(Sr₆N)[CoN₂][CN₂]₂: The first low-valency nitridometalate carbodiimide

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Abstract

The first nitridocobaltate carbodiimide (Sr₆N)[CoN₂][CN₂]₂ has been synthesized from the elements Sr, Co, and graphite powder and Na₃N (as a nitrogen source). The crystal structure was determined from X-ray single-crystal diffraction data as orthorhombic (space group P2₁2₁2). (Sr₆N)[CoN₂][CN₂]₂ is the first low-valency 3d-transition nitridometalate containing additional [CN₂]⁻ groups. The crystal structure can be described as an array of rocksalt-like columns of Sr and N linked via common corners and connected by [N–C=N]⁻ units located within structural channels running along [0 0 1]. The magnetic susceptibility follows the Curie–Weiss law with an effective moment of 3.26 μB consistent with two unpaired spins (d⁷, CoI). The compound is a bad metallic conductor with a resistivity of 3.8569(3) Ω cm at 300 K. Vibrational spectroscopic data support the existence of carbodiimide [N–C=N]⁻ species. The Co K-edge X-ray absorption spectra (XAS) of Ca₅[CoN₂]₂ and (Sr₆N)[CoN₂][CN₂]₂ confirm the presence of Co⁴⁺ within the complex anions.

Keywords: Nitridometalate; Synthesis; Crystal structure; Electrical resistivity; Magnetic susceptibility; Vibrational spectroscopic properties; XAS

1. Introduction

The quest for novel materials with interesting structural and physical properties requires an in-depth survey of possible combinations of different elements of the periodic table. Indeed, carbodiimides and cyanamides were obtained with alkali metals, alkaline-earth metals, transition metals, main-group metals, and even rare-earth metals. In general, carbodiimide compounds contain symmetric anionic units [N≡C–N]⁻ while cyanamides possess asymmetric units [N≡C=N]⁻ [1]. Though cyanamides/carbodiimides and nitrides have lately attracted much experimental effort, there is still a wide field to be explored. Many group II cyanamidates/carbodiimides have been obtained (Ca[CN₂] [2,3], Cu₁₁N₄[CN₂] [4], Cu₄N₂[CN₂] [4], Sr[CN₂] [5], Ba[CN₂] [5], Sr[CN₂][CN₂] [6], Sr₂[CN₂][CN₂] [7], Ba₃[CN₂][CN₂] [7]). These compounds have been prepared using a variety of starting materials and methods: carbides, carbonates, HCN gas, alkaline-earth nitrides, graphite, and melamine. However, the family of cyanamides/carbodiimides containing transition metals still encompasses only 15 compounds. Therein, the transition metal sometimes plays the role of the cation, as encountered in the compounds Mn[CN₂] [8], Ag₂[CN₂] [9], Zn[CN₂] [10], Cd[CN₂] [11], Hg[CN₂] [12,13] (orthorhombic and monoclinic), Hg₃[CN₂]Cl₂ [14], Hg₃[CN₂]Cl₂ [14], Cu[CN₂] [15], Cu₄[CN₂]₂NH₃ [16], or forms nitridometalate anions [MN₃⁻]⁻ like in Ba₉[ NbN₄]O [CN₂] [17], Ba₈[WN₄][CN₂] [18], (Ba₉N)[MoN₄][CN₂] [18], (Ba₉N)[WN₄][CN₂] [18], and Ba₈[MoN₄][CN₂] [18]. The synthesis of most of these latter compounds was accomplished using precursors (e.g. binary nitrides, cyanamides).

In nitridocobaltates the following nitridocobaltate complexes have been observed so far: linear units [Co¹¹N₃]⁻ in Sr₅₉Co₁₂₃N₃₁ [19], LiSr₂[CoN₂] [20], Ca₃[CoN₂] [21], and BaCu₄[CoN₂] [22], or infinite chains in Ba[CoN] [23]. In general, the family of nitridometalates of the transition metals seems to cover a much larger number of compounds by taking into account the inherently more stable multinary alkaline-earth phases containing [CN₂]⁻.

In addition, isolated N³⁻ species were reported for some nitridometalates, e.g. (Ca₃N)₂[FeN₃] [24], Ba₅(Ba₆N) [NiN]₆ [25].

