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$^{2}_{\infty}[Yb_2(NH_2)_2(Pz)_4][Yb(NH_3)_2(Pz)_3PzH]$: Electride Induced Synthesis of a 2D-Ytterbium-Pyrazolate Network[#]

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Summary. $^{2}_{\infty}[Yb_2(NH_2)_2(Pz)_4][Yb(NH_3)_2(Pz)_3PzH]$, $Pz^- =$ pyrazolate anion, $PzH =$ pyrazole, $C_3H_4N_2$ is obtained by the reaction of ytterbium metal with pyrazole in liquid ammonia and subsequent increase of the temperature to 200°C resulting in the formation of colorless single crystals of the compound. The X-ray single crystal analysis reveals that the structure consists of $^{2}_{\infty}[Yb_2(NH_2)_2(Pz)_4]$ planes with neutral $[Yb(NH_3)_2(Pz)_3PzH]$ monomeric molecules that are located between the planes and ytterbium is trivalent. This is the first example of a two-dimensional network structure of an organic amine of the rare earth elements that derives from an electride induced synthesis. The product decomposes under release of ammonia outside its sealed reaction vessel, *viz.* if the NH_3 pressure is removed.

Keywords. Lanthanoids; X-Ray crystal structure; Amides; Network structures; Electrides.

Introduction

The ability of liquid ammonia to dissolve alkaline and alkaline earth metals giving deeply blue colored solutions of solvated electrons and homoleptic ammine complexes has attracted attention of chemists since the late 19th century [1–6]. At ambient pressure europium and ytterbium give analogous reactions, which was *e.g.* used to obtain first divalent metallocene complexes [7, 8] or amides of the formula $[Ln(NH_2)_2]$ [9–12].

We successfully used electrides to have a suitable reducing agent for organic amines and to thereby synthesize organic amides of the lanthanides at low temperatures [13–16]. Subsequent heating of the amides $[Ln(NH_2)_2]$ results in nitride formation [17, 18]. Referring redox and deprotonation reactions gave the first molecular nitride of a rare earth element: $[Yb_3N(Dpa)_6][Yb(Dpa)_3]$, $Dpa^- =$ dipyridylamide anion [19], with the organic amine 2,2′-dipyridylamine. Recently, cyclopentadienide amide and ammine complexes like Cp_3LnNH_3 or $Cp_4Ln_2(NH_2)_2$ [20] have been shown to function as suitable precursors for nanocrystalline nitrides [21] or amorphous Ln/C/N/O solids [22] by pyrolysis.

Our studies on the influence of temperature on the formation of rare earth pyrrolates from liquid ammonia illuminate that prior to pyrolysis the amides perform condensation reactions under release of ammonia molecules, which result in the formation of the one-dimensional coordination polymers $^{1}_{\infty}[Eu_2(Pyr)_4(PyrH)_2(NH_3)] \cdot PyrH$, $Pyr^- =$ pyrrolate anion, $PyrH =$ pyrrole, C_4H_4NH [15], and $^{1}_{\infty}[Yb_5(Pyr)_{12}(NH_3)_4(NH_2)] \cdot 2PyrH$ [16]. Higher dimensionalities like in the title compound have not yet been observed.

Here we present that the reaction of ytterbium metal with pyrazole, $PzH = C_3H_3NNH$, in liquid ammonia gives a two-dimensional network structure upon heating.

Results and Discussion

Synthesis

The formation of organic rare earth amides from liquid ammonia can be subdivided into two steps

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[#] Dedicated to Prof. *Dieter Naumann* on the occasion of his 65th birthday

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of reaction. Within the first reaction the metal is dissolved in ammonia giving homoleptic ammonia complexes and solvated electrons:

$$Yb + xNH_3 \xrightarrow{T > -78^\circ C} [Yb(NH_3)_8]^{y+} + ye^-(NH_3)_z \tag{1}$$

Though described as hexaammine complexes [3, 18, 23, 24] vapour pressure investigations [24] as well as crystallizations of the monomeric trivalent salts $[Yb(NH_3)_8][Cu(S_4)_2] \cdot NH_3$, $[La(NH_3)_9][Cu(S_4)_2]$ [25], $NH_4[La(NH_3)_9](S_5)S$ [26], or $[Yb(NH_3)_8][Yb(Pyr)_6]$ [27] and $[Sm(NH_3)_9][Sm(Pyr)_6]$ [28] show that higher coordination numbers are much more likely (eight for ytterbium).

