Synthesis, Crystal Structure, Magnetic, Thermal and Fluorescent Properties of $[Co(H_2O)_4(nia)_2](suc)\cdot(H_2suc)$

Selcuk Demir[a], Veysel T. Yilmaz[b], Jerzy Mroziński[c], Tadeusz Lis[c], and Małgorzata Hołyńska[c]

[a] Department of Chemistry, Faculty of Arts and Sciences, Rize University, 53100, Rize, Turkey
[b] Department of Chemistry, Faculty of Arts and Sciences, Uludag University, 16100, Bursa, Turkey
[c] Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50383 Wrocław, Poland

Reprint requests to Dr. Selcuk Demir. Fax: +90 464 223 5376. E-mail: selcuk.demir@rize.edu.tr

Z. Naturforsch. **2010**, *65b,* 695 – 700; received February 2, 2010

A new cobalt(II) complex, $[Co(H_2O)_4(nia)_2](suc)\cdot(H_2suc)$ [nicotinamide = nia, succinate = suc^{2-}], has been synthesized and characterized by elemental analysis, IR, TG-DTA and single-crystal X-ray diffraction. It contains $[Co(H_2O)_4(nia)_2]^{2+}$ complex cations, uncoordinated suc^{2-} anios and H_2suc species. In the complex cation the cobalt(II) ion is coordinated by four aqua and two nia ligands in a distorted octahedral geometry. The suc^{2-} dianion acts as a counter-ion, while H_2suc is present as a molecule of solvation. A three-dimensional network is formed by O–H···O and N–H···O hydrogen bonds. The title complex exhibits luminescence in the solid state at room temperature. The magnetism of the complex was studied over the temperature range 1.8 – 300 K.

Key words: Succinate Complexes, Nicotinamide, Crystal Structure, Thermal Analysis, Magnetic Interaction

Introduction

Metal carboxylates are particularly interesting since they not only form open-framework structures, but also because the carboxylate group may act as a linker between inorganic moieties [1]. α,ω-Alkane-dicarboxylates, such as succinate [suc^{2-}, $(C_4H_4O_4)^{2-}$], have conformational freedom, and they can give novel frameworks, with for instance bidentate and monodentate linking modes, *cis-cis*, *trans-trans* and *cis-trans* orientation *etc*.

Some complexes containing suc^{2-} as the counter-ion have been reported [2 – 7]. Apart from this, some complexes comprise suc^{2-} as both a ligand and a counter-ion [8 – 10] or as a ligand together with a H_2suc molecule [9, 11]. In an extension of our work on succinate complexes [12 – 14] we have observed that the reactions of H_2suc or $Na_2(suc)$ with nickel(II) salts yield two different compounds, *i. e.*, $\{[Ni(\mu\text{-suc})(H_2O)_2(nia)_2]\cdot 2H_2O\}_n$ and $[Ni(H_2O)_4(nia)_2](suc)\cdot(H_2suc)$. The latter is one of the rare examples which shows simultaneous presence of uncoordinated suc^{2-} and H_2suc [14, 15].

It is known that the presence of infinite *M*–O–*M* connectivities in metal dicarboxylate structures enables the electronic and magnetic exchange in one, two or three dimensions [1], but the *M*–O–C–O–*M* pathway also needs to be taken into account for weak coupling [16]. Furthermore, it has ben reported that magnetic exchange interactions through hydrogen bonds are also possible [17]. Because of the diversity of the inorganic networks and their complexity, metal carboxylate frameworks show different and usually extremely complicated magnetic behavior [16].

Herein we present the synthesis of the title complex $[Co(H_2O)_4(nia)_2](suc)\cdot(H_2suc)$, which has been characterized by elemental analyses, IR, TG-DTA, and single-crystal X-ray diffraction. In addition to fluorescence properties, the magnetic properties are described for the temperature range of 1.8 – 300 K. The magnetic behavior of the title mononuclear complex of $[Co(H_2O)_4(nia)_2](suc)\cdot(H_2suc)$ and of the 1D polymeric complex $\{[Co(\mu\text{-suc})(H_2O)_2(nia)_2]\cdot 2H_2O\}_n$ which contains N-bonded nia and suc^{2-} dianions as ligands is also discussed briefly.

