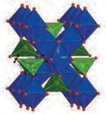
IUCr Chemistry

Selected chemistry articles from IUCr journals

Phase transition

IUCrJ (2016). **3**, 354–366
https://doi.org/10.1107/S2052252516012574

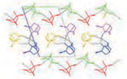


Cooperative Jahn–Teller effect and the role of strain in the tetragonal-to-cubic phase transition in $Mg_xCu_{1-x}Cr_2O_4$
S. C. Tarantino, M. Giannini, M. A. Carpenter and M. Zema

In the $Mg_xCu_{1-x}Cr_2O_4$ solid solution, progressive substitution of the Jahn–Teller and d^9 Cu^{2+} cation with the spherical and closed-shell Mg^{2+} cation results in a gradual reduction of the splitting of *a* and *c* unit-cell parameters, until transformation occurs from the tetragonal $I4_1/amd$ to the cubic $Fd\bar{3}m$ archetype spinel structure.

Packing principles

Acta Cryst. (2016). **B72**, 807–821
https://doi.org/10.1107/S2052520616017297



High-*Z'* structures of organic molecules: their diversity and organizing principles
C. P. Brock

An in-depth investigation of the $Z' > 4$ structures of organic molecules archived in the Cambridge Structural Database has shown that the group is very diverse but that most structures are the result of a simple modulation and/or of a hydrogen-bonded aggregate that has at most approximate symmetry.

Charge transfer

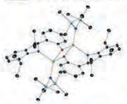
Acta Cryst. (2016). **C72**, 923–931
https://doi.org/10.1107/S2053229616016387

Synthesis and structures of 11,11,12,12-tetracyano-2,6-diiodo-9,10-anthraquinodimethane and its 2:1 cocrystals with anthracene, pyrene and tetrathiafulvalene
Y. Ren, S. Lee, J. Bertke, D. L. Gray and J. S. Moore

In the structures of 11,11,12,12-tetracyano-2,6-diiodo-9,10-anthraquinodimethane (DITCAQ) and its 2:1 cocrystals with tetrathiafulvalene, pyrene, and anthracene, the saddle-shaped DITCAQ molecule gradually transforms into a less bent geometry as the charge-transfer interactions between DITCAQ and the electron donors strengthens.

Solvent effects

Acta Cryst. (2016). **C72**, 990–996
https://doi.org/10.1107/S2053229616018593



Solvent dependence of the solid-state structures of salicylaldiminate magnesium amide complexes
J. A. Rood, A. M. Landis, D. R. Forster, T. Goldkamp and A. G. Oliver

Two new salicylaldiminate-magnesium complexes have been synthesized and structurally characterized. This study has shown that these specific systems are prone to ligand redistribution in solution and that the isolation of heteroleptic salicylaldiminate-magnesium amides is solvent dependent.

In situ crystallization

Acta Cryst. (2016). **C72**, 753–757
https://doi.org/10.1107/S2053229616015047

Acetic anhydride at 100 K: the first crystal structure determination
R. W. Seidel, R. Goddard, N. Nöthling and C. W. Lehmann

Acetic anhydride is a widely used acetylation reagent in organic synthesis. The crystal and molecular structure, as determined by single-crystal X-ray analysis at 100 K, is reported for the first time. The molecule adopts an exact C_2-symmetric conformation about a crystallographic twofold axis.

Instrumentation and computer programs

J. Synchrotron Rad. (2016). **23**, 1264–1271
https://doi.org/10.1107/S1600577516012443

***CTM4DOC*: electronic structure analysis from X-ray spectroscopy**
M. U. Delgado-Jaime, K. Zhang, J. Vura-Weis and F. M. F. de Groot

CTM4DOC, a new graphical user interface for electronic structure calculations in X-ray spectroscopy, is introduced and examples in transition metal complexes are described.

J. Synchrotron Rad. (2016). **23**, 1409–1423
https://doi.org/10.1107/S1600577516012625

A multi-MHz single-shot data acquisition scheme with high dynamic range: pump-probe X-ray experiments at synchrotrons
A. Britz *et al.*

A time-resolved X-ray absorption spectroscopy setup has been developed and tested, comprising a synchronized MHz fiber amplifier laser system with a multi-MHz data acquisition scheme capable of detecting multi-photon events in a single X-ray photon pulse. This system permits recording time-resolved X-ray absorption spectra with quasi-static signal quality.

