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COMMUNICATION
Douglas W. Stephen *et al.*
N-Heterocyclic carbene stabilized parent sulfenyl, selenenyl, and tellurenyl cations (XH^+, X = S, Se, Te)

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COMMUNICATION

A New Polar Perovskite Coordination Network with Azaspiroundecane as A-site Cation

Stefan Burger,[a] Silva Kronawitter,[a] Hanna L. B. Boström,[b] Jan Zaręba[c] and Gregor Kieslich[a]

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ABX_3 perovskite coordination networks are a rapidly growing sub-class of crystalline coordination networks. At present, synthetic efforts in the field are dominated by the use of commercially available building blocks, leaving the potential for tuning properties *via* targeted compositional changes largely untouched. Here we apply a rational crystal engineering approach, using 6-azaspiro[5.5]undecane ($[ASU]^+$) as A-site cation for the synthesis of the polar perovskite $[ASU][Cd(C_2N_3)_3]$.

Dense and porous coordination networks offer a fascinating material platform in the search for new chemistries and physics. By combining inorganic coordination chemistry and organic linker chemistry, coordination networks provide experimentalists with access to intriguing crystal chemistries and the full range of chemical bond strength *via* composition.[1,2] In turn coordination networks exhibit many fundamentally interesting and scientifically relevant properties such as the recent discoveries of unusual elastic properties of cadmium halide polymeric chains[3] and $[Cu(acac)_2]^4$, the colossal negative linear compressibility observed in $Zn[Au(CN)_2]_2{}^5$, and the discovery of spin-crossover phenomena in a dicyanometallate-based perovskite-type coordination network[6] to name just a few.

Among the various existing dense coordination networks is the rapidly growing class of ABX_3 perovskite-type coordination networks which we refer to as molecular perovskites.[7] This nomenclature highlights the use of molecular building blocks on the A and X-site and draws a clear line to hybrid organic-inorganic perovskites such as $[CH_3NH_3]PbI_3$ and $[(NH_2)_2CH]PbI_3$.[8,9] Similar to inorganic perovskites, molecular perovskites crystallise in an ABX_3 perovskite structure, with both the A-site and X-site occupied by molecular moieties. The molecular A-site cation sits in the void of the ReO_3-type 3D $[BX_3]^-$ network and can interact with the $[BX_3]$-network *via* hydrogen bonds and dispersion interactions. The phase space of molecular perovskites appears to even exceed that of inorganic perovskites, and materials such as $[(CH_3)_2NH_2][M(HCOO)_3]$ ($M = Mn^{2+}$, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and $Na^{+}{}_{0.5}Fe^{3+}{}_{0.5}$)[10–13], $[(CH_3)_2NH_2][M(N_3)_3]$ ($M = Mn^{2+}$, Cd^{2+})[14,15], $[TriBuMe][M(C_2N_3)_3]$ (TriBuMe = tributylmethylammonium, $M = Mn^{2+}$, Fe^{2+}, Co^{2+}, Ni^{2+})[16], $[DMA][Mn(H_2POO)_3]$ (DMA = dimethylammonium, guanidinium)[17,18] and $[BTba][M(C_2N_3)_3]$ (Btba = benzyltributylammonium, $M = Mn^{2+}$, Co^{2+})[19] nicely demonstrate the chemical variability of molecular perovskites. Conceptually, this variability originates from the use of a molecular building block on the X-site which leads to an enlargement of the ReO_3-type network and in turn to additional chemical freedom on the A-site, see Figure 1. It is this chemical variability that in principle allows for studying and manipulating the physicochemical properties of molecular perovskites as a function of small chemical changes. In turn, molecular perovskites show a range of interesting properties such as promising barocaloric performances[20], tuneable mechanical responses[16] and multiferroic properties.[11,14] Since the perovskite building principle as structure motif is retained in molecular perovskites, the relative packing density as captured by the Goldschmidt's Tolerance Factor has proved to be an important tool in understanding the building principle of molecular perovskites.[21–24] When comparing molecular perovskites to inorganic perovskites, the use of molecular

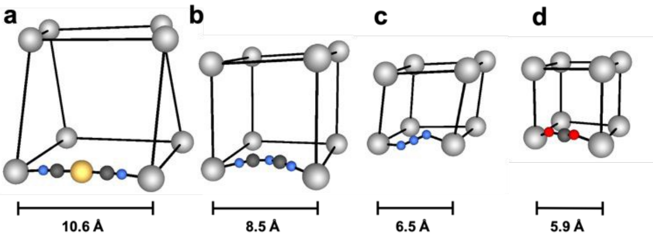

Figure 1. Illustrating the size dependence of the ReO_3-type network in molecular perovskites as a function of the X-site anion with X = $[Au(CN)_2]^-$ (**a**), $[C_2N_3]^-$ (**b**),[16] $[N_3]^-$ (**c**)[15] and $[HCOO]^-$ (**d**)[25]. For better visualisation, the A-site cation was deleted; colour code: Au – yellow, N – blue, C – dark grey, O – red and B-site cation in light grey.

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building units in molecular perovskites leads to chemical and structural degrees of freedom such as unconventional tilts and shifts when compared to the conventional tilt systems as captured by the Glazer notation [25,26], the incorporation of (correlated) defects[27] and the manipulation of dynamic properties via A-site solution amongst others.[28,29] Currently these additional degrees of freedom are mostly of scientific relevance although their role in design concepts based on tilt and shift engineering towards improper ferroelectrics has recently been highlighted.[30,31] These additional degrees of freedom nicely showcase the opportunities that come with the use of molecular building units and understanding their interplay and chemical origin can be considered as a milestone in the understanding of composition–structure–property relations in molecular perovskites.

In the pursuit to address these degrees of freedom synthetically current research efforts focus on the use of commercially available components.[7,32] In other words, one of the unique features of coordination networks — *the nearly unlimited chemical parameters space in the synthesis of tailor-made building blocks* — is broadly untouched, offering large opportunities for material tunability and for creating fundamental knowledge *via* systematic chemical manipulations. In this communication, we follow on from this idea, presenting a route towards a new molecular perovskite with a tailor-made A-site cation which is based on the azaspiro motif. We show how to rationally select A-B-X permutations for the synthesis of a new molecular perovskite, reporting $[ASU][Cd(dca)_3]$ as a new molecular perovskite with an unusual tilt system.

When looking for A-site cations with chemically interesting features, azaspiro compounds such as $[ASU]^+$ (6-azaspiro[5.5]undecane), $[ASD]^+$ (5-azaspiro[4.5]decane) and $[ASN]^+$ (5-azaspiro[4.4]nonane) are interesting candidates.[33] These molecular A-site cations seem to exhibit all ingredients that facilitate the discovery of interesting composition–symmetry–structure relations. They are accessible by standard organic substitution chemistry, the number of carbon atoms can be varied *via* the choice of the precursors, the synthesis of asymmetric azaspiro compounds such as ASD is possible and ring puckering[34] of incorporated azaspiro compounds with larger carbon rings can be expected. Therefore, azaspiro compounds are representing excellent candidates for studying the impact of size and symmetry on the formation and physicochemical properties of molecular perovskites. In this proof-of-principle study we focus on $[ASU]^+$ as A-site cation for the synthesis of molecular perovskites. $[ASU]^+$ can be prepared *via* nucleophilic substitution starting from piperidine and 1,5-dibromopentane, see Figure 2a.[33] After A-site cation selection and synthesis, the Tolerance Factor concept can guide us in choosing a suitable A-B-X combination that is expected to form a perovskite-type structure. As for the X-site anion, the dicyanamide $[C_2N_3]^-$ anion seems suitable. $[C_2N_3]^-$ is a relatively large anion compared to other regularly used X-site anions such as $[N_3]^-$, $[CN]^-$ or $[HCOO]^-$ (Fig. 1)[35–37] and allows for using A-site cations with more than four atoms. In the past, $[C_2N_3]^-$ has proved robust for the synthesis of molecular perovskites with different A-site cations and metals such as $[BTba][Co(C_2N_3)_3]$[19], $[Et_3(n\text{-}Pr)P][Cd(C_2N_3)_3]$[38] and $[TPrA][Mn(C_2N_3)_3]$[39], with $Et_3(n\text{-}Pr)P$ = propyltriethylphosphonium and TPrA = tetrapropylammonium. Together with a suitable divalent B-site cation the size of the resulting three-dimensional $[B(C_2N_3)_3]^-$ network is expected to be large enough to incorporate $[ASU]^+$ for the formation of $[ASU][B(C_2N_3)_3]$. Following the idea of the Tolerance Factor approach, the B-site metal can be used to fine-tune the size of the $[B(C_2N_3)_3]^-$ network, of which we tested B = Cd^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+}. Along the series the Shannon ionic radius[40] decreases and hence the Tolerance Factor increases. Please note that due to the distorted 3D network we here use the Tolerance Factor as qualitative guideline rather than a strict concept. Finally, for the synthesis attempts of $[ASU][B(C_2N_3)_3]$ with B = Cd^{2+}, Mn^{2+}, Co^{2+}, and Ni^{2+} a standard mild-solution route was chosen, following the successful synthesis of related dicyanamide-based molecular perovskites.[41,42] The synthetic approach involves the mixing of precursor salts in an aqueous solution mixture and single crystal formation at room temperature, see supporting information (SI) for experimental details.

