JOURNAL OF CHEMICAL EDUCATION

Article

pubs.acs.org/jchemeduc

3D Printed Molecules and Extended Solid Models for Teaching Symmetry and Point Groups

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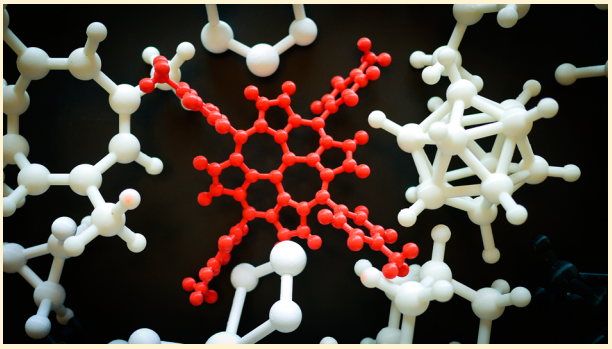
Supporting Information

ABSTRACT: Tangible models help students and researchers visualize chemical structures in three dimensions (3D). 3D printing offers a unique and straightforward approach to fabricate plastic 3D models of molecules and extended solids. In this article, we prepared a series of digital 3D design files of molecular structures that will be useful for teaching chemical education topics such as symmetry and point groups. Two main file preparation methods are discussed within this article that outlines how to prepare 3D printable chemical structures. Both methods start with either a crystallographic information file (.cif) or a protein databank (.pdb) file and are ultimately converted into a 3D stereolithography (.stl) file by using a variety of commercially and freely available software. From the series of digital 3D chemical structures prepared, 18 molecules and 7 extended solids were 3D printed. Our results show that the file preparation methods discussed within this article are both suitable routes to prepare 3D printable digital files of chemical structures. Further, our results also suggest that 3D printing is an excellent method for fabricating 3D models of molecules and extended solids.



KEYWORDS: *3D Printing, Molecular Models, Hands-On Learning, Group Theory, Symmetry, Inorganic Chemistry*

INTRODUCTION

Three-dimensional (3D) representations of chemical structures in the form of tangible models have been used for many decades in chemistry research and instruction. Numerous models have been developed such as those constructed from polystyrene spheres,[1−5] plastic bottle caps,[6] glass marbles,[7] folded paper,[8,9] and plastic beads.[10] Commercially available molecular model kits containing plastic spheres and connecting rods are also readily available (e.g., Molymod). However, the majority of commercial model kits have limitations on the variety of molecular structures they are capable of representing. It is often difficult or impossible to represent complex molecules and extended solids via these conventional techniques. In addition, many of the fabrication processes reported are system-specific; that is, they excel at representing a particular class or group of chemical structures but fail to provide a technique capable of fabricating a large variety of chemical structures.

3D printing is a modern additive manufacturing process that can overcome the aforementioned limitations of traditional molecular model constructs. In 3D printing, the object is built from a series of fused cross-sectional layers. The process is additive, resulting in minimal design and production restrictions; exquisite one-piece shapes can be readily produced with 3D printing. This is in direct contrast to subtractive techniques where an object is sculpted from a solid material.[11−13] There are a variety of different 3D printing technologies and materials available. For example, some 3D printers deposit thermoplastics or UV resins for the individual layers, whereas other 3D printers fuse composite powder particles together through the use of liquid binders or lasers. For the interested reader, Castle Island's Worldwide Guide to Rapid Prototyping[14] and Make Magazine's Ultimate Guide to 3D Printing[15] provide a good introduction to current 3D printing technology.

In the context of fabricating molecular models, 3D printing eliminates the often tedious process of the additive combining of individual pieces such as spheres and rods at specific angles and combinations (that can quickly become very complex!). With 3D printing, molecules can be created in one piece directly from a digital 3D design file, greatly simplifying the process of fabricating molecular models.