Results and Discussion

The composition of the complex was determined by elemental analyses, FT-IR, DTA-TG, and magnetic measurement analysis. The elemental analysis data agree well with the calculated values. The complex is

0932–0776 / 10 / 0600–0695 \$ 06.00 © 2010 Verlag der Zeitschrift für Naturforschung, Tübingen · http://znaturforsch.com

soluble in water. The room temperature magnetic moment is 5.09 μ_B, significantly higher than the spin only value of 3.87 μ_B, indicating orbital contributions.

The IR spectrum of the complex displays characteristic bands of suc^{2-}, H_2suc and nia. The strong and broad peaks centered at *ca.* 3380 cm^{-1} were assigned to the ν(OH) vibrations of the water molecules. The ν(NH) absorption bands of the amide group of the free nia molecule are split for the complex and appear in the 3450 – 3220 cm^{-1} region at higher wave number than those of the free nia because of involvement in hydrogen bonding. The bands at around 2920 – 3080 cm^{-1} are attributed to the ν(CH) stretching vibrations of the aromatic and aliphatic groups. The stretching bands of the amide carbonyl group in the free nia and in the complex are similar and observed at 1680 and 1677 cm^{-1}, respectively, indicating absence of coordination through the amidic carbonyl group. The very strong band centered at 1704 cm^{-1} is characteristic of the ν(C=O) stretch of the COOH group, and the strong absorptions at 1542 and 1393 cm^{-1} arise from the asymmetric (ν_{as}) and symmetric (ν_s) vibrations of the carboxylate group of suc^{2-} [14].

Description of the crystal structure

The title complex consists of tetraaquabis(nicotinamide)cobalt(II) cations, succinate dianions and succinic acid molecules (Fig. 1). Two systems with similar constituents (catena-(μ_2-succinato)diaquabis(nicotinamide)cobalt(II)) have been reported provioulsy [13, 18]. They both crystallize in the triclinic space group $P\bar{1}$. However, in these compounds the succinate anion is involved in coordination leading to a polymeric structure.

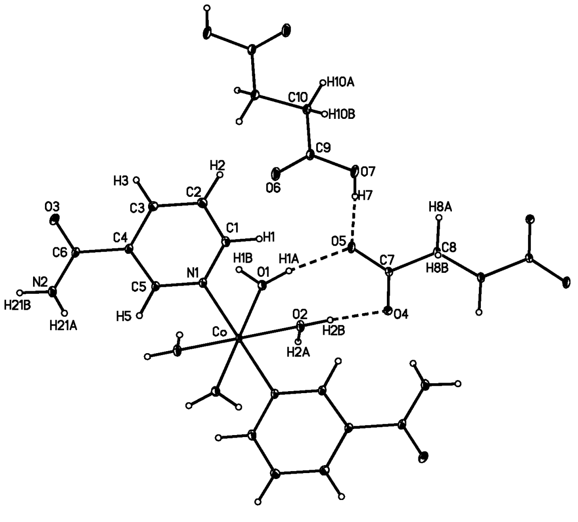

Fig. 1. Molecular structure of the title compound. Displacement ellipsoids are drawn at the 30 % probability level. Hydrogen bonds are indicated with dashed lines. The non-labelled part is generated with the symmetry operation (i) $1-x$, $1-y$, $1-z$.

Table 1. Selected geometrical parameters of the complex cation (Å, deg)[a].

Co–O1	2.074 (1)	Co–O2	2.094 (2)
Co–N1	2.178 (1)		
O1–Co–O2	89.1 (1)	O1–Co–O2^i	90.9 (1)
O2–Co–O2^i	180.0 (1)	O1–Co–N1	88.9 (1)
O2–Co–N1	87.6 (1)	O2^i–Co–N1	92.4 (1)

[a] Symmetry code: (i) $1-x$, $1-y$, $1-z$.