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Here, we report on the first cobalt carbodiimide (Sr6N)[CoN2][CN2]2, containing isolated nitride N3− species and nitridocobaltate [CoN2]5− complexes as well as [N=C=−N]2− anions, and alkaline-earth cations in the crystal structure. Up to now no IR spectroscopic investigations of nitridometalates of the transition metals with [CN2]2− units have been published.

2. Experimental section

2.1. Synthesis

All manipulations were performed in an argon-filled glove box due to the air and moisture sensitivity of these compounds. Sr2N was prepared by reaction of strontium metal (dendritic pieces, Alfa, 99.9%), and Co (Praxair, 99.999%, further purified by molecular sieve (3 Å, Merck) and BTS catalyst (MERCK)) under nitrogen flow of ambient back pressure (700 °C, 25 h). The resulting black strontium nitride preserved the shape of the dendritic pieces. The product was characterized by X-ray diffraction and identified as single-phase Sr2N [26].

Single crystals of (Sr6N)[CoN2][CN2]2 were grown by the reaction of a mixture of Sr/Sr2N, Co (Merck 1 μm, 99.9%), graphite powder (Chempur 99.9%), and NaN3 (Roth 99.9%, added as a nitrogen source) in an iron ampoule (length 50 mm) sealed under argon. The samples were protected from the iron ampoule using a thin Co foil (length 50 mm) sealed under argon. The samples were isolated from the bulk under dried paraffin oil by mechanical fragmentation and sealed in thin-walled glass capillaries. The product was characterized by X-ray diffraction and identified as single-phase Sr2N [26].

2.2. Crystal structure determination

Black, needle-like single crystals of (Sr6N)[CoN2][CN2]2 were isolated from the bulk under dried paraffin oil by mechanical fragmentation and sealed in thin-walled glass capillaries. Crystal structure data collection was performed on a Rigaku AFC7 four-circle diffractometer, equipped with a Mercury CCD detector with Mo Kα radiation and a graphite monochromator (scan types φ/ω). 5310 reflections were observed (1633 unique reflections), 2θmax = 59.99°, number of refined parameters 76. Structure solution and refinements were performed using the SHELXL-86 and SHELXS-97 [27] programs, and representations of the crystal structure were drawn with DIAMOND [28]. The program Structure Tidy [29] was used to standardize the crystal structure data.

2.3. Physical measurements

Magnetization measurements in external fields μ0H between 10 mT and 7 T within the temperature range 1.8–400 K were performed on a SQUID magnetometer (MPMS XL-7, Quantum Design). The cleaned polycrystalline sample (71.8 mg, finely ground) was sealed in a quartz tube under helium atmosphere (p = 0.4 bar). Corrections for the sample container were applied. The susceptibility χ = M/H at 400 K was almost identical for μ0H = 7 T and 3.5 T; thus the sample did not contain detrimental concentrations of ferromagnetic phases (e.g. Co or Fe metal).

The electrical resistance ρ(T) was determined in situ on a pellet pressed from cleaned powder in a cylindrical sapphire die cell. A four-contact dc van-der-Pauw method was used between 4 and 300 K (estimated inaccuracy ±30%). A cryostat integrated in a glove box system allowed one to prepare and mount the sample under argon gas.

The FT-IR spectra were collected with a Bruker IFS 66/S spectrometer under argon. For the infrared spectroscopic measurements 1.5 mg of the cleaned compound was mixed with 150 mg of dried KBr (Merck 99.9%) and pressed into a pellet. The FT Raman spectra were collected from a polycrystalline sample placed between two glass plates with a Bruker RFS 100/S spectrometer.

X-ray absorption spectroscopy (XAS) spectra at the K-threshold of cobalt were measured to investigate the electronic state of cobalt. To prevent contamination the air-sensitive samples needed special preparation. The cleaned samples were mixed in a glove box with B2C in a ratio of 1:3 and loaded in a steel holder with Be windows. The data were collected at the DORIS III storage ring in the HASYLAB laboratory at DESY in Hamburg.