Our interest in 3D printed molecules was driven by the desire to create a series of classic and unique chemical structures that are challenging to represent via traditional fabrication techniques or commercially available model kits. One such example is inorganic coordination compounds,[16] often used in teaching symmetry and point groups in an inorganic chemistry course.[17] More importantly, with 3D printing technology, *any* model can be fabricated, from simple organic structures to coordination compounds to extended solid structures, both experimentally discovered and undiscovered.

Published: April 18, 2014

3D printed molecules have received little attention in the chemical literature, despite the growing availability of 3D printers on academic campuses.[18] To our knowledge, there have only been two prior articles concerning 3D printed molecules in the literature.[19,20] Chakraborty and Zuckermann recently developed a custom 3D printed design and fabrication procedure for representing physical models of biomacromolecules.[19] Although their models are quite useful for understanding protein structures and protein folding, the custom 3D printed design is system-specific and would prove difficult to adapt for use in representing small molecules and extended solid structures. Another recent article discussed the use of computational chemistry and 3D printed molecules to aid blind and visually impaired student learning.[20] However, a detailed description of chemical structure file preparation for 3D printing was not provided. Further, much of the available information on 3D printing molecules is scattered throughout the Internet on blogs and forums,[21−25] which has led to incomplete and difficult to locate information.

The purpose of this article is twofold: (1) present a set of 3D chemical structure .stl (stereolithography) files that can be 3D printed and useful for chemical education, particularly in the teaching of symmetry and point groups and (2) discuss how to prepare chemical structure .stl files for 3D printing from .cif (crystallographic information) or .pdb (protein databank) files.

SELECTION OF MOLECULES AND EXTENDED SOLIDS FOR 3D PRINTING

We selected a variety of molecules and extended solid structures that are useful for teaching inorganic symmetry and group theory (Table 1). For each of the molecules and extended solids in Table 1, a .stl file is included in the Supporting Information. The majority of these .stl files were 3D printed in our facilities to confirm the feasibility of printing the models. Molecules chosen for inclusion met one or more of the following criteria: (1) the structure would be difficult or impossible to assemble from a standard molecular model kit, (2) the structure illustrates a particular symmetry principle (e.g., chirality), (3) the structure contains symmetry elements that are more easily discerned in a 3-dimensional model compared to a 2-dimensional illustration, or (4) the structure was generated from .cif data from our own research and/or from the primary literature to illustrate this method's utility in creating unique and specific models.

For example, $[Cd(en)_3]^{2+}$ cannot be created in most organic molecular model kits (an inorganic kit is required). A 3D model is helpful in demonstrating its C_3 axis and, especially, its three perpendicular C_2 axes. The $[Cd(en)_3]^{2+}$ cation is chiral, and its chirality has the same origin as that in "hexol" (three bidentate ligands in an octahedral coordination geometry around a metal center), the first inorganic complex in which chirality was demonstrated.[26] We have printed both the Δ and Λ enantiomers of $[Cd(en)_3]^{2+}$, so that the mirror-image relationship of the two enantiomers (and their nonsuperimposability) can be demonstrated (see Figure 1C). Another molecule that is useful in a discussion of chirality is 1,3,5,7-tetramethylcyclooctatetraene. It is a rare example of a molecule that contains neither a reflection plane nor an inversion center yet is achiral due to its S_4 improper rotation axis. Two copies of 1,3,5,7-tetramethylcyclooctatetraene can be printed to demonstrate that they are mirror images and also superimposable.

Models of ferrocene generally exist only as expensive permanent models. The 3D printing of ferrocene models is an affordable alternative; thus, we selected ferrocene in both the staggered and eclipsed conformations of the two cyclopentadienyl rings. Models are especially useful in showing the sets of C_2 axes for ferrocene.

The series of cyclopropane, 1,1,2-trifluorocyclopropane, and *cis*- and *trans*-1,2-difluorocyclopropane yield a nice demonstration of how point groups change with variations in the substitution pattern on the same parent molecule. The fluorocyclopropane derivatives provide simple examples of low-symmetry point groups.