Table 2. Hydrogen bonding parameters (Å, deg)[a].

D–H···A	D–H	H···A	D···A	D–H···A
N2–H21A···O4^i	0.89	2.12	3.005 (2)	177
N2–H21B···O6^{ii}	0.92	1.99	2.899 (2)	171
O7–H7···O5	0.84	1.72	2.559 (2)	176
O1–H1A···O5	0.87	1.87	2.729 (2)	171
O1–H1B···O3^{ii}	0.82	2.05	2.858 (2)	167
O2–H2A···O3^{iii}	0.81	2.04	2.804 (2)	156
O2–H2B···O4	0.89	1.81	2.690 (2)	172

[a] Symmetry codes: (i) $1-x$, $1-y$, $1-z$; (ii) $2-x$, $2-y$, $1-z$; (iii) $1-x$, $2-y$, $1-z$.

In the complex cation, the cobalt(II) ion is surrounded by two N-bonded nicotinamide ligands and four water molecules. If nicotinamide molecules are considered as axial ligands, the four water molecules lie in the equatorial plane. Geometrical parameters expected for such a cation are well documented in the literature [19 – 22]. For the present case, the reported geometrical parameters given in Table 1 do not deviate significantly from expectations. The coordination sphere around the cobalt(II) ion is distorted octahedral. The geometrical parameters of the nicotinamide ligands are normal [23]. The planar pyridine ring and the amide group plane are mutually twisted by 5.4(1)°.

A three-dimensional O–H···O and N–H···O hydrogen bonding network (Table 2, Fig. 2) stabilizes the crystal structure of the title compound. The only weak C–H···O contact to be considered is C5–H5···O4^i (symmetry code as in Table 2; C5···O5 distance 3.256(2) Å, C5–H5···O4 angle 153°; for details see Table 2 and Figs. 1 and 2). The carboxyclic group of the succinic acid molecule is the donor to a particularly short hydrogen bond to the succinate dianion O5 atom. This hydrogen bond may be one of the reasons for specific crystal structure packing with short contacts created between nicotinamide O atoms (O3···O3^{iv} dis-

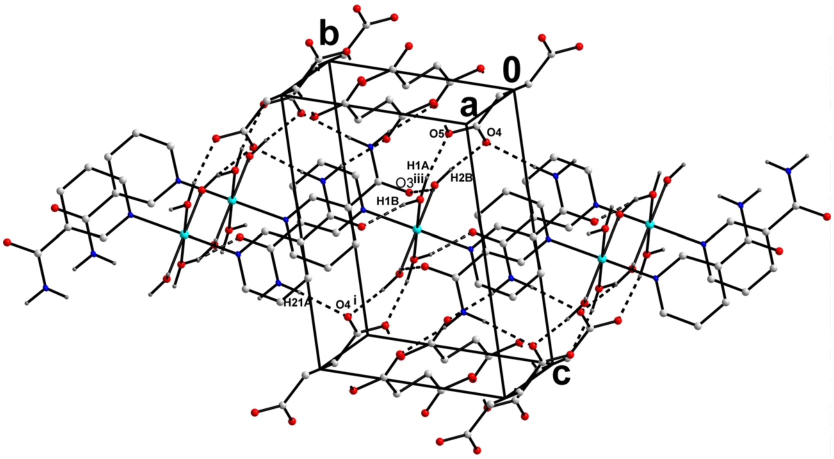

Fig. 2. Packing diagram of the title compound with hydrogen bonding scheme. Hydrogen bonds are denoted with dashed lines. Symmetry codes: (i) $1-x$, $1-y$, $1-z$; (iii) $1-x$, $2-y$, $1-z$. C-bonded H atoms are omitted for clarity.

tance 2.855(2) Å, (iv) $2-x$, $3-y$, $1-z$). The arrangement of the carbonyl groups rather excludes the possibility of carbonyl···carbonyl interactions and a column-like arrangement of the complex cations along [100] (Fig. 2). Also, each nicotinamide pyridyl ring is involved in stacking interactions with a symmetry-related ($1-x$, $2-y$, $1-z$) nicotinamide pyridyl ring (the ring planes are parallel; the distances of atoms constituting one ring from the plane of the interacting ring are at approximately 3.55 Å). The shortest Co···Co distances correspond to the *a* and *b* axes directions (7.281(3) and 8.287(3) Å).

