

LiSr₂(NCN)I₃: the first empty tetrahedral strontium(II) entity coordinated by carbodiimide units but without strontium–strontium bonding

Wuping Liao, Jörg von Appen and Richard Dronskowski*

Institut für Anorganische Chemie der RWTH Aachen, Professor-Pirlet-Straße 1, D-52056 Aachen, Germany. E-mail: drons@HAL9000.ac.rwth-aachen.de; Fax: +49-241-80 92642; Tel: +49-241-80 93642

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LiSr₂(NCN)I₃, the first extended compound containing empty tetrahedral Sr₄ entities, is synthesized using a new flux route, and it exhibits two interpenetrating three-dimensional networks made up from Sr tetrahedra capped by NCN²⁻ anions on their triangular faces and vertex-sharing LiI₆ octahedra.

Cyanamides and carbodiimides have gained an increasing amount of attention within the last decade because they have great potential for both solid-state and molecular chemistry. The classic solid-state cyanamide is CaNCN,¹ prepared in the laboratory from calcium carbonate and HCN gas; industrially, calcium cyanamide is made from calcium carbide and molecular nitrogen. The other alkaline-earth metal cyanamides (*i.e.* MgNCN, SrNCN and BaNCN), also being carbodiimides structurally, are synthesized by the reaction of melamine with metal nitrides.² In comparison, EuNCN results from a reaction between EuN, elemental carbon and NaN₃ at 1030 °C.³ Nonetheless, most metal cyanamides or carbodiimides such as those of Zn,⁴ Cd,⁵ Hg,⁶ Ag,⁷ Pb⁸ and Tl⁹ may simply be precipitated from aqueous cyanamide solutions. There are also few reports on synthetic routes targeted at metal cyanamides using organosilicon carbodiimides as precursor compounds.¹⁰ Inspired by the reaction of EuN, BN and NaN₃ to form Eu₃(NBN)₂¹¹ and the totally unforeseeable synthesis of In_{2.24}(NCN)₃¹² from InBr and NaCN, we have found mixtures of metal halides, sodium cyanide and sodium azide to act as promising precursors for the synthesis of novel cyanamides and carbodiimides resulting, for example, in compounds such as MNCN and M₂(NCN)Cl₂ (M = Sr and Eu) at relatively low temperatures of *ca.* 700 °C. The addition of LiI lowers the temperatures even further and leads, in the case of Sr, to LiSr₂(NCN)I₃ for which we present synthesis,[†] crystal and electronic structure.

The crystal structure was determined by single-crystal X-ray diffraction,[‡] and it is constructed from two interpenetrating sub-networks (one containing strontium and NCN²⁻, the other hosting vertex-sharing LiI₆ octahedra), which are linked by Sr–I bonds. A single crystallographic site (32e) was found for Sr, which experiences nine-fold coordination through the three nearest N atoms (2.610(3) Å) of the NCN²⁻ anions and another six iodide anions (three at 3.452(1) Å, three at 3.750(1) Å). The iodide anion exhibits the I^{i-a-a} functionality¹³ by simultaneously binding to one edge of a tetrahedral Sr entity and also by coordinating to the two vertices of two neighboring tetrahedra. It is also connected to two lithium atoms.

The essential feature of LiSr₂(NCN)I₃ is given by the *empty tetrahedra* of the formally divalent Sr atoms (Fig. 1(a), left) which is out of the ordinary for strontium. Although *ab initio* calculations have indicated the relative stability of neutral Sr₄ clusters¹⁴ which can also be produced in molecular beams and are observed in TOF mass spectra,¹⁵ the only examples from the solid state are *O-centered* Sr tetrahedra in Sr₄OX₆ (X = Cl and I)¹⁶ and *H-centered* ones in Sr₂AlH₇.¹⁷ To the best of our knowledge, LiSr₂(NCN)I₃ is the first compound with such empty tetrahedra. The Sr–Sr distance of 3.982(2) Å almost coincides with the distance in the neutral Sr₄ system (4.01 Å)¹⁴ and thus might suggest metal–metal interactions between the Sr²⁺ cations.