As an alternative to printing all of the fluorocyclopropane derivatives above, it is possible to print only cyclopropane itself and then mark some of the hydrogen atoms to indicate that they are fluorine. We have found that wrapping the atoms in aluminum foil is a convenient, inexpensive, and reversible method that labels the appropriate atoms in a visually distinctive manner. Alternatively, if permanent models of the fluorocyclopropane derivatives are desired, then multiple copies of cyclopropane can be 3D printed and the appropriate atoms painted to indicate their identity as fluorine. In any case, we

Table 1. Selected Molecules and Extended Solids for 3D Printing

Molecule	Point Group	Reference
cyclopropane	D_{3h}	*b*
1,1,2-trifluorocyclopropane	C_1	*b*
cis-1,2-difluorocyclopropane	C_s	*b*
trans-1,2-difluorocyclopropane	C_2	*b*
$[Re_2Cl_8]^{2-}$	D_{4h}	32
Δ-$[Cd(en)_3]^{2+}$	D_3	33
Λ-$[Cd(en)_3]^{2+}$	D_3	33
$[(\eta^5\text{-}C_5H_5)_2Fe]$ eclipsed	D_{5h}	34
$[(\eta^5\text{-}C_5H_5)_2Fe]$ staggered	D_{5d}	35
$[B_{12}H_{12}]^{2-}$	I_h	36
cis-$[FeCl_2(2\text{-(aminomethyl)pyridine})_2]$	C_2	29
trans-$[FeCl_2(2\text{-(aminomethyl)pyridine})_2]$	C_{2h}	29
1,3,5,7-cyclooctatetraene	D_{2d}	37
1,3,5,7-tetramethylcyclooctatetraene	S_4	38
adamantane ($C_{10}H_{16}$)	T_d	39
$[Mo_6Cl_{14}]^{2-}$	O_h	40
triphenylphosphine[a]	C_3	41
biphenyl (planar)[a]	D_{2h}	42
biphenyl (twisted)[a]	D_2	43
9-Borabicyclo[3.3.1]nonane (9-BBN)[a]	D_{2h}	44
S_8[a]	D_{4d}	45
$Th[(NO_3)_6]^{2-a}$	T_h	46
(C═C)tetra-*p*-tolylporphyrin	C_1	28
$[Ge(i\text{Pr}_2\text{NHC})_3]^{2+}$	C_3	30
Extended Solid	**Space Group**	**Reference**
NaCl	$Fm\bar{3}m$	47
CsCl	$Pm\bar{3}m$	48
CaF_2	$Fm\bar{3}m$	49
diamond	$Fd3m$	50
ZnS-wurtzite	$P6_3mc$	51
ZnS-zincblende	$F\bar{4}3m$	52
TiO_2-rutile[a]	$P4_2/mnm$	53
TiO_2-anatase[a]	$I4_1/amd$	53
NiAs[a]	$P6_3/mmc$	51
$Pb_3C_6S_6$	$P6/mmm$	31

[a]Only the .stl files were prepared for these structures; all other structures have been 3D printed. [b]Structures were created in PerkinElmer Chem3DPro.

dx.doi.org/10.1021/ed400887t | J. Chem. Educ. 2014, 91, 1174−1180

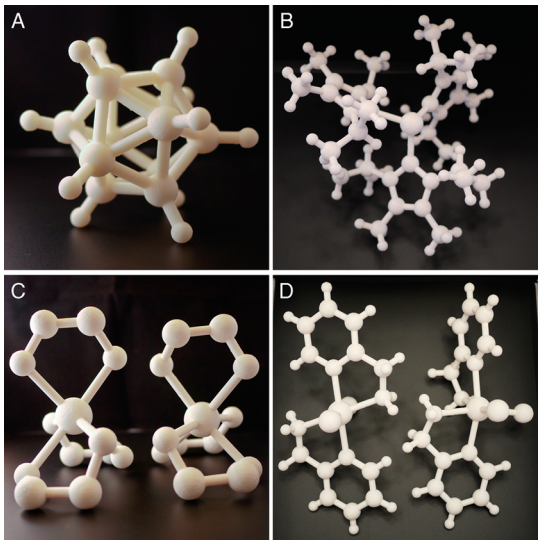


Figure 1. Representative samples of 3D printed molecules: (A) $[B_{12}H_{12}]^{2-}$; (B) $[Ge(iPr_2NHC)_3]^{2+}$; (C) Δ-$[Cd(en)_3]^{2+}$ and Λ-$[Cd(en)_3]^{2+}$; (D) *trans*- and *cis*-$[FeCl_2(2\text{-(aminomethyl)pyridine})_2]$. The approximate dimensions of the models are on the order of 15−25 cm in all directions.