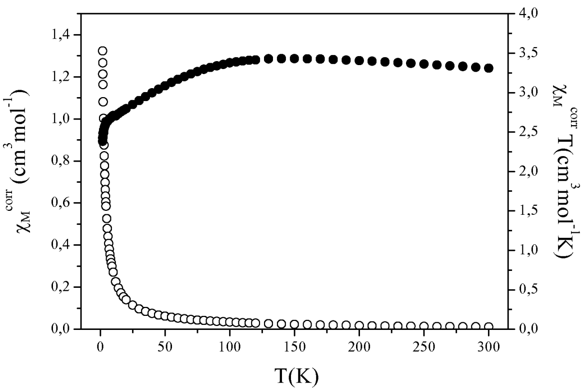

Fig. 3. Temperature dependence of experimental χ_M (○) and $\chi_M T$ (●) *vs.* *T* for [Co(H$_2$O)$_4$(nia)$_2$](suc)(H$_2$suc).

Thermal decomposition studies

The thermal degradation of the complex in nitrogen atmosphere has been studied by DTA and TG. The complex looses its aqua ligands in the range 62–139 °C. The experimental mass loss is 11.5 %, consistent with the calculated value of 11.8 %. After dehydration, removal of the nia as well as the succinate components occurs simultaneously in the range 139–738 °C. Three DTA maxima are observed at 187(+), 249(+), and 439(−) °C. The final decomposition product is the metal oxide. Found and calculated weight losses are in good agreement (found 75.3 % and calculated 75.9 %).

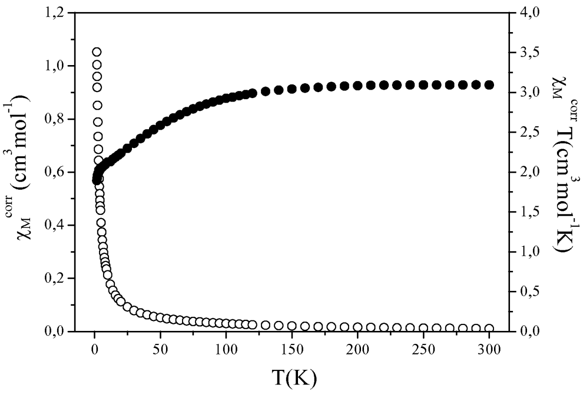

Fig. 4. Temperature dependence of experimental χ_M (○) and $\chi_M T$ (●) *vs.* *T* for {[Co(μ-suc)(H$_2$O)$_2$(nia)$_2$]·2H$_2$O}$_n$.

Magnetic behavior

The complex {[Co(μ-suc)(H$_2$O)$_2$(nia)$_2$]·2H$_2$O}$_n$ was synthesized as reported in the literature [13] in order to compare its magnetic behavior with that of [Co(H$_2$O)$_4$(nia)$_2$](suc)·(H$_2$suc). The {[Co(μ-suc)(H$_2$O)$_2$(nia)$_2$]·2H$_2$O}$_n$ complex is a 1D coordination polymer, in which the suc^{2-} ligand bridges the metal centers through its carboxylate groups. The Co(II) ions exhibit an octahedral geometry with two suc^{2-}, two nia and two aqua ligands. The magnetic properties of both complexes over the temperature range 1.8 – 300 K are illustrated as magnetic susceptibility χ_M and $\chi_M T$ *vs.* T in Figs. 3 and 4.