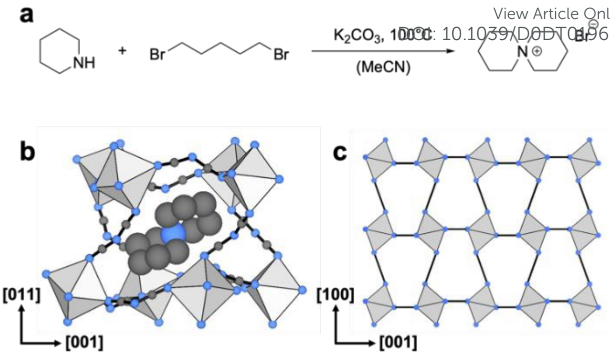

Figure 2. (a) Synthetic scheme of $[ASU]^+$ based on nucleophilic substitution. (**b**) shows the distorted 3D ReO_3-type network formed of Cd^{2+} and $(C_2N_3)^-$ with $[ASU]^+$ as the void-filling A-site cation. In (**c**) a 2D representation of the unconventional M_5^+ tilt is shown. The tilt direction alternates along the axis of rotation, *i.e.* it is out of phase.

The crystal structures of the materials were obtained by single crystal X-ray diffraction, see SI for details of the crystal structure solution. For the large second row divalent metal B = Cd^{2+} with an Shannon ionic radius of $r_{Cd2+} = 95$ pm we observe the formation of the perovskite coordination network $[ASU][Cd(C_2N_3)_3]$, whilst for the smaller cations B = Mn^{2+}, Ni^{2+} and Co^{2+} (all $r_{M2+} < 84$ pm) a different network structure with the formula $[ASU]_2[B_2(C_2N_3)_6]\cdot 2H_2O$ is obtained.[40] Therefore, the observed structures highlight once more the importance of size criteria in the formation step of crystalline molecular perovskites as captured by the Tolerance Factor approach and confirm the applied synthetic approach. As-synthesised crystals of $[ASU][Cd(C_2N_3)_3]$ crystallise in the orthorhombic non-centrosymmetric polar space group $Pna2_1$ with unit cell parameters $a = 17.1022(9)$ Å, $b = 10.7274(5)$ Å,