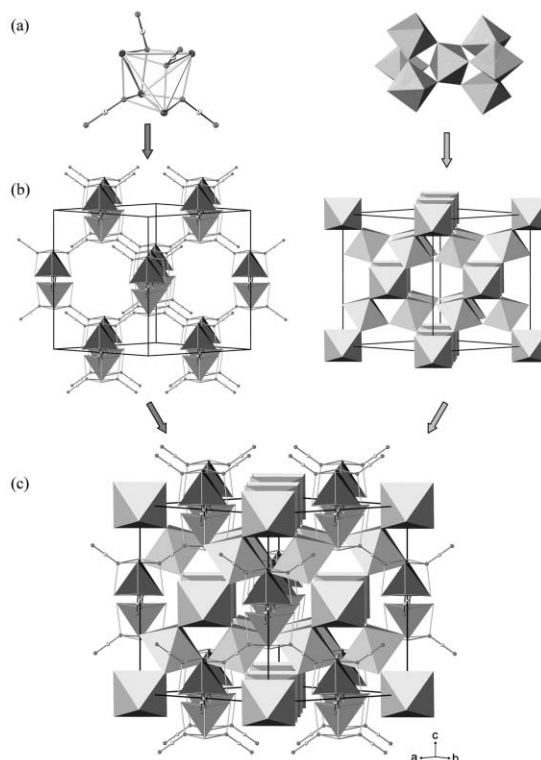


Fig. 1 (a) The empty Sr₄ tetrahedral unit in LiSr₂(NCN)I₃ capped by NCN²⁻ anions (left) and the interconnection of the LiI₆ octahedra (right); (b) sub-networks built from Sr₄ tetrahedra capped by NCN²⁻ anions (left) and condensed LiI₆ octahedra (right); (c) view of the LiSr₂(NCN)I₃ structure along [110], with strontium atoms given in dark grey, nitrogen atoms in grey and carbon atoms in white.

All faces of a single strontium tetrahedron are capped by NCN²⁻ anions, and these interconnect all tetrahedra to form a three-dimensional network. This is easily visible when the Li/I sub-structure is momentarily suppressed (Fig. 1(b), left). The latter is constructed from octahedral LiI₆ units (Li–I = 2.918(1) Å), and each octahedron shares all of its corners with six adjacent octahedra (Fig. 1(a), right) such that all octahedra are part of another three-dimensional network (Fig. 1(b), right) which fills the cavities of the strontium/NCN²⁻ network. As was said before, the structure of LiSr₂(NCN)I₃ is the result of two interpenetrating ionic networks (Fig. 1(c)), similar to a classic *double salt*. To clearly express the connectivity pattern, the LiSr₂(NCN)I₃ formula might alternatively be written as Sr₄(NCN)_{4/2}·(LiI_{6/2})₂.

We note that the NCN²⁻ unit has been found both in symmetrical (carbodiimide) as well as in asymmetrical (cyanamide) configurations, corresponding to the two Lewis formulations ⁻N=C=N⁻ and N=C–N²⁻ but most metal cyanamides contain the linear carbodiimide unit because it fits better with the hard metal cations in terms of Pearson hardness.⁸ Likewise, SrNCN (with

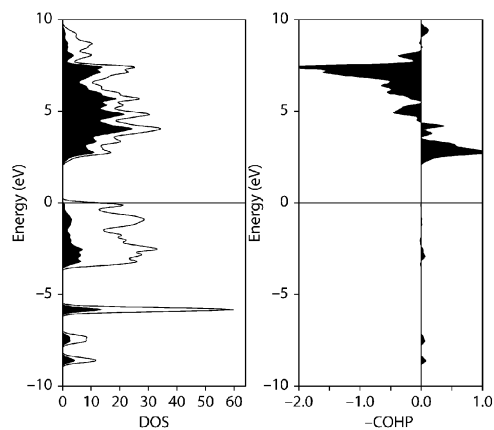


Fig. 2 Density-of-states (DOS) with Sr projections in black (left) and Crystal Orbital Hamilton Population (COHP)²² analysis for the Sr–Sr interactions in $\text{LiSr}_2(\text{NCN})\text{I}_3$ (right); spikes to the right/left indicate bonding/antibonding interactions. In both plots, the Fermi level (horizontal line) is set to zero energy.