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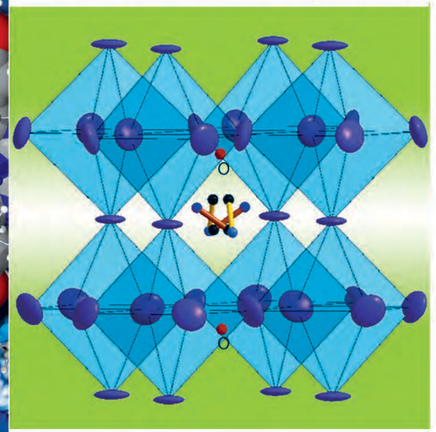
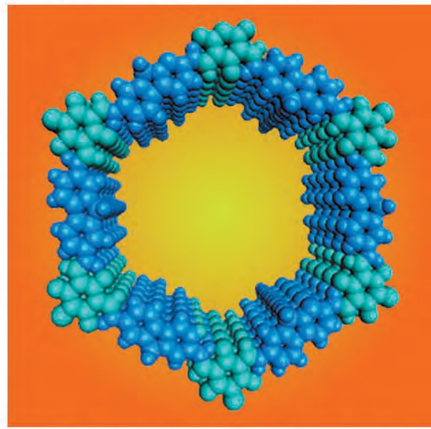
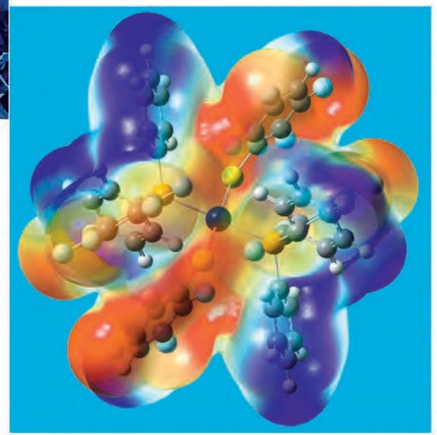
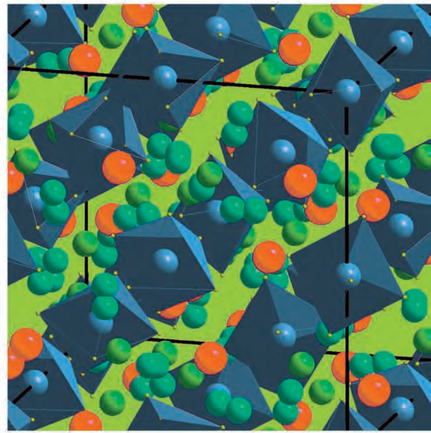
Innovation with Integrity

Crystallography









journals.iucr.org

X-ray crystallography provides accurate information about the molecular structure and conformation, bond distances and resonance, hydrogen bonding and intermolecular interactions, π-stacking, and salt-cocrystal continuum. The crystal structures are in turn related to properties such as solubility, dissolution, solvation, drug-like behaviour, isostructurality and polymorphism. Methods to obtain crystal structures of liquids and those compounds that do not crystallize easily as well as NMR and computations to complement crystallography are covered in the chemistry journals of the IUCr.

– Ashwini Nangia

Pharmaceuticals and natural products

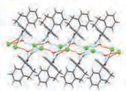
Acta Cryst. (2016). **B72**, 20–28
https://doi.org/10.1107/S2052520615018582

Salt screening and characterization of ciprofloxacin

G. Zhang, L. Zhang, D. Yang, N. Zhang, L. He, G. Du and Y. Lu

This paper presents a study of the structures and physicochemical properties of ciprofloxacin's novel salts.

Acta Cryst. (2016). **C72**, 155–160
https://doi.org/10.1107/S2053229616001133



Salt forms of the pharmaceutical amide dihydrocarbamazepine

A. R. Buist and A. R. Kennedy

Although organic amides are often thought of as being nonbasic and hence non-ionizable, it is possible to protonate them using strong acids and to isolate their salt forms in the solid. We present here the structures of three salt forms of the pharmaceutically relevant amide dihydrocarbamazepine and compare their molecular and supramolecular structures with those of dihydrocarbamazepine and carbamazepine analogues.

