From crystal to crystal: a new polymorph of (4-carboxylatopyridine)silver(I) by topotactic dehydration of its monohydrate†‡

Irmgard Kalf, Patrick Mathieu and Ulli Englert*

Received (in Montpellier, France) 22nd February 2010, Accepted 28th April 2010
DOI: 10.1039/c0nj00144a

The dehydration of the coordination polymer (4-carboxylatopyridine)silver(I) monohydrate to a new polymorph of the unsolvated compound occurs even at room temperature under vacuum. In the course of this conversion, space filling increases; the new polymorph is closer packed than the one described earlier in the literature. The reaction proceeds as single-crystal-to-single-crystal transformation, with a close three-dimensional relationship between reactant and product crystals. The dehydration may also be conducted in the bulk, leading to a phase pure product. During the topotactic desolvation, the 3D framework of the monohydrate transforms into a two-dimensional layer structure. The reaction is irreversible: crystals of the unsolvated polymer cannot be re-hydrated when exposed to humid atmosphere or even immerged into water.

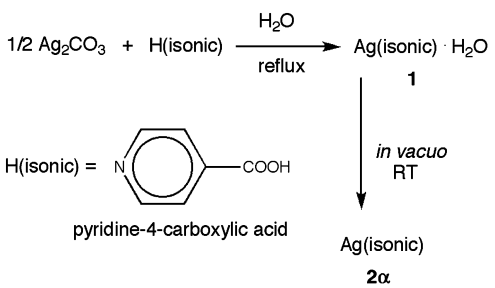
Coordination polymers and organic–inorganic hybrid materials represent widely studied classes of compounds because of their potential applications,[1–3] their enormous versatility in building up extended structures[4–8] and their fascinating dynamic behaviour.[9–11] Not only systems based on cations derived from a single element but also more complex bimetallic networks have been obtained and structurally characterized.[12–16] Polymers based on silver cations are particularly attractive: their lability facilitates crystallization and dissolution processes,[17] and closed-shell interactions between Ag(I) cations have been exploited for crystal engineering.[18–20] These so-called "argentophilic[18,19,21–23] interactions" involve Ag···Ag contacts of *ca.* 3 Å and bring about energies comparable to hydrogen bonds.[24] The fast-growing field of silver coordination polymers has been addressed by several review articles.[17,25,26] In our earlier work, we have used silver salts of weakly coordinating anions, among them silver acetate[27] and alkylbenzoates[28] as starting materials. The successful preparation of Ag(I) oligomers *via* reaction of silver 4-aminobenzoate and 4,4′-bipyridine[29] supports the idea that bidentate *N* donor ligands can in general replace the harder oxygen atoms in the coordination sphere of silver carboxylates and related compounds. We have recently reported on competitive coordination between carboxylates and the *N* donor pyrazine.[30] The ligand isonicotinate (isonic) unites both functionalities and acts as an *N*, *O* coordination partner for Ag(I) cations. Our interest in (4-carboxylatopyridine)silver(I) monohydrate, however, goes beyond its static polymer structure and mainly stems from its topotactic reactivity. Single-crystal-to-single-crystal transformations have been studied for several types of reactions, in particular for the photodimerization of olefins;[31] they usually do not involve the transport of matter over longer distances but rather occur with a minimum of atomic movement.[32] In the past years, several examples for single-crystal-to-single-crystal dehydrations have been documented.[33–39] We had encountered a case of reversible release and uptake of a coordinated water molecule in a europium complex.[40] In this contribution, we show that the irreversible dehydration of $[Ag(isonic)]_n{\cdot}nH_2O$ results in the formation of a hitherto unknown polymorph of the title compound. Both coordination polymers, the starting material (4-carboxylatopyridine)silver(I) monohydrate, **1**, and the reaction product of the topotactic transformation, **2α**, are represented in Scheme 1.

Several compounds containing isonicotinate and Ag(I) cations have been documented in the literature: the monohydrate **1** which represents the starting material of our single-crystal-to-single-crystal reaction was first described by Lu and co-workers.[41] Although this earlier structure determination and our result agree well and the structure of **1** will only be referred to for comparison, its re-determination was mandatory for two

Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany. E-mail: ullrich.englert@ac.rwth-aachen.de; Fax: +49 241 809228; Tel: +49 241 8094666

† This article is part of a themed issue on Coordination polymers: structure and function.