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c = 10.7037(5) Å, V = 1963.72(17) Å^3 at 100 K. To back-up the assignment of a polar space-group we performed a Kurtz-Perry powder test, confirming the absence of an inversion centre through the detection of a second harmonic generation signal (see SI for details). To the best of our knowledge, this is the first reported dicyanamide perovskite to crystallise in a polar space group[30] although examples with piezoelectric symmetries are known such as $[Et_3(CH_2CHCH_2)P][Mn(C_2N_3)_3]$[43] and $[(C_3H_7)_4N][Mn(C_2N_3)_3]$[44]. As expected for a molecular perovskite, each Cd^{2+} is octahedrally coordinated to its neighbouring Cd atoms *via* six $\mu_{1,5}$-$[C_2N_3]$-bridges to form the 3D ReO_3-type $[Cd(C_2N_3)_3]^-$ network, see Figure 2b. $[ASU]^+$ is sitting in the void of the pseudocubic ReO_3-type cavities of the resulting $[Cd(C_2N_3)_3]^-$ network. Given the absence of any acidic hydrogen atoms in $[ASU]^+$, the cation can only interact through dispersion interactions with the 3D network. In turn, any structure- directing properties of the A-site cation are linked to its shape as it was discussed for the group of formate-based molecular perovskites.[45] As highlighted previously, the use of molecular building units on the X-site leads to the availability of unconventional tilts and shifts within the ReO_3-type network which can be decomposed and described by group theory.[46] For $[ASU][Cd(C_2N_3)_3]$, such a decomposition shows that the symmetry is accounted for by three primary order parameters, a checkerboard shift (irrep M_2^-), a conventional out-of-phase tilt (R_5^-) and an unconventional tilt (M_5^+). While the former two distortions are frequently found in dicyanamide perovskites, the M_5^+ tilt is rare, see Figure 2c.[30] So far, substantial activation of this mode has only been observed in two other molecular perovskites, the ABX_3 solvate $[PPN]Cd[Ag(CN)_2]_3 \cdot 3EtOH$[47] and $[(CH_3)_2NH_2][Mn(N_3)_3]$[15], and a few A-site deficient systems.[48] Importantly, it is this distortion that in combination with the M_2^- shift leads to the polarity of $[ASU][Cd(C_2N_3)_3]$ as previously suggested in a tilt and shift design concept towards molecular perovskites with improper ferroelectrcity.[31] Having the prevalence of the M_2^- distortion in mind, incorporating the M_5^+ tilt is an appealing strategy towards the development of additional polar dicyanamide perovskites, nicely demonstrating the benefit of using tailor-made cations in crystal structure engineering attempts. Looking at the thermogravimetric analysis of the as-synthesised sample, $[ASU][Cd(C_2N_3)_3]$ decomposes at approximately T = 323 °C with no indication of any mass loss until decomposition (Fig. S6). Calorimetry shows an irreversible heat event during the first heating cycle at approximately T = 55 °C and a reversible heat event at T = 20 °C (heating)/ T = 22 °C (cooling) during subsequent cycles (Fig. S5). This behaviour is known from $[CH_3NH_2NH_2][Mn(HCOO)_3]$[49] and $[TriBuMe][Mn(C_2N_3)_3]$[16] and presumably relates to an irreversible phase transition of $[ASU][Cd(C_2N_3)_3]$ during the first heating step. The investigation of this phase transition which was previously understood as activation mechanism is currently under way and goes beyond the concept of this study which focuses on the incorporation and synthesis of molecular perovskites with a tailor-made A-site cation.

For the smaller divalent cations B = Mn^{2+}, Co^{2+}, and Ni^{2+}, the 3D network decreases in size and a different structure is formed, which exhibits a diamond topology (see SI). It can be assumed that for smaller cations the void within the 3D ReO_3-type network is too small to host $[ASU]^+$, and hence, a different crystal structure becomes energetically more favourable. The Mn^{2+}, Co^{2+} and Ni^{2+} compounds with the general formula $[ASU]_2[B_2(C_2N_3)_6] \cdot 2H_2O$ crystallise in the monoclinic space-group $P2_1/n$ and are isostructural, see SI for details. The structure consists of MN_5O octahedra where the divalent metal is coordinated by five terminal N-atoms of the $[C_2N_3]$-ligands and one H_2O molecule. Only four of five $[C_2N_3]^-$ anions are used as $\mu_{1,5}$-$[C_2N_3]$ linkers, and together with H_2O, only 4 of 6 ligands contribute to the connectivity of the 3D network. In total this leads to a diamond-type network connectivity with a ring of six linked octahedra as structure motif, see Fig. S11 and 12. Notably, the $[ASU]^+$ is disordered within this diamond network, whilst no disorder is observed in $[ASU]Cd(C_2N_3)_3$.

In conclusion, we show how a new molecular perovskite with a rare tilt system can be synthesised by applying a crystal engineering approach based on the tailor-made A-site cation $[ASU]^+$. The size of the transition metal allows for fine tuning the size of the 3D $[B(C_2N_3)_3]^-$ host network to a size that is suitable for incorporating the molecular A-site cation $[ASU]^+$. A detailed analysis of the structure *via* group theory reveals that polarity in $[ASU]Cd(C_2N_3)_3$ originates from the presence of an unconventional M_5^+ tilt, nicely highlighting the opportunities of the large but still untouched chemical parameter space. The results and approach presented here offer a blueprint on how to access structural degrees of freedom within molecular perovskites *via* a crystal engineering based on chemical concepts and intuition. Looking forward, it will be interesting to see to which extent chemical and compositional changes can be used to alter and introduce distinct tilts and shifts. In this context, we would like to advocate that the analysis of the underlying tilt and shifts becomes standard for the report of new molecular perovskites, facilitating the identification of overarching composition-structure trends within molecular perovskites.

Conflicts of interest

There are no conflicts to declare.

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