Cobalt has the highest Curie temperature among the three ferromagnets of the first-row transition metals and is magnetically also the most anisotropic one. For octahedral coordination geometry, the ground state is $^4T_{1g}$. If the spin-only formula for $S = 3/2$ and a g-value of 2 are used, the effective moment is expected to be 3.87 μ_B [24]. However, the value of $\chi_M T$ at 300 K equal to 3.22 cm^3 mol^{-1} K (5.09 μ_B) for the [Co(H_2O)$_4$(nia)$_2$]·(suc)·(H_2suc) complex is higher than the expected value because of an unquenched orbital moment as a consequence of spin-orbit coupling [24]. As seen in Fig. 3, the value of $\chi_M T$ increases only slightly to 3.92 cm^3 mol^{-1} K (5.21 μ_B) at 140 K as the temperature is lowered. In the low-temperature range (below 140 K), a more evident decrease is observed reaching 2.38 cm^3 mol^{-1} K (4.37 μ_B) at 1.8 K. The slight decrease in the low-temperature range is due to very weak antiferromagnetic interactions and/or single ion zero-field splitting of the Co(II) ions [25].

For the polymeric complex {[Co(μ-suc)(H_2O)$_2$(nia)$_2$]·2H_2O}$_n$ (Fig. 4), the value of $\chi_M T$ at 300 K equals 3.09 cm^3 mol^{-1} K (4.98 μ_B) and decreases only slightly as the temperature is lowered. In the low-temperature range (below 50 K), a more evident decrease in its value is observed reaching 1.89 cm^3 mol^{-1} K (3.89 μ_B) at 1.8 K.

A negative value of the Weiss constant confirms the occurrence of antiferromagnetic interactions between the Co centers for the polymeric complex {[Co(μ-suc)(H_2O)$_2$(nia)$_2$]·2H_2O}$_n$. This result corresponds well to the known fact that the carboxylate group may play the role of an antiferromagnetic coupler in carboxylate-bridged cobalt(II) complexes [25].

When both complexes are compared, it is seen that the orbital contribution for the mononuclear complex is higher than for the polymer (magnetic momentums of 5.09 μ_B and 4.98 μ_B, respectively). The variation of the magnetization M *versus* the magnetic field H for both complexes is linear in the whole field range and indicates values of magnetic momentum of 2.63 μ_B and 2.35 μ_B at 5 T, respectively.

Photoluminescence

The solid-state photoluminescence spectra of nia and of the title complex at room temperature are shown in Fig. 5. Upon excitation at 275 nm, the free nia emits fluorescence at 372 and 442 nm, and the Co complex emits fluorescence at 376 and 437 nm. The fluorescence spectrum of the complex is similar to that of the free nia with only negligible shifts, suggesting that the fluorescence of this cobalt(II) complex mainly originates from the nia ligand, and the emissions can be tentatively assigned to intra-ligand π-π^* transitions.

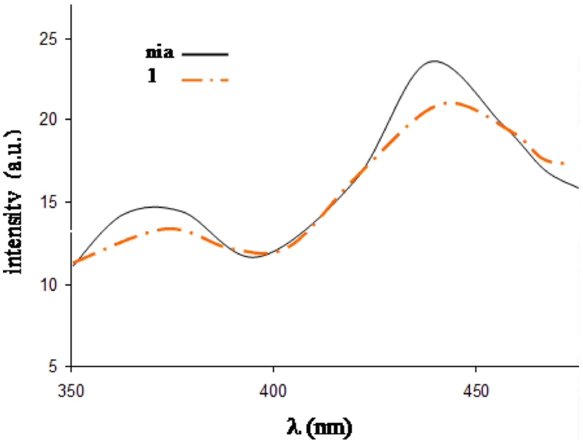

Fig. 5. The solid-state photoluminescence spectra of nia and the title complex at room temperature.

