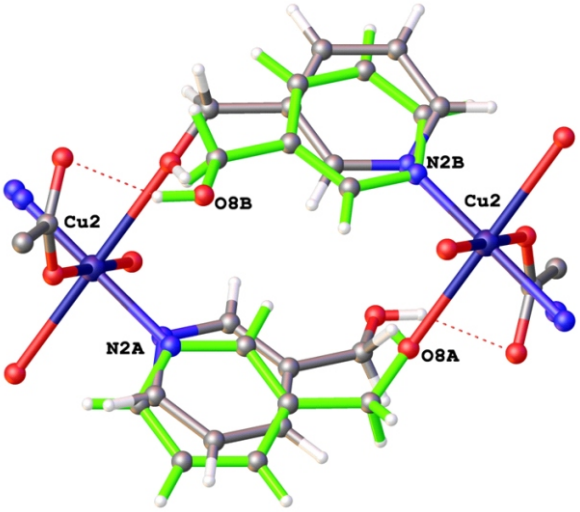


Figure 6. Disorder of 3-pyridylmethanol ligand forming coordination chain or hydrogen-bonding supramolecular chain.

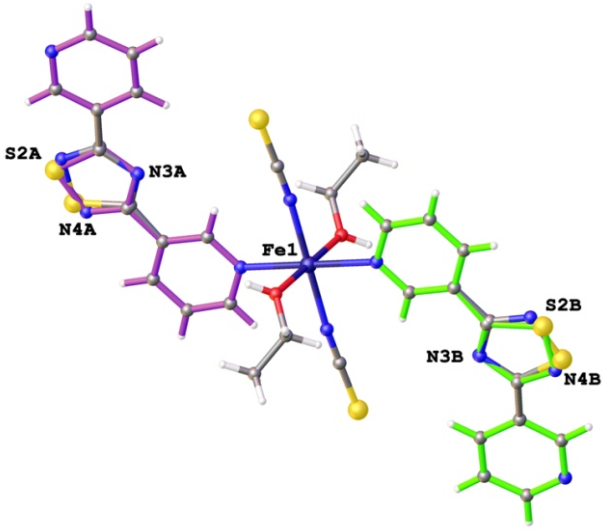


Figure 7. Disorders of 3,3'-(1,2,4-thiadiazole-3,5-diyl) dipyridine ligands forming three structural isomers ron(II) complex.

SL24

STRUCTURAL SURPRISES IN ORGANOMETALLIC CHEMISTRY

P. Štěpnička

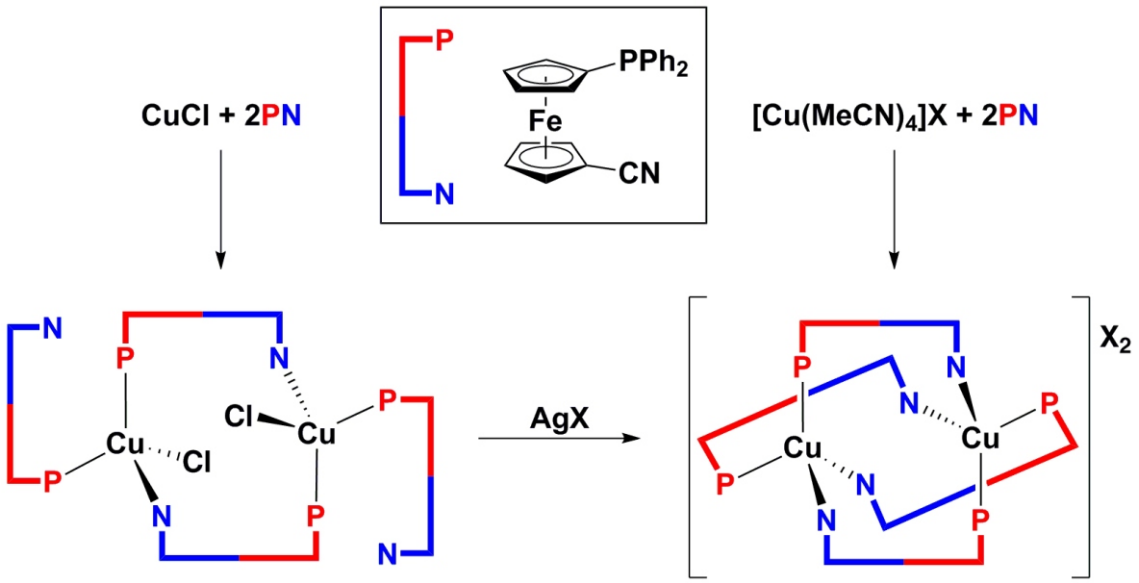
Department of Inorganic Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030, 12840 Czech Republic
stepnic@natur.cuni.cz

