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Recent Advances of Single-Crystal to Single-Crystal Transformation for Discrete Coordination Compounds

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REVIEW ARTICLE

Abstract | In this short review we highlight the diversity of single-crystal to single-crystal transformations that has been discovered in the last few years in the field of coordination cluster chemistry. In particular, we focus on phase transformations which involve a chemical change such as bond formation, oxidation–reduction, electron-transfer, and ligand exchange, which will, for example, cause spin-crossover or switch nonlinear optical activity. We first deal with crystals without guests followed by those losing guest or exchange ligands during the transformations and discuss how guests are involved before focusing on the rare occurrence of chemical reactions that take place on molecular components within crystalline solids without destroying the long-range crystalline state. Finally, a perspective following these advances made in the field is developed.

1 Introduction

The renaissance of inorganic chemistry of the Fifties was principally concerned with the coordination of ligands around one metal centre followed by development of an understanding of their bonding and electronic properties, and that of the Nineties goes beyond one metal centre to extended clusters and polymeric materials.[1] The latter, known as coordination polymers (CP) or metal–organic frameworks (MOF), have brought about several new aspects in the field of coordination chemistry attracting both academic and industrial interests.[2] Importantly, the acquired information allowed for the design of these materials to be developed with the introduction of desired functionalities such as gas storage, catalysis, separation, magnetism, optical properties and also both electron and proton conductions made possible.[3, 4]

Consequently, this vast area of research has progressed very rapidly and in doing so several novel branches of inorganic chemistry have evolved. One is the unusual occurrence of phase transformation from one single crystal to another during a physical or chemical event which is now classified under the heading single-crystal to single-crystal (SC–SC) transformation. Several reviews have dealt with this subject in great details, but they are focused on infinite extended frameworks[5–12] and discrete cage coordination compounds with occluded guests,[13, 14] as well as a review which concentrates on solid-state reactions between or within crystals involving compounds that can be activated mechanically.[15] the strong connectivity through a combination of covalent and dative bonds within the infinite frameworks help to retained the crystalline and most importantly, their porous character that provides the space for the reactants to get to the reaction sites. For the case of the non-porous discrete coordination compounds, guests could be transport via rearrangement of the molecular, or expansion of the entire solid, attributed to the dynamic van der Waals cooperativity.

Since we have experienced such transformations in our research work on finite sized coordination clusters it prompted us to do a survey on related examples.[16] In this context we mainly concentrate on discrete coordination compounds without occluded guests involving chemical changes during SC–SC transformations, for example: solvent ordering, removal of solvent, replacement of solvent, agglomeration in the solid state, and reactions on the ligands or at the metal sites, as a function of time, temperature and/or pressure.

Single-crystal to single-crystal (SC-SC) transformation: Crystalline state phase transitions that involve significant changes in structure without appreciable loss of crystal mosaicity.

Discrete coordination compound: A compound is a substance packing by discrete units in which metal atom or ion is associated with a group of neutral molecules or anions ligands. Moreover, the discrete units connect with each other via supramolecular interaction.

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Our aim is to first familiarise the readers to this specialised field of research with some examples developing a general view of the diversity of phase transformations that one can encounter as well as introducing methods for their characterisations. The information that can be derived will be important in progressing an understanding of the chemical reaction processes for both chemists and material scientists. On one hand correlation between the original and final structures provides information for one to choose effective strategies in developing novel materials as well as their syntheses. On the other hand, crystallographers and researchers working on soft matter are interested in the short- and long-range ordering during the SC–SC transformation processes. Therefore, we collected these examples in this review and show their relevance in the field of coordination chemistry involving SC–SC transformation from discrete coordination compounds (Fig. 1). There are four possible types of content within crystal structures of discrete coordination compounds; those that contain (I) only neutral molecules, (II) neutral molecules and guests, (III) charged molecules and counter-ions, and (IV) charged molecules, counter-ions and guests. The constituents are held by supramolecular interactions and often packed effectively and invariably lead to non-porous solids. We have to point out that more often than not it is the optical appearances, colour and shape, that have led the researchers to look further at characterising these kinds of phase transformations. Based on experience, we also argue that the SC–SC transformation can only retain the crystallinity if the transformation is progressive and slow that allow for annealing of the lattice. If this is absent the long-range order is destroyed.

In the following we introduce those involving discrete coordination compounds and discuss the relationship between changes of crystalline lattices and guests. In this review, selected examples have been discussed. We distinguish four types of SC–SC transformation involving discrete coordination compounds; the first is guest-independent, the second one is guest removal, the third one is ligand exchange, and the fourth is transformation by redox reaction. The first one is energetically easier to proceed requiring only rearrangement of some atoms within the crystal lattice. In contrast for the second and third types the lattice has to adjust to accommodate the space for departing guests and ligands or the incoming ones. The fourth type does not only require rearrangement of the atoms, but also digest the heat released from the redox reaction.