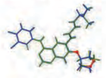
Acta Cryst. (2016). **E72**, 1628–1632
https://doi.org/10.1107/S2056989016016789

Crystal structure and Hirshfeld surface analysis of 1-carboxy-2-(3,4-dihydroxyphenyl)ethan-1-aminium chloride 2-ammonio-3-(3,4-dihydroxyphenyl)propanoate: a new polymorph of L-dopa HCl and isotypic with its bromide counterpart

P. Kathiravan, T. Balakrishnan, P. Venkatesan, K. Ramamurthi, M. J. Percino and S. Thamotharan

L-Dopa is a precursor for neurotransmitter molecules and is used in the treatment of Parkinson's disease. For the L-dopa HCl salt, a second polymorph is now reported, which crystallizes in the monoclinic space group *I*2.

Acta Cryst. (2017). **E73**, 417–422
https://doi.org/10.1107/S2056989017002626



A new solvate of afatinib, a specific inhibitor of the ErbB family of tyrosine kinases

M. Zeller, G. L. B. de Araujo, T. Parker, A. Singh Rai and S. R. Byrn

Two afatinib molecules are found in the asymmetric unit, along with other species. The API molecules are related across a pseudo centre of symmetry but this is broken down by the location of the oxygen atom and CH_2 moieties in the outer tetrahydrofuranyl substituent.

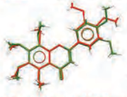
Acta Cryst. (2016). **E72**, 1714–1717
https://doi.org/10.1107/S2056989016017321

Crystal structure of a 2:1 piroxicam–gentisic acid co-crystal featuring neutral and zwitterionic piroxicam molecules

E. M. Horstman, J. A. Bertke, T. J. Woods and P. J. A. Kenis

Piroxicam is a non-steroidal anti-inflammatory drug classified as a BCS Class II drug due to its low aqueous solubility. Co-crystallization of an API and an FDA-approved counter-ion is a common technique employed to increase the solubility of the API. A new co-crystal of piroxicam and gentisic acid has been characterized, in which the ratio of piroxicam (one neutral molecule and one zwitterion) to gentisic acid is 2:1.

Acta Cryst. (2016). **C72**, 124–127
https://doi.org/10.1107/S2053229616000577



Nobiletin: a citrus flavonoid displaying potent physiological activity

S. Noguchi, H. Atsumi, Y. Iwao, T. Kan and S. Itai

Based on its potent physiological activities, the citrus flavonoid nobiletin has become an attractive candidate for use as a therapeutic agent. The crystal structure analysis revealed it to be conformationally chiral because of the conformational arrangement of the four methoxy groups bound to the chromene ring of the flavone moiety.

Powder diffraction

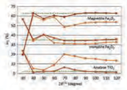
Acta Cryst. (2016). **E72**, 1159–1162
https://doi.org/10.1107/S2056989016011506

Crystal structure of anhydrous tripotassium citrate from laboratory X-ray powder diffraction data and DFT comparison

A. Rammohan and J. A. Kaduk

The complex crystal structure of anhydrous potassium citrate was solved from powder diffraction data and optimized with the aid of density functional theory to reveal the citrate tri-anion in a *trans,trans*-conformation and a three-dimensional network of edge- and corner-sharing KO_6 and KO_8 polyhedra.

J. Appl. Cryst. (2016). **49**, 1508–1516
https://doi.org/10.1107/S1600576716010451



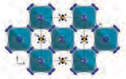
A new method for quantitative phase analysis using X-ray powder diffraction: direct derivation of weight fractions from observed integrated intensities and chemical compositions of individual phases

H. Toraya

A new method for the quantitative phase analysis of multi-component polycrystalline materials using the X-ray powder diffraction technique is proposed. The method can derive weight fractions from single-measurement integrated intensity datasets for individual phases and their chemical compositions. No standard reference material, reference intensity ratio or crystal structural parameter is required.

