Structure Elucidation

Deutsche Ausgabe: DOI: 10.1002/ange.201601585
Internationale Ausgabe: DOI: 10.1002/anie.201601585

Infinite Polyiodide Chains in the Pyrroloperylene–Iodine Complex: Insights into the Starch–Iodine and Perylene–Iodine Complexes

Sheri Madhu, Hayden A. Evans, Vicky V. T. Doan-Nguyen, John G. Labram, Guang Wu, Michael L. Chabinyc, Ram Seshadri, and Fred Wudl**

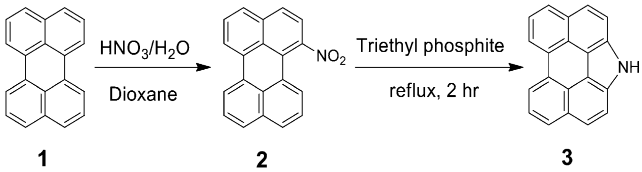
Abstract: *We report the preparation and X-ray crystallographic characterization of the first crystalline homoatomic polymer chain, which is part of a semiconducting pyrroloperylene–iodine complex. The crystal structure contains infinite polyiodide* $I_\infty^{\delta-}$*. Interestingly, the structure of iodine within the insoluble, blue starch–iodine complex has long remained elusive, but has been speculated as having infinite chains of iodine. Close similarities in the low-wavenumber Raman spectra of the title compound and starch–iodine point to such infinite polyiodide chains in the latter as well.*

According to Saenger,[1] the starch–iodine complex was discovered by Colin and de Claubry, over two hundred years ago.[2] The complex is better described as amylose–iodine[1] and has continuously, over the years, been considered as a clathrate of polyiodide and carbohydrate. The nature of the polyiodide in this complex still remains to be fully characterized, and many of the references on iodine chain-containing compounds in the literature draw analogies with the elusive starch-iodine structure. For example, Kahr et al.[3] established the crystal structure of so-called herapathite: a quinine iodine complex with iodide trimers. Redel et al.[4] have reported a complex copper iodide with chains of up to 5 iodine atoms. Lin et al.[5] have reported bent anionic I_7 chains stabilized by complex multivalent organic ammonium cations. Schroder and co-workers[6] have reviewed the rich structural chemistry that emerges when macrocylic thioethers are employed to stabilize oligomeric iodine chains. Yin et al.[7] have reported a metal–organic framework based on Cu^{II} cations and I_5^- and I_7^- chains. Kloo et al.[8] have also employed ab-initio techniques to study the structure and stability of short I_n^- moieties in the vacuum. These descriptions of iodide chains, as well as numerous others, are better described as oligomeric rather than polymeric chains of iodine, with lengths typically shorter than 10 iodine units and usually containing molecular iodine within the chain.[9] Indeed, a seminal resonance Raman spectroscopic study of starch iodine carried out in 1978 allowed the authors inferred the presence predominantly I^{5-} species.[10]

A separate and highly relevant structural mystery involving iodine is that of one of the earliest organic electronic conductors; the perylene–iodine charge-transfer complex,[11] which to this day, has not been fully resolved. It is clear that the hydrocarbon is partially oxidized and the iodine shows hints of iodine and triiodide[12] but the latter are disordered in essentially, all examined cases.

Here we relate these stories and shed light on the science of these functional organic materials. We have determined the structure of a pyrroloperylene–iodine complex that comprises helical, infinite iodine chains interspersed between π-stacks of the pyrroloperylene. The electrical conductivity of this compound is found to be close to $10^{-2}\,\mathrm{S\,cm^{-1}}$ at room temperature, and a change in the temperature coefficient of the conductivity at temperatures close to 150 K is suggested as corresponding to a structural transition. Based on similarities between the published low-frequency Raman spectroscopic signatures of starch-iodine and the spectrum measured on the title compound, it is suggested that starch–iodine must similarly comprise infinite iodine chains.

Pyrroloperylene **3** was prepared in 80 % to 85 % yield by a simple Cadogan reaction shown in Scheme 1.[13] The preparation of the pyrroloperylene–iodide complex from solution by slow cooling was straightforward, and employed a benzene solution containing 15 mg (0.0566 mmol) of pyrroloperylene **3** and 51 mg (0.198 mmol) of iodine, kept at 65 °C in a vial with a screw cap. The solution was allowed to cool slowly from 65 °C to 30 °C over a period of five days in a doubly insulated container. Shiny needles with a dark yellow-green lustre were obtained at the bottom of the vial. The crystals were found to be quite stable at room temperature under STP conditions, but lost iodine at higher temper-



Scheme 1. Synthetic route for pyrroloperylene **3**.

---

[*] Dr. S. Madhu, H. A. Evans, Dr. V. V. T. Doan-Nguyen, Prof. Dr. R. Seshadri, Prof. Dr. F. Wudl
Materials Research Laboratory, University of California
Santa Barbara, CA 93106 (USA)
E-mail: seshadri@mrl.ucsb.edu
wudl@chem.ucsb.edu

H. A. Evans, Dr. G. Wu
Department of Chemistry and Biochemistry, University of California
Santa Barbara, CA 93106 (USA)

Dr. V. V. T. Doan-Nguyen, Dr. J. G. Labram
California NanoSystems Institute, University of California
Santa Barbara, CA 93106 (USA)

Prof. Dr. M. L. Chabinyc, Prof. Dr. R. Seshadri, Prof. Dr. F. Wudl
Materials Department, University of California
Santa Barbara, CA 93106 (USA)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201601585.

ature (see the thermogravimetric analysis in the Supporting Information) The concentration most favorable for the formation of large (>1 mm) single crystals was 10 mg of pyrroloperylene and 35 mg of iodine per 5 mL benzene solution. The dimensions of these crystals varied in length from 1 mm to 5 mm, the width from 100 μm to 200 μm, and thickness from 10 μm to 50 μm.

The crystal structure of pyrroloperylene–iodine complex solved at 100 K, refined to a composition of pyrrolloperylene-$I_{2.2}$ and is displayed in Figure 1. The structure is monoclinic, space group $C2/c$ (No. 15), solved with $R1 = 5.91\,\%$. In the crystal structure of the complex, pyrroloperylene exhibits a nearly planar molecular conformation with an interplanar distance of 3.47 Å. In the asymmetric unit, one of the pyrroloperylene molecules exhibits disorder of the N over two orientations related by the inversion center. The pyrroloperylene stacks are interspersed with polyiodide chains in close proximity and parallel to each other. The 100 K crystal structure showed the presence of nearly linear polyiodide chains, with shallow helicity, and interatomic distances varying from 3.054 Å to 3.174 Å. Key interatomic distances for the 100 K and room temperature crystal structure are presented in the SI. The interiodine distances in the chain both in the 100 K and room temperature structure are all greater than 3.00 Å, supporting the conclusion that no neutral I_2 units (interatomic distance: 2.70 Å)[14] are part of the chains. This implies that all the iodine atoms in the polyiodide chain carry a partial negative charge. So far, with very few exceptions, the geometry of polyiodide chains (I^{5-}, I^{7-}, and I^{9-}) reported in the literature is non-linear,[11] whereas the polyiodide chain found in the pyrroloperylene–iodine complex at 100 K and room temperature is nearly linear.

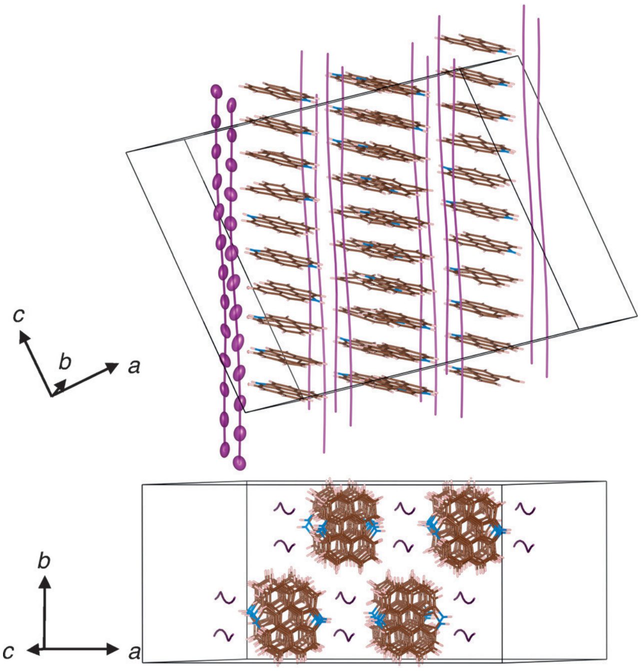


Figure 1. Views of the crystal structure of pyrroloperylene–iodine complex at 100 K, showing pyrroloperylene π-stacks separated by racemic pairs of helical chains of $I_{\infty}{}^{\delta-}$. In the top panel, the 99 % probability thermal ellipsoids of I in two of the chains are displayed.

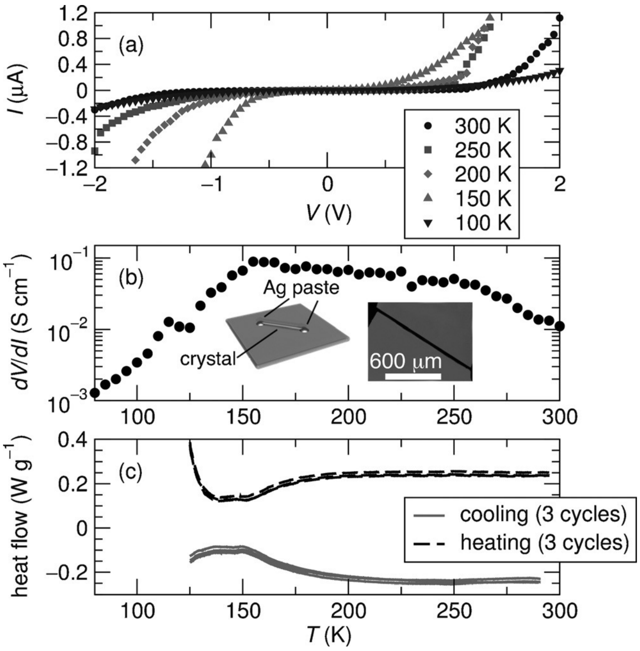


Figure 2. a) Current as a function of voltage applied along the length of a single crystal of pyrroloperylene–iodine complex, measured at various temperatures. b) Average differential conductivity between −2 V and −1.5 V and between 1.5 V and 2 V, acquired upon forward sweep, as a function of measurement temperature T. The inset displays an optical microscope image of a single crystal on silica. At the edge of the image the silver paste employed to contact the crystal is visible. The crystal was assumed to be cylindrical with a length of 1.2 mm and a diameter of 50 μm. All measurements were carried out under vacuum (10^{-4} mbar). c) DSC heating and cooling traces suggesting a highly reproducible incident near 150 K, corresponding to the temperature at which the temperature-coefficient of conductivity changes slope.

We examined the electrical properties of four single crystals of the complex and found some variation in their electrical behavior attributable to mechanical defects and cracking near the contacts during temperature changes (see the Supporting Information). Because of their fragility, we did not attempt four-probe measurements and our electrical data includes effects due to injection at the contacts. A successful measurement of the electrical behavior is shown in Figure 2a displaying nonlinear I–V relationship over the range of applied biases examined. The differential conductivity (dI/dV) was extracted from the data and shows a ten-fold increase in conductivity from 300 K to 150 K across the entire range of applied bias, followed by a significant decrease [Figure 2b]. There is some asymmetry in the I–V data which we attribute to imperfect contacts. We believe that the increase in differential conductivity is a materials property because poorly injecting contacts would be expected to have the opposite temperature dependence (injection would be worse at lower temperature). Some hysteresis is observed between forward and reverse measurements at higher voltages (see SI, Figure S5) and is hypothesized to be due to small structural instabilities in the contact interface between the silver paste and the pyrrolopyrelene–iodine crystal, or even perhaps some electromigration. Overall the data is suggestive of metallic behavior above 150 K. The decrease in differential conductivity near 150 K coincides with a phase transition with no hysteresis observed using differential scanning calorimetry [Figure 2c] further suggesting that the electrical behavior is representative of the crystal. Because the structure is one-dimensional, it is possible that Peierls physics is involved.[15] Differential scanning calorimetry carried out on the complex indeed suggests a reproducible solid-state phase transition at approximately 150 K, as shown in Figure 2c, with no hysteresis. This led us to closely examine the structure of the complex at room temperature, reported in detail in the Supporting Information, which indeed suggests a slightly less distorted polyiodide chain, consistent with the 150 K incident corresponding to a structural distortion.

The Kubelka–Munk transformation of the diffuse reflectivity of solid pyrroloperylene and the pyrroloperylene–iodine complex, acquired in dispersion in $BaSO_4$ is shown in Figure 3a. The crystals of the pyrroloperylene–iodine complex appear shiny and metallic and with an absorption extending through visible range of the visible region into the near-infrared. This, as well as the feature observed near 1750 nm suggests the presence of free carriers, and is consistent with the electrical transport measurement.[16] Both spectra show identical overlapping bands in the region of 450 nm, which is also seen in the solution spectrum of pyrroloperylene (Figure S1a). Figure 3b compares the infrared spectra of pyrroloperylene and the pyrroloperylene–iodine complex. The spectrum of the complex is dominated by free charge carriers, starting in the 500 cm^{-1} extending all the way to NIR region. The intramolecular vibrational peaks of pyrroloperylene are very weak and are clearly masked by the free charge carriers in the complex. The presence of these free carriers also influences the lineshape of the room temperature electron spin resonance (ESR) spectrum of the pyrroloperylene–iodine complex, displayed in Figure 3c. The open-shell complex displays an asymmetric signal centered at $g = 2.0022$, with some complex features potentially arising from the powder averaging of a crystalline material.

Finally, Figure 4 displays a Raman spectrum of the pyrroloperylene–iodine complex, in the low-energy regions associated with I-I modes. The strongest vibrational modes are found to be at 106.8 cm^{-1} and 150.1 cm^{-1}. Previous reports on compounds with finite chains of I^{5-}, I^{7-}, and I^{9-} display higher wave number signatures[4,6,9,17,18] *ie.* varying from 160 cm^{-1} to 180 cm^{-1}, which can also include signatures of I_2 at 215 cm^{-1} in the solid.[19] This supports the assertion of polymeric iodine speculated to be found in starch-iodine, as reported in the spectrum from Teitelbaum et al.[10]

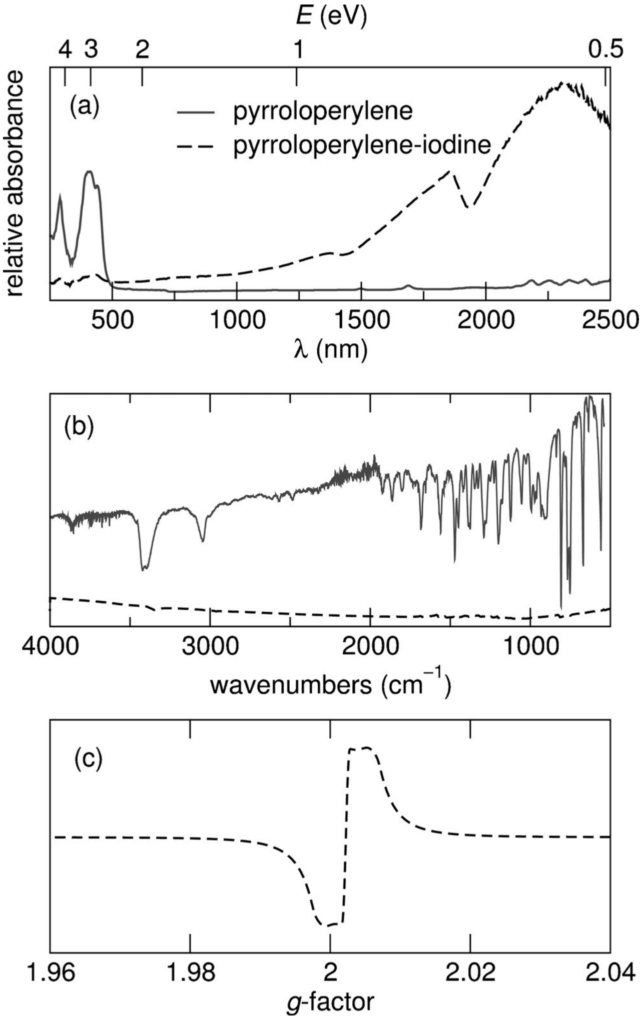


Figure 3. Solid state a) UV/Vis absorption (in $BaSO_4$) and b) infrared spectra of the pyrroloperylene and pyrroloperylene–iodine complex. c) Solid-state ESR spectrum of the pyrroloperylene–iodine complex at room temperature.

Experimental Section

Synthesis of 1-nitroperylene (**2**):[13] To a hot solution of perylene (5.0 g, 19.8 mmol) dissolved in 1,4-dioxane (200 mL) was added a mixture of 5.0 mL of water and 4.5.0 mL of nitric acid ($d = 1.5$) dropwise while stirring. The resulting solution was heated at 60 °C with vigorous stirring for 30 minutes, and the initial yellow solution completely turned to brick red color. The reaction mixture was cooled and transferred into 1 L of water. The solid was filtered, dried under vacuum, and purified by column chromatography on silica gel with hexane/toluene (75/25) as eluent to afford **2** as a brick-red crystal. Yield (1.77 g, 30 %). ^{1}H NMR (DMSO, 600 MHz): $\delta = 8.56$ (dd, 2 H), 8.02–7.95 (m, 4 H), 7.83 (d, $J = 8.4$ Hz, 1 H), 7.77 (dd, 2 H), 7.69 (t, $J = 7.6$ Hz, 1 H), 7.59 ppm (t, $J = 8.0$ Hz, 1 H). EI-MS, m (%), 297 (M^+, 100 %).

Synthesis of Pyrroloperylene or 6H-Phenanthro [1,10,9,8-c,d,e,f,g] carbazole (**3**):[13] A mixture of 0.50 g (1.7 mmol) of 1-Nitroperylene (**2**) and 5 mL of triethyl phosphite was heated at reflux under argon for 2 h. Upon cooling the reaction mixture to room temperature, the yellow brown amine **3** crystallized and crystals were collected by filtration. Yield (0.38 g, 85 %). ^{1}H NMR (DMSO, 600 MHz): $\delta = 12.20$ (s, 1 H), 8.74 (d, $J = 8.2$ Hz, 2 H), 8.19 (d, $J = 8.4$ Hz, 2 H), 7.99 (dd, 4 H), 7.94 ppm (t, $J = 7.4$ Hz, 2 H). ^{13}C NMR (DMSO, 150 MHz): $\delta = 131.1$, 130.2, 128.8, 125.5, 125. 1, 124.7, 121.3, 117.4, 116.0 ppm. EI-MS, m (%), 265 (M^+, 100 %).

For electrical transport measurements, a single crystal of the pyrroloperylene-iodine complex was deposited onto a vitreous silica substrate with a hypodermic needle. Using a stereo microscope, a small volume of colloidal silver paste (Pelco) was deposited onto the substrate at each end of the crystal, again using a hypodermic needle.