Since its discovery in early 1950's [1] when it was looked upon as a real structural surprise, ferrocene and its derivatives gradually spread over and influenced nearly all chemistry fields, finding applications in areas as diverse as catalysis, material design and bioinorganic chemistry [2]. Probably the most spectacular applications of ferrocene compounds were achieved in organometallic catalysis where ferrocene-based ligands, predominantly phosphines, have often played a pivotal role [2]. The numerous successful practical applications of ferrocene ligands in catalysis naturally encouraged search for new ferrocene phosphines with specific physicochemical and coordination properties and investigations into the reactions of ferrocene compounds in general.

This contribution will present some unexpected reactions of ferrocene alkynes with 6,9-$(Me_2S)_2$-*arachno*-$B_{10}H_{12}$ encountered during our studies on ferrocenyl-substituted 1,2-dicarba-*closo*-dodecaboranes [3] and will further focus on the structurally unpredictable Cu(I) complexes resulting from the reactions of a simple phosphinoferrocene ligand 1 -(diphenylphosphino) -1-cyanoferrocene with Cu(I) precursors (Scheme 1) [4]. In both these cases, single-crystal X-ray diffraction analysis played a vital role in elucidation of the structures of the compounds formed.

1. a) P. L. Pauson, T. J. Keally, *Nature*, **168**, (1951), 1039; b) S. A. Miller, J. A. Tebboth, J. F. Tremaine, *J. Chem. Soc.*, (1952), 632; c) G. Wilkinson, M. Rosenblum, M. C. Whiting, R. B. Woodward, *J. Am. Chem. Soc.*, **74**, (1952), 2125; d) E. O. Fischer, W. Pfab, *Z. Naturforsch.*, **7b**, (1952), 377.
2. *Ferrocenes: Ligands, Materials and Biomolecules*, edited by P. Štěpnička (Chichester: Wiley), 2008.
3. A. Korotvička, I. Šnajdr, P. Štěpnička, I. Císařová, Z. Janoušek, M. Kotora, *Eur. J. Inorg. Chem.*, (2013), 2789.
4. K. Škoch, I. Císařová, P. Štěpnička, *Inorg. Chem.*, **53**, (2014), 568.

The results presented in this contribution were obtained with financial support from the Czech Science Foundation (project nos. P207/11/0705 and 13-08890S).



Scheme 1. Reactions of 1 -(diphenylphosphino)-1-cyanoferrocene with various Cu(I) precursors.

L9

BREAKING THE PROBLEM COMPLEXITY LIMITS FOR POWDER DIFFRACTION BASED STRUCTURE SOLUTION

M. Hušák

Institute of Chemical Technology Prague, Technická 5,166 28 Praha 6
husakm@vscht.cz