Conclusions

In summary, [Co(H_2O)$_4$(nia)$_2$](suc)·(H_2suc) has been synthesized and characterized by its elemental analysis, magnetic properties, IR spectrum and TG-DTA. The crystal structure was determined by X-ray diffraction. The complex exhibits luminescence in the solid state at r. t. because of intra-ligand π-π^* transitions. The complexes [Co(H_2O)$_4$(nia)$_2$](suc)·(H_2suc) and {[Co(μ-suc)(H_2O)$_2$(nia)$_2$]·2H_2O}$_n$ exhibit magnetic moments showing an important orbital contributions at high temperature, however, for the [Co(H_2O)$_4$(nia)$_2$](suc)·(H_2suc) complex this magnetic phenomenon is more pronounced.

Experimental Section

All chemicals were bought and used without further purification. IR spectra were recorded on a Perkin Elmer 100 FTIR spectrophotometer from KBr pellets at 4000 – 450 cm^{-1}. The elemental analyses (C, H and N contents) were performed at TUBITAK-ATAL. Thermal analysis curves (TG and DTA) were obtained using a Pyris Diamond TG/DTA (DSC) thermal analyzer in nitrogen atmosphere. Sample sizes of 5 – 10 mg and a heating rate of 10 °C

Table 3. Crystallographic and structure refinement data for $[Co(H_2O)_4(nia)_2](suc)\cdot(H_2suc)$.

Formula	$[C_{12}H_{20}CoN_4O_6][C_4H_6O_4][C_4H_4O_4]$
M_r	609.41
Temperature, K	100(2)
λ (MoK_α), Å	0.71073
Crystal size, mm^3	0.39 × 0.31 × 0.27
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	7.281(3)
b, Å	8.287(3)
c, Å	11.340(4)
α, deg	91.37(3)
β, deg	104.24(3)
γ, deg	108.17(3)
V, Å^3	626.4(4)
Z	1
D_{calcd}, g cm^{-3}	1.62
$F(000)$, e	317
μ, mm^{-1}	0.8
Absorption correction	analytical
Min. / max. transmission	0.743 / 0.859
θ range, deg	4.31 – 38.54
Refl. total / unique / R_{int}	12526 / 6426 / 0.015
Data / ref. parameters	6426 / 180
$R1$ [$I \geq 2\ \sigma(I)$] / $wR2$ (all data)	0.025 / 0.085
GoF (F^2)	1.02
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.59 /–0.50

min^{-1} between 30 – 1000 °C were used. The magnetization of the powdered samples was measured over the temperature range 1.8 – 300 K using a Quantum Design SQUID-based MPMSXL-5-type magnetometer. Measurements were made at a magnetic field of 0.5 T. The effective magnetic moment was calculated from the equation $\mu_{eff} = 2.83.(\chi_M\ T)^{1/2}$ (μ_B). Fluorescence spectra of solid samples at room temperature were run on a Varian Cary Eclipse fluorescence spectrophotometer with excitation and emission slits of 10 and 20 nm, respectively.

*Synthesis of $[Co(H_2O)_4(nia)_2](suc)\cdot(H_2suc)$ (**1**)*

$[Co(H_2O)_4(nia)_2](suc)\cdot(H_2suc)$ was prepared as its Ni(II) analogs [14]. 5 mL of an aqueous solution of $CoSO_4\cdot 7H_2O$ (1 mmol, 0.28 g) was mixed with 10 mL of an aqueous solution of H_2suc (1.0 mmol, 0.12 g), and the nia ligand (4.0 mmol, 0.49 g) dissolved in 5 mL water was added dropwise to this solution with stirring at r. t. The resulting solution was filtered and allowed to stand at r. t. X-Ray quality orange crystals of the complex were formed after a few weeks. Yield 37 %. – Anal. for $C_{20}H_{30}CoN_4O_{14}$: calcd. C 39.09, H 4.83, N 9.12; found C 39.41, H 4.96, N 9.23. – IR (KBr disc, cm^{-1}): ν = 3382s, 3206s, 3077vw, 2923vw, 2488m, 1936m, 1704vs, 1677vs, 1619s, 1572s, 1542vs, 1426s, 1393vs, 1332vs, 1225s, 1195vs, 1121m, 1050w, 1034w, 1021w, 894w, 805m, 775m, 684m, 644s, 628m, 535w.