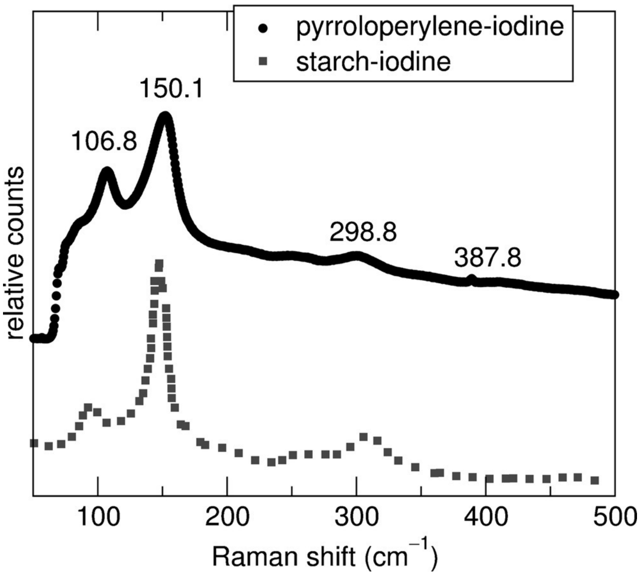


Figure 4. Comparative Raman spectra of pyrroloperylene–iodine complex and starch iodine. The latter spectrum is digitized from Teitelbaum et al.[10]

The silver paste was allowed to dry at room temperature in air for 1 h before the sample was transferred to a cryogenic probe station. The chamber was evacuated to a pressure of 1×10^{-4} mbar. The current was then measured as a function of voltage applied across the length of the crystal using a Keithley 2400 SourceMeter. The conductance was extracted from the measured current–voltage characteristics using 3-point differentiation and taking an average across all applied voltages (-2 V to $+2$ V). The conductivity was derived from the conductance by approximating the crystal as a cylinder with a length of 1.2 mm and a diameter of 50 μm, as determined by optical microscopy. Raman spectroscopy was performed using a Horiba Jobin–Yvon Lab ARAMIS instrument equipped with a 785 nm laser and confocal microscope, equipped with a 10× objective lens. The single crystals were measured using a 400 μm aperture, 400 μm slit, and 1200 gratings *per* mm, with exposure time of 1 s, averaged 20 times.

Single-crystal X-ray diffraction data acquisition was carried out on a Bruker Kappa APEX II CCD diffractometer with graphite-monochromatized (MoK$\alpha = 0.71073$ Å) radiation at a temperature of $T = 100(2)$ K. Data were collected with omega scan width of 0.5° at 3 different settings with exposure time of 15 s keeping the sample-to-detector distance fixed at 60 mm. The X-ray data collection was monitored by the APEX2 program.[20] The data were corrected for Lorentz, polarization and absorption effects using SAINT and SADABS. SHELXTL was used for structure solution and full matrix least-squares refinement on F2.[21] All the H-atoms were placed in geometrically idealized position and constrained to ride on their parent atoms. For the solution of the crystal structure of pyrroloperylene–iodine complex, the details are as: Molecular formula $C_{130}H_{70.5}I_{14.5}N_{6.5}$, $M = 3563.48$ g mol^{-1}, plate, $0.25\times0.05\times0.05$ mm^3, monoclinic, space group $C2/c$, $a = 37.939(7)$, $b = 18.507(3)$, $c = 29.839(5)$ Å, $\beta = 101.376(10)°$, $V = 20540(6)$ Å^3, $Z = 8$, $T = 100(2)$ K, $2\theta_{max} = 60.00°$, $D_{calc} = 2.305$ g cm^{-3}, $F(000) = 13316$, $\mu = 4.430$ mm^{-1}, 66320 reflections collected, 20967 unique reflections ($R_{int} = 0.509$), 1635 observed [$I > 2\sigma(I)$] reflections, multi-scan absorption correction, $T_{min} = 0.404$, $T_{max} = 0.809$, 633 refined parameters, $S = 0.684$, $R1 = 0.0591$, $wR2 = 0.0893$ (all data $R = 0.5242$, $wR2 = 0.1756$), maximum and minimum residual electron densities are $\Delta_{max} = 1.061$ e$^-$ Å^{-3} and $\Delta_{min} = -1.520$ e$^-$ Å^{-3}.