Inorganic and mineral chemistry

Acta Cryst. (2016). **B72**, 716–722
https://doi.org/10.1107/S2052520616010428



$CH_3NH_3PbI_3$: precise structural consequences of water absorption at ambient conditions

A. Arakcheeva, D. Chernyshov, M. Spina, L. Forró and E. Horváth

Structure, symmetry and hydrogen bonds have been determined for pristine and aged tetragonal $CH_3NH_3PbI_3$ crystals upon H_2O absorption from air at room temperature. Single-crystal X-ray diffraction data obtained on a synchrotron light source was used for the study. H_2O insertion into the structure changes hydrogen bonds and, consequently, the space group from *I*422 (pristine crystal) to $P4_22_12$ (aged crystal).

Acta Cryst. (2016). **E72**, 287–289
https://doi.org/10.1107/S2056989016001924

Symmetry reduction due to gallium substitution in the garnet $Li_{6.43(2)}Ga_{0.52(3)}La_{2.67(4)}Zr_2O_{12}$

L. Robben, E. Merzlyakova, P. Heitjans and T. M. Gesing

In recent years, 'Li-stuffed' garnets have gained considerable interest as promising electrolyte materials for all-solid-state Li-ion batteries because of an increased Li-ion mobility. Gallium-substituted lithium lanthanum zirconate is such an 'Li-stuffed' garnet, with gallium atoms found both on two lithium sites and on the lanthanum position. It shows a reduction of the symmetry to space group *I*43*d* compared with *Ia*3̄*d* typically observed for these structures.

Acta Cryst. (2015). **B71**, 619–640
https://doi.org/10.1107/S2052520615018508

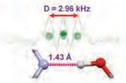
The crystal chemistry of inorganic metal borohydrides and their relation to metal oxides

R. Černý and P. Schouwink

Single- and poly-cation inorganic homoleptic metal borohydrides are discussed on the basis of their structural relationship to metal oxides.

MOFs and crystal engineering

IUCrJ (2017). **4**, 466–475
https://doi.org/10.1107/S205225251700687X

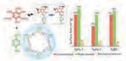


Exploring the salt–cocrystal continuum with solid-state NMR using natural-abundance samples: implications for crystal engineering

L. Rajput, M. Banik, J. R. Yarava, S. Joseph, M. K. Pandey, Y. Nishiyama and G. R. Desiraju

The salt–cocrystal continuum is a well known phenomenon in crystal engineering and has been studied here in several multicomponent solids with solid-state NMR (700 MHz) using ^{15}N–^{1}H heteronuclear dipolar coupling. The measurement is made at ultrafast (60–70 kHz) magic angle spinning (MAS) frequency. The experiment is sensitive enough to determine the proton position even in a continuum situation.

IUCrJ (2016). **3**, 402–407
https://doi.org/10.1107/S2052252516013762



Constructing covalent organic frameworks in water *via* dynamic covalent bonding

J. Thote *et al.*

The present work effectively highlights the utilization of Dynamic Covalent Chemistry (DCC) principles in conjunction with the keto-enol tautomerism to synthesize useful, stable, crystalline and porous Covalent Organic Frameworks (COFs) in water, which thereby merits over the conventional solvothermal COF synthesis protocol with its simpler and greener appeal.

IUCrJ (2016). **3**, 139–151
https://doi.org/10.1107/S2052252515024379

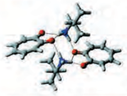
The crystalline sponge method updated

M. Hoshino, A. Khutia, H. Xing, Y. Inokuma and M. Fujita

The protocols of the crystalline sponge method, particularly those in the soaking, data collection and refinement processes, are considerably improved to give reliable structural information.

Intermolecular interactions

Acta Cryst. (2016). **C72**, 730–737
https://doi.org/10.1107/S2053229616013474

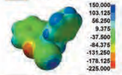


The tropolone–isobutylamine complex: a hydrogen-bonded troponoid without dominant π–π interactions

Z. N. Vealey, B. Q. Mercado and P. H. Vaccaro

The organic salt formed by transfer of a proton between tropolone and isobutylamine has been studied by crystallographic, computational, and statistical methods, revealing an extensive hydrogen-bonding network but a surprising absence of the π-mediated interactions that characterize many other troponoid-based crystals.