3. Results and discussion

(Sr6N)[CoN2][CN2]2 crystallizes with an orthorhombic unit cell (space group P212121, No. 18, α = 9.8807(6) Å, b = 14.6474(9) Å, c = 3.8569(3) Å, V = 558.2 Å3, Z = 2, R1 = 0.0265, wR2 = 0.0383). Crystallographic data are given in Tables 1a–c; the crystal structure is shown in Fig. 1. The predominant structural features of (Sr6N)[CoN2][CN2]2 are near-linear carbodiimide [N−C=−N]2− (< (N−C−N) = 173.3(4)) ions and linear nitridocobaltate [CoN2]5− units (< (N−Co−N) = 178.6(2)). Moreover, the structure...
contains isolated nitride ions $N^3\text{--}$, octahedrally coordinated by strontium. The average Sr–N distance $d = 2.77 \text{ Å}$ is similar to other compounds (e.g. LiSr$_2$CoN$_2$ [20] $d = 2.60 \text{ Å}$, Sr$_2$[CN$_3$] [5] $d = 2.63 \text{ Å}$, Sr$_2$[FeN$_3$] [30] $d = 2.68 \text{ Å}$, Sr$_3$MnN$_3$ [31] $d = 2.72 \text{ Å}$). Strontium atoms are always octahedrally coordinated by six nitrogen atoms. The linear [Co$\text{N}_3$]$^-$ unit consists of only one crystallographically independent nitride species ($d$(N2–Co) = 1.836(3) Å), the octahedral coordination sphere of N2 is completed by five additional Sr atoms (Fig. 2a). The Co–N distances are in agreement with related compounds containing [Co$^1$N$_2$]$^-$ units (LiSr$_2$CoN$_2$ [20] $d = 1.81 \text{ Å}$, Ca$_3$[CoN$_2$]$_2$ [21] $d = 1.82 \text{ Å}$, BaCa$_2$[CoN$_2$]$_2$ [22] $d = 1.81 \text{ Å}$). The carbodiimide [N == C == N]$^-$ anion contains two crystallographically independent nitrogen species with nearly equal bond distances ($d$(C–N3) = 1.231(5), $d$(C–N4) = 1.235(5) Å). The coordination spheres of N3 and N4 are completed by altogether eight Sr atoms forming two highly distorted octahedra sharing a common Sr–C face (Fig. 2b).

A simple description of the crystal structure is based on rocksalt-like N$_7$Sr$_4$Sr$_2$N$_4$ slabs (Fig. 3). The slabs are connected to form infinite columns which are interconnected via common corners to form a 3D framework with channels running along [0 0 1]. C and Co are located within the channels, thereby connecting the infinite columns.

Infrared and Raman spectroscopy were used to investigate the nature of the [CN$_2$]$^2-$ anions in the crystal structure of (Sr$_6$N)[CoN$_2$][CN$_2$]. The vibrational frequencies of the anion were observed around 1950 and 1978 cm$^{-1}$ for asymmetric stretching, around 1240 cm$^{-1}$ for symmetric stretching, and about 663 and 676 cm$^{-1}$ for deformation vibration (Fig. 4). A similar split of the asymmetric stretching and deformation vibration frequencies was observed in Sr[CN$_2$] ($v_{as}$: 1989 and 2023 cm$^{-1}$; $v_1$: 1251 cm$^{-1}$; $\delta$: 663 and 677 cm$^{-1}$) at $d$(C–N1) = 1.228(10) Å and $d$(C–N2) = 1.222(11) Å [5] and in other quasibinary cyanamides as well, e.g. in Ca$_{11}$N$_6$[CN$_2$]$_2$ [4], Ca$_4$N$_2$[CN$_2$] [4], Cd[CN$_2$] [11], Hg[CN$_2$] [13]. The distinction between symmetrical carbodiimide [N == C == N]$^-$ and asymmetric cyanamide [N–C == N]$^-$ ions in ionic solids is challenging at best; often only gradual changes are observed. Historically, inorganic compounds containing [CN$_2$]$^2-$ were described generally as cyanamides. IR and Raman investigations of alkaline-earth cyanides, cyanamides, and carbodiimides [11] revealed a strong relationship between C–N bond lengths, cation mass, electronegativity, and coordination environments. In most alkaline-earth-containing ionic compounds, the slightly differing C–N distances may be attributed to the different coordination spheres of the N species in the [CN$_2$]$^2-$ anion. In the title compound there are no indications for different bonding characteristics in the [CN$_2$]$^2-$ anion. We therefore assume that the [CN$_2$]$^2-$ anions in (Sr$_6$N)[CoN$_2$][CN$_2$]