All crystallographic representations were carried out with VESTA.[22]

Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award No. DE-SC-0012541. V.D.N. is supported by the UC President's Postdoctoral Fellowship and the Elings Prize Fellowship. The use of shared experimental facilities of the Materials Research Laboratory: A National Science Foundation MRSEC supported by grant number NSF DMR 1121053 is gratefully acknowledged.

Keywords: conducting materials · perylenes · polyhalides · solid-state structures · X-ray diffraction

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 8032–8035
Angew. Chem. **2016**, *128*, 8164–8167

[1] W. Saenger, *Naturwissenschaften* **1984**, *71*, 31.
[2] J. J. Colin, H. G. de Claubry, *Ann. Chim.* **1814**, *90*, 87.
[3] B. Kahr, J. Freudenthal, S. Phillips, W. Kaminsky, *Science* **2009**, *324*, 1407.
[4] E. Redel, C. Röhr, C. Janiak, *Chem. Commun.* **2008**, 2103–2105.
[5] J. Lin, J. Martí-Rujas, P. Metrangolo, T. Pilati, S. Radice, G. Resnati, G. Terraneo, *Cryst. Growth Des.* **2012**, *12*, 5757–5762.
[6] A. J. Blake, F. A. Devillanova, R. O. Gould, W.-S. Li, V. Lippolis, S. Parsons, C. Radek, M. Schröder, *Chem. Soc. Rev.* **1998**, *27*, 195–205.
[7] Z. Yin, Q.-X. Wang, M.-H. Zeng, *J. Am. Chem. Soc.* **2012**, *134*, 4857–4863.
[8] L. Kloo, J. Rosdahl, P. H. Svensson, *Eur. J. Inorg. Chem.* **2002**, 1203–1209.
[9] P. H. Svensson, L. Kloo, *Chem. Rev.* **2003**, *103*, 1649–1689.
[10] R. C. Teitelbaum, S. L. Ruby, T. J. Marks, *J. Am. Chem. Soc.* **1978**, *100*, 3215–3217.
[11] J. Kommandeur, F. R. Hall, *J. Chem. Phys.* **1961**, *34*, 129–133.
[12] R. C. Teitelbaum, S. L. Ruby, T. J. Marks, *J. Am. Chem. Soc.* **1980**, *102*, 3215–3217.
[13] a) J. I. G. Cadogan, M. Cameron-Wood, R. K. Mackie, R. J. G. Searle, *J. Chem. Soc.* **1965**, 4831–4837; b) J. J. Looker, J. Org. Chem. **1972**, *37*, 3379–3381.
[14] J. M. Reddy, K. Knox, M. B. Robin, *J. Chem. Phys.* **1964**, *40*, 1082–1089.
[15] P. W. Anderson, P. A. Lee, M. Saitoh, *Solid State Commun.* **1973**, *13*, 595–598.
[16] J. B. Torrance, B. A. Scott, B. Welber, F. B. Kaufman, P. E. Seiden, *Phys. Rev. B* **1979**, *19*, 730–741.
[17] E. M. Nour, L. H. Chen, J. Laane, *J. Phys. Chem.* **1986**, *90*, 2841–2846.
[18] F. W. Parrett, N. J. Taylor, *J. Inorg. Nucl. Chem.* **1970**, *32*, 2458–2461.
[19] A. G. Maki, R. Forneris, *Spectrochim. Acta* **1967**, *23*, 867–880.
[20] *SMART Apex II*, Version 2.1; Bruker AXS Inc.: Madison, WI, **2005**.
[21] *SHELXTL PC*, Version 6.12; Bruker AXS Inc.: Madison, WI, **2005**.
[22] K. Momma, F. Izumi, *Comm. Crystallogr. Comput.* **2006**, *7*, 106–119.

Received: February 15, 2016