‡ Electronic supplementary information (ESI) available: IR spectra of **1** (as synthesized and stored over a saturated solution of NaCl) and **2α** (obtained after drying **1** for 12 h in vacuum); powder diffractograms of **1** and **2α**; and channels in **1** occupied by water molecules. CCDC reference numbers 766378 (**1**) and 766379 (**2α**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0nj00144a



Scheme 1

reasons: (a) we intended to establish the three-dimensional relationship between the crystal structures of the monohydrate and the dehydrated compound. (b) A comparison between **1** and **2α** with respect to space filling is more informative if both the structure determinations are performed at the same temperature. The product of our topotactic dehydration is not the first anhydrous silver isonicotinate: Ng and co-workers have described an alternative polymorph of the compound obtained under hydrothermal conditions;[42] we will refer to this compound as **2β**.

The remaining silver isonicotinates which have been structurally characterized comprise a coordination polymer containing un-deprotonated isonicotinic acid in addition to isonicotinate,[43,44] a hydrate with lower water content[45] and a methanol/water solvate.[46] They do not represent polymorphs of **1** and **2** and are not structurally related to the compounds documented in this study.

Results and discussion

When crystalline silver isonicotinate monohydrate, **1**, is dried in a desiccator or *in vacuo*, the unsolvated reaction product **2α** is also obtained in the form of crystals, many of them directly suitable for X-ray diffraction. Powder diffraction and IR spectra (see ESI‡) confirm that the conversion is complete with respect to the bulk and does not only occur in individual crystals. The lattice parameters of **1**[41] and **2α** already suggest a close relationship between these structures. In the context of this comparison, we do not refer to the earlier report on **1**[41] but rather to the numerical results of our own experiment because it was conducted at the same temperature as the diffraction study of the new compound **2α**. In addition to the starting material and the product of the topotactic reaction, the alternative polymorph **2β** by Ng *et al.*[42] has been included in Table 1.

Strictly spoken, a topotactic reaction requires not only a close structural relationship between the two compounds involved but also a three-dimensional correlation between their lattices.[47,48] This is best proven by determining the orientation matrices of the reactant and the product crystals. Fig. 1 shows the relative orientation of the reciprocal cells obtained on the same crystal before and after the single-crystal-to-single-crystal reaction

Table 1 Unit cell parameters and space filling requirements

	1	**2α**	**2β**
Reference	This work and ref. 41	This work	Ref. 42
Formula	$C_6H_6AgNO_3$	$C_6H_4AgNO_2$	$C_6H_4AgNO_2$
Temperature/K	110	110	298
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/a$
a/Å	3.6519(5)	3.6484(7)	7.763(6)
b/Å	12.1512(18)	10.844(2)	9.152(4)
c/Å	15.070(2)	14.425(3)	8.619(6)
β/°	90.982(4)	92.790(3)	98.08(6)
V/Å^3	668.63(16)	569.45(19)	606.3(7)
Z	4	4	4
V/Z/Å^3	167.16(4)	142.36(5)	151.6(2)
Packing coeff.	0.783	0.802	0.758
Shortest Ag···Ag/Å	2.9876(14)	3.2322(10)	4.189(3)

Fig. 1 Reciprocal unit cells of the reactant (dashed black and white) and product crystals (dark grey).

and confirms that this correlation is indeed observed for the reaction under study.

The antiparallel orientation of two lattice parameters $a_1^* \approx -a_{2\alpha}^*$ and $b_1^* \approx -b_{2\alpha}^*$ was chosen to ensure conventional obtuse monoclinic unit cells for both crystal structures.§ In the course of the single-crystal-to-single-crystal dehydration, no intermediates can be detected based on diffraction. The solid state reaction even occurs under ambient conditions but is considerably slower than under vacuum, *cf.* Experimental. We collected intensity data on a crystal of **1** in regular intervals. During the first 20 hours, the diffraction pattern corresponded to that of the hydrate **1**. After 30 hours, diffraction intensity was considerably lower and the diffraction pattern of **2α** was obtained. Subsequent data collections after 40 and 50 hours showed increasingly better crystal quality with respect to the criteria R_{int}, R_σ ($R_\sigma = \sum\sigma(F_o^2)/\sum F_o^2$), R_1 and wR_2. The similarity between **1** and **2α** extends to their atomic arrangement as shown by the projection of both the structures along the shortest direct lattice parameter in Fig. 2: the close match with respect to unit cell parameters, relative orientation of reactant and product crystals and atomic positions before and after the transformation underlines that the crystal-to-crystal reaction proceeds with a minimum of atomic movement, in agreement with the topochemical principle.[32]

