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A Historical Perspective on Crystallography in Croatia and the Career of Biserka Kojić-Prodić from the Viewpoint of the CSD

Peter A. Wood,* Clare A. Tovee, Andrew G. P. Maloney, Suzanna C. Ward

Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK

* Corresponding author's e-mail address: wood@ccdc.cam.ac.uk

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THIS PAPER IS DEDICATED TO DR. BISERKA KOJIĆ-PRODIĆ ON THE OCCASION OF HER 80TH BIRTHDAY

Abstract: There is a long history of chemical crystallography and use of the Cambridge Structural Database (CSD) in Croatia, which dates back to 1985 when the CSD first became accessible there thanks to the efforts of Biserka Kojić-Prodić as head of the National Affiliated Centre. On the occasion of Dr Kojić-Prodić's 80th birthday we take the opportunity to look back at the history of crystallography in Croatia, and particularly in Biserka's career, from the point of view of the CSD. Biserka has been a prolific author and contributor of crystal structures over the years sharing over 400 structures and collaborating with over 270 different co-authors on a wide range of different types of structure.

Keywords: Crystallographic database, Cambridge Structural Database, CSD, crystal structure, molecular structure, crystallography.

INTRODUCTION

THE relationship between Croatian crystallography and the Cambridge Structural Database (CSD)[1] began in 1985 with the establishment of a local National Affiliated Centre (NAC). This development was significantly driven by the efforts of Biserka and she became the head of this NAC from its inception in 1985 until 2007. The role of an NAC was initially to support the dissemination of the CSD to academic users within a region, and over time it has evolved more towards acting as a local advocate for the CSD and its applications. It is safe to say that Biserka has had a huge impact in both aspects over the years, initially bringing access to the CSD to Croatia for the first time, then encouraging the use of the database through many publications and local workshops.

Croatian chemical crystallographers, and Biserka in particular, have made a huge contribution to the CSD since its inception. Dr Kojić-Prodić, along with her co-authors, has shared over 400 crystal structures with the international research community through the CSD and here we look back over her crystal structures in the context of the CSD and Croatian crystallography in general.

CROATIAN CHEMICAL CRYSTALLOGRAPHY

One of the first chemical crystallography groups in Croatia was started by Drago Grdenić in Zagreb in 1948.[2] Professor Grdenić mainly studied organo-mercury compounds in the 1950s and has some of the earliest structures containing mercury in the CSD, like the ring structure, mercury diethylene oxide, with two bridged mercury centres (Figure 1, CSD refcode DOHGCD).[3]

From these early structures, the volume of crystallographic publications has continued to grow and there are now thousands of structures from Croatia in the CSD. These structures cover a broad range of chemistry from structures with a small molecular volume such as the organic zwitterion, 3-carboxypyridinium-2-olate, (molecular volume of just 142 Å^3, CSD refcode PIMBAP01).[4] At the other end of the volume scale there are organic salts of

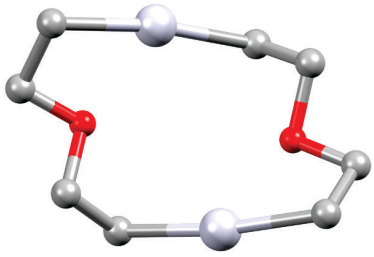

Figure 1. One of the first Croatian structures in the CSD, mercury diethylene oxide (CSD refcode DOHGCD).[3]

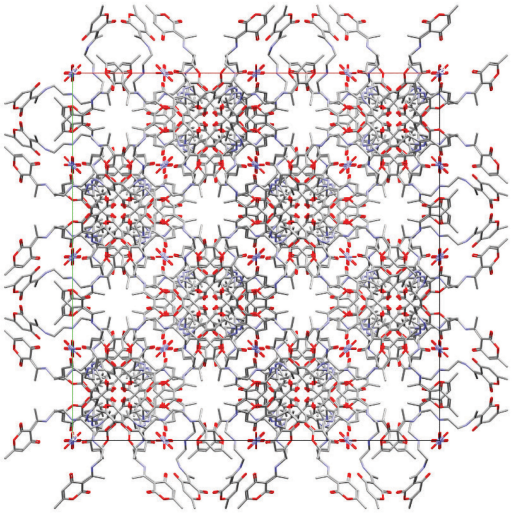

Figure 2. One of the largest Croatian structures in the CSD by unit cell volume, an organic salt in space group *Fd*-3*c* (CSD refcode YOHFUX).[5]