have had success only with single-color 3D printing of the models, and either temporary or permanent marking of the fluorine atoms in the fluorocyclopropane derivatives will be helpful in making them visually distinguishable from the hydrogen atoms.

A model for the classic quadruply bonded metal complex $[Re_2Cl_8]^{2-}$ is included. The $[Re_2Cl_8]^{2-}$ dianion belongs to the D_{4h} point group. Although we have not included .stl files for various isomers such as $[Re_2Cl_6Br_2]^{2-}$ or $[Re_2Cl_4Br_4]^{2-}$, it is possible to 3D print the $[Re_2Cl_8]^{2-}$ model and then use one of the methods outlined above to either temporarily or permanently mark some of the chloride anions to indicate that they are bromides. A number of molecular models with somewhat challenging-to-assign point groups are thus created.[27]

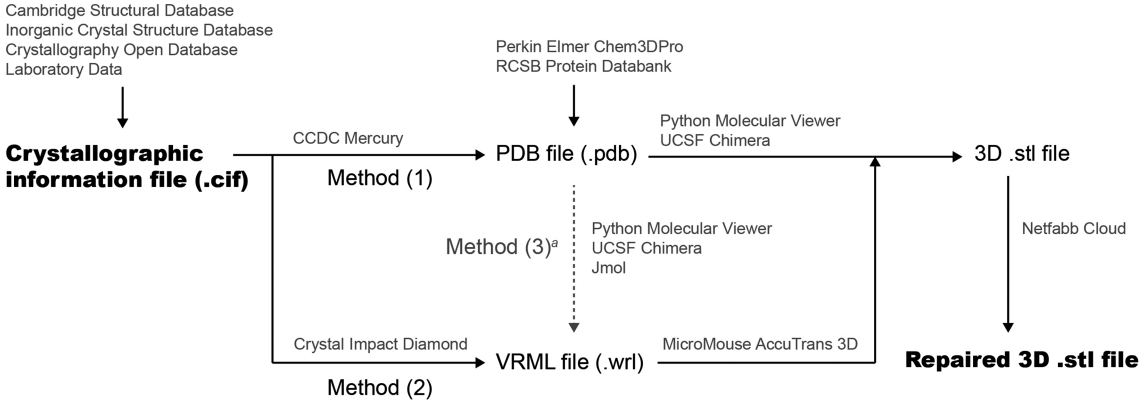
Other models are useful for teaching the very high symmetry point groups, including $[B_{12}H_{12}]^{2-}$ (I_h), adamantane (T_d), $[Mo_6Cl_{14}]^{2-}$ (O_h), and $Th[(NO_3)_6]^{2-}$ (T_h). 3D models are particularly useful in illustrating the higher-order rotation axes for these point groups. The models of adamantane and $[Mo_6Cl_{14}]^{2-}$ enable demonstration of the T_d and O_h point groups in molecules that are not simply tetrahedral and octahedral metal complexes (or similar simple molecules such as CH_4 and SF_6).

A few unique structures were selected that would not generally appear in inorganic or group theory textbooks such as the (C═C)tetra-*p*-tolylporphyrin (C_1) from our own research,[28] a *cis* and *trans* $[FeCl_2(2\text{-(aminomethyl)pyridine})_2]$ coordination complex (*cis* (C_2), *trans* (C_{2h})) reported by Bürgi and co-workers,[29] and a germanium complex, $[Ge(iPr_2NHC)_3]^{2+}$ (NHC = *N*-heterocyclic carbene, C_3) reported by Baines and co-workers.[30] Selecting and creating molecules not generally discussed in the context of symmetry and point groups allows for the demonstration of interesting molecules that are selected directly from the primary literature. This is quite useful in developing and tailoring a series of molecules to a particular instruction class.

Similarly to the commercially available ferrocene models, many models of extended solids are available for purchase; however, they are often costly. 3D printing offers an affordable alternative. Several of the selected extended solids, including NaCl, CsCl, CaF_2, and diamond, have structures that are taught in general chemistry, and will be useful in that capacity. Other structure types, including NiAs, ZnS (wurtzite and zincblende), and TiO_2 (rutile and anatase), are often taught in upper-level inorganic chemistry courses. One capacity in which these 3D models are particularly useful is in the observation of various lattice planes (such as (100), (110), (111), etc.) in the solid-state structure. Furthermore, in a class where space-group symmetry is taught, these models would be useful in demonstrating all of the symmetry elements present in a given structure. Finally, $Pb_3C_6S_6$ was included as an example of a model of an extended structure created in our research laboratory.[31]

Lastly, we note that a multitude of .cif chemical structures are readily available from data repositories such as the Cambridge Structural Database, Inorganic Crystal Structure Database, Crystallography Open Database, or from researchers' own laboratory data. There are hundreds of thousands of unique molecular structures in these databases. Moreover, programs such as PerkinElmer's Chem3D can be used to create 3D molecular structures when crystal structure data is not readily available or if hypothesizing new molecular structures yet to be

Scheme 1. Preparation of 3D Printable Chemical Structure .stl Files: Method 1 (top), Method 2 (bottom), and Method 3 (center)



[a]Method 3 is an alternative method to create .wrl files (see Supporting Information and ref 21).

discovered. By using a combination of repositories and 3D structure drawing software, educators and researchers can obtain or create a 3D structure for *any* molecule.

METHODOLOGY FOR 3D PRINTING MOLECULES AND EXTENDED SOLIDS

3D printers, or more precisely the software that operates them, require specific file formats of digital models. A common format accepted by many 3D printing software packages is the stereolithography, or .stl format. A .stl file is a continuous 3D surface representation composed of many triangles. The .stl file is used by the 3D printer software to create the final build file for the printer. The build file contains the *xyz* coordinate instructions (i.e., a tool path) for each layer of the object, including any directions for using temporary support material (see Supporting Information). 3D printing software is often specific to the particular manufacturer and model of the printer. For this reason, details of building the .stl molecular files have been omitted from this article (i.e., slicing layers and adding support). However, we have found 3D printer .stl build preparation software from a variety of manufactures including Stratasys (Catalyst EX), Bits from Bytes (Axon), and Makerbot (MakerWare) intuitive and straightforward to use when converting .stl files into the final print-ready 3D printer build file.

Two main methods to prepare molecular structure .stl files were used in this article (Scheme 1). These methods were developed and adapted from various sources found on the open Web Internet.[21−25] We have included detailed instructions for both file preparation methods in the Supporting Information. Briefly, Method 1 starts with a .cif file and converts this file into a .pdb file using CCDC Mercury. The .cif files were obtained from either the Cambridge Structural Database or the Crystallography Open Database. For structures where .cif files were not readily available, .pdb files were created in PerkinElmer Chem3DPro (Table 1). The .pdb file is then imported into a suitable 3D software package such as UCSF Chimera[54] or Python Molecular Viewer (PMV)[55] and modified to the desired 3D chemical representation. We chose to exclusively use the ball and stick representation for our models as these are very useful representations for teaching symmetry and point groups; however other representations such as space-filling or wire can also be selected. This 3D representation is then exported as a .stl file. In Method 2, a .cif file is exported as a .wrl (a modeling language text file) from Crystal Impact Diamond; the text file is modified and adjusted to the desired chemical representation settings and then converted to a .stl file using MicroMouse AccuTrans 3D, a 3D object conversion program. In both methods, the .stl files are checked for any errors with Netfabb Cloud, repaired if necessary, and then loaded into the 3D printing build software (in our case, Catalyst EX). We have achieved successful 3D prints of equal resolution and quality from these two methods. All molecules and extended solids were fabricated on a Stratasys Dimension Elite 3D printer using ABS P430 (acrylonitrile-butadiene-styrene based copolymer) model material and P400SR (acrylic copolymer based) soluble support material (see Supporting Information). The approximate material cost of the models produced from ABS P430 and P400SR ranged from $10−75 depending upon the overall size of the structure.