$\text{N}=\text{C}$ equal to 1.23(1) and 1.22(1) Å, $\text{N}-\text{C}-\text{N} = 179(1)^\circ$) turns out to be carbodiimide.² Indeed, $\text{LiSr}_2(\text{NCN})\text{I}_3$ can also be formulated as a carbodiimide because of its NCN^{2-} shape with two $\text{N}=\text{C}$ double bond lengths of 1.250(7) Å and an angle of exactly 180° due to space group symmetry. This is confirmed by the IR spectra in which the characteristic frequencies of the carbodiimide anion (around 1668 and 2108 cm^{-1} for the asymmetric stretching of NCN^{2-} and 669 cm^{-1} for the deformation vibration) are clearly detected. As required by the selection principle for molecules containing an inversion center, the symmetric stretching is forbidden in the IR spectrum.

The possibility of metal–metal bonding in the tetrahedra by the formally divalent Sr is disfavored by classic bond-valence calculations¹⁸ which yield partial Sr charges of 1.08 due to Sr–N and 0.92 due to Sr–I interactions, perfectly summing up the divalent state such that there are no excess electrons left for covalent bonding. A similar result is derived from DFT band-structure calculations according to the TB-LMTO-ASA method^{19,20} and the generalized gradient approximation.²¹ The contributions of the Sr 5s orbitals are mostly restricted to the virtual bands (Fig. 2, left), and small covalent interactions occur with N and I. There is negligible Sr–Sr bonding in the occupied bands (Fig. 2, right), and it lowers the band-structure energy²² by less than only 10 kJ per tetrahedron. Although the structural fragment alludes to such bonding, there is almost none.

The cations Sr^{2+} and Eu^{2+} exhibit a rather similar structural chemistry. Isotypic or structurally closely related compounds such as $\alpha\text{-SrNCN}^2$ and EuNCN ,³ $\text{Sr}_2\text{NCNCl}_2$ and $\text{Eu}_2\text{NCNCl}_2$,²³ or Sr_4OCl_6 ¹⁵ and Eu_4OCl_6 ²⁴ are just a few examples. Not surprisingly, the Sr atoms in this compound can be substituted by Eu atoms to form $\text{LiEu}_2(\text{NCN})\text{I}_3$,²⁵ isotypic with $\text{LiSr}_2(\text{NCN})\text{I}_3$. However, the Sr substitution also leads to the formation of yet another phase, $\text{LiEu}_4(\text{NCN})_3\text{I}_3$,²⁵ in which face-sharing of the Eu tetrahedra results in bitetrahedral units which connect further, via two opposing vertices, into one-dimensional linkages and the LiI_6 octahedra share common faces to also yield one-dimensional linkages.

In conclusion, $\text{LiSr}_2(\text{NCN})\text{I}_3$ is the first structural example of an empty tetrahedron of divalent Sr atoms, and it is also the first phase containing both alkali and alkaline-earth metals in a carbodiimide compound. This structural chemistry can probably be extended to other alkaline-earth metals as well. Further synthetic investigations are in progress.

Notes and references

† Colorless transparent single crystals of $\text{LiSr}_2(\text{NCN})\text{I}_3$ were synthesized in high yields from the reactions of SrI_2 , NaCN (or KCN), NaN_3 and LiI in a 2 : 1 : 1 : 2 ratio at elevated temperatures. All physical manipulations were performed in a glovebox (MBraun) under argon with oxygen and moisture levels well below 1 ppm. SrI_2 (99.9%, Aldrich) was used directly as a reagent, and NaCN (95%, or KCN 96%, Merck), NaN_3 (99%, Alfa) and $\text{LiI}\cdot 2\text{H}_2\text{O}$ (LiI > 80%, Merck) were thoroughly dried at 160°C for 3 days *in vacuo*. It is important to follow this procedure because even traces of moisture or oxygen will lead to the formation of Sr_4OI_6 . The mixtures were transported into tantalum ampoules which were sealed with an arc welder and jacketed with quartz, both under argon. The samples were heated to 880°C for three days and then slowly cooled to room temperature at about 6°C min^{-1} .

‡ Crystal data: $\text{LiSr}_2(\text{NCN})\text{I}_3$, $M = 602.91\text{ g mol}^{-1}$, cubic, $a = 15.2312(13)\text{ \AA}$, $V = 3533.5(5)\text{ \AA}^3$, $T = 293(2)\text{ K}$, space group $F\bar{4}3m$ (no. 227), $Z = 16$, $\mu(\text{MoK}\alpha) = 22.479\text{ mm}^{-1}$; diffraction data collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$), empirical absorption correction, 11679 reflections measured, 248 unique ($R_{\text{int}} = 0.0595$) which were all used in the refinements. The final values for $wR2$ (all data) and $R1$ [$I > 2\sigma(I)$] were 0.0475 and 0.0189 respectively. Crystal structure solution/refinement by means of SHELX programs.²⁶ CCDC 241601. See <http://www.rsc.org/suppdata/cc/b4/b408647c/> for crystallographic data in .cif or other electronic format.