2 Guest Independent Transformation

In this section we deal with the transformation where no guests are involved in the crystal lattices. The transformation process modifies the lattices slightly, while always retaining the same space group. We look at examples where the coordination numbers and stereochemistry changes followed by those exhibiting charge transfer.

2.1 Change of Coordination Number

Sun et al. observed that by either heating to 176 °C for 15 min or ball milling at room temperature the blue crystals of the mononuclear Cu(II) complex, $[Cu(NH_3)_3(pmbsdb)]\cdot(H_2O)_{0.66}$, pmbsdb = 2,2′-(1,2-phenylenebis(methylene)) bis(sulfanediyl) dibenzoate, their colour changes to green, while retaining the same space group R-3 (Fig. 2).[17] Crystallography reveals that one of the two terminal carboxylate groups of the flexible ligand adopts an anti-mode of coordination with Cu–O distance of 1.968 Å, while the other is free. This means the metal complex is a Zwitterion with a positively charged head at the Cu end and a negatively charged tail at the free carboxylate end. The coordination geometry of the copper ion is square-planar with one O atom from carboxylate and three N atoms from ammonia. In the crystal structure, pairs of monomers are packed head-to-tail and the distance from the copper centre in one monomer to the O atom of its nearest neighbour is 3.796 Å. After transformation the uncoordinated carboxylate group coordinates to its neighbour's copper ion causing a dimerization of monomers. The coordination number of each copper increases from 4 to 5, and the Cu···O distance decreases from a supramolecular non-bonded 3.796 Å to a bonded 2.031 Å while the Cu···Cu distance decreases from 10.37 to 10.28 Å. This dimerization removes the charge
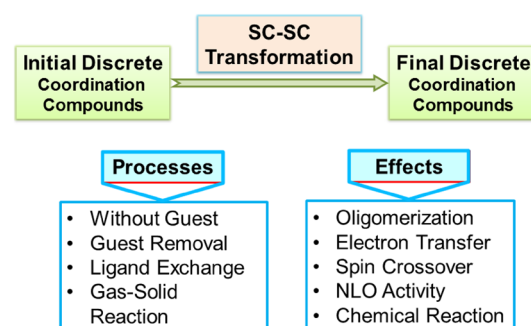
Figure 1: General processes and effects on the physical properties during single-crystal to single-crystal transformation in discrete coordination compounds
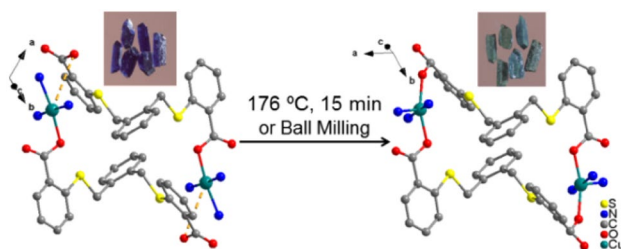
Figure 2: Transformation from supramolecular interacted pairs to dative bonded pairs involving change of coordination number from 4 to 5

imbalance and it is not a Zwitterion anymore. The colour change is associated to the different crystal fields. It is highly probable that this successful transformation relies on the unsaturated coordination of copper ion and the short distance of copper and oxygen atom in the lattice.

2.2 Change of Stereochemistry

Since silver compounds are very reactive to light it is usually required that they are kept in the dark and this is the reason for their application in photographic plates where they decompose to give nanoparticles of silver metal. On rare occasion they can be transformed without destruction to the metal. Avdeeva et al. found a complex that change from colourless to light-brown upon UV irradiation using a Xe lamp for 4 h while retaining its crystallinity and space group $P2_1/c$ (Fig. 3).[18] They reported a silver-based complex, $\{Ag_2(PPh_3)_6[trans\text{-}B_{20}H_{18}]\}$, in which two cationic $[Ag(PPh_3)_3]^+$ are connected to one anionic

$[trans\text{-}B_{20}H_{18}]^{2-}$ by Ag···H-B bonds. X-ray diffraction analysis shows that the configuration of $[B_{20}H_{18}]^{2-}$ change form *trans* to *iso*, accompanying contraction of Ag···Ag distance from 13.168 to 12.298 Å. The reason for the colour change has not been revealed. The monomer $[Ag(PPh_3)]^+$ holds the confined space for stabilising the *iso* configuration of $[B_{20}H_{18}]^{2-}$. The authors also mentioned that after all non-hydrogen atoms were refined, a high residual electron density was still observed in the region of the boron cage. This could be explained, as the authors mentioned, either an incomplete SC–SC reaction or disorder of the macropolyhedral borane.

In contrast to the above examples Vittal et al. reported the phase transformation without change of colour which is concerned with a mononuclear Zn(II) complex, $[ZnBr_2(4spy)_2]$, 4spy = *trans*-4-styrylpyridine (Fig. 4).[19] The distance between the double bonds in the nearest neighbour monomers is 3.71-3.73 Å. Because of the close proximity of the C=C bonds of neighbouring pairs they successfully incite a [2 + 2] cycloaddition reaction from the monomers to dimers in a SC–SC manner by irradiating the compound with UV light.
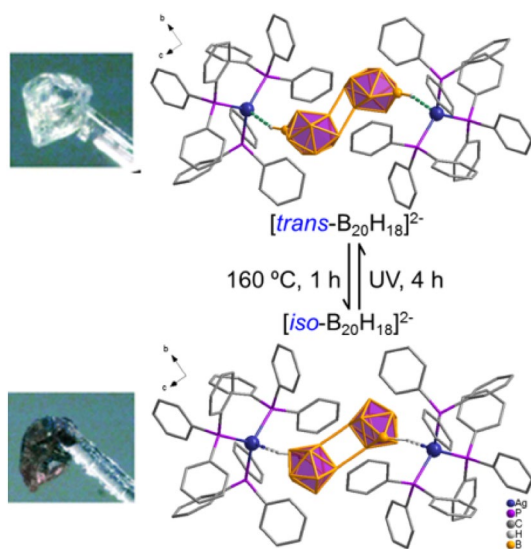
Figure 3: Transformation from $[trans\text{-}B_{20}H_{18}]^{2-}$ to $[iso\text{-}B_{20}H_{18}]^{2-}$ in the silver borane adducts
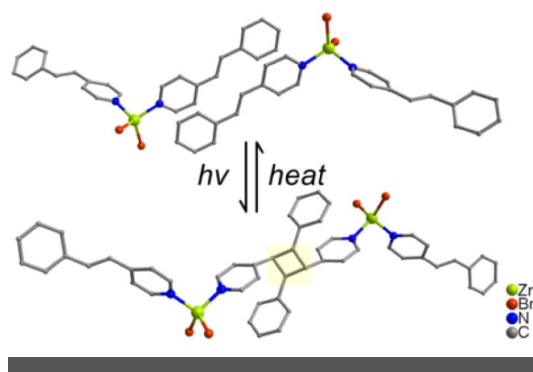
Figure 4: [2 + 2] cycloaddition reaction between two ligands on a zinc monomer complex during SC–SC transformation

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Both the initial and final phases crystallise in the same space group $P2_1/n$. Furthermore, the cyclobutane ring in the dimer could be cleaved reversibly to the *trans*-olefins by heating at ~238 °C. The light-driven cycloaddition reaction leads to the molecules mobility within the lattice as seen by a reduction of the Zn···Zn distance from 13.86 to 13.79 Å.

2.3 Transfer of Charge

Chorazy et al. reported a pentadecanuclear cyano-bridged $\{Fe_9[W(CN)_8]_6(MeOH)_{24}\}\cdot xMeOH$ cluster with a double $Fe^{II/III}$-$W^{IV/V}$ mixed valence nature.[20] Differential scanning calorimetry located a phase transition at 210 K having a small hysteresis. This was accompanied by a very subtle change of the interplanar distance and a very small anomaly in the magnetic susceptibility for it to be associated with a proper SCO transition of the Fe^{II} or Fe^{III}. Mössbauer spectroscopy confirms that the bimetallic compound undergoes a rare concerted double charge transfer (CT) phase transition from $^{HS}Fe_7^{II HS}Fe_2^{III}W_2^{IV}W_4^{V}$ high temperature to $^{HS}Fe_3^{II HS}Fe_6^{III}W_6^{IV}$ low temperature. The challenge in this kind of transformation is that it is difficult to determine the fraction of ions undergoing intervalence charge transfer. In the present case Mössbauer spectroscopy provided one solution, but complementary characterizations are always welcomed.

3 Molecule-Controlled Transformation

In this section we deal with the transformation where guests are involved in the crystal lattice. First we focus on examples where guests were removed and then followed by exchange of ligands, accompanied by a discussion of their changes of optical and magnetic properties, as well as structure–property correlations.

3.1 Guest Removal

There are numerous example of desolvation of solids in the literature where the solvent molecules are derived from those in the lattice or from those coordinated or both. It is sometime difficult to stop the desolvation partially at one stage and this leads to difficulty in producing SC–SC transformation. When these chemical changes are made on cobalt compounds dramatic changes of colour can be observed, for example, from pink when the cobalt is a regular six-coordinated centre to blue for tetrahedral ones or dark purple for five-coordinated ones. In the rare case, Mobin and Mohammad have reported two monomeric cationic cobalt(II) complexes, $[Co^{II}(hep-H)(H_2O)_4]SO_4$ and $[Co^{II}(hep-H)(H_2O)_2](NO_3)_2$ (hep-H = 2-(2-hydroxyethyl)pyridine) where the removal of coordinated water induces coordination of the counter-anions (Fig. 5).[21] The colour change in this case was more subtle where the former changes from orange to pink by heating at 120 °C for 1 h as the cobalt centre retains six-coordination.

By analysing the single-crystal diffraction data of the former, two coordinated water molecules were removed from each monomer and the vacant positions were taken by two SO_4^{2-} which bridge a pair of cobalt monomers head-to-head forming a square. This dimerization introduces a glide plane and the space group changes from being chiral $P2_1$ to achiral $P2_1/n$. In the structure of $[Co^{II}(hep-H)_2(H_2O)_2](NO_3)_2$, the Co displays six-coordination with two chelating hep-H occupied four equatorial positions and two water molecules occupied axial positions. After keeping the crystals at 110 °C for 1 h, the space group changes from triclinic P-1 to orthorhombic $Pbcn$. The two water molecules have been removed, and the two vacant axial positions were coordinated by one O atom for a chelating hep-H and one O atom
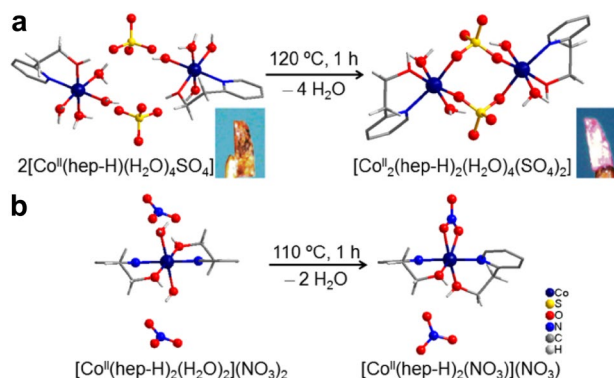
Figure 5: Dehydration induces counter-anion coordination: **a** Monomer to dimer SC–SC transformation; **b** uncoordinated nitrate ion to coordination by replacing water and *trans–cis* reversal

302

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J. Indian Inst. Sci.|VOL 97:2|299–309 June 2017|journal.iisc.ernet.in

from NO_3^- ion. The four equatorial positions are occupied by one N atom and one O atom from a chelating hep-H ligand, one N from another hep-H and one O atom from NO_3. Importantly, there has been a change of stereochemistry from the two hep-H moving from *trans*- to *cis*-positions. This will suggest a tetrahedral intermediate for Co(hep-H)$_2$. In these two examples, the synergistic effect of water removal and anion coordination drives a dramatic mobility of the molecules in the lattice while introducing several symmetry elements resulting into the change of space group.

Using a similar approach, but this time with Cu(II), Mobin et al. reported two more examples using the same ligand which undergo SC–SC transformation by dehydration of two discrete hydrated dimeric copper complexes, [(OAc)Cu(μ-hep)$_2$Cu(OAc)]·2H$_2$O and [(OAc) Cu(μ-hep)$_2$Cu(O^{n}Pr)]·2H$_2$O (OAc = acetate and O^{n}Pr = n-propionate).[22] After dehydration of the former, X-ray analyses reveal the structures possess the same *P*-1 space group, but the volume of the unit cell decreased by 16% from 593 to 496 Å^3, consistent with the loss of two lattice water molecules per unit formula. A similar decrease of 11% from 1143 to 1017 Å^3 of the unit cell volume is also observed for the later.

In another case, the colour change from navy blue to cyan is responsible for Mobin et al. to study the transformation of the dimeric copper complex, [Cu(μ_2-hep)(TFA)(H$_2$O)]$_2$ (TFA = trifluoroacetic acid) to the tetrameric complex, [Cu$_4$(μ_3-hep)$_2$(μ_2-hep)$_2$(μ_2-TFA)$_2$(μ_2-TFA)$_2$] (Fig. 6).[23] Surprisingly, the coordinated water molecule is removed by exposure to methanol vapour. During the SC–SC transformation, four new coordination bonds were formed, two Cu–O(μ_2-hep) and Cu–O(μ_2-TFA), leading to a butterfly arrangement of the copper atoms in the tetramer.

While removal of neutral molecules from a solid is quite common, the departure of an amine through the decomposition of a charged ammonium counter-anion to a bare proton is quite unusual. Our group found such a case for a cobalt-based complex with a multifaceted cage, NHEt$_3$[Co$_6$(phendc)$_6$⊃Cl]·MeOH·3H$_2$O (phendc = 1,10-phenanthroline-2,9-dicarboxylate), which crystallised in trigonal space group *R*-3.[24] Thermogravimetric analysis was found to exhibit a weight loss of 8.6% weight from 25 to 120 °C, corresponding to the loss of three H$_2$O, one methanol and one Et$_3$N (Fig. 7). The latter was confirmed using pyrolysis–gas chromatography-mass spectrometry (Py-GC/MS) method. When crystals of the complex are heated from 25 to 130 °C at a rate of 10 °C/min and kept at 130 °C for 15 min, their crystallinity are surprisingly retained. X-ray analyses reveal the same space group as the solvated crystal, and the volume of the unit cell decreased by 10.6% from 6698.8 to 5991.6 Å^3, as a compression of mainly along the unique *c*-axis. Since these changes do not affect the internal structure of the clusters the magnetic properties are unchanged.