In a second step the organic amine pyrazole is reduced by the solvated electrons to form hydrogen and ammonia complexes of ytterbium pyrazolates. As the product could not be crystallized directly from the low-temperature reaction in liquid ammonia subsequent treatments at temperatures up to 200°C were applied. At these temperatures single crystalline ${}^2_\infty[Yb_2(NH_2)_2(Pz)_4][Yb(NH_3)_2(Pz)_3PzH]$ is formed in good yields (see Eq. (2)) as a condensation product of a partial release of ammonia as well as an internal deprotonation reaction leading to linking NH_2^- groups, as observed for the classical rare earth and alkaline rare earth amides [12, 18, 29, 30] or the ytterbium carbazolate $[Yb_2(Cbz)_4(NH_2)_2(NH_3)_4] \cdot 3CbzH$ (**2**) (Cbz^- = carbazolate anion, $CbzH$ = carbazole, $C_{12}H_8NH$) [15].

$$\begin{aligned} &3[Yb(NH_3)_8]^{3+} + 7e^-(NH_3)_z + 8C_3H_4N_2 \\ &\longrightarrow {}^2_\infty[Yb_2(NH_2)_2(C_3H_3N_2)_4][Yb(NH_3)_2 \\ &\qquad (C_3H_3N_2)_3C_3H_4N_2] + z - 4NH_3 + \frac{9}{2}H_2 \end{aligned} \tag{2}$$

${}^2_\infty[Yb_2(NH_2)_2(Pz)_4][Yb(NH_3)_2(Pz)_3PzH]$ is highly air and moisture sensitive and cannot be maintained if removed from the ammonia overpressure of the sealed ampoule, but decomposes under release of NH_3. Accordingly, microanalysis shows significantly lower amounts of N and H. However this decomposition is much less rapid than for $[Yb(NH_3)_8][Yb(Pyr)_6]$ [27], as IR spectroscopy still reveals stretching modes of NH_2^-, NH_3 groups [31], and coordinating pyrazole ($\nu(N-H) = 3126, 3280, 3364\,cm^{-1}$) as well as deformation bands ($\delta(N\text{–}H) = 1524, 1595, 1603\,cm^{-1}$). Stretching modes of the metal-N vibrations are also evident in the FarIR spectrum ($\nu(Yb-N) = 237, 164\,cm^{-1}$). The Yb–N vibrations are in the expected region found for other ammino ytterbium amides [15, 16, 19, 27, 28], and cannot be identified with the pyrazole ligand [32].

Crystal Structure

The crystal structure of ${}^2_\infty[Yb_2(NH_2)_2(Pz)_4][Yb(NH_3)_2(Pz)_3PzH]$ consists of two dimensional layers of the formula ${}^2_\infty[Yb_2(NH_2)_2(Pz)_4]$ and monomeric $[Yb(NH_3)_2(Pz)_3PzH]$ molecules that are positioned in-between the layers.

All ytterbium ions are trivalent and octa-coordinated by nitrogen atoms, two of them being η^2-N-coordinations by pyrazolate anions so that distorted octahedral coordination spheres result for each Yb^{3+}

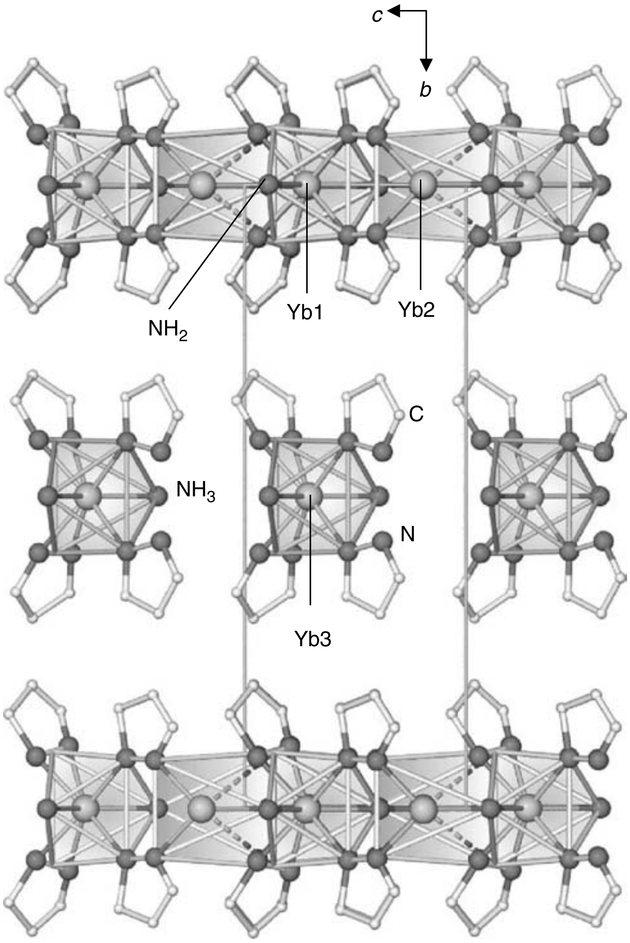

Fig. 1. The crystal structure of ${}^2_\infty[Yb_2(NH_2)_2(Pz)_4][Yb(NH_3)_2(Pz)_3PzH]$ with a view along [100]. Monomeric molecules of the formula $[Yb(NH_3)_2(Pz)_3PzH]$ are positioned between layers of the formula ${}^2_\infty[Yb_2(NH_2)_2(Pz)_4]$ along [010]. The coordination polyhedra around the Yb^{3+} ions are depicted

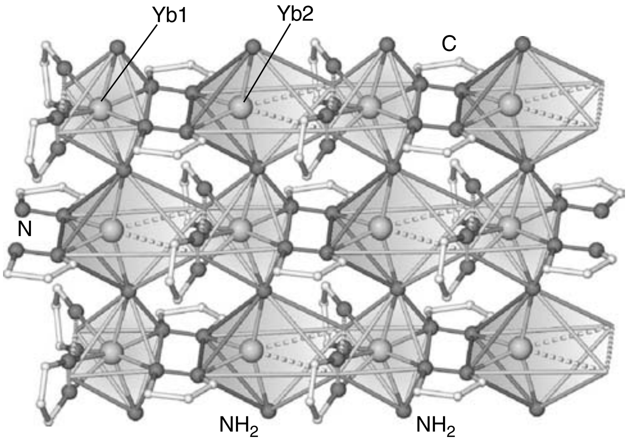

Fig. 2. View on one layer $^{2}_{\infty}[\mathrm{Yb_2(NH_2)_2}(Pz)_4]$. The coordination polyhedra illuminate the asymmetric coordination sphere of Yb2 due to the μ-η^3:η^2 bridging to Yb1. H atoms are left out for clarity

ion. Both anionic species, $\mathrm{NH_2}^-$ (μ_2) and Pz^- ($\mu-\eta^1$:η^1 and $\mu-\eta^2$:η^3) are linking the Yb ions within the layer (see Fig. 2).

Yb1 is thus coordinated by two $\mathrm{NH_2}^-$ groups, η^2 by two Pz^- as well as η^1 by another two Pz^- anions with Yb1-N distances of 222(2)–250(2) pm, the shortest distances reflecting the η^2 coordination (see Fig. 3). This finding is in good agreement with a study on the referring binding mode in other pyrazolates like $[\mathrm{Nd_3}(Pz)_9(Pz\mathrm{H})_2]$ including DFT and ELF calculations [33]. As the $\mu-\eta^2$:η^3 bridging in $^{2}_{\infty}[\mathrm{Yb_2(NH_2)_2}(Pz)_4]$ is strongly asymmetric reflecting a weak $\eta^3-\pi$ bonding to Yb2, its coordination sphere is asymmetric, too. A combination of η^2:η^3 coordinations of a pyrazolate ring resulting in a bridging of metal cations was previously reported for $[\mathrm{K}\{\mathrm{Er}(tBu_2Pz)_4\}_n]$ [34]. The Yb2-N distances range from 232(2)–243(2) pm, the Yb2-(η^3-C,N)-π distances are 275(2)–355(3) pm. An η^1:η^1 bridging is common for linked unsubstituted Pz^- anions in rare earth pyrazolates like $[\mathrm{Gd_2}(Pz)_6(Pz\mathrm{H})_4]$, $[\mathrm{Nd_3}(Pz)_9(Pz\mathrm{H})_2]$ [33], and is also found for coordination polymers like $^{1}_{\infty}[\mathrm{Ho}(Pz)_3(Pz\mathrm{H})_3]$ [35]. In contrast it is rather seldom for substituted pyrazolates and only found for small substituents like methyl groups in $[\mathrm{Nd_2}(Me_2Pz)_6(thf)_2]$ [36]. The larger the substituents on the pyrazolate rings get the more non-bridging η^2 coordinations are observed [34, 36, 37]. Large substituents also prevent formation of coordination polymers. So far all coordination polymers of rare earth pyrazolates contain unsubstituted pyrazolate groups and are one-dimensional. Addition of $\mathrm{NH_2}^-$ groups now renders bridging in a second direction and thus formation of $^{2}_{\infty}[\mathrm{Yb_2(NH_2)_2}(Pz)_4]$ layers in $^{2}_{\infty}[\mathrm{Yb_2(NH_2)_2}(Pz)_4]$ $[\mathrm{Yb(NH_3)_2}(Pz)_3Pz\mathrm{H}]$.

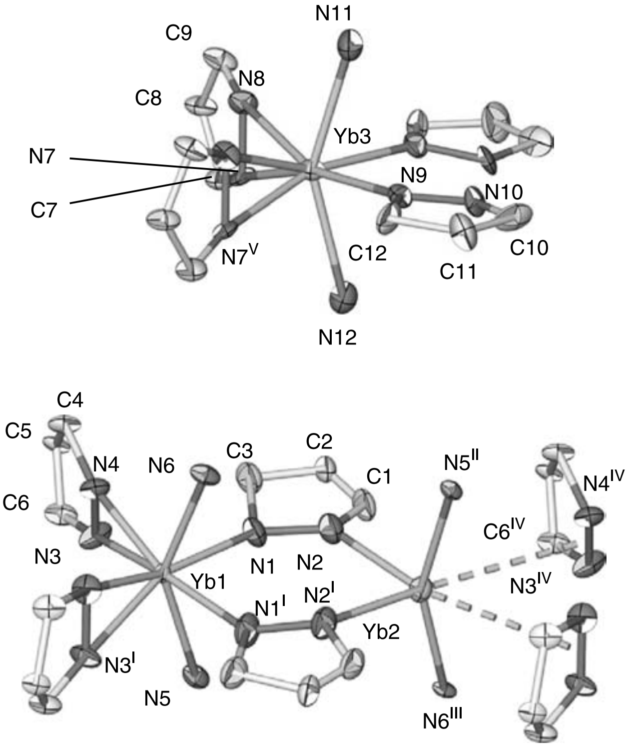

Fig. 3. Depiction of the thermal ellipsoids of the atoms of $^{2}_{\infty}[\mathrm{Yb_2(NH_2)_2}(Pz)_4][\mathrm{Yb(NH_3)_2}(Pz)_3Pz\mathrm{H}]$. A monomer is displayed at the top, a section of a layer of the formula $^{2}_{\infty}[\mathrm{Yb_2(NH_2)_2}(Pz)_4]$ at the bottom. The thermal ellipsoids represent a probability level of the atoms of 35%. H atoms are left out for clarity. Selected interatomic distances/pm and angles/°: Yb1–N1: 227(2), Yb1–N3: 222(2), Yb1–N4: 240(2), Yb1–N5: 248(2), Yb1–N6: 250(2), Yb2–N2: 232(2), Yb2–N5$^{\mathrm{II}}$: 240(2), Yb2–N6$^{\mathrm{III}}$: 243(2), Yb2–C6$^{\mathrm{IV}}$: 275(2), Yb2–N3$^{\mathrm{IV}}$: 355(3), Yb3–N7: 232(2), Yb3–N8: 231(2), Yb3–N9: 240(2), Yb3–N11: 245(2), Yb3–N12: 245(2); N1–Yb1–N3: 89.7(5), N1$^{\mathrm{I}}$–Yb1–N3: 162.2(6), N1–Yb1–N4: 158.9(6), N4–Yb1–N6: 84.5(4), N5–Yb1–N6: 146.4(6), N2–Yb2–N2$^{\mathrm{I}}$: 79.2(5), N2–Yb2–N6$^{\mathrm{III}}$: 94.3(4), N5$^{\mathrm{II}}$–Yb2–N6$^{\mathrm{III}}$: 155.4(6), N7–Yb3–N7$^{\mathrm{V}}$: 95.1(4), N8–Yb3–N8$^{\mathrm{V}}$: 95.8(4), N7–Yb3–N9: 159.5(4), N9–Yb3–N12: 81.0(4), N11–Yb3–N12: 150.0(5). Symmetry operations: I: $x, -y, z$; II: $x, y, z-1$; III: $x-1, y, z$; IV: $x-1, y, z-1$; V: $x, -y+1, z$

In the monomeric unit $[\mathrm{Yb(NH_3)_2}(Pz)_3Pz\mathrm{H}]$ two $\mathrm{NH_3}$ molecules as well as one end-on η^1-coordinating pyrazole molecule and pyrazolate anion each saturate the coordination sphere of Yb3 in addition to two η^2-coordinating Pz^- anions (see Fig. 3). The Yb3-N distances range from 231(2) pm for Pz^- to 245(2) pm for the $\mathrm{NH_3}$ molecules. All Yb–N distances in $^{2}_{\infty}[\mathrm{Yb_2(NH_2)_2}(Pz)_4][\mathrm{Yb(NH_3)_2}(Pz)_3Pz\mathrm{H}]$ are in the expected range for $\mathrm{Yb^{III}}$ [38].

Experimental

All manipulations were carried out under inert atmospheric conditions using glove box, *Schlenk* and ampoule techniques. Yb metal (Strem, 99.99%), pyrazole (Acros, 99.9%), and NH_3 (Linde, 99.9999%) were used as purchased. The IR spectra were recorded using a Bruker FTIR-IS66V-S spectrometer. For MIR investigations KBr pellets, and PE pellets for FIR were used under vacuum. Elemental analyses (C, H, N) were conducted using the Elemental Analyser Euro EA (Hekatech), their results were found to be in good agreement (±0.2%) with the calculated values reflecting that the compound releases ammonia once outside the ammonia atmosphere. The data collection for the single crystal X-ray investigation was carried out on a STOE IPDS-II diffractometer (Mo K_α radiation $\lambda = 0.7107$ Å) at 170 K.

The best out of five single crystals of **1** was selected for the single crystal X-ray investigation under glovebox conditions and sealed in glass capillaries. The structure was determined using direct methods [39]. All non-hydrogen atoms were refined anisotropically by least squares techniques [40]. All hydrogen positions were calculated into pre-set positions adjusting their thermal parameters to 1.2 of the referring carbon atoms. $^{2}_{\infty}[\mathrm{Yb_2(NH_2)_2}(Pz)_4][\mathrm{Yb(NH_3)_2}(Pz)_3Pz\mathrm{H}]$ (**1**) crystallizes in the monoclinic space group *P* m. A numerical absorption correction was applied by determination of the trigonal prismatic needle like crystal habitus on the Stoe IPDS-II diffractometer and refining the five crystal faces [41]. Crystallographic data are summarized in Table 1.

Table 1. Crystallographic data for $^{2}_{\infty}[\mathrm{Yb_2(NH_2)_2}(Pz)_4]$ $[\mathrm{Yb(NH_3)_2}(Pz)_3Pz\mathrm{H}]$

Formula	$Yb_3C_{24}H_{39}N_{20}$
molar mass/g mol^{-1}	1122.83
crystal system	monoclinic
space group	*P* m
a/pm	666.4(2)
b/pm	1893.1(4)
c/pm	669.2(2)
$\beta/°$	90.70(3)
$V/10^6$ pm^3	844.2(3)
Z	1
d_{calc}/g cm^{-3}	2.209
μ/cm^{-1}	82.91
T/K	170
Flack-x parameter [42]	0.05(4)
data range	$4.3 \leq 2\theta \leq 52.0$
X-ray radiation	Mo K_α, $\lambda = 71.073$
absorption correction, faces, $T_{\min}/T_{\max}$ [41]	numerical, 5, 0.1444, 0.5138
R_{int} (previous/after absorption corr.)	0.113/0.061
no. unique reflections	3272
no. of parameters/restraints	223/0
ratio refl./parameters	15
R_1[a] for n reflections with $F_o > 4\sigma(F_o)$; n	0.061; 2439
R_1 (all)	0.093
wR_2[b] (all)	0.143
rem. electron density/e/(10^6 pm^3)	1.5/−1.7

[a] $R_1 = \Sigma[|F_o| - |F_c|]/\Sigma[|F_o|]$

[b] $wR_2 = (\Sigma w(F_o{}^2 - F_c{}^2)^2/(\Sigma w(F_o{}^4))^{1/2}$ [40]

Further information was deposited at the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223336033 or e-mail: deposit@ccdc.cam.ac.uk) and may be requested by citing the deposition number CCDC-642036, the names of the authors, and the literature citation.

[$Yb_2(NH_2)_2(C_3H_3N_2)_4$][$Yb(NH_3)_2(C_3H_3N_2)_3C_3H_4N_2$]
(**1**, $C_{24}H_{35}N_{20}Yb_3$)

Yb (173 mg, 1 mmol) and 545 mg pyrazole (8 mmol) were filled in a Duran glass ampoule. Subsequently 4 cm^3 ammonia were condensed with liquid nitrogen into the ampoule. Upon melting of the ammonia at −78°C the colour of the reaction mixture changed to blue followed by dark red. Further increase of temperature to −50°C gave a yellow solution of liquid NH_3 and a red precipitate that was orange in thin layers. The excess ammonia was evaporated giving lighter colours of the same types becoming more and more colourless. The ampoule was cooled with liquid nitrogen and sealed under vacuum keeping a slight excess of ammonia. The reaction mixture was then heated to 100°C in 5 h and to 130°C in another 3 h. This temperature was kept for 168 h. The reaction mixture was then cooled down to 80°C in 150 h and to room temperature within 24 h. The crystalline colourless product of **1** was formed on the walls of the ampoule in addition to a microcrystalline bulk of **1** and excess pyrazole. No excess ytterbium metal was observed. **1** is highly air and moisture sensitive and prone to decomposition once the ampoule is opened due to the release of NH_3. Yield: 718 mg (64%). IR (KBr): $\bar{\nu} = 3364$, 3280, 3126, 3080, 2983, 1780, 1603, 1595, 1524, 1489, 1439, 1410, 1363, 1261, 1252, 1243, 1154, 1130, 1039, 989, 951, 922, 883, 764, 677, 626, 590 cm^{-1}; FarIR (PE): $\bar{\nu} = 449$, 237, 165, 148 cm^{-1}; Analysis: $M = 1126.83$ g mol^{-1}, calc: C 25.58, N 24.86, H 3.49; after release of ammonia: $M = 1092.83$ g mol^{-1}, calc (found): C 26.35 (26.6), N 23.14 (23.0), H 2.56 (2.8).

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References

[1] Weyl W (1864) Poggendorff Ann **121**: 601
[2] Kraus CA (1908) J Am Chem Soc **30**: 1323
[3] Symons MCR (1976) Chem Soc Rev **5**: 337
[4] Dye JL (1984) Prog Inorg Chem **32**: 327