### Table 1a

| Crystal data      | Orthorhombic, $P2_12_12$ (No. 18) black needle, size 0.2, 0.1, 0.1 mm |
|-------------------|------------------------------------------------------------------------|
| $a$               | 9.8807(6) Å                                                           |
| $b$               | 14.674(9) Å                                                           |
| $c$               | 3.8560(3) Å                                                           |
| Flack parameter   | $-0.013(14)$                                                          |
| Wavelength        | Mo K$_x$ radiation (0.71073 Å)                                         |
| $\mu$             | 29.87 mm$^{-1}$                                                       |
| $\lambda$         | Rigaku AFC7 and mercury CCD, $\omega/\phi$                           |
| $2\theta_{\text{max}}$ | 61.99°                                                                 |
| $N(hkl)_{\text{measured}}$ | 5310/1770                                                            |
| $N(hkl)_{\text{unique}}$ | 75                                                                    |
| $N(\text{param})_{\text{refined}}$ | 0.0265/0.0383                                                       |
| Programs          | SHEXL97-27 [27], SHEXL88-26 [27], DIAMOND [28], STRUCTURE TIDY [29] |

### Table 1b

| Site | $x$     | $y$     | $z$     | $U_{eq}$ |
|------|---------|---------|---------|----------|
| Sr1  | 4c      | 0.07717(3) | 0.38964(2) | 0.93964(10) | 0.01055(8) |
| Sr2  | 4c      | 0.40465(3) | 0.33567(2) | 0.55092(9)  | 0.01156(8)  |
| Sr3  | 4c      | 0.25404(3) | 0.05813(2) | 0.55886(9)  | 0.01020(8)  |
| Co1  | 2a      | 0       | 0       | 0.0232(2)  | 0.01005(15) |
| N1   | 2b      | 0       | 1/2     | 0.4361(12) | 0.0115(9)   |
| N2   | 4c      | 0.3323(3) | 0.4461(2) | 0.9711(9)   | 0.0120(6)   |
| N3   | 4c      | 0.3306(3) | 0.1939(2) | 0.0317(10)  | 0.0168(7)   |
| N4   | 4c      | 0.1340(4) | 0.2486(2) | 0.3647(8)   | 0.0191(8)   |
| Cl   | 4c      | 0.2282(4) | 0.2205(3) | 0.1831(10)  | 0.0128(8)   |

### Table 1c

|      | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|------|----------|----------|----------|----------|----------|----------|
| Sr1  | 0.01072(16) | 0.00925(15) | 0.01168(17) | 0.00125(14) | -0.00043(15) | -0.00025(13) |
| Sr2  | 0.01228(16) | 0.01033(15) | 0.01208(18) | -0.00176(15) | -0.00081(16) | 0.00120(13) |
| Sr3  | 0.01101(16) | 0.00920(16) | 0.01041(17) | 0.00102(14) | -0.00016(16) | -0.00011(13) |
| Co   | 0.0095(3)   | 0.0005(3)   | 0.0105(4)   | 0.0000(4)   | 0.0000(4)   | 0.00026(7)  |
| N1   | 0.013(2)    | 0.012(2)    | 0.009(2)    | 0.000(2)    | 0.000(2)    | 0.00026(7)  |
| N2   | 0.0126(13)  | 0.0120(14)  | 0.0115(15)  | -0.0009(14) | -0.0003(14) | -0.0004(12) |
| N3   | 0.0150(15)  | 0.0148(15)  | 0.0206(19)  | -0.0013(15) | 0.0000(16)  | 0.0015(12)  |
| N4   | 0.0167(18)  | 0.0188(19)  | 0.022(2)    | 0.0085(15)  | 0.0022(15)  | -0.0028(15) |
| C1   | 0.015(2)    | 0.0038(17)  | 0.020(2)    | 0.0055(15)  | -0.0081(16) | -0.0028(15) |
have to be regarded as carbodiimide anions. Not only the fact of equal C–N distances (within the margin of error) has to be emphasized, but also the split of νas bands seems to be a sign for a symmetric carbodiimide anion [13].

XAS was used to investigate the K-threshold of Co. XAS spectra of Ca₄[CoN₂]₂ [30], (Sr₆N)[CoN₂][CN₂]₂, and CoO (as a reference material) were measured (Fig. 5). Both nitridocobaltates show a good separation of the pre-edge
feature (at about 7713 eV) with the pre-edge peaks assigned to a $1s\rightarrow 3d$ transition [32], as expected for a non-centrosymmetric environment of Co. The main absorption edge reflects the $1s\rightarrow 4p$ transition; the shift of the main absorption edge at 0.6 of the total edge jump was employed to assign the oxidation states of Co with higher energies being associated with an increase in oxidation states. Since no nitridocobaltates and cobalt nitrates with oxidation states above +1 are known, we choose to use Co$^{10}$O as a reference material, being fully aware of the shift of the absorption edge to higher energies with increasing electronegativity of the ligands [33]. For (Sr$_6$N)[CoN$_2$][CN$_2$]$_2$ and Ca$_3$[CoN$_2$]$_2$ the main absorption edge is observed at that same energy at about 7721 eV. The corresponding value for CoO was deduced at 7724 eV, a difference of about 3 eV, indicating a significantly higher oxidation state even taking the different ligands into account [32]. This indicates that both (Sr$_6$N)[CoN$_2$][CN$_2$]$_2$ and Ca$_3$[CoN$_2$]$_2$ contain [Co$^1$N$_2$]$_2^-$ complex anions.

The inverse magnetic susceptibility $H/M$ (Fig. 6) of (Sr$_6$N)[CoN$_2$][CN$_2$]$_2$ follows a Curie–Weiss law at elevated temperatures. A fit of $\chi(T)$ in the temperature range 80–400 K yields an effective magnetic moment ($\mu_{eff}$) of 3.26 $\mu_B$. This value is in the range of values found for Ni$^{2+}$.

**Fig. 4.** Vibrational spectra of [NCN]$^-$ anions: IR (top) and Raman (bottom) spectra of (Sr$_6$N)[CoN$_2$][CN$_2$]$_2$.

**Fig. 5.** Co K-edge X-ray absorption spectra of cobalt compounds. The main absorption edge is taken at 0.6 of the total edge jump, as indicated by the horizontal line at 0.6.

**Fig. 6.** Inverse magnetic susceptibility $H/M$ versus temperature $T$ in a field $\mu_0 H = 3.5$ T. The inset shows the electrical resistivity $\rho$ versus temperature $T$. 
species with $d^8$ configuration ($2.80-3.50 \mu_B$ [34]), i.e. cobalt is present with a spin of $S = 1$ ($d^8$ configuration spin-only value $2.83 \mu_B$, Co$^5$), consistent with the chemical formula. The Weiss temperature is small and positive ($\Theta = +7.4 \, K$), indicating weak ferromagnetic interactions. No magnetic ordering or other phase transitions are observed above 2.0 K.

The electrical resistivity $\rho(T)$ (Fig. 6) merely shows a linear temperature dependence for $T>40 \, K$, indicating metallic conduction. The deviations above 200 K can be attributed to changes of the contacts between the grains of this loosely cold-pressed pellet. At 300 K the resistivity is about 1 m$\Omega$cm. Regarding the relatively low residual resistivity compared to $\rho(300 \, K)$, the intrinsic resistivity of the material cannot be much lower. Thus, $(\text{Sr}_6\text{N})[\text{CoN}_2][\text{CN}_2]_2$ is a metal with $\rho(300 \, K) \approx 0.1 \, m\Omega\text{cm}$, displaying so-called bad metal behavior.

4. Conclusion

$(\text{Sr}_6\text{N})[\text{CoN}_2][\text{CN}_2]_2$ is the first phase containing both linear nitridocobaltate (I) and $[\text{CN}_2]^2$ groups. The novel structure type contains nitridocobaltate complexes $[\text{Co}N_2]^5^-$, carbodiimide $[\text{N}==\text{C}==\text{N}]^2^-$ ions, isolated nitride ions, and alkaline-earth metal cations.

The magnetic susceptibility of $(\text{Sr}_6\text{N})[\text{CoN}_2][\text{CN}_2]_2$ follows a Curie–Weiss law with an effective moment of 3.26 $\mu_B$ consistent with two unpaired spins ($d^8$, Co$^5$). From electric resistivity measurements the compound is a metallic conductor. The X-ray absorption spectroscopy (XAS) spectra confirmed that the $[\text{NCoN}]^5^-$ complex contains Co$^4$.