Lanthanide ions are sensitive to their coordination environments which vary their optical properties and magnetic anisotropy. Here we introduce a chiral lanthanide based compound undergoing reversible SC–SC transformation. Liu et al. reported a monomeric dysprosium(III) compound, [Dy(bpb)$_2$(acac)$_2$]·MeOH·3H$_2$O, bpb = (−)-4,5-bis(pinene)-2,2′-bipyridine, acac = acetylacetonate, which crystallised in a chiral polar space group *P*2$_1$ due to the chirality of the single enantiomer of the ligand used as the starting material which exhibits second-order non-linear-optical (NLO) activity.[25] Single-crystal analysis reveals that the structure of the monomer is transformed to [Dy(bpb)$_2$(acac)$_2$]·H$_2$O, by either heating the crystals at 373 K or pumping at 2 × 10^6 Pa at 291 K (Fig. 8). During the transformation, methanol and part of the water were removed, while the space group changes to a chiral nonpolar *C*222$_1$, exhibiting no NLO properties. The structure could be changed reversibly by exposure of the crystals to methanol vapour. The
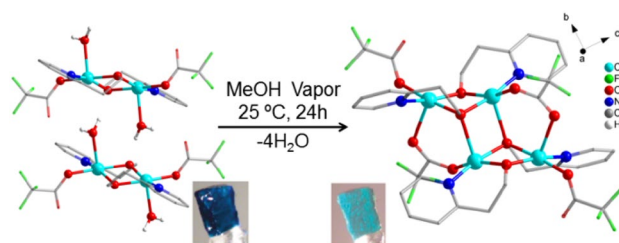
Figure 6: Dimer to tetramer SC–SC transformation
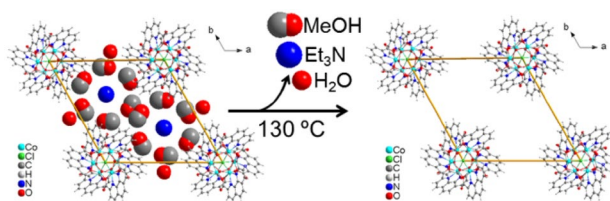
Figure 7: Removal of guests and decomposition of charged ammonium during SC–SC transformation
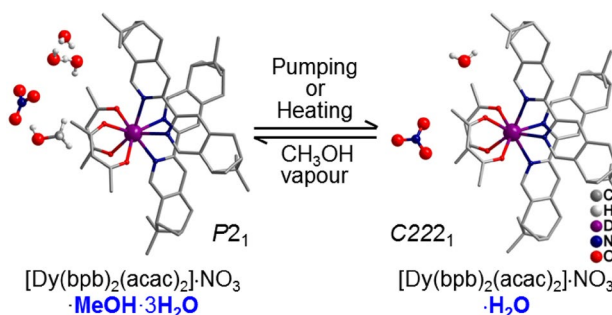
Figure 8: Guest removal induced SC–SC transformation changing space group from polar to nonpolar in a Dysprosium(III) structure

SC–SC transformation not only affects the optical properties, but also magnetic properties.
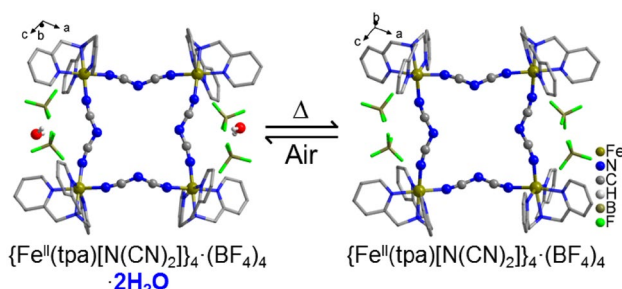
Cao et al. reported of the change of spin state of a cyano-bridged {Fe$_2$Co$_2$} complex, {[(Tp)Fe(CN)$_3$]$_2$ [Co(4,4′-bcbpy)$_2$]$_2$} (ClO$_4$)$_2$·2MeOH, Tp = hydrotris (pyrazolyl) borate, 4,4′-bcbpy = 4,4′-bis (ethoxycarbonyl)-2,2′-bipyridine).[26] Its green colour and the Co–N bond lengths (1.877 to 1.936 Å), implies that the complex is in a low-spin state with Fe^{II}(µ-CN)Co^{III} linkage. The green colour turns to red soon after exposure of the crystals to the atmosphere at room temperature to give {[(Tp) Fe(CN)$_3$]$_2$[Co(4,4′-bcbpy)$_2$]$_2$} (ClO$_4$)$_2$, with removal of two methanol per formula. The single-crystal to single-crystal transformation could be reversed by re-absorption of methanol. Its magnetic properties were studied and showed that diamagnetic and paramagnetic states switched specifically by losing and absorbing methanol at room temperature in the solid state upon reversible SC–SC transformation via charge transfer induced spin transition (CTIST). It is notable that this process is specific to methanol and not responsive to other alcohols, ammonia, other protic or aprotic solvents, as well as dilute acids and bases.

Wei et al. reported a spin-crossover (SCO) for the square tetramer Fe$_4^{II}$ compound, {Fe^{II}(tpa) [N(CN)$_2$]}$_4$ (BF$_4$)$_4$·2H$_2$O (tpa = tris(2-pyridylmethyl)amine).[27] Single-crystal diffraction analysis showed that the four Fe centres are liked by µ-N(CN)$_2^-$ groups in a square arrangement adopting an alternating Fe1-Fe2-Fe1-Fe2 geometric configuration (Fig. 9). After heating the compound to 340 K, the water molecules were removed. The magnetic susceptibility exhibits two-step spin transition from a four low-spin (LS) state below 150 K to a two low-spin and two high-spin (HS) state up to 250 K, and then to a four high-spin state up to 350 K. Reversible SC–SC transformation via desorption and resorption of guest water molecules was evidenced.

Liu et al. reported a Co(II)-Dy(III)-Co(II) complex, [Co$_2^{II}$Dy^{III}(L^{Br})$_2$(H$_2$O)]·NO$_3$·3H$_2$O (L^{Br} = 2,2′,2″-(((nitrilotris(ethane-2,1-diyl)) tris(azanediyl)) tris (methylene))tris-(4-bromophenol))), in which L^{Br} was obtained by in situ reaction of 5-bromo-salicylaldehyde and tris(2-aminoethyl)amine.[28] Its relaxation dynamics can be greatly improved by removing water in the lattice via SC–SC transformation process. The effective energy barrier can be increased from 293 cm^{-1} (422 K) to 416 cm^{-1} (600 K), and the tunnelling relaxation time can be slowed down 100-fold from 8.5 × 10^{-4} to 7.4 × 10^{-2} s.

Wu et al. reported a binuclear iron compound, [Fe$_2$(µ$_2$-btz)$_3$(btz)$_2$(NCS)$_4$]·2CH$_3$CH$_2$OH (btz = 4-benzene-1,2,4-triazole). The temperature dependence of the magnetic susceptibility of this compound suggests an incomplete spin-crossover (SCO) behaviour ($T_{1/2}$ = 122 K).[29] Interestingly, after exposure of the binuclear Fe(II) compound to water vapour,

304

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$\{Fe^{II}(tpa)[N(CN)_2]\}_4 \cdot (BF_4)_4$
$\cdot 2H_2O$

$\{Fe^{II}(tpa)[N(CN)_2]\}_4 \cdot (BF_4)_4$

Figure 9: Reversible SC–SC transformation via desorption and resorption of water molecules in a square Fe_4^{II} discrete coordination compound

SC–SC transformation process was observed by diffraction analysis, and water molecule was inserted to the crystal lattice in the formation of $[Fe_2(\mu_2\text{-btz})_3(btz)_2(NCS)_4]\cdot 2CH_3CH_2OH\cdot 1.5H_2O$, while the space group changes from chiral $P2_12_12_1$ to achiral P-1. The temperature-dependent magnetic susceptibility of the new compound reveals typical antiferromagnetic interactions.

During removal of guest from the crystal lattice, the balance of deformation and formation of interactions between molecules holds the long-range order of the crystal. To maintain the long-range order of the crystals for collection the single-crystal diffraction, gentle change of the driven-force and slow control of the progress of the transformation is essential.

3.2 Ligand Exchange

Zenkina et al. reported a single-crystal to single-crystal reaction of monomer rhodium-based organometallic compound. The rhodium dinitrogen complex, $[Rh^I(N_2)(SIPr)Cl]$ (SIPr = N,N'-(2,6-iPr$_2$C$_6$H$_3$)$_2$C$_3$H$_4$N$_2$) crystallised in space group $P2_12_12$ where the rhodium atom adopts a pseudo square-planar coordination, with two carbene SIPr ligand, one terminal chloride and one dinitrogen molecule.[30] Exposure of the rhodium dinitrogen complex to O_2 atmosphere, Rh^I singlet dioxygen complex was obtained by a SC–SC transformation, in which O_2 takes the position of the N_2, accompanied by a dramatic colour change from yellow to blue. After exposure of rhodium dioxygen complex to CO for 7 days, CO replaces the O_2 in the lattice to give the brown complex, $[Rh^I(CO)(SIPr)Cl]$ (Fig. 10a). Single-crystal structure analysis revealed that all these three crystalline complexes possess the same orthorhombic $P2_12_12$ space group, with almost identical unit cells with minor rearrangement of molecules in the lattice. This gas

position exchange upon double SC–SC transformation study is so unusual and very unique as well as being a sole example with three exchangeable ligands. The mechanism of the gas–solid exchange reactions while retaining the crystalline states in each case remains a challenging project for chemists and crystallographers.

As for the case above Supriya and Das found that the a trimeric cluster, $[Fe_3(\mu_3\text{-O})(\mu_2\text{-CH}_3\text{COO})_6(C_5H_5NO)_2(H_2O)]ClO_4\cdot 3H_2O$ can exchange the coordinated water at one of the three iron centres with methanol or pyridine whole keeping the same coordination of the other two coordinate iron centre to its 2-pyridone ligands.[31] After exposure of the single crystals to methanol vapour at room temperature for 25 h, the coordinated H_2O molecule was exchanged to methanol, generating the new compound, $[Fe_3(\mu_3\text{-O})(\mu_2\text{-CH}_3\text{COO})_6(C_5H_5NO)_2(MeOH)]ClO_4\cdot 3H_2O$, but retains the red colour and the same $Pbca$ space group (Fig. 10b). Surprisingly the water of crystallisation is not replaced. This suggests they may be strongly connected by supramolecular interactions. Yet it is also surprising that the exchange can take place in a non-porous solid without destroying the crystallinity. The coordinated methanol can be reversibly exchanged with water. The authors finally replace the water by pyridine upon exposure of the crystals to pyridine vapour.[32] In this case both the coordinated water molecule and the three lattice water molecules were exchanged to pyridine, generating the compound, $[Fe_3(\mu_3\text{-O})(\mu_2\text{-CH}_3\text{COO})_6(C_5H_5NO)_2(C_5H_5N)]ClO_4\cdot 3C_5H_5N$, but this time the colour has changed from red to green. It is notable that the authors establish a strategy to study the reversible crystal-to-crystal transformation using a combination of IR spectroscopy and PXRD, while no suitable single crystal of the green crystal was available for structure determination.
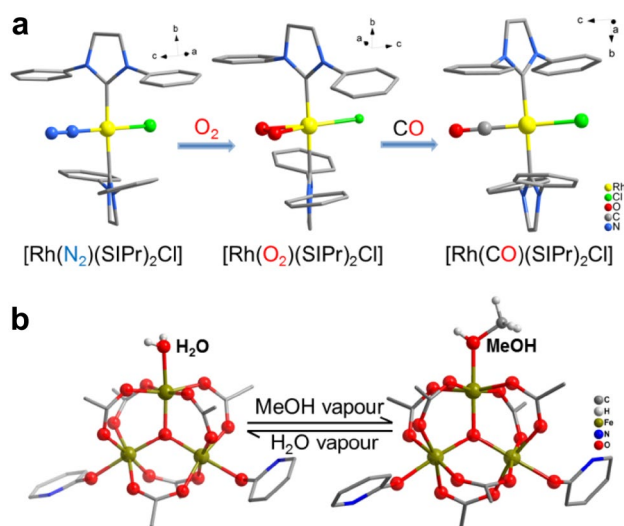
Figure 10: **a** Molecular gas exchange in the non-porous structure consisting of discrete clusters. Isopropyl groups were omitted for clarity. **b** Reversible exchange of methanol and water molecular on an iron monomer during SC–SC transformation

The suitable size of the new guest is essential during exchange during SC–SC transformation. The lattice conforms to provide the space needed for the new guests and builds on the interactions between the new guests and the lattice.
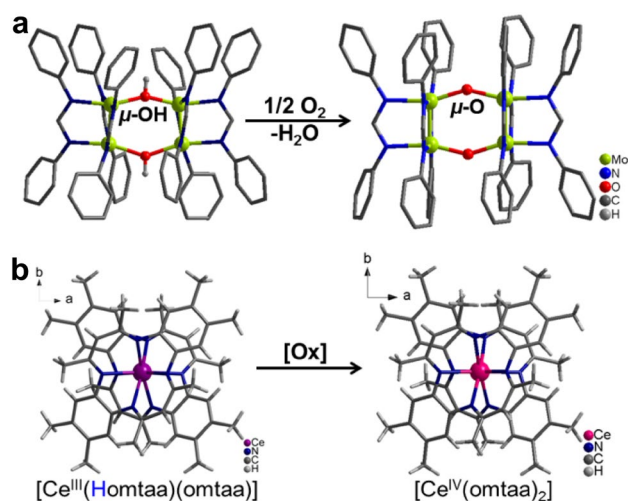
4 Transformation by Redox Reaction

In the last section, we presented examples of molecule-controlled SC–SC transformations involving breaking and forming of coordination bonds, in which the charge of the metal ion is not altered. We introduce two examples involving the partial oxidation of a tetranuclear Mo(II) cluster to its mixed-valent(II/III) states, a coupled oxidation-proton transfer for a mononuclear Ce(III) complex to its tetravalent state, and one tetranuclear Fe(II) complex to it trivalent state.

Cotton et al. reported a yellow tetramer molybdenum based complex, $[(DAniF)_3Mo_2^{II}(\mu\text{-}OH)_2Mo_2^{II}(DAniF)_3]$, (DAniF = N,N'-di-p-anisylformamidinate). The tetramer could be considered as two (μ-OH) connecting two $[Mo_2^{II}(DAniF)_3]^+$ units.[33] The yellow crystals quickly turn to green on the surface then to an unidentified orange-brown amorphous powder after exposure to air. The authors showed their problem-solving skills by coating a single-crystal with mineral or Paratone oil to slow down the reaction process. After exposure to air for a long period of 420 h, a black compound was obtained, $[(DAniF)_3Mo_2(\mu\text{-}O)_2Mo_2(DAniF)_3]$, upon deprotonation process; the (μ-OH)$_2$ linker was oxidised

to (μ-O)$_2$ by atmospheric dioxygen. During the SC–SC transformation, the Mo(II) ion changed to mixed-valent II/III, while the space group P-1 was retained. The obtained molecule could be considered as two (μ-O) connecting two $[Mo^{II}Mo^{III}(DAniF)_3]^{2+}$ unit (Fig. 11a). The authors tried to find out if there is an intermediate during the transformation. It was expected as the dimer $[Mo_2^{II}(DAniF)_3]^+$ is charged +1 and $[Mo^{II}Mo^{III}(DAniF)_3]^{2+}$ is species with one oxo and one hydroxo bridging group, and resulting in a paramagnetic state. However, the lack of EPR signals was explained by the weak accumulation of the expected intermediate in the crystal. Fortunately, the compound $[(DAniF)_3Mo_2(\mu\text{-}OH) (\mu\text{-}O)Mo_2(DAniF)_3]\cdot BF_4$ was obtained independently, which containing the proposed intermediate.

The other redox-driven SC–SC transformation was found by exposure of a red-brown Paratone-convered crystal of monomer cerium(III) coordination compound, $[Ce^{III}(Homtaa) (omtaa)]$, ($H_2$omtaa = octamethyl tetraazaannulene), to air atmosphere for a period of 24 h.[34] The colour of the crystal changed to dark green and yield the tetravalent $[Ce^{IV}(omtaa)_2]$ complex (Fig. 11b). The monoclinic space group $C2/c$ was retained during the transformation and exhibited only small change to the unit cell parameters. It is notable that the bond lengths of Ce-N become shorter from a range of 2.526–2.569 to 2.437–2.460 Å, which suggested Ce(III) was oxidised to Ce(IV). This redox-driven SC–SC transformation

306

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J. Indian Inst. Sci.|VOL 97:2|299–309 June 2017|journal.iisc.ernet.in

Figure 11: SC–SC transformation upon gas–solid redox reaction involving **a** deprotonation of μ-OH and **b** deprotonation of coordination ligand. Methoxy groups were omitted for clarity

is quite unprecedented in lanthanide coordination chemistry.

For the examples above, both contain metal ions which can be easily oxidised under ambient conditions. The oxidation of ferrous to ferric compound in air is also facile. In this context we have synthesised clear yellow crystals of an iron(II)-based discrete coordination cluster, $[Fe_4^{II}(mbm)_4Cl_4(MeOH)_4$, $(mbm$ = (1-methyl-1H-benzo[d]imidazol-2-yl) methanolate)], with distorted Fe_4O_4 cubic core in the structure.[35] On exposure of the yellow crystals to the atmosphere its colour changes gradually to opaque black over a few days, but without apparent change of crystal size and shape. After 2 days the black crystal diffracts just as well and its structure reveals a chemical reaction to a new compound, $[Fe_4^{III}(mbm)_4Cl_4(OH)_4]\cdot2H_2O$, also having the cubic core has taken place. OH^- group come from water molecule in air atmosphere. The Combination of single crystal diffraction and Mössbauer spectroscopy reveals four changes during the transformation: an exchange of methanol to hydroxide, complete oxidation of Fe(II) to Fe(III) with the expected changes in bond parameters, change of stereochemistry by rearrangement of the Cl atom and solvation by two water molecules. This is a rare observation that four chemical changes in a non-porous molecular solid in air upon SC–SC transformation have been recorded.

5 Summary and Perspective

In summary, the results discussed herein demonstrated that SC–SC transformation occurring in crystals containing discrete coordination clusters

is rather limited. This is often caused by the loss of crystallinity. We have argued that retention of the crystallinity is possible if the transformation is progressive and slow. During the transformation, the challenge is to have the changes and rearrangement of supramolecular interactions to auto-repair the crystallinity. The strategy for slowing down the transformation process is sometimes beneficial to give enough time for repairing the long-range order. However, in many case it is not possible. So even though SC–SC transformation is becoming a common occurrence with the advances made in porous coordination polymers, it is still in its infancy for crystals that are made up of molecules of small coordination clusters.

A single-crystal of a discrete coordination compound can be transformed to various structures by controlled adjustment of the synergistic balance between the strength of the coordination bond within the clusters and the supramolecular interactions between them. The investigating procedures to reveal the underlying reasons for this kind of SC–SC transformations will turn the challenge to an opportunity for us to study the transformation progress for post-modification and functionalization of the discrete clusters using gas–solid reactions or exchange of the metal ion. The studies of SC–SC transformation of discrete compounds may open a subclass of crystal engineering in inorganic chemistry.

307

J. Indian Inst. Sci. |VOL 97:2|299–309 June 2017|journal.iisc.ernet.in

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308

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309

J. Indian Inst. Sci. |VOL 97:2|299–309 June 2017|journal.iisc.ernet.in   Springer   IISc Press