- N. G. Vannerberg, *Acta Chem. Scand.*, 1962, **16**, 2263.
- U. Berger and W. Schnick, *J. Alloys Compd.*, 1994, **206**, 179.
- O. Reckeweg and F. J. DiSalvo, *Z. Anorg. Allg. Chem.*, 2003, **629**, 177.
- M. Becker and M. Jansen, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2001, **57**, 347.
- G. Baldinozzi, B. Malinowska, M. Rakib and G. Durand, *J. Mater. Chem.*, 2002, **12**, 268.
- M. Becker and M. Jansen, *Z. Anorg. Allg. Chem.*, 2000, **626**, 1639; X. Liu, P. Müller, P. Kroll and R. Dronskowski, *Inorg. Chem.*, 2002, **41**, 4259.
- M. Becker, J. Nuss and M. Jansen, *Z. Naturforsch., B: Chem. Sci.*, 2000, **55**, 383.
- X. Liu, A. Decker, D. Schmitz and R. Dronskowski, *Z. Anorg. Allg. Chem.*, 2000, **626**, 103.
- K. M. Adams, M. J. Sole and M. J. Cooper, *Acta Crystallogr.*, 1964, **17**, 1449.
- R. Riedel, E. Kroke, A. Greiner, A. O. Gabriel, L. Ruwisch and J. Nicolich, *Chem. Mater.*, 1998, **10**, 2964; N. Hering, K. Schreiber, R. Riedel, O. Lichtenberger and J. Woltersdorf, *Appl. Organomet. Chem.*, 2001, **15**, 879.
- W. Carrillo-Cabrera, M. Somer, K. Peters and H. G. von Schnering, *Z. Kristallogr. -New Cryst. Struct.*, 2001, **216**, 43.
- R. Dronskowski, *Z. Naturforsch., B: Chem. Sci.*, 1995, **50**, 1245.
- H. Schäfer and H. G. von Schnering, *Angew. Chem.*, 1964, **76**, 833.
- Y. Wang, H.-J. Flad and M. Dolg, *J. Phys. Chem. A*, 2000, **104**, 5558.
- P. Dugourd, J. Chevalere, C. Bordas and M. Broyer, *Chem. Phys. Lett.*, 1992, **193**, 539.
- H. Hagemann, F. Kubel and H. Bill, *Eur. J. Solid State Inorg. Chem.*, 1996, **33**, 1101; O. Reckeweg and H. J. Meyer, *Z. Kristallogr.*, 1997, **212**, 235; M. G. Barker, M. G. Francesconi, T. H. Shutt and C. Wilson, *Acta Crystallogr., Sect. E*, 2001, **57**, 144.
- Q. Zhang, Y. Nakamura, K. Oikawa, T. Kamiyama and E. Akiba, *Inorg. Chem.*, 2002, **41**, 6547.
- N. Brese and M. O'Keeffe, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1991, **47**, 192.
- O. K. Andersen, *Phys. Rev. B*, 1975, **12**, 3060; O. K. Andersen and O. Jepsen, *Phys. Rev. Lett.*, 1984, **53**, 2571.
- G. Krier, O. Jepsen, A. Burkhardt and O. K. Andersen, The TB-LMTO-ASA program, version 4.7; Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany, 1995.
- J. Perdew, J. Chevary, S. Vosko, K. Jackson, M. Pederson, D. Singh and C. Fiolhais, *Phys. Rev. B*, 1992, **46**, 6671.
- R. Dronskowski and P. E. Blöchl, *J. Chem. Phys.*, 1993, **97**, 8617.
- W. Liao and R. Dronskowski, *Z. Anorg. Allg. Chem.*, 2004, submitted.
- T. Schleid and G. Meyer, *Z. Anorg. Allg. Chem.*, 1987, **554**, 118.
- W. Liao, C. Hu, R. K. Kremer and R. Dronskowski, *Inorg. Chem.*
- G. M. Sheldrick, SHELXS/SHELXL programs, version 5.1, Universität Göttingen, Germany, 1998.