X-Ray structure determination

The X-ray diffraction measurement was carried out on an Xcalibur PX diffractometer with the use of graphite-monochromatized MoK_α radiation. The crystal structure of the title complex was solved by Direct Methods with SHELXS and refined with the SHELXL software [26]. H atoms bonded to C atoms were included assuming a model molecular geometry with U_{eq} = 1.2 U_{eq} (parent atom). All remaining H atoms were found on difference Fourier maps and refined initially with DFIX restraints for O–H and N–H bond lengths. Next AFIX 3 constraints were applied to these H atoms with U_{eq} = 1.2 U_{eq} or 1.5 U_{eq} for N-bonded and O-bonded H atoms, respectively. The details of data collection, refinement and crystallographic data are summarized in Table 3.

CCDC 755484 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

---

[1] C. N. R. Rao, S. Natarajan, R. Vaidyanathan, *Angew. Chem.* **2004**, *116*, 1490 – 1521; *Angew. Chem. Int. Ed.* **2004**, *43*, 1466 – 1496.

[2] S.-M. Ying, J.-G. Mao, Y.-Q. Sun, H.-Y. Zeng, Z.-C. Dong, *Polyhedron* **2003**, *22*, 3097 – 3103.

[3] H. Mao, C. Zhang, G. Li, H. Zhang, H. Hou, L. Li, Q. Wu, Y. Zhu, E. Wang, *Dalton Trans.* **2004**, 3918 – 3925.

[4] X. Xu, Y. Ma, E. Wang, *J. Solid State Chem.* **2007**, *180*, 3136 – 3145.

[5] S. Jin, W. Chen, *Inorg. Chim. Acta* **2007**, *360*, 3756 – 3764.

[6] J. Jin, S. Y. Niu, G. D. Yang, L. Ye, *Z. Anorg. Allg. Chem.* **2006**, *632*, 2350 – 2354.

[7] A. K. Ghosh, A. D. Jana, D. Ghoshal, G. Mostafa, N. R. Chaudhuri, *Crystal Growth Design* **2006**, *6*, 701 – 707.

[8] Y. Q. Zheng, J. L. Lin, J. Sun, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1059 – 1065.

[9] Y. Q. Zheng, W. H. Liu, J. L. Lin, *Z. Anorg. Allg. Chem.* **2002**, *628*, 620 – 624.

[10] M. Padmanabhan, S. M. Kumary, X. Huang, J. Li, *Inorg. Chim. Acta* **2005**, *358*, 3537 – 3544.

[11] Y. Q. Zheng, J. Sun, J. L. Lin, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1501 – 1504.

[12] V. T. Yilmaz, S. Demir, O. Andac, W. T. A. Harrison, *J. Coord. Chem.* **2002**, *55*, 863 – 872.

[13] S. Demir, V. T. Yilmaz, F. Yilmaz, O. Buyukgungor, *J. Inorg. Organomet. Polym.* **2009**, *19*, 342 – 347.

[14] S. Demir, V. T. Yilmaz, B. Sariboga, O. Buyukgungor, J. Mrozinski, *J. Inorg. Organomet. Polym.* **2010**, *20*, 220 – 228.

[15] S. L. Li, A. Usman, I. A. Razak, A. A. Rahman, H. K. Fun, J. Y. Wu, Y. P. Tian, M. H. Jiang, Z. Y. Chen, *Acta Crystallogr*. **2003**, *E59*, m199 – m201.

[16] N. Guillou, C. Livage, G. Ferey, *Eur. J. Inorg. Chem.* **2006**, 4963 – 4978.

[17] D. Valigura, J. Moncol, M. Korabik, Z. Pucekova, T. Lis, J. Mroziński, M. Menlik, *Eur. J. Inorg. Chem.* **2006**, 3813 – 3817.

[18] T. A. Azizov, Kh. T. Sharipov, N. A. Parpiev, Z. Karimov, M. