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Reversible single-crystal-to-single-crystal photoisomerization of a silver(I) macropolyhedral borane

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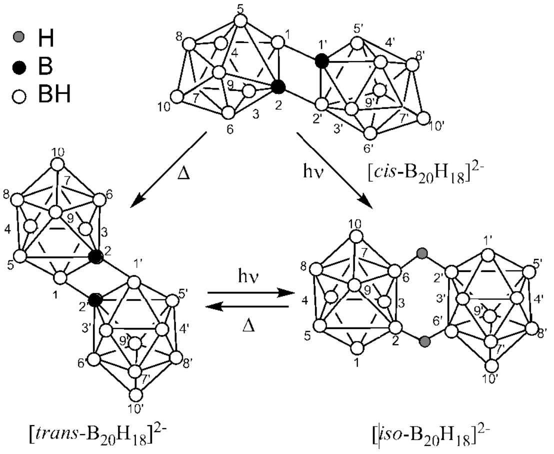
We report a new family of photoactive molecular compounds for which reversible solid state transformations and linkage isomerism have been observed using *in situ* X-ray diffraction. Interaction of tris(triphenylphosphine)silver(I) with eicosaborate $[B_{20}H_{18}]^{2-}$ afforded a binuclear complex with a bridging boron cluster that underwent a series of isomerization transformations occurring in a single-crystal-to-single-crystal manner without crystal degradation and obeying the criteria for an effective molecular switch.

Introduction

Solid state linkage isomerism under variation of external conditions (temperature, pressure, UV radiation or magnetic field) has been used over the last two decades for investigation of metastable and short-lived species[1] and reaction intermediates.[2] Reversible photo- and thermally-controlled isomerization of metal complexes to long-lived metastable isomers can be used in optical switches and data storage devices;[1a,3] however, a further progress in this field requires new solids that exhibit high level of conversion at room temperatures while maintaining the reversibility of the transition. Up to date, some metal complexes with small inorganic ligands (SO_2, N_2, NO and others) have been found to produce long-lived metastable switches, but no metal complexes with polyhedral boranes are known to undergo isomerization reactions in the solid.

The octadecahydro-eicosaborate dianion $[B_{20}H_{18}]^{2-}$ undergoes in solutions a series of transformations (scheme 1),[4] both reversible and irreversible. A reversible 100% conversion of its *trans*-isomer to $[\textit{iso}\text{-}B_{20}H_{18}]^{2-}$, which is stable up to 100°C was selected as the target reaction to produce an effective molecular switch. We expected a crystallization of the borane with a d^{10} metal complex to not prevent it from isomerization due to highly polar nature of B–H…M and B...M bonding.[5] Both stable and metastable complexes may also exhibit linkage isomerism upon heating, as the cation migration under the surface of a polyhedral borane has relatively low energy barrier.[6] Nevertheless, neither coordination chemistry of macropolyhedral boranes nor solid state linkage isomerism of widely used *closo*-borates ($[B_6H_6]^{2-}$, $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$) have been studied before. We have chosen $[B_{20}H_{18}]^{2-}$ and a bulky $[(PPh_3)_3Ag]^+$ counter ion to prevent crystal degradation and to perform the desired reaction as a single-crystal-to-single-crystal (SCSC) process with high photoconversion. Note that recent efforts in photocrystallography aiming to produce a large 'reaction cavity' within which photoisomerization may proceed allowed obtaining reversible systems with conversion up to 100%.[7]



Scheme 1. Schematic representation of eicosaborate $[B_{20}H_{18}]^{2-}$ isomers.

Experimental

General Procedures

Infrared spectra were recorded on an InfraLum FT-02 FT-IR spectrometer (Lumex, St.-Petersburg, Russia) in the range 600—4000 cm^{-1} (Nujol, NaCl pellets). The elemental analysis was carried out on an EA1108 automatic CHN analyzer (Carlo Erba Instruments). Determination of boron and silver by ICP MS was performed on iCAP 6300 Duo ICP emission spectrometer with inductively coupled plasma. Powder patterns were measured on a Bruker D8 Advance Vario diffractometer at RT with LynxEye detector and Ge (111) monochromator, λ(CuKα$_1$) = 1.54060 Å, θ/2θ scan from 4° to 65°, stepsize 0.0191°. The calorimetric studies were performed on a DSC Mettler-822e calorimeter. The heating and cooling rates were both equal to 10K/min under argon atmosphere in the temperature range 150 – 420 K.

Synthetic procedure

All organic solvents and liquid organic reagents used for preparation of the initial reagents and products were purified and dried according to the standard procedures. $AgNO_3$ and PPh_3 were purchased from Aldrich. $(HN\mathit{Et}_3)_2[B_{10}H_{10}]$ was synthesized from decaborane-14 as described in ref.[8]. $[Ag(PPh_3)_3NO_3]$ was prepared from $AgNO_3$ and PPh_3 according to the known procedure.[9] $(HN\mathit{Et}_3)_2[\mathit{trans}\text{-}B_{20}H_{18}]$ was prepared by oxidative coupling of $(HN\mathit{Et}_3)_2[B_{10}H_{10}]$ proceeding in aqueous solution using $FeCl_3$ as an oxidizer as described in ref. [4a].

(μ^2-*trans*-octadecahydro-eicosaborato)-hexakis(triphenylphosphine)-disilver(I) $\{Ag_2(PPh_3)_6[\mathit{trans}\text{-}B_{20}H_{18}]\}$ (**1**) A light-yellow solution of $(HN\mathit{Et}_3)_2[B_{20}H_{18}]$ (0.1 mol) in DMF (5 ml) was added to a solution of $[Ag(PPh_3)_3NO_3]$ (0.2 mmol) in DMF (5 ml). From the resulting light-yellow reaction solution, colorless crystals **1** were precipitated after 24 h. $Ag_2C_{108}H_{108}P_6B_{20}$ (**1**): yield: 85 %. *Anal. calcd.* C 64.09, H 5.38, Ag 10.66, B 10.68; *found* C 63.87; H 5.21; Ag 10.52; B 10.50. FTIR (NaCl) ν/cm^{-1}: 2521, 2507, 2486 (ν(BH), 2410 (ν(BH)$_{BHAg}$), 1585-700 (a number of bands corresponding to coordinated PPh_3 molecules).

(μ^2-*iso*-octadecahydro-eicosaborato)-hexakis(triphenylphosphine)-disilver(I) $\{Ag_2(PPh_3)_6[\mathit{iso}\text{-}B_{20}H_{18}]\}$ (**2**). The single crystal of **1** was irradiated over 4 hours with Xe laser. Yield recovered from X-ray data was 100 %. FTIR (NaCl) ν/cm^{-1}: 2544, 2534, 2495 (ν(BH)), 2350 (ν(BH)$_{BHAg}$), 1778, weak (ν(BH)$_{bridge}$; corresponds to two bridged BHB groups between the two 10-vertex boron cages), 1585-700 (the same bands corresponding to coordinated PPh_3 molecules).

Crystallography

A colorless single crystal of $\{Ag_2(PPh_3)_6[B_{20}H_{18}]\}$ was obtained from reaction mixture. The intensities of reflections were measured with a Bruker Apex II CCD diffractometer using graphite monochromated MoK$_\alpha$ radiation (λ = 0.71073 Å) at 120 K. The structure was solved by the direct method and refined by full-matrix least squares against F^2. Non-hydrogen atoms were refined anisotropically. *Trans* configuration and ordered atomic positions of non-hydrogen atoms of the $[B_{20}H_{18}]^{2-}$ anion were confirmed.† The positions of all H(C) and H(B) atoms (with an exception of H10A) were calculated, and the H(C) and H(B) atoms were included in the refinement by the riding model with U_{iso}(H) = 1.2U_{eq}(X). The H10A is involved in B10 – H10...Ag1 bonding, thus, its position and U_{iso} were freely refined with the B – H distance fixed at 1.10Å.

Then, the single crystal was irradiated over 4 hours with Xe laser (λ = 365 nm; 200 W source used with 40 % of the full intensity). The crystal was found to be undamaged after irradiation although changed its colour; and intensities of reflections for reaction product were measured at 120 K (2θ$_{max}$ = 76°). The structure of **2** was solved by the direct method and refined by full-matrix least squares against F^2. Although refinement confirmed the *iso* configuration of the $[B_{20}H_{18}]^{2-}$ anion, high residual electron density in the region of the anion (up to 3.5 e Å^{-3}) and significant anisotropic displacement of a number of boron atoms indicated disorder of the anion (or incomplete SCSC reaction). Thus, positions of some boron atoms were splitted on two parts. Neither B – B distances, no any thermal parameters were restrained. Occupation of two positions was freely refined and resulted in the ratio of occupation factors equal to 0.593 : 0.407; those were further fixed at 0.6 : 0.4 values.

Heating of **2** with the Oxford Cryosystem up to 120°C slightly affects the ratio of the occupation factors for major and minor parts of the disordered anion (0.560 : 0.440 as compared with 0.593 : 0.407) but is not accompanied with the reverse process. Thus, the crystal was heated to 160°C for 1 hour in electric muffle and after slow cooling at room temperature the X-ray data confirmed full reverse conversion to **1**. We also studied **1** at 363 K and revealed disorder of two phenyl moieties (these were splitted over two sites with equal occupancies) and of the $[\mathit{trans}\text{-}B_{20}H_{18}]^{2-}$ anion. Following the procedure described above, we obtained occupation factors 0.75 : 0.25 for two parts of the anion. For a minor part a number of B – B distances were fixed at 1.7 Å, and thermal parameters of boron atoms were constrained using the EADP instruction. For **2** and **1** at 363 K the disordered boron and carbon atoms were refined in isotropic approximation, and the others non-hydrogen atoms were refined in isotropic approximation. Taking the disorder of the anion into account, the positions of all H(C) and H(B) atoms were calculated, and these were included in the refinement by the riding model with U_{iso}(H) = 1.2U_{eq}(X).†

All calculations were made using the SHELXS, SHELXL2013[10] and OLEX2[11] program packages.

Thermogravimetry and DSC analyses

Six single crystals of **1** were taken from reaction mixture for TGA and DSC analyses, and their composition was approved using the SCXRD. Completeness of the direct and the reverse processes was controlled using the SCXRD. The TGA analysis showed that compound is stable until 475 K. The mass loss takes place as a two-step process.

Results and discussion

Interaction of $[Ag(PPh_3)_3(NO_3)]$ and $(HN\mathit{Et}_3)_2[B_{20}H_{18}]$ in DMF afforded the complex $\{Ag_2(PPh_3)_6[\mathit{trans}\text{-}B_{20}H_{18}]\}$ (**1**) with a high yield. Single crystal X-ray analysis revealed that **1** crystallized in the monoclinic $P2_1/c$ space group with half of the complex in the asymmetric unit; the second half of the complex is obtained through an inversion centre situated between two condensed $B_{10}H_9$ cages of the macropolyhedral borane. The borane, which adopts *trans*-configuration, bridges two silver atoms, both of them coordinating three triphenylphosphines and a hydrogen atom of [*trans*-$B_{20}H_{18}$]$^{2-}$ to form the *AgHP$_3$* coordination polyhedron (Fig. 1, **a**). The polyhedron has a trigonal pyramidal geometry with the hydrogen atom in its vertex and the metal atom situated 0.470(1) Å above the *P$_3$* pyramid base. The hydrogen atom is in the apical vertex of the macropolyhedral borane that has the most negative charge, as shown by DFT calculations.[12] As a result, the linkage type of the complex can be termed as [10,10'-**1**].

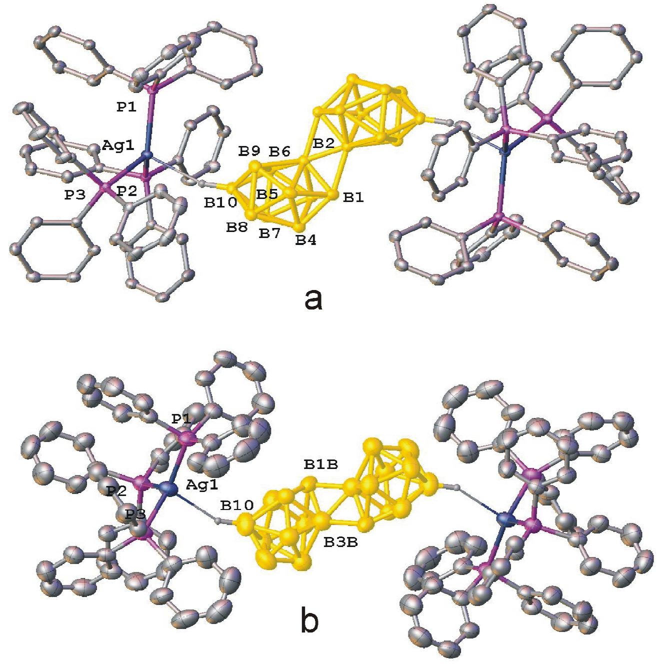


Figure 1. Molecular view of (a) [10,10'-**1**] at 120 K and (b) [7,7'-**1**] at 363 K given in representation of atoms with thermal ellipsoids (given at p = 50%). Hydrogen atoms (with an exception of those involved in B–H...Ag bonding) are omitted for clarity.

At 120 K, the complex is ordered, and the position of the hydrogen atom was refined to produce the geometry of the (AgHB) bond, which is almost linear with r(B...Ag) = 3.382(3) Å and BHAg = 161.8(15)°. This is the first example of a linear B-H…Ag bond, as silver ion was thought to coordinate boranes through edges or faces only.[13] A relatively high B…Ag distance – in silver(I) *closo*-borates, the value of r(B...Ag) does not exceed 2.9 Å – and the linear coordination are indicative of a low coordination ability of the eicosaborate as compared to other polyhedral boranes.

The crystal structure of **1** may be assigned to a family of isotypical compounds with a [$(PPh_3)_3$AgAn] composition (An = carboxylates, cyanides, thiolates and other ligands) that crystallize in the *$P2_1/c$* space group and have similar unit cell parameters (*ca.* a = 13, b = 25, c = 16 Å for the reduced cell). Numerous dispersive interactions clearly govern how the bulky [$(PPh_3)_3$Ag]$^+$ species are packed together. The remaining crystal space is occupied by anions, and it may be used as a 'reaction cavity' for the photoinduced processes.[7a,c] As the isomerization of [*trans*-$B_{20}H_{18}$]$^{2-}$ should not be accompanied by significant changes in its volume, and the structure of the target anion [*iso*-$B_{20}H_{18}$]$^{2-}$ does not prevent the crystal from keeping the inversion center, we expected to obtain the complex {$Ag_2(PPh_3)_6$[*iso*-$B_{20}H_{18}$]} in the SCSC manner. Indeed, the crystal of **1** changed its color (from colourless to light-brown, Fig. S1) upon UV irradiation using Xe lamp for 4 hours but retained its single crystal character. The X-ray diffraction analysis confirmed the transformation of **1** to {$Ag_2(PPh_3)_6$[*iso*-$B_{20}H_{18}$]} (**2**) with a moderate unit cell contraction (from 5131.8(4) to 5093.1(6) Å^3).

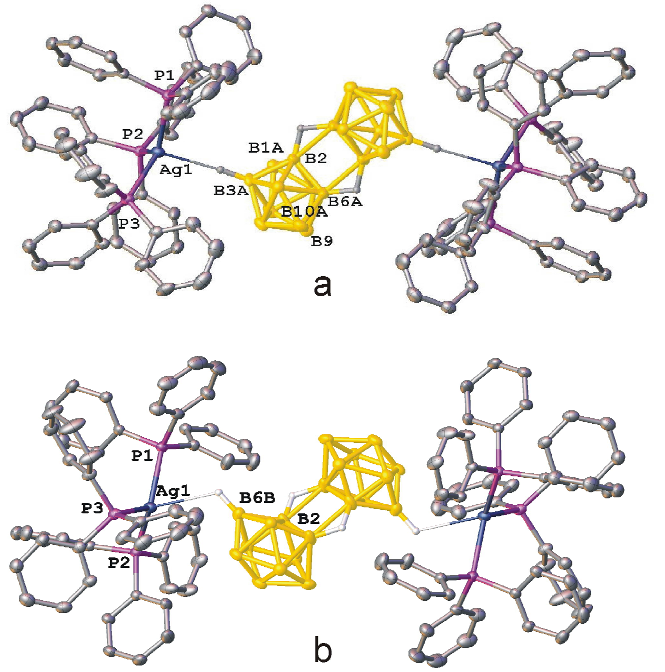


Figure 2. Molecular view of (a) [3,3'-**2**] and (b) [1,1'-**2**] linkage isomers at 120 K isomers after photoactivation of **1** with occupancies of 0.60 and 0.40, respectively, given in representation of atoms with thermal ellipsoids (given at p = 50%). Hydrogen atoms (with an exception of those involved in B–H…Ag bonding) are omitted for clarity.

After localization and refinement of all non-hydrogen atoms, high residual electron density was still observed in the region of the boron cage; it could be indicative of either an incomplete SCSC reaction or a disorder of the macropolyhedral borane. We succeeded to split the positions of boron atoms without applying any restraints, thus proving that a 100 % conversion of [*trans*-$B_{20}H_{18}$]$^{2-}$ to [*iso*-$B_{20}H_{18}$]$^{2-}$ occurred in the solid and that two linkage isomers of the eicosaborate ([3,3'-**2**] and [1,1'-**2**] with occupancies 0.60 and 0.40 (Fig. 2)) co-existed in the crystal. In both these isomers, the macropolyhedral borane remains coordinated with silver ions through the vertex; however, the BHAg angle remains linear (172°) in [3,3'-**2**] only, while its value of 116° in [1,1'-**2**] is more typical for B-

H…Ag bonds. The corresponding B…Ag distances increased to 3.517(5) and 3.394(8) Å.

It is well known that a topochemical drawback for a solid state reaction to occur requires a minimum of atomic or molecular movement.[14] Polyhedral borane rearrangements should also proceed through simultaneous break of edge(s) common to two triangular faces and formation of new edge(s) perpendicular to it.[15] In the latter case, the disposition of atoms on rotation axes of an order 3 or more is forbidden, although the presence of substituents around the critical face at which the process occurs may help to lower the reaction barrier. Unfortunately, no DFT calculations of an isomerization reaction in ‘condensed’ macropolyhedral boranes are reported in literature; however, the shift of relatively stable decaborane cages along common edges or vertices was proposed.[4g] The average shifts of equivalent boron atoms in the isomers [3,3'-**2**] and [1,1'-**2**] as compared to **1** are similar; the corresponding values of 1.4 and 1.3 Å are much greater than those for other SCSC reactions (0.1 – 0.2 Å). Also note that the shift of the apical atoms B1 and B10 is as high as 2.4 Å. At the same time, the difference between the positions of the closest boron atoms in **1** and **2** is much smaller (0.6 and 0.8 Å in average for [3,3'-**2**] and [1,1'-**2**]); so the rearrangement of decaborane cages under photoisomerization can be proposed.

To confirm the reversible character of the SCSC reaction, the single crystal of **2** has been heated. While in acetonitrile solutions the reverse process began at 373 K,[4c] the rearrangement of **2** to **1** started above 435 K only (Fig. 3) and below this temperature the ratio of the isomers [3,3'-**2**] and [1,1'-**2**] was constant. The reverse process also retains the single crystal character of the solid with a 100% conversion. Note that the X-ray analysis at high temperature revealed the disorder of the anion [*trans*-$B_{20}H_{18}$]$^{2-}$ and, hence, the co-existence of the linkage isomers [10,10'-**1**] and [7,7'-**1**] with occupancies 0.75 and 0.25. Major part of disordered at high temperatures anion is similar with [10,10'-**1**] at low temperature and is depicted in Supplementary (Fig. S2); minor part is depicted on Fig. 1, **b**. Cooling of **1** caused the minor component to disappear with the ordering of the borane cage.

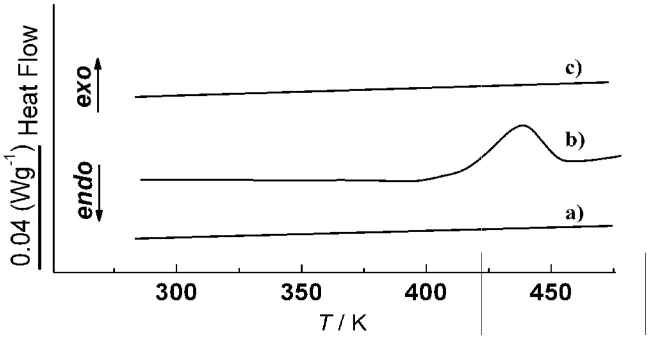


Figure 3. DSC curves for the crystalline samples obtained at a heating rate of 10 K/min under an argon atmosphere. a) Observed from **1** at first heating. b) Observed from **2** obtained by UV irradiation of **1**. c) Observed at second heating of irradiated **2**.

We have also studies the isomerization reactions of **1** in the solid by differential scanning calorimetry (DSC) and powder X-ray diffraction (PXRD) techniques. Thermogravimetry analysis showed that the compound **1** was stable in an inert atmosphere up to 475 K. The DSC curve (*vide infra*) for single crystals of **1** lacks any extremes up to the beginning of thermal degradation (Fig. 3); thus, the thermal effects associated with the linkage isomerism of **1** are absent. The DSC curve for single crystals of **2** exhibits an exothermic peak with a maximum at 437 K (ΔH = 3.64 kJ mol^{-1}). As the DSC curve for the second heating of the same crystals is similar to that of the starting compound **1**, the observed exothermic effect corresponds to the reverse isomerization of the metastable **2** to the thermodynamically stable phase **1**.

The PXRD plots showed that photoisomerization of **1** occurs after 15 min of irradiation, the direct process was completed after 4 h only.[‡] Significant redistribution of reflection intensities gives evidence of reaction occurred (Fig. 4). Rietveld refinement with Bruker TOPAS[16] confirmed the completeness of the **1** ↔ **2** reaction (full description of PXRD analysis is given in ESI). The reverse process was finished after 30 min of heating at 440 K; slight differences in PXRD plots of **1** before and after irradiation (Figs. 4, **a** and **c**) were attributed to different distribution of crystallite sizes.

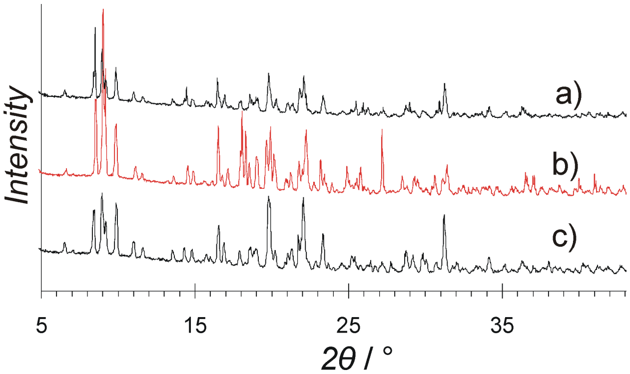


Figure 4. Overlay plots (offset for clarity) of the powder XRD patterns (λ = 1.54060 Å). a) Observed from **1**. b) Observed from **2** obtained by UV irradiation of **1**. c) Observed from **1** obtained by heating of **2** at 440 K for 30 min.