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References

[1] R.G. Pearson, Chemical Hardness, Wiley, Weinheim, New York, NY, 1997.
[2] U. Dehlinger, Z. Kristallogr. 65 (1927) 286.
[3] N.G. Vannerberg, Acta Chem. Scand. 16 (1962) 2263.
[4] O. Reckeweg, F.J. DiSalvo, Angew. Chem. Int. Ed. 39 (2000) 412.
[5] U. Berger, W. Schnick, J. Alloys Compounds 206 (1994) 179.
[6] Z.A. Gal, P.M. Mallinson, S.J. Clarke, Acta Crystallogr. E 61 (2005) i221.
[7] U. Berger, W. Milius, W. Schnick, Z. Anorg. Allg. Chem. 621 (1995) 593.
[8] X. Liu, M. Krott, P. Mueller, C. Hu, H. Lueken, R. Dronskowski, Inorg. Chem. 44 (2005) 3001.
[9] M. Becker, J. Nuss, M. Jansen, Z. Naturforsch. 55b (2000) 383.
[10] M. Becker, M. Jansen, Acta Crystallogr. C 57 (2001) 347.
[11] G. Baldinozzi, B. Malinowska, M. Rakib, G. Durand, J. Mater. Chem. 12 (2002) 268.
[12] M. Becker, M. Jansen, Z. Anorg. Allg. Chem. 626 (2000) 1639.
[13] X. Liu, P. Mueller, P. Kroll, R. Dronskowski, Inorg. Chem. 41 (2002) 4259.
[14] X. Liu, R. Dronskowski, Z. Naturforsch. 57b (2002) 1108.
[15] X. Liu, M.A. Wankeu, H. Lueken, R. Dronskowski, Z. Naturforsch. 60b (2005) 593.
[16] X. Liu, P. Mueller, R. Dronskowski, Z. Anorg. Allg. Chem. 631 (2005) 1071.
[17] O. Reckeweg, F.J. DiSalvo, Z. Naturforsch. 58b (2003) 201.
[18] P. Höhn, R. Kniep, Z. Anorg. Allg. Chem. 628 (2002) 2173.
[19] G.R. Kowach, H.Y. Lin, F.J. DiSalvo, J. Solid State Chem. 141 (1998) 1.
[20] P. Höhn, R. Kniep, Z. Natur. 47b (1992) 434.
[21] J. K. Bendyna, P. Höhn, R. Kniep, Z. Kristallogr. NCS, in press.
[22] J. K. Bendyna, P. Höhn, R. Kniep, Z. Kristallogr. NCS, in press.
[23] A. Tennstedt, R. Kniep, Z. Anorg. Allg. Chem. 620 (1994) 1781.
[24] G. Cordier, P. Höhn, R. Kniep, A. Rabenau, Z. Anorg. Allg. Chem. 591 (1990) 58.
[25] A. Gudat, W. Milius, S. Haag, R. Kniep, A. Rabenau, J. Less-Common Met. 168 (1991) 305.
[26] J. Gaude, P. l’Haridon, Y. Laurent, J. Lang, Bull. Soc. Fran. Miner. Crist. 95 (1972) 56.
[27] G.M. Sheldrick, SHELXL-97: Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
[28] K. Brandenburg, DIAMOND: Visual Crystal Structure Information System, Version 2.0f, Crystal Impact, Bonn, Germany, 1998.
[29] L.M. Gelato, E. Parthe, J. Appl. Crystallogr. 20 (1987) 139.
[30] P. Höhn, R. Kniep, Z. Naturforsch. 47b (1992) 477.
[31] A. Tennstedt, C. Roehr, R. Kniep, Z. Naturforsch. 48b (1993) 794.
[32] R. Niewa, Z. Hu, R. Kniep, Eur. J. Inorg. Chem. 8 (2003) 1632.
[33] Z. Hu, G. Kaindl, G. Meyer, J. Alloys Compounds 246 (1997) 186.
[34] Landoldt-Börnstein, in: K.H. Hellwege (Ed.), Neue Serie, vol. 12, Springer, Berlin, 1984.