It can be predicted from theoretical calculations, how much complex structure can be solved from powder diffraction data [1]. The theoretical limit for perfect synchrotron data is about 300 DOF (degree of freedom) while current existing record solves only 42 DOF problem simplified by heavy atom presence [2]. We have tried to determine a realistic DOF limit based on perfect simulated powder diffraction data. For the simulation we have chosen peptide structures from CSD: 1 single peptide molecule in asymmetric unit cell, 2-8 amino acids, 10-39 DOF. The parameters of the simulated powder diffractogram used were close to typical perfect measurement on ID31 of ESRF - wavelength 0.5 Å, range 0.5 -15 , step 0.002 , FWHM 0.01 . The structure solution tests were done by SA (simulated annealing) in DASH 3.2 software [3]. To speed up the computation of structures with more than 20 DOF we have used parallel processing obtained by MDASH extension. Influence of Mogul CSD based torsion angles bias on the calculation effectiveness was investigated as well. The results demonstrate the required number of SA steps depends exponentially on the problems DOF. This requires for problems close to 30 DOF about 10E+10 SA steps and years of single CPU computational time. The Mogul based bias can significantly help for compounds like peptides - e.g. for simulation based on compound CSD code AHAREH (4 peptides, DOF 24) the Mogul based calculation gives 50 times more often correct result than non-restricted SA run. We believe the 40 DOF structures can be solved routinely on 16-32 CPU clusters from perfect data not influenced by preferred orientation when the Mogul CSD torsion angels biased will be used (required total computational time about 1 month). Without developing a more efficient algorithm than SA solution we do not see a way how to get really close to the 300 DOF theoretical limits. The promising new algorithm can be a brute-force solution space sampling followed by local minimization as described in [4]. R&D of a code utilizing this idea is under progress.

1. David, W.I.F., Shankland, K. (2008). *Acta Cryst* A**64**, 52-64.
2. Fernandes, P., Shankland, K., Florence, A. J.,Shankland N., Johnston A. (2007) *Journal of Pharmaceutical Science* **96-5**, 1192-1202.
3. David, W.I.F., Shankland, K., Streek J., Pidcock, E., Motherwell S., Cole J. (2006). *J. Appl. Cryst*. **39**, 910-915.
4. Shankland K., Markvardsen A.J., Rowlatt Ch., Shankland N., David W.I.F.: (2010). *J. Appl. Cryst*. **43**,401-406.

This work was supported by the Grant Agency of Czech Republic, Grant No. 106/14/03636S.

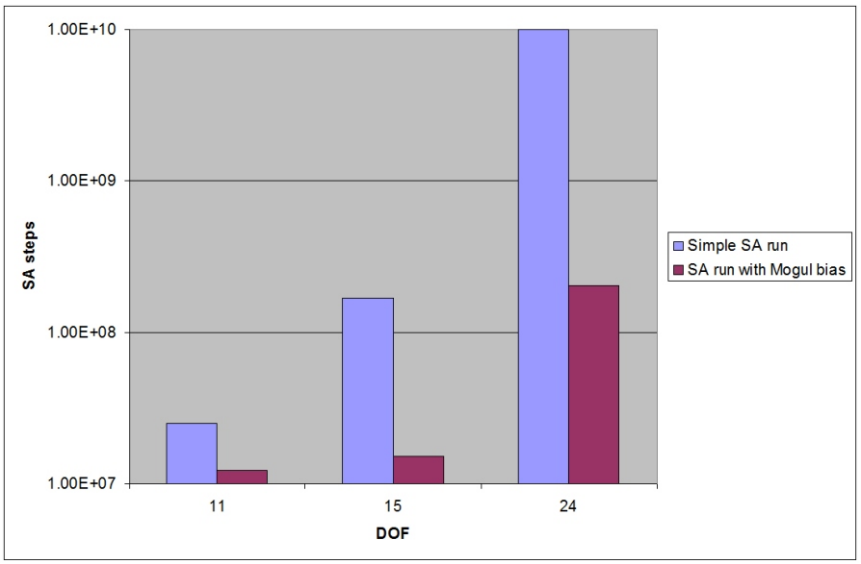


Figure 1. Dependence of required simulated annealing steps number required to get one solution on DOF and the use of Mogul based bias**.**