RESULTS AND DISCUSSION OF 3D PRINTED MOLECULES AND EXTENDED SOLIDS

A total of 18 molecules and 7 extended solids were 3D printed. All structures appeared to print with equal quality and resolution, regardless of the file preparation method or complexity of the structure. Notably, a very wide range of structures were fabricated demonstrating this method is not system-specific like many traditional molecular model fabrication techniques. Numerous molecules and extended solids were created with the 3D printing methodology described herein (Table 1). Several representative examples are shown in Figures 1 and 2.

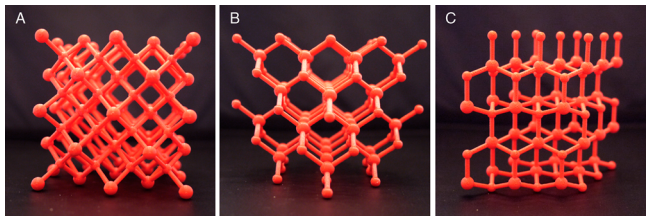


Figure 2. Representative samples of 3D printed solids: (A) CaF_2, (B) ZnS-zincblende, and (C) ZnS-wurtzite. The approximate dimensions of the models are on the order of 10−20 cm in all directions.

These 3D printed models are currently being used for teaching symmetry and point groups in an upper-level inorganic chemistry class. Preliminary feedback from the students is very positive; the students enjoy manipulating the models and viewing unique examples from the literature. Although 3D printing overcomes many limitations of traditional fabrication techniques, one potential limitation with 3D printed molecules is the inability for students to learn from assembling the models piecewise themselves. Students are only able to manipulate models postassembly as one-piece units. As a result, tactile learning may be limited using one-piece models. However, we believe the benefits of introducing unique models of chemical structures that cannot be easily constructed with molecular model kits or other fabrication techniques outweigh the potential tactile learning limitations. A combination of piece-wise model kits and 3D printed one-piece models can also be used to circumvent this limitation.

The majority of molecules and solids within this article were prepared via Method 1. We found Method 1 to be faster and more straightforward compared to Method 2 (Scheme 1). In addition, all of the software used in Method 1 is freely accessible. One potential limitation to Method 1 is that the software including UCSF Chimera and PMV are designed for biomacromolecules, so there are limited options for manipulating small molecules and extended solids. In contrast, many researchers, particularly those familiar with single crystal X-ray diffraction, will likely find Crystal Impact Diamond as used in Method 2 more comfortable and more powerful to use compared to UCSF Chimera or PMV. One potential limitation to Method 2 is that both Crystal Impact Diamond and MicroMouse AccuTrans 3D are only commercially available. Thus, the accessibility of this software is dependent on purchasing a license. Both methods have produced successful high quality 3D prints of molecular structures, so in the end, both are suitable.

The Stratasys Dimension Elite 3D printer used to create the models deposits thermoplastics in the melt-phase (ABS P430

dx.doi.org/10.1021/ed400887t | J. Chem. Educ. 2014, 91, 1174−1180

was selected for the model material and P400SR for the soluble support material). The soluble support material is a sacrificial component and is removed in a basic solution (see Supporting Information). This particular 3D printer and many others using similar thermoplastic extrusion technology are only capable of printing the model with one material type at a time. As a result, the molecules and extended solids in this article were limited to a single color. If atom sizes were not significantly different, it was difficult to differentiate similar atoms. This was only apparent on a few of the solid structures as the overall atom sizes were much smaller compared to the molecular structures. We plan to selectively mark or paint atoms in the extended solids where it is difficult to differentiate.

There are several full-color 3D printers available that can print multiple colors within one object. Color printers such as the 3D Systems ProJet 460Plus series printer use composite particles that are fused together with a liquid binder. Unfortunately, our preliminary efforts using a color .wrl molecular structure file (produced with Method 2, see Scheme 1) and a 3D Systems ProJet 460Plus color powder printer were unsuccessful. We found that the molecular models are very brittle prior to the permanent solidification process. As such, all of our models cracked during the removal of excess powder, prior to the postprinting solidification process.

In contrast to the fragile color printing molecular model attempts, models printed on the Stratasys Dimension Elite 3D printer reported in this article using the ABS P430 model material and P400SR dissolvable support material consistently produced structures with excellent mechanical integrity. The Stratasys Dimension printer is a professional grade thermoplastic extrusion printer; we also explored using a hobbyist level (<$5,000) thermoplastic extrusion printer to fabricate one of the molecules in this article. We 3D printed the molecule on a Bits from Bytes (BFB) 3D Touch printer using polylactide for both the model and support material. The resulting quality and finish of the model was very good. However, because both the model itself and the sacrificial support material were polylactide, the support could not be selectively dissolved away in a basic solution, and mechanically trimming away the support was unsuccessful. Printing the model with ABS plastic and the support with polylactide on the BFB 3D Touch failed due to disconnection between the model and support during printing.

For those who wish to acquire a 3D printer for fabricating molecular models, we recommend a professional thermoplastic extrusion printer capable of using a soluble support. To our knowledge, the current lowest cost system is the Stratasys Mojo that sells for approximately $10,000.[56] As an alternative to purchasing a 3D printer, there are many commercial 3D printing services such as Shapeways, Sculpteo, and Ponoko where users can submit digital models (e.g., .stl and .wrl files) to be professionally printed for a reasonable fee.

CONCLUSIONS

We have created a unique series of 3D printed molecules and extended solids useful for teaching symmetry and group theory. Two main digital file preparation methods were reported that successfully converted .cif or .pdb chemical structure files into 3D printable .stl files. Both file preparation methods produced successful 3D prints of equal quality using a Stratasys Dimension Elite 3D printer. 3D printing has made it feasible to create tangible models of molecular structures that were difficult or impossible to replicate with traditional fabrication techniques or commercially available molecular model kits. Several challenging structures were easily fabricated in this article such as ferrocene, $[B_{12}H_{12}]^{2-}$, ZnS, and CaF_2.

The ability to create custom 3D printed tangible representations of molecular structures will be applicable in many areas of research and teaching. We are currently using these 3D printed models in an upper-level inorganic chemistry class to help teach symmetry and group theory. All .stl files of molecules and extended solids discussed in this article have been compiled and included in the Supporting Information. These files can be freely used by instructors, researchers, and students seeking to reproduce models within this article.

ASSOCIATED CONTENT

Supporting Information

Detailed instructions for the creation of .stl files; additional photographs of 3D printed molecules and extended solids; molecular and solid structure .stl files for the models in Table 1. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank The University of Alabama Libraries and The University of Alabama Department of Engineering for financial support of this project, Doug Cannon and the student technicians in the UA 3D Printing Lab for assistance with printing the models, and the anonymous reviewers and *Journal* editors for excellent suggestions and feedback to improve this article.

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NOTE ADDED IN PROOF

During production of this paper, two related papers also in production came to our attention: (1) Kitson, P.; Macdonell, A.; Tsuda, S.; Zang, H.; Long, D.-L.; Cronin, L. Bringing Crystal Structures to Reality by 3D Printing. *Cryst. Growth Des.* **2014**, 10.1021/cg5003012; (2) Chen, T.-H.; Lee, S.; Flood, A. H.; Miljanic, O. How to Print a Crystal Structure Model in 3D. *CrystEngComm* **2014**, 10.1039/C4CE00371C.