

DOI: 10.1002/zaac.202300121

Special
Collection

Formation of $[K(18\text{-crown-6})]_2\text{Bi}_2$ and the influence of 18-crown-6 on the crystallization of bismuth-based Zintl clusters obtained from Bi_2^{2-}

Andreas Schmidt,^[a] Benjamin Peerless,^[a] and Stefanie Dehnen^{*[a]}*Dedicated to the late Professor Eduard Zintl on the occasion of his 125th birthday*

So far, homoatomic polybismuthide Zintl anions, which can be used as starting materials for larger binary or ternary, bismuth-based clusters, have always been isolated from potassium-based Zintl phases using 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (crypt-222) to sequester the K^+ counterions. The formation of larger clusters from such anions is still poorly understood, and a change of the sequestering agent might lead to the crystallization of missing links in the cluster formation pathways, which is why – in addition to cost considerations – such variants are being investigated. Herein, we present the synthesis and characterization of the first

homoatomic polybismuthide salt with a 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) complex as counterion, $[K(18\text{-crown-6})]_2\text{Bi}_2$ (**1**). By means of mass spectrometry, we show that compound **1** behaves, generally, alike $[K(\text{crypt-222})]_2\text{Bi}_2$ in reactions with $[\text{CpRu}(\text{NCMe})_3]^+$, forming the previously reported cluster anion $[\{\text{CpRu}\}_3\text{Bi}_6]^-$. However, crystallization of this cluster can only be achieved in the presence of $[\text{PF}_6]^-$ anions, yielding $[\{K(18\text{-crown-6})\}_2\{\text{PF}_6\}][\{\text{CpRu}\}_3\text{Bi}_6]^-$ (**2**). This shows that $[K(18\text{-crown-6})]^+$, if paired up with an additive like $[\text{PF}_6]^-$, indeed is a (cheaper) alternative for the crystallization of anionic bismuth-based clusters.

Introduction

Bismuth-based clusters – both in cationic or anionic form – enjoy worldwide attention for their various chemical and physical properties.^[1–4] First homoatomic anionic species, polybismuthide anions, were observed in the early 1930s by Eduard Zintl in the potentiometric titration of BiI_3 with sodium in liquid ammonia, suggesting Bi_3^{3-} , Bi_5^{3-} , Bi_7^{3-} and Bi_9^{3-} as possible products.^[5,6] However, no details about the structure of these species were obtainable, and to date only one of the predicted polyanions has been crystallized: $[K(\text{crypt-222})]_3\text{Bi}_7$ (crypt-222 = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) was obtained by extraction of K_5Bi_4 with pyridine in the presence of $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$.^[7] The common practice in Zintl chemistry to use a sequestering agent to aid in the crystallization of the anions is dominated by crypt-222. And this is true of polybismuthides where, Bi_2^{2-} ,^[8] Bi_4^{2-} ,^[9] Bi_7^{3-} ,^[7] and

Bi_{11}^{3-} ^[10] have been isolated in crystalline form. The discrepancy between Zintl's original postulation and the structurally observed anions lies in the diverse and flexible nature of polybismuthide anions. Though exact mechanistic detail is still unclear, small polybismuthide units can be oxidized to give both homoatomic and heteroatomic cluster anions with a wide structural diversity and number of Bi atoms from as low as one up to 18,^[11–23] and with Bi_2^{2-} apparently playing a central role in the initial steps of such processes.^[24] The Bi-based clusters span over different classes of architectures including electron precise two electron two center bonds, deltahedral and intermetaloid clusters. This highlights how further understanding of the chemistry of Bi_2^{2-} is crucial to understanding cluster formation and synthesis.^[3,4,25–27] Studies in solution are limited due to a lack of a suitable spectroscopic handle, and mass spectrometry often does not give a true picture of the processes taking place in solution. Absorption spectroscopy could offer possible insight, however there is limited preliminary data to aid in further investigations. All meaning that, fractional crystallization, coupled with in-depth quantum chemical calculations, remains as the primary method in elucidating these pathways.^[28] However, to further diversify such studies, new starting materials are required.^[27]

The balance between the size of counterions with regards to the crystallization of Zintl salts is a crucial part in the outcome of the reaction. Therefore, substituting crypt-222 will have a significant effect on the crystallization process of potential intermediates or products.^[12,29–31] We report, herein, the use of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) as a sequestering agent on the extraction of K_5Bi_4 and investigate the resulting $[K(18\text{-crown-6})]_2\text{Bi}_2$ with regards to its spectroscopic properties and synthetic potential.

[a] A. Schmidt, Dr. B. Peerless, Prof. S. Dehnen
Institute of Nanotechnology
Karlsruhe Institute of Technology (KIT)
Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen
E-mail: stefanie.dehnen@kit.edu

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/zaac.202300121>

This article is part of a Special Collection to celebrate Professor Eduard Zintl on the occasion of his 125th anniversary. Please see our homepage for more articles in the collection.

© 2023 The Authors. Zeitschrift für anorganische und allgemeine Chemie published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

Results and Discussion

In a similar method to obtain $[\text{K}(\text{crypt-222})]_2\text{Bi}_2$, K_5Bi_4 was extracted with four equivalents of 18-crown-6 in ethane-1,2-diamine (en). This results in a blue solution, which already differs significantly from the greenish-turquoise solution obtained when using crypt-222 instead.^[32] Red crystalline needles of $[\text{K}(\text{18-crown-6})]_2\text{Bi}_2$ (**1**) were obtained upon layering the solution with 1.5 eq of methyl tert-butyl ether (MTBE). The structure of one formula unit, as observed in the crystal structure of **1** by means of single-crystal X-ray diffraction (SCXRD), is presented in Figure 1.

The Bi_2 dumbbell is enclosed by two $[\text{K}(\text{18-crown-6})]^+$ cations that are angled towards each other with a $\text{K}\cdots\text{Bi}\cdots\text{K}$ angle of 110.45° and an average $\text{K}\cdots\text{Bi}$ distance of $3.7107(6)$ Å. No such interaction is observed in $[\text{K}(\text{crypt-222})]_2\text{Bi}_2$, where the potassium atom is completely encapsulated by the crypt-222 and the $\text{K}\cdots\text{Bi}$ distance is 9 Å.^[8] Through the coordination to the potassium atoms, the $\text{Bi}\text{--}\text{Bi}$ distance increases from $2.8377(7)$ to $2.8743(6)$ Å compared to the discrete Bi_2^{2-} dumbbell in $[\text{K}(\text{crypt-222})]_2\text{Bi}_2$.^[8] The crystal structure is isostructural to that of $[\text{K}(\text{18-crown-6})]_2\text{Te}_2$ with the same butterfly-like structural motif and the same trend in the elongation of the dumbbell bond.^[33] Furthermore, the $\text{Bi}\text{--}\text{Bi}$ bond length is in the range of other side-on coordinated $\text{Bi}\text{--}\text{Bi}$ double bonds that have previously been described. While in $[(\text{Cp}^*\text{RE})_2(\text{Bi}_2)]$ ($\text{RE}=\text{Y}, \text{Sm}, \text{Gd}, \text{Tb}, \text{and Dy}$; $\text{Cp}^*=\text{pentamethylcyclopentadienyl}$) the bond lengths are slightly shorter ($2.842\text{--}2.855$ Å), the one for $\{[(\text{hmds})_2\text{Mn}]_2(\text{Bi}_2)^{2-}\}$ is slightly longer with 2.902 Å.^[14,34,35]

Two side products – the phase KBi_2 and bismuth powder – formed alongside the desired product in the crystallization process, verified via powder X-ray diffraction (PXRD, Figure S1). Additional, small, unidentified reflexes are present in the diffractogram. It is possible these reflexes belong to that of $[\text{K}(\text{18-crown-6})]_2\text{Bi}_4$, however no comparative data is available to confirm this. Identification of KBi_2 upon extraction of bismuth intermetallics with 18-crown-6 has been

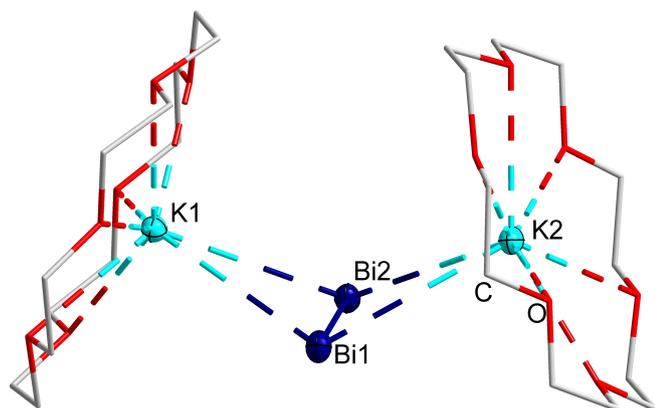


Figure 1. Structure of one formula unit of **1** in the crystal. Thermal displacement ellipsoids are presented with a 50% probability, C and O atoms are presented as wires and sticks, and H atoms are omitted for clarity.

made before.^[36] No such by-product has been observed in the extraction of $[\text{K}(\text{crypt-222})]_2\text{Bi}_2$. Hence, the influence of the solvent on the stability of the crystals was analyzed. Dissolution of **1** in en gave a blue solution that turned colorless after approximately 6 hours with concurrent formation of a black powder containing bismuth, whereas a DMF solution of redissolved crystals of **1** gave a green solution which turned into a brown solution after approximately 24 h that persisted for several weeks. It is worthy to note that in a previous publication, it was reported that DMF extraction solutions of K_5Bi_4 in the presence of 18-crown-6 were less stable than when en was used, though both persisted for only a few days.^[36] It seems that the behavior of isolated **1** is different to that of a freshly prepared extraction solution, which is not surprising given that extraction solutions usually contain a wide range of polybismuthides, which are likely to undergo follow-up (redox) reactions.^[4,23] In contrast, $[\text{K}(\text{crypt-222})]_2\text{Bi}_2$ is stable in en solution for several days, hinting that en may have a significant influence on the stability of **1**. To limit the exposure to en during the extraction process, rather than crystallizing the product, the solvent was removed *in vacuo* after a 15 min extraction time, instead. The residue was analyzed by PXRD (Figure S2), showing reflexes of the two side-products KBi_2 and bismuth, similar to the one recorded from the crystallized product. The residue was then extracted with DMF affording a green solution, similar to dissolution of crystalline **1**. Removal of the solvent *in vacuo* led to a residue that was identified primarily as **1** by PXRD (Figure S3), however, in the diffractogram minor reflexes in the lower 2θ angle region were observed. Coupling this fact with that of the green color suggests that the oxidatively coupled product $[\text{K}(\text{18-crown-6})]_2\text{Bi}_4$ may be present in traces, though this could not be verified so far and is drawn from a comparison with the known outcomes of crypt-222 extraction processes (Figure S4).

As previously mentioned, the en solutions of redissolved **1** and $[\text{K}(\text{crypt-222})]_2\text{Bi}_2$ have different colors, blue and green respectively. The colors of the crystals however are similar. Therefore, UV-visible absorption spectra were recorded on en solutions of the two crystalline compounds, Figure 2. For both samples, three prominent signals are obtained. Compound **1** shows peaks at 416, 579, and 725 nm, while $[\text{K}(\text{crypt-222})]_2\text{Bi}_2$ has peaks at 423, 633, and ~780 nm (shoulder). The apparent blueshift of the peaks in the spectrum of **1** hints to an influence of the en molecules on the absorption properties of the two compounds, as the color of the crystalline solids are the same.

To investigate the reactivity of **1**, it was treated with $[\text{CpRu}(\text{NCMe})_3][\text{PF}_6]$ and $[\text{Ir}(\text{cod})\text{Cl}]_2$, complexes which have recently been used as reactants towards $[\text{K}(\text{crypt-222})]_2\text{Bi}_2$ to great success.^[15] Combination of **1** and either of the two transition metal compounds in en gave brown solutions. *In situ* electrospray ionization mass spectrometry (ESI-MS) showed the presence of $[\text{Cp}_3\text{Ru}_3\text{Bi}_6]^-$ and $[(\text{cod})_3\text{Ir}_3\text{Bi}_6]^-$, as observed upon using $[\text{K}(\text{crypt-222})]_2\text{Bi}_2$ (see Figures S5 and S6). Upon layering the reaction solutions with toluene and

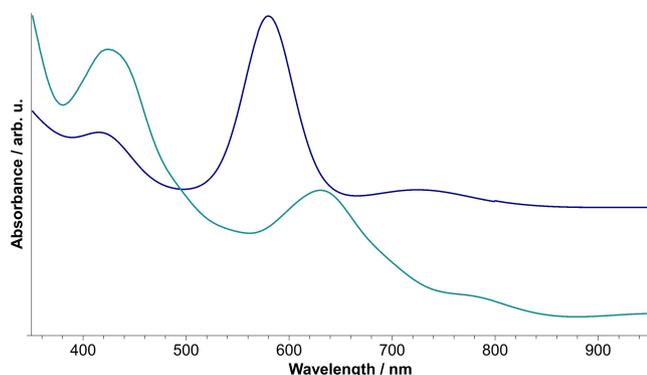


Figure 2. UV-visible spectra of solutions of **1** (blue line) and $[K(\text{crypt-222})]_2\text{Bi}_2$ (green line) in en ($c=0.5$ mmol/L).

n-hexane, crystals of $[[K(18\text{-crown-6})]_2\text{PF}_6][\{\text{CpRu}\}_3\text{Bi}_6] \cdot \text{en}$ (**2**) were obtained, while no crystals were observed in the Ir example. The structure of one formula unit, together with an adjacent $[K(18\text{-crown-6})]^+$ cation, is shown in Figure 3. The $[\{\text{CpRu}\}_3\text{Bi}_6]^-$ cluster in **2** is nearly identical with the one reported previously, although being even more regular. We therefore assume that it possesses the same uncommon φ -aromatic properties which were outlined in the quoted literature. Like in **1** and in $[K(18\text{-crown-6})]_2\text{Te}_2$, the $[K(18\text{-crown-6})]^+$ complexes seek bridging by an anion, which in the case of **2** is realized by one $[\text{PF}_6]^-$ molecule. The selection of this anion instead of the cluster anion (with the same charge) can be attributed to better matching sizes of the molecular units. Although the latter is generally known to be very important for observing crystalline products in Zintl cluster chemistry, we emphasize here that the $[K(18\text{-crown-6})]^+$ salt of the $[\{\text{CpRu}\}_3\text{Bi}_6]^-$ Zintl cluster could only be crystallized in the presence of additional $[\text{PF}_6]^-$ anions. This may explain the failure of crystallizing such Zintl cluster anions with $[K(18\text{-crown-6})]^+$ counterions alone in previous work.^[15]

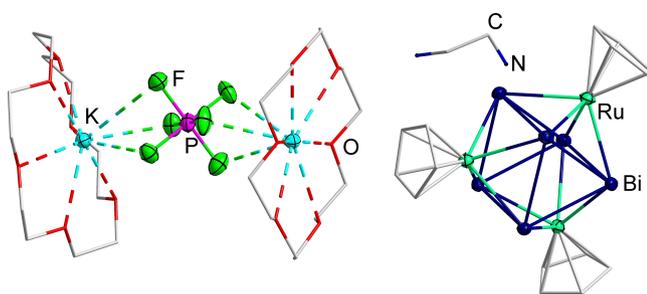


Figure 3. Structure of one formula unit of **2** in the crystal. Thermal displacement ellipsoids are presented with a 50% probability, C, N and O atoms are presented as wires and sticks, and H atoms are omitted for clarity.

Conclusions

In conclusion, the first homoatomic polybismuthide with 18-crown-6 as a sequestering agent $[K(18\text{-crown-6})]_2\text{Bi}_2$ could be crystallized and investigated in terms of absorption and reactivity properties. While the stability of **1** was found to be lower than that of the crypt-222 analogue, it was still successful as a reagent for the formation of larger anionic clusters. The use of crypt-222 is still the predominant method in Zintl chemistry, however, 18-crown-6 may be able to take a place alongside as a cheaper alternative. The most important consideration is to acknowledge the influence of ion sizes in cluster chemistry. $[K(\text{crypt-222})]^+$ has so far been an ideal candidate in this regard. However, in this work we have shown that additives such as $[\text{PF}_6]^-$ partnered with $[K(18\text{-crown-6})]^+$ may influence crystalline stability opening up new avenues into the formation of Zintl anions, or aid in the isolation in missing links previously not possible with crypt-222 in cluster formation pathways.

Experimental Section

Materials and Methods: All reactions were carried out using standard Schlenk line and glovebox techniques under an argon atmosphere. Solvents were dried as follows: en (Aldrich, 99.8%) was refluxed over CaH_2 ; MTBE (Fluka, >99.5%) and toluene (Acros Organics) were refluxed over Na for 24 hours, distilled, and stored over 4 Å sieves. All filtrations were performed via a cannula fitted with a microfiber glass filter that was fixed with Teflon tape; 18-crown-6 (Sigma-Aldrich, >99%) was recrystallized from acetonitrile and dried under vacuum for 16 hours. $[K(\text{crypt-222})]_2\text{Bi}_2$ was prepared by the published procedure.^[15,32] All other chemicals were used as received: K (Acros Organics, 98%), Bi powder (ChemPur, >99.5%), $[\text{Ir}(\text{cod})\text{Cl}]_2$ (Chempur) and $[\text{CpRu}(\text{NCMe})_3][\text{PF}_6]$ (Sigma-Aldrich). For the synthesis of K_5Bi_4 , stoichiometric amounts of K and Bi were weighed in a niobium ampule, which was sealed by arcwelding. The niobium ampule was then sealed in a silica glass ampule, which was placed in an oven and kept at 700 °C for 7 days.

Synthesis of compound 1. 103 mg of K_5Bi_4 (1.0 eq, 0.1 mmol) and 106 mg of 18-crown-6 (4.0 eq, 0.4 mmol) were weighed into a Schlenk tube and dissolved in 2 mL of en. The mixture was stirred for 15 min, showing a blue color immediately. (a) The blue solution was filtered and layered with 3 mL of MTBE. After 7 days, red needles of $[K(18\text{-crown-6})]_2\text{Bi}_2$ (alongside KBi_2) formed on the wall of the Schlenk tube, which were washed with 2×2 mL of toluene and dried under vacuum. (b) The blue solution was filtered and the solvent was removed *in vacuo*. Then, the residue was redissolved in DMF and a green suspension was obtained. The suspension was filtered and the solvent was removed again, resulting in 415 mg (0.40 mmol, 40%) of a brown powder containing $[K(18\text{-crown-6})]_2\text{Bi}_2$ (**1**).

Synthesis of compound 2. 51 mg (1.0 eq., 0.05 mmol) of **1** and 22 mg (1.0 eq., 0.05 mmol) of $[\text{CpRu}(\text{NCMe})_3][\text{PF}_6]$ were weighed into a Schlenk tube and dissolved in 2 mL of en. The mixture was stirred for 2 h and a brown colored solution was obtained, which was filtered and layered with 3 mL of MTBE. This led to the formation of brown block-like crystals of **2** on the wall of the Schlenk tube.

Single crystal X-ray diffraction. The SCXRD measurement for **1** was performed on a Bruker D8 Quest, and for **2** on an IPDS-2T, both equipped with a Mo-K α -radiation source ($\lambda = 0.71073 \text{ \AA}$). The crystals were cooled down to 100 K. The structures were solved by dual space methods of SHELXT15.^[37] Refinements were done using the full-matrix-least-squares methods against F^2 with SHELXL15, using the software Olex² version 1.5.^[38,39] The software DIAMOND version 4.6.8 was used to draw the crystal structures. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2267362–2267363. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internat.) +44 1223/336–033; e-mail: deposit@ccdc.cam.ac.uk];

Powder X-ray diffraction. PXRD measurements were performed on a Stoe Stadi MP using a capillary. A Debye-Scherrer construction was used and the samples were radiated with a Cu-K α radiation in an 2θ -angle from 2° to 60° . For the interpretation of the obtained diffractograms and removal of the background the program WinXPow Version 3.5.0.2 was used and the program QtiPlot version QT: 5.12.2 was used to create the data plots.

Optical absorption spectroscopy. UV-visible spectra were recorded on an Agilent Varian Cary 5000 spectrometer. The samples were prepared in a glovebox, as solutions with a concentration of 0.5 mmol/L. The data was recorded by the Cary WinUV Scan Application Version 6.2.0.1588 and plotted with QtiPlot version QT: 5.12.2.

Electrospray ionization mass spectrometry. ESI mass spectrometry on compound **2** was performed on a Finnigan LTQ-FT spectrometer. The measurements were done upon filtering the reaction solution after 2 h, which was then drawn into a 250 μL Hamilton syringe and injected into the mass spectrometer that was purged with the solvent beforehand. The procedure was similar for recording the ESI mass spectra presented in Figure S6; in the reaction only half an equivalent of the $[\text{Ir}(\text{cod})\text{Cl}]_2$ complex was used. The program Xcalibur 2.2 Version Foundation 2.0 SP1 build 57 was used to interpret the data.

Acknowledgements

The authors thank the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) for financial support. The work was co-funded by the European Union (ERC, BiCMat, 101054577). Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Research Council. Neither the European Union nor the granting authority can be held responsible for them. We thank J. Rienmüller for help with the X-ray diffraction measurement of **1** and we thank J. Bamberger and Dr. U Linne for recording the ESI mass spectra. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Zintl anions · Polybismuthide compounds · Sequestering agent · X-ray diffraction · UV-visible spectra

- [1] M. Ruck, F. Locherer, *Coord. Chem. Rev.* **2015**, *285*, 1–10.
- [2] E. Ahmed, M. Ruck, *Coord. Chem. Rev.* **2011**, *255*, 2892–2903.
- [3] J. Heine, B. Peerless, S. Dehnen, C. Lichtenberger, *Angew. Chem. Int. Ed.* **2023**.
- [4] F. Pan, B. Peerless, S. Dehnen, *Acc. Chem. Res.* **2023**, *56*, 1018–1030.
- [5] E. Zintl, J. Goubcau, *Z. Phys. Chem. Abt. A* **1931**, *154*, 1–46.
- [6] E. Zintl, W. Dullenkopf, *Z. Phys. Chem. Abt. B* **1932**, *16*, 183–194.
- [7] L. G. Perla, A. G. Oliver, S. C. Sevov, *Inorg. Chem.* **2014**, *54*, 872–875.
- [8] L. Xu, S. Bobev, J. El-Bahraoui, S. C. Sevov, *J. Am. Chem. Soc.* **2000**, *122*, 1838–1839.
- [9] A. Cisar, J. D. Corbett, *Inorg. Chem.* **1977**, *16*, 2482–2487.
- [10] B. Weinert, A. R. Eulenstein, R. Ababei, S. Dehnen, *Angew. Chem. Int. Ed.* **2014**, *53*, 4704–4708.
- [11] L. Xu, A. Ugrinov, S. C. Sevov, *J. Am. Chem. Soc.* **2001**, *123*, 4091–4092.
- [12] J. M. Goicoechea, M. W. Hull, S. C. Sevov, *J. Am. Chem. Soc.* **2007**, *129*, 7885–7893.
- [13] P. Zhang, F. Benner, N. F. Chilton, S. Demir, *Chem* **2022**, *8*, 717–730.
- [14] P. Zhang, R. Nabi, J. K. Staab, N. F. Chilton, S. Demir, *J. Am. Chem. Soc.* **2023**, *145*, 9152–9163.
- [15] B. Peerless, A. Schmidt, Y. J. Franzke, S. Dehnen, *Nat. Chem.* **2023**, *15*, 347–356.
- [16] L. G. Perla, S. C. Sevov, *Inorg. Chem.* **2015**, *54*, 8401–8405.
- [17] N. Lichtenberger, R. J. Wilson, A. R. Eulenstein, W. Massa, R. Clérac, F. Weigend, S. Dehnen, *J. Am. Chem. Soc.* **2016**, *138*, 9033–9036.
- [18] N. Lichtenberger, N. Spang, A. Eichhöfer, S. Dehnen, *Angew. Chem. Int. Ed.* **2017**, *56*, 13253–13258.
- [19] N. Lichtenberger, W. Massa, S. Dehnen, *Angew. Chem. Int. Ed.* **2019**, *58*, 3222–3226.
- [20] M. Kaas, N. Korber, *Z. Anorg. Allg. Chem.* **2019**, *645*, 146–148.
- [21] A. R. Eulenstein, Y. J. Franzke, N. Lichtenberger, R. J. Wilson, H. Lars Deubner, F. Kraus, R. Clérac, F. Weigend, S. Dehnen, *Nat. Chem.* **2021**, *13*, 149–155.
- [22] L. Qiao, D. Chen, J. Zhu, A. Muñoz-Castro, Z. M. Sun, *Chem. Commun.* **2021**, *57*, 3656–3659.
- [23] F. Pan, S. Wei, L. Guggolz, A. R. Eulenstein, F. Tambornino, S. Dehnen, *J. Am. Chem. Soc.* **2021**, *143*, 7176–7188.
- [24] K. Beuthert, B. Peerless, S. Dehnen, *Commun. Chem.* **2023**, *6*, 1–8.
- [25] S. Scharfe, F. Kraus, S. Stegmaier, A. Schier, T. F. Fässler, *Angew. Chem. Int. Ed.* **2011**, *50*, 3630–3670.
- [26] T. F. Fässler, *Zintl Phases: Principles and Recent Developments (Structure and Bonding Book 139)*, Springer, Berlin, Heidelberg [u.A.], **2011**.
- [27] R. J. Wilson, N. Lichtenberger, B. Weinert, S. Dehnen, *Chem. Rev.* **2019**, *119*, 8506–8554.
- [28] S. Mitzinger, L. Broeckart, W. Massa, F. Weigend, S. Dehnen, *Nat. Commun.* **2016**, *7*, 1–10.
- [29] F. Lips, M. Raupach, W. Massa, S. Dehnen, *Z. Anorg. Allg. Chem.* **2011**, *637*, 859–863.
- [30] S. Chen, Z. Li, B. Yuan, L. Lin, M. H. Whangbo, L. Xu, *Inorg. Chem.* **2020**, *59*, 10628–10633.

- [31] Z. Liang, L. Lin, Y. Liang, Y. Wang, *New J. Chem.* **2023**, *47*, 3993–3998.
- [32] H. T. Sun, T. Yonezawa, M. M. Gillett-Kunnath, Y. Sakka, N. Shirahata, S. C. Rong Gui, M. Fujii, S. C. Sevov, *J. Mater. Chem.* **2012**, *22*, 20175–20178.
- [33] G. Thiele, N. Lichtenberger, R. Tonner, S. Dehnen, *Z. Anorg. Allg. Chem.* **2013**, *639*, 2809–2815.
- [34] J. Evans, S. L. Gonzales, J. W. Ziller, *J. Am. Chem. Soc.* **1991**, *113*, 9980–9982.
- [35] J. Rienmüller, A. Schmidt, N. J. Yutronkie, R. Clérac, C. G. Werncke, F. Weigend, S. Dehnen, *Angew. Chem. Int. Ed.* **2022**, *61*, e202210683.
- [36] A. N. Kuznetsov, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2002**, *628*, 2537–2541.
- [37] G. M. Sheldrick, *Acta Crystallogr., Sect. A Found. Adv.* **2015**, *71*, 3–8.
- [38] G. M. Sheldrick, *Acta Crystallogr. C Struct. Chem.* **2015**, *71*, 3–8.
- [39] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

Manuscript received: June 5, 2023

Revised manuscript received: June 30, 2023

Accepted manuscript online: July 3, 2023