[5] Korber N, Richter F (1997) Angew Chem **109**: 1575; (1997) Angew Chem Int Ed Engl **36**: 1512
[6] Klein W, Jansen M (2000) Z Anorg Allg Chem **626**: 847
[7] Fischer EO, Fischer H (1964) Angew Chem **76**: 134; (1964) Angew Chem Int Ed Engl **3**: 132
[8] Hayes RG, Thomas JL (1969) J Am Chem Soc **91**: 6876
[9] Juza R, Hadenfeldt C (1968) Naturwissensch **55**: 229
[10] Hadenfeldt C, Juza R (1969) Naturwissensch **56**: 282
[11] Warf JC, Korst WL (1956) J Phys Chem **60**: 1590
[12] Hadenfeldt C, Jacobs H, Juza R (1970) Z Anorg Chem **379**: 144
[13] Müller-Buschbaum K (2005) Z Anorg Allg Chem **631**: 811
[14] Müller-Buschbaum K (2004) Z Anorg Allg Chem **630**: 895
[15] Müller-Buschbaum K, Quitmann CC (2005) Z Kristallogr **220**: 158
[16] Quitmann CC, Müller-Buschbaum K (2004) Z Anorg Allg Chem **630**: 2422
[17] Klemm W, Winkelmann G (1956) Z Anorg Allg Chem **288**: 87
[18] Jacobs H, Fink U (1978) Z Anorg Chem **438**: 151
[19] Quitmann CC, Müller-Buschbaum K (2004) Angew Chem **116**: 6120; (2004) Angew Chem Int Ed Engl **43**: 5994
[20] Baisch U, Pagano S, Zeuner M, Schmedt auf der Günne J, Oeckler O, Schnick W (2006) Organometallics **25**: 3027
[21] Baisch U, Pagano S, Zeuner M, Barros N, Maron L, Schnick W (2006) Chem Eur J **12**: 4785
[22] Baisch U, Pagano S, Zeuner M, Schnick W (2006) Eur J Inorg Chem 3517
[23] Oesterreicher H, Mammano M, Sienko MJ (1969) J Solid State Chem **1**: 10
[24] Thompson DS, Stone MJ, Waugh JS (1966) J Phys Chem **70**: 934
[25] Young DM, Schimek GL, Kolis JW (1996) Inorg Chem **35**: 7620
[26] Schimek GL, Young DM, Kolis JW (1997) Eur J S State Inorg Chem **34**: 1037
[27] Müller-Buschbaum K (2007) Z Anorg Allg Chem **633**: in press
[28] Quitmann CC, Müller-Buschbaum K (2005) Z Anorg Allg Chem **631**: 564
[29] Stuhr A, Jacobs H, Juza R (1973) Z Anorg Allg Chem **398**: 1
[30] Jacobs H, Kistrup H (1977) Z Anorg Allg Chem **435**: 127
[31] Nakamoto K (1978) Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd edn., Wiley VCH, New York, p 196
[32] Schrader B (1989) Raman/Infrared Atlas of Organic Compounds, 2nd edn., Wiley VCH, New York
[33] Quitmann CC, Bezugly V, Wagner FR, Müller-Buschbaum K (2006) Z Anorg Allg Chem **632**: 1173
[34] Deacon GB, Delbridge EE, Forsyth CM (1999) Angew Chem **111**: 1880; (2004) Angew Chem Int Ed Engl **38**: 1766
[35] Quitmann CC, Müller-Buschbaum K (2005) Z Anorg Allg Chem **631**: 1191
[36] Deacon GB, Gatehouse BM, Nickel S, Platts SN (1991) Aust J Chem **44**: 613
[37] Deacon GB, Forsyth CM, Gitlits A, Harika R, Junk PC, Skelton BW, White AH (2002) Angew Chem **114**: 3383; (2002) Angew Chem Int Ed Engl **41**: 3249
[38] Shannon RD (1976) Acta Crystallogr **A32**: 751
[39] Sheldrick GM (1997) SHELXS-97 – Program for the solution of Crystal Structures, Univ. Göttingen
[40] Sheldrick GM (1997) SHELXL-97 – Program for the refinement of Crystal Structures, Univ. Göttingen
[41] STOE Software Package v.1.16 (2001) XRED – Program for the numerical absorption correction of X-ray single crystal data; XSHAPE – Program for the identification and refinement of Crystal shapes, Wiesbaden
[42] Flack HD (1983) Acta Cryst **A39**: 876