N,N'-3-azoniapentane-1,5-diylbis(3-(1-aminoethylidene)-6-methyl-2H-pyran-2,4(3H)-dione) that have an extremely large unit cell volume (72951 Å^3, Figure 2, CSD refcode YOHFUX).[5] This huge unit cell contains 96 individual formula units (Z = 96) but only half of the formula unit is symmetry unique (Z' = 0.5).

The studies carried out by Croatian crystallographers include many metal-organic structures, which have been explored in diverse areas from magnetic properties (CSD refcode BAWFOX)[6] to the limits of halogen-bonding interactions (CSD refcode WEKNOS).[7] They are also not limited to single crystal studies and the CSD contains, amongst others, the powder structure of a metal-organic framework generated by mechanochemsitry (CSD refcode OFERUN08).[8]

In recent years, Croatian crystallographers have contributed to the international community on the editorial boards of journals and several high-profile international crystallographic meetings have been held in Croatia. These highly successful meetings include the European Crystallographic Meeting (ECM29) in 2015, the European Crystallography School (ECS3) in 2016 and the Hot Topics in Contemporary Crystallography meetings in 2014, 2017 and 2018.

BISERKA AND THE CSD

In a chemical crystallography career spanning five decades and dating back almost to the inception of the CSD itself, Dr Kojić-Prodić has so far contributed 439 crystal structures to the CSD (Figure 3). The crystal structures she has shared span an impressive range of chemistries from her simplest structure with only 12 atomic coordinates (the organic compound tetrabromo-semiquinone, CSD refcode TBBENQ02),[9] to her most complex including 544 atomic coordinates (a Z' = 4 structure of an adamantane bisurea salt, CSD refcode LETLUT).[10]

Some of Biserka's most high-profile structures in the CSD include those of supramolecular organic gelators based on amino acid and amino alcohol oxalamides (Figure 4) – the publications associated with these structures have each been cited over 100 times.[11,12] Other key studies include the structural analysis of interaction behaviour in calixarene amino acid derivatives[13] and the structures of palladium(II) quinolinylaminophosphonate complexes.[14] Roughly two thirds of Biserka's CSD structures are organic, the remaining third containing at least one metal atom with an increasing fraction of polymeric coordination compounds since 2009.

Experimental crystal structures can be highly precise, and they can be extremely challenging. The lowest *R*-factor structure of Dr Kojić-Prodić is a low temperature, charge density structure from 2015 of a potassium salt (*R*-factor of 1.3 %, CSD refcode UHOTAN01).[15] In contrast, the highest *R*-factor structure is that of a muramic acid derivative from 1998 which could not be easily crystallised,

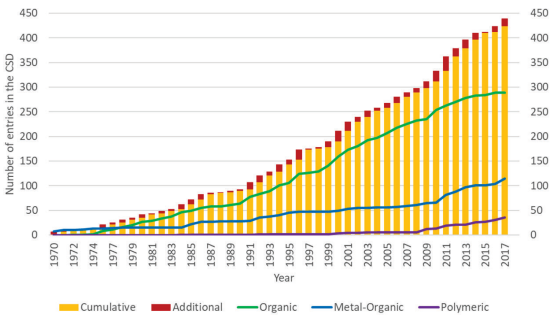

Figure 3. Chart of the number of crystal structures contributed by Dr Kojić-Prodić to the CSD over the years with breakdown into organic (green line), metal-organic (blue line) and polymeric systems (purple line).

has a Z' = 2 and only very tiny plates could be obtained (*R*-factor of 17 %, CSD refcode BEFQUY).[16] This pair of structures really capture the challenges associated with experimental crystallography and the need to obtain structures of appropriate precision for the research in question. If you want to study charge density, you need incredibly precise, high resolution data; if you are simply aiming to prove the 3D structure and conformation of the compounds studied then a different level of precision is required.

Through Biserka's 439 crystal structures, there are a wide range of space groups represented including the most common space groups in the CSD, namely $P2_1/c$, *P*-1 and *C*2/*c*, as well as some of the least common (Figure 5). There are a number of extremely rare space groups observed within these structures including *Ccc2*,[17] $P42_12$[13] and *P*31*m*[18] which have just 114, 77 and 19 examples in the CSD respectively. This again highlights the breadth of crystallography encountered by Dr Kojić-Prodić over her career.

A wide range of experimental conditions have been sampled across Biserka's CSD structures – her coolest structures were determined at just 90 K, the polymorphs of

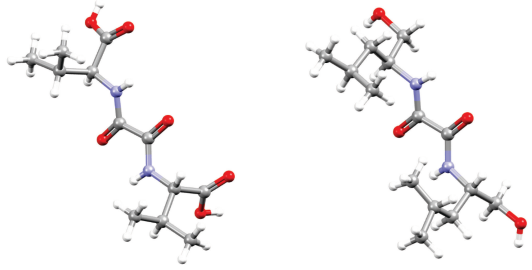

Figure 4. Molecular structures of supramolecular organic gelators by Dr Kojić-Prodić – CSD refcodes ACETAD (left)[11] and UNEGOJ (right).[12]

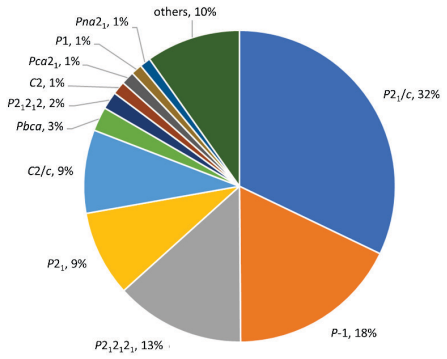

Figure 5. Pie chart of frequency of space groups observed within Dr Kojić-Prodić's CSD entries.

p-benzosemiquinone radical (CSD refcodes JEMROJ and JEMROJ02),[19] as part of a variable temperature study to assess dynamical disorder of a proton. The hottest structure was done at 340 K, the structure of di-potassium chloranilate chloranilic acid,[20] again as part of a variable temperature study to investigate proton dynamics.

Crystallography is also a very collaborative science and Biserka's career in chemical crystallography is no exception to this; she has worked with 270 different co-authors across her 439 different structures in the CSD from many different countries around the world. There isn't space here to adequately reflect all the many collaborations she has had on these structures, but the list of high-profile names includes Nobel Prize winner Jean-Marie Lehn, with whom Biserka published the structure of two cyclo-bis-intercaland receptor molecules(CSD refcodes TIVTOH and TIVTUN).[21] She has also worked with many well-known crystallographers from across the globe like Bill Duax,[22] George Sheldrick[23] and Ton Spek.[24]

It is important of course to recognise not just the big names, but also the very frequent collaborators - there are a few scientists that have shared many crystal structures in collaboration with Dr Kojić-Prodić over the years. Aleksandar Višnjevac has published 19 structures in the CSD with Biserka, Živa Ružić-Toroš has shared 35 and Krešimir Molčanov a mighty 38 structures! To paraphrase the well-known saying, "no research scientist is an island", and Biserka has shown the clear benefits of active collaboration throughout her career.

SUMMARY

The history of both chemical crystallography and the use of the CSD in Croatia is rich and Biserka's contribution has been particularly impactful. With over 400 crystal structures across a wide range of structural types, her footprint in the CSD is significant. Biserka's efforts in setting up the National Affiliated Centre and running it for over 20 years have also made an enormous difference to structural chemistry research in Croatia. There is now also a country-wide agreement for the CSD licence, so all Croatian academics can get easy access to the database. We look forward to seeing the very strong relationship between the CSD and Croatian crystallography continue well into the future.

Acknowledgements. The authors would like to thank all the many Croatian crystallographers that have contributed structures to the Cambridge Structural Database over the years. Without this sharing of fundamental structural data by the crystallographic community we wouldn't have this amazing resource to utilise for research.

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