Acta Cryst. (2017). **C73**, 2–8
https://doi.org/10.1107/S2053229616018702



C–I...N and C–I...π halogen bonding in the structures of 1-benzyliodoimidazole derivatives

C. I. Nwachukwu, N. P. Bowling and E. Bosch

The role of halogen bonding, *i.e.* C–I...N and C–I...π, as a major intermolecular force is investigated in the crystal structures of three iodoimidazole derivatives.

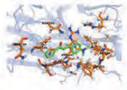
IUCrJ (2017). **4**, 411–419
https://doi.org/10.1107/S2052252517004262

Halogen bonding in hypervalent iodine and bromine derivatives: halonium salts

G. Cavallo, J. S. Murray, P. Politzer, T. Pilati, M. Ursini and G. Resnati

The presence of halogen bonds in some hypervalent iodine and bromine derivatives is demonstrated. Hypervalent atoms in polyatomic cations and anions do have σ-holes on the extensions of their covalent bonds and the cation holes are influential on the crystal lattice structures of halonium salts.

Acta Cryst. (2017). **E73**, 476–480
https://doi.org/10.1107/S2056989017003437



Crystal structure of (2*E*)-3-[4-(dimethylamino)phenyl]-1-(thiophen-2-yl)prop-2-en-1-one

G. P. de Oliveira, L. Bresolin, D. C. Flores, R. L. de Farias and A. B. de Oliveira

Chalcone derivatives show a wide range of applications, especially in medicinal chemistry. This report describes the synthesis and crystal structure of a chalcone formed during the reaction between 4-(dimethylamino)benzaldehyde and 2-acetylthiophene in basic ethanolic solution. A Hirshfeld surface analysis indicates the H...H and H...C interactions to be most important. A docking study of the compound in the active site of neuramidase shows similar H...*Cg*(thiophene) contacts as observed in the centrosymmetric dimers present in the crystal packing.

Bond-valence parameters

Acta Cryst. (2015). **B71**, 562–578
https://doi.org/10.1107/S2052520615016297

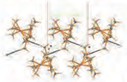
Comprehensive derivation of bond-valence parameters for ion pairs involving oxygen

O. C. Gagné and F. C. Hawthorne

Published bond-valence parameters for cation–oxygen bonds are evaluated with regard to their agreement with the valence-sum rule, and new bond-valence parameters are derived for 135 cations bonded to oxygen.

Coordination chemistry

Acta Cryst. (2016). **E72**, 1301–1304
https://doi.org/10.1107/S2056989016012822

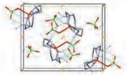


Crystal structure of bis(η^2-ethylene)(η^5-pentamethylcyclopentadienyl)cobalt

C. D. Ramful, K. N. Robertson and K. E. O. Ylijoki

The compound $[Co(C_{10}H_{15})(C_2H_4)_2]$ or $Cp^*Co(CH_2CH_2)_2$, where Cp^* is pentamethylcyclopentadienyl, is an important precursor for the generation of fragments used in C–H bond activation, cyclotrimerization of alkynes or in C–S activation. Although all atoms of the molecule are located on general positions, the complex essentially has point group symmetry *C*2*v*, in agreement with solution ^1H NMR data.

Acta Cryst. (2017). **E73**, 31–34
https://doi.org/10.1107/S2056989016019563



Crystal structure of (perchlorato-κ*O*)(1,4,7,10-tetraazacyclododecane-κ^4*N*)copper(II) perchlorate

J. L. Gray, D. L. Gerlach and E. T. Papish

$[Cu(ClO_4)(cyclen)]ClO_4[Cu(ClO_4)(cyclen)]ClO_4$ (cyclen = 1,4,7,10-tetraazacyclododecane, $C_8H_{20}N_4$), prepared without solvent molecules of crystallization, exhibits a square-pyramidal CuN_4O coordination geometry for the metal ion, with a perchlorate-O atom occupying the apical site. An N–H...O hydrogen bond from one of the cyclen NH groups reinforces the linkage between the Cu^{2+} ion and the anion.