The crystal structure of **1** features two major voids with a volume of 45 Å^3 each, located in the origin of the cell and in the center of the *bc* plane. The resulting void volume of *ca.* 22.5 Å^3 per water molecule in the unit cell is in good agreement with the value obtained from searches[50] in the CSD.[51] In the

§ In the case of parallel orientation of all three reciprocal lattice vectors, $\beta^* < 90°$ for one and (unconventionally) $\beta^* > 90°$ for the other structure would result.

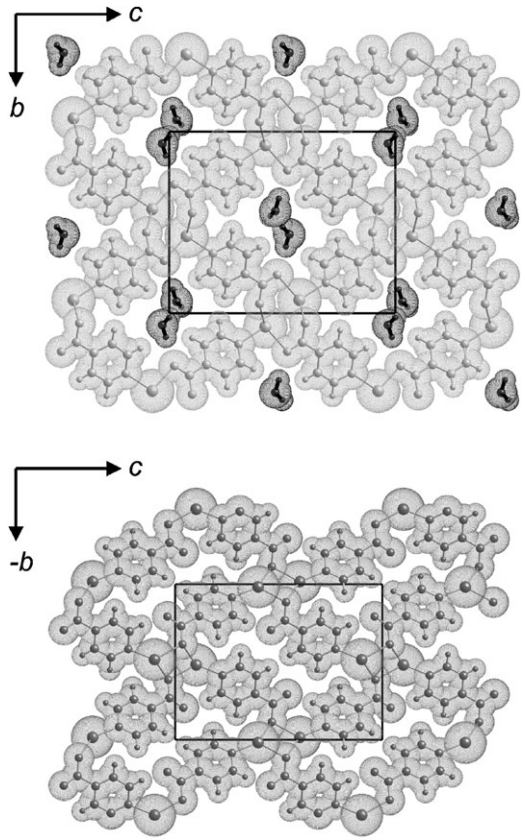


Fig. 2 Projections[49] of **1** (along $-a$) and **2α** (along a). The hydrate water molecules in **1** have been emphasized in dark grey, the alternative position of a bridging H between two neighbouring water molecules has been omitted.

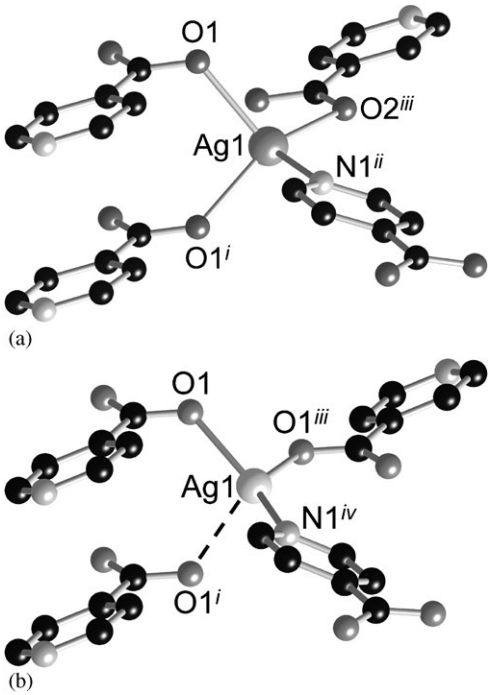


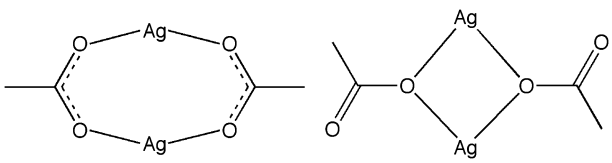
Fig. 3 (a) Silver coordination in **1** in the [001] direction. Selected interatomic distances and angles: Ag1–O1 2.455(9), Ag1–O1^{i} 2.402(9), Ag1–O2^{iii} 2.385(10), Ag1–N1^{ii} 2.278(8) Å, O1–Ag1–O1^{i} 97.5(3), O1–Ag1–O2^{iii} 105.7(3), O1–Ag1–N1^{ii} 118.5(4), O1^{i}–Ag1–O2^{iii} 145.0(3), O1^{i}–Ag1–N1^{ii} 85.8(4), O2^{iii}–Ag1–N1^{ii} 105.0(4)°. Symmetry operators $i = x - 1, y, z$; $ii = 1 - x, 0.5 + y, 0.5 - z$, $iii = 2 - x, 1 - y, -z$. (b) Silver coordination in **2α** in the [001] direction. Selected interatomic distances and angles: Ag1–O1 2.346(5), Ag1–O1^{i} 2.669(5), Ag1–O1^{iii} 2.297(4), Ag1–N1^{iv} 2.191(6) Å, O1–Ag1–O1^{i} 93.13(15), O1–Ag1–O1^{iii} 75.45(18), O1–Ag1–N1^{iv} 147.1(2), O1^{i}–Ag1–O1^{iii} 99.16(15), O1^{i}–Ag1–N1^{iv} 98.10(17), O1^{iii}–Ag1–N1^{iv} 132.22(19)°. Symmetry operators $i = x - 1, y, z$, $iii = 2 - x, 1 - y, -z$; $iv = 1 - x, y - 0.5, 0.5 - z$.

course of the topotactic reaction, the isonicotinate groups close to the co-crystallized water molecules approach each other, and the former cavity is efficiently filled. The cell parameters b and c shrink significantly whereas the shortest lattice constant a remains almost constant. Despite the pronounced overall similarity between **1** and **2α** with respect to packing, clear-cut changes occur in the coordination environment of the silver cations. The hydrate **1** represents a three-dimensional structure, and the coordination polyhedron around silver (Fig. 3a) is a distorted tetrahedron, with three Ag–O bonds around 2.4 Å and a shorter Ag–N distance.

In contrast, the product **2α** is best described as a layer structure; Fig. 3b corresponds to the same view direction [001] as Fig. 3a above and shows that the metal cation is co-ordinated by three donor atoms at unexceptional bond distances whereas the fourth interaction corresponds to a much longer and presumably weaker inter-layer contact and therefore has been shown as dashed line.

The shortest Ag···Ag distances in **1** are due to the formation of 1,3-carboxylato bridges as shown in Scheme 2 (left) and amount to only 2.9876(14) Å. In **2α**, only one of the carboxylato O atoms bridges inversion-related silver cations at a longer intercationic distance of 3.6728(11) Å (Scheme 2, right).

The different coordination modes of the carboxylato group in **1** and **2α** are reflected in well-distinguishable absorption



Scheme 2 Carboxylato bridges between closest Ag(I) cations in **1** (left) and **2α** (right).

bands in the frequency range between 1700 and 1300 cm^{-1} of the IR spectra (see ESI‡).

The alternative polymer of anhydrous silver isonicotinate, **2β**,[42] represents a chain polymer of lower density. The silver cations are coordinated in an almost linear fashion by one carboxylato O and a pyridine N atom. Fig. 4a shows the environment around an Ag(I) cation, and in Fig. 4b the projection along the resulting isolated strands in b direction is provided.

The structural outcome of the dehydration has not only been monitored by single-crystal experiments but also by powder diffraction (see ESI‡): the reaction yields the new polymorph **2α** as a phase pure product. The dehydration is irreversible: when macroscopic samples of **2α** are exposed to

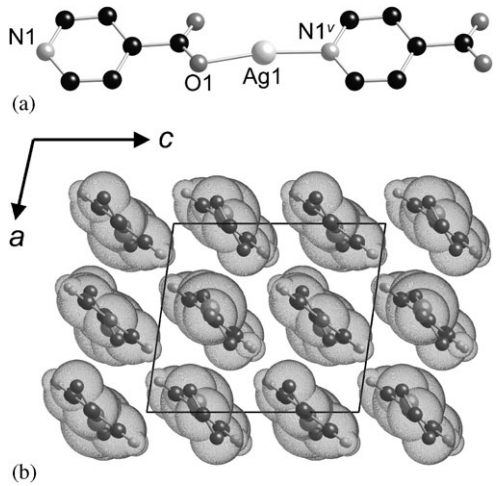


Fig. 4 (a) Silver coordination in **2β**. Selected interatomic distances and angles: Ag1–O1 2.175(7), Ag1–N1$^{\nu}$ 2.149(8) Å, O1–Ag1–N1$^{\nu}$ 170.4(3)°. Symmetry operator $\nu = x, 1 + y, z$. (b) Projection[49] of **2β** (along *b*).

humidity, no significant increase in weight is observed. Powder diffraction and experiments on single crystals confirm that no re-hydration occurs.

Conclusions

In this contribution, we have reported the formation of a new, close-packed polymorph of silver isonicotinate *via* irreversible dehydration of its monohydrate: the reaction proceeds in the solid state, and we have shown that it is not reconstructive. Its single-crystal-to-single-crystal character is not due to serendipity but rather to a combination of the following favourable facts: (a) in crystals of the starting material **1** short hydrogen bonds with donor···acceptor distances of *ca.* 2.60 Å only occur between hydrate water molecules; interactions between these water molecules leaving the crystal in the solid state reaction and the coordination polymer framework are significantly longer (2.86 Å) and weaker. (b) The voids filled by the solvent molecules extend to a continuous channel along [100] (see ESI‡) and thus allow the dehydration by diffusion without disrupting the surrounding host structure. (c) The structures of **1** and **2α** differ with respect to the coordination distances and angles around the silver cations (*cf.* Fig. 3) and the dihedral angle subtended by the pyridine and the carboxylato plane in the ligand; the latter increases from 12.1(14)° in **1** to 21.8° in **2α**. These changes in soft degrees of freedom allow to balance the atomic movements which are required to fill the empty space when the water molecules leave **1** and **2α** forms.

Experimental

Our study relies on single crystal and powder X-ray diffraction, microanalysis and IR spectroscopy. Ag_2CO_3 (Aldrich) and isonicotinic acid (Aldrich) were used as received.

IR spectra were recorded with a Nicolet Avatar 360 E.S.P. FT instrument as nujol mulls and as KBr pellets; we did not find any indication of artefacts due to the formation of AgBr in the latter samples. Selected absorption bands below refer to the spectra in KBr and are reported in cm^{-1}. Elemental analyses were carried out on a Heraeus CHNO-Rapid apparatus.

Synthesis

Synthesis of (4-carboxylatopyridine)silver(I) monohydrate, 1. 16.3 mmol (4.5 g) of Ag_2CO_3 and 32.5 mmol (4.0 g) of isonicotinic acid are ground in a mortar for 5 min. The resulting solid is suspended in 900 mL of water and heated to reflux for 2.5 h. The solid is filtered off and the hot filtrate is allowed to cool from 100 °C to 20 °C overnight. 13.0 mmol (3.23 g, 41.5% yield) of **1** are obtained in the form of colourless, needle-shaped crystals. From the filtrate, additional microcrystalline products may be recovered by evaporation of the solvent. Calc. for $C_6H_6AgNO_3$: C 29.06, H 2.44, N 5.65%. Found: C 29.59, H 2.59, N 5.74%. IR 1608 (vs), 1550 (s), 1410 (sh), 1395 (vs).

Stability of **1**: single crystal diffraction of the same crystal at regular intervals under ambient conditions, microanalysis and IR spectra indicate that loss of water proceeds even at ambient conditions; when kept in a closed container over a saturated solution of NaCl in water, crystals of the product are stable for at least one month.

Synthesis of (4-carboxylatopyridine)silver(I), 2α. 11.5 mmol (2.84 g) of **1** are placed in a Schlenk tube and kept at 20 °C under vacuum for 12 h. A weight loss of *ca.* 8% is observed. The resulting solid corresponds to **2α**. Calc. for $C_6H_4AgNO_2$: C 31.34, H 1.75, N 6.09%. Found: C 31.68, H 2.03, N 6.08%; dec. *ca.* 231 °C. IR 1650 (sh), 1630 (s), 1602 (s), 1550 (s), 1415 (m), 1390 (m), 1330 (vs), 1310 (sh).

No re-hydration of **2α** to **1** occurs when (micro)crystalline samples are stored over a saturated solution of NaCl in water. The solubility of **2α** in water is very low: when single crystals of the compound are suspended in water for up to three weeks, no re-hydration occurs.

X-Ray diffraction studies

Powder diffractograms were recorded with a Stoe Imageplate-detector IP-PSD.

Single-crystal X-ray structure determination: geometry and intensity data were obtained with a Bruker D8 goniometer equipped with sealed tube generator (Mo-Kα radiation, $\lambda = 0.71073$ Å, graphite monochromator). Temperature was controlled using an Oxford Cryostream 700 instrument. Intensities were integrated with SAINT+[52] and corrected for absorption with SADABS.[53] The structure was solved by a Patterson synthesis and refined on F^2 with SHELXL-97.[54] Non-hydrogen atoms were assigned anisotropic displacement parameters; in the case of **1**, isotropicity restraints were applied to the displacement parameters of the carboxylato O atoms. H atoms on C were included as riding in standard geometry, and H atoms associated with the water molecule were located as local electron density maxima. The short distance of 2.607(18) Å between inversion-related neighbouring water molecules requires the presence of a bridging hydrogen atom and hence necessarily implies disorder for this H position. O–H distances were idealized to 0.85 Å. After the intensity

data collection for the monohydrate **1**, the goniometer head with the single crystal was transferred into a desiccator, kept *in vacuo* for 12 h, and again mounted on the diffractometer in a stream of cold N_2 for intensity data collection of the product crystal **2α**. Refinement results for this new structure: 6745 reflections, $\theta_{max} = 27°$, $R_{int} = 0.0703$, 1254 independent reflections, 91 parameters, wR_2 (all data) = 0.0929, R_1 (979 data with $I > 2\sigma I$) = 0.0434.‡

Calculations of packing coefficients and voids

The packing coefficient is defined as the ratio of occupied to total unit cell volume.[55,56] This overall indicator for space filling efficiency has been included in Table 1. The numerical values for the packing coefficients and the volume occupied by the water molecules in the hydrate **1** were determined with the help of PLATON;[57] for Ag, a van der Waals radius of 1.7 Å was assumed.[27]

References

1 C. Janiak, *Dalton Trans.*, 2003, 2781.
2 S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334.
3 D. Maspoch, D. Ruiz-Molina and J. Veciana, *Chem. Soc. Rev.*, 2007, **36**, 770.
4 B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
5 L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247.
6 D. Braga, L. Brammer and N. R. Champness, *CrystEngComm*, 2005, **7**, 1.
7 S. Kitagawa and R. Matsuda, *Coord. Chem. Rev.*, 2007, **251**, 2490.
8 U. Englert, *Coord. Chem. Rev.*, 2010, **254**, 537.
9 C. Hu and U. Englert, *Angew. Chem., Int. Ed.*, 2005, **44**, 2281.
10 C. Hu and U. Englert, *Angew. Chem., Int. Ed.*, 2006, **45**, 3457.
11 J. J. Vittal, *Coord. Chem. Rev.*, 2007, **251**, 1781.
12 V. D. Vreshch, A. N. Chernega, J. A. K. Howard, J. Sieler and K. V. Domasevitch, *Dalton Trans.*, 2003, 1707.
13 V. D. Vreshch, A. B. Lysenko, A. N. Chernega, J. A. K. Howard, H. Krautscheid, J. Sieler and K. V. Domasevitch, *Dalton Trans.*, 2004, 899.
14 G. Margraf, R. Pattacini, A. Messaoudi and P. Braunstein, *Chem. Commun.*, 2006, 3098.
15 A. D. Burrows, K. Cassar, M. F. Mahon and J. E. Warren, *Dalton Trans.*, 2007, 2499.
16 M. Kondracka and U. Englert, *Inorg. Chem.*, 2008, **47**, 10246.
17 A. N. Khlobystov, A. J. Blake, N. R. Champness, D. A. Lemenovskii, A. G. Majouga, N. V. Zyk and M. Schröder, *Coord. Chem. Rev.*, 2001, **222**, 155.
18 X. Liu, G.-C. Guo, M.-L. Fu, X.-H. Liu, M.-S. Wang and J.-S. Huang, *Inorg. Chem.*, 2006, **45**, 3679.
19 L. Dobrzanska, H. G. Raubenheimer and L. Barbour, *Chem. Commun.*, 2005, 5050.
20 R. P. Feazell, C. E. Carson and K. K. Klausmeyer, *Inorg. Chem.*, 2006, **45**, 2635.
21 M. A. Omary, T. R. Webb, Z. Assefa, G. E. Shankle and H. H. Patterson, *Inorg. Chem.*, 1998, **37**, 1380.
22 C. J. Shorrock, B.-Y. Xue, P. B. Kim, R. J. Batchelor, B. O. Patrick and D. B. Leznoff, *Inorg. Chem.*, 2002, **41**, 6743.
23 Q. Chu, D. C. Swenson and L. R. MacGillivray, *Angew. Chem., Int. Ed.*, 2005, **44**, 3569.
24 P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597.
25 A. Y. Robin and K. M. Fromm, *Coord. Chem. Rev.*, 2006, **250**, 2127.
26 C.-L. Chen, B.-S. Kang and C.-Y. Su, *Aust. J. Chem.*, 2006, **59**, 3.
27 I. Kalf, M. Braun, Y. Wang and U. Englert, *CrystEngComm*, 2006, **8**, 916.
28 Y. Wang and U. Englert, *Inorg. Chim. Acta*, 2010, DOI: 10.1016/j.ica.2010.04.030.
29 Y. Wang and U. Englert, *Eur. J. Inorg. Chem.*, 2007, 5623.
30 Y. Wang, M. Serb and U. Englert, *Struct. Chem.*, 2010, **21**, 203–211.
31 T. Friščić and L. R. MacGillicray, *Z. Kristallogr.*, 2005, **220**, 351.
32 M. D. Cohen and G. M. J. Schmidt, *J. Chem. Soc.*, 1964, 1996.
33 E. Y. Lee and M. P. Suh, *Angew. Chem., Int. Ed.*, 2004, **43**, 2798.
34 A. Michaelides and S. Skoulika, *Cryst. Growth Des.*, 2005, **5**, 529.
35 T. Pretsch, K. W. Chapman, G. J. Halder and C. J. Kepert, *Chem. Commun.*, 2006, 1857.
36 H. A. Habib, J. Sanchiz and C. Janiak, *Dalton Trans.*, 2008, 1734.
37 D.-X. Xue, W.-X. Zhang, X.-M. Chen and H.-Z. Wang, *Chem. Commun.*, 2008, 1551.
38 M.-L. Cao, H.-J. Mo, J.-J. Liang and B.-H. Ye, *CrystEngComm*, 2009, **11**, 784.
39 C. D. Ene, A. M. Madalan, C. Maxim, B. Jurca, N. Avarvari and M. Andruh, *J. Am. Chem. Soc.*, 2009, **131**, 4586.
40 U. Englert, B. Ganter, T. Wagner and W. Kläui, *Z. Anorg. Allg. Chem.*, 1998, **624**, 970.
41 W.-G. Lu, J.-Z. Gu, L. Jiang, C.-Y. Su and T.-B. Lu, *Chin. J. Inorg. Chem.*, 2006, **22**, 1977.
42 Y.-Y. Yang, Z.-Q. Huang, G.-F. Ouyang and S. W. Ng, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2004, **60**, m1158.
43 B. Cova, A. Briceno and R. Atencio, *New J. Chem.*, 2001, **25**, 1516.
44 F.-T. Xie, H.-Y. Bie, L.-M. Duan, G.-H. Li, X. Zhang and J.-Q. Xu, *J. Solid State Chem.*, 2005, **178**, 2858.
45 B. Liu and Q. Yuan, *Inorg. Chem. Commun.*, 2005, **8**, 1022.
46 Z. Liu, P. Liu, Y. Chen, J. Wang and M. Huang, *New J. Chem.*, 2005, **29**, 474.
47 F. K. Lotgering, *J. Inorg. Nucl. Chem.*, 1959, **9**, 113.
48 H. Morawetz, S. Z. Jakabhazy, J. B. Lando and J. Hafer, *Proc. Natl. Acad. Sci. U. S. A.*, 1963, **49**, 789.
49 D. C. Palmer, *CrystalMaker: Interactive Crystallography for MacOS, Version 7.2.1*, Oxford, 2007.
50 J. van de Streek and S. Motherwell, *CrystEngComm*, 2007, **9**, 55.
51 F. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **58**, 380.
52 Bruker AXS, *SAINT+: Program for Reduction of Data collected on Bruker CCD Area Detector Diffractometer V. 7.23A*, Bruker AXS Inc., Madison, Wisconsin, USA, 2005.
53 Bruker AXS, *SADABS: Program for Empirical Absorption Correction of Area Detector Data V 2004/1*, Bruker AXS Inc., Madison, Wisconsin, USA, 2004.
54 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.
55 A. I. Kitaigorodsky, *Molecular Crystals and Molecules*, Academic Press, New York, USA and London, England, 1973.
56 A. Gavezzotti, *J. Am. Chem. Soc.*, 1983, **105**, 5220.
57 A. L. Spek, *Acta Crystallogr., Sect. D: Biol. Crystallogr.*, 2009, **65**, 148.