Conclusions

In conclusion, the reversible *trans*-to-*iso* transformation of the [$B_{20}H_{18}$]$^{2-}$ anion in the solid {$Ag_2(PPh_3)_6[B_{20}H_{18}]$} has been observed, for the first time. The B...Ag bonds in these isomers are longer than others reported for silver *closo*-borates; and eicosaborates interact very weakly with silver. As the result of weak bonding, both the [*trans*-$B_{20}H_{18}$]$^{2-}$, and the [*iso*-$B_{20}H_{18}$]$^{2-}$ anions exhibit the linkage isomerism. Based on isomerization reactions of metal complexes with macropolyhedral boranes a novel family of molecular switches can be constructed that exhibits 100 % solid state photoconversion and high-temperature reverse process. This process can be repeated several times without significant degradation of the crystal quality.

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† $\{Ag_2(PPh_3)_6[B_{20}H_{18}]\}$ is monoclinic, space group P 2_1/c, Z = 4, crystal dimensions 0.52 × 0.38 × 0.29, MoK_α radiation. Crystal data for **1** at 120 K: a = 12.8280(6), b = 25.0953(11), c = 21.3666(9) Å, β = 131.748(1)°, V = 5131.8(4) $Å^3$, ρ_{calcd} = 1.310 g sm^{-3}, μ = 0.523 mm^{-1}, R_1 = 0.038 for 18384 observed reflections, wR_2 = 0.093 for 23755 independent reflections (R_{int} = 0.040), GOF = 1.032, 617 parameters. Crystal data for **2** at 120 K: a = 12.9112(9), b = 25.0981(18), c = 21.0634(14) Å, β = 131.739(1)°, V = 5093.1(6) $Å^3$, ρ_{calcd} = 1.320 g sm^{-3}, μ = 0.527 mm^{-1}, R_1 = 0.046 for 18152 observed reflections, wR_2 = 0.106 for 23939 independent reflections (R_{int} = 0.039), GOF = 1.00, 650 parameters. Crystal data for **1** at 363 K: a = 12.9900(8), b = 25.1550(14), c = 21.7332(14) Å, β = 131.733(2)°, V = 5299.6(6) $Å^3$, ρ_{calcd} = 1.268 g sm^{-3}, μ = 0.507 mm^{-1}, R_1 = 0.050 for 10904 observed reflections, wR_2 = 0.139 for 18906 independent reflections (R_{int} = 0.046), GOF = 1.01, 608 parameters and 18 restraints.

‡ *Caution!* High intensity of radiation may cause strong heating of the sample accompanied with its redox decomposition with explosion.

Electronic Supplementary Information (ESI) available: details of powder X-ray diffraction data, TGA and DSC. CCDC 1053534-1053536. For ESI and crystallographic data in CIF format see DOI: 10.1039/c000000x/

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V. V. Avdeeva, M. I. Buzin, E. A. Malinina,
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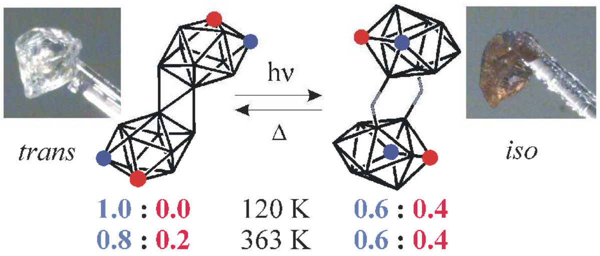
Reversible single-crystal-to-single-crystal photoisomerization of a silver(I) macropolyhedral borane



A reversible conversion [*trans*-$B_{20}H_{18}$]$^{2-}$ to [*iso*-$B_{20}H_{18}$]$^{2-}$ and linkage isomerism occur in a single crystal of {$Ag_2(PPh_3)_6[B_{20}H_{18}]$} (the positions of [$Ag(PPh_3)_3$]$^+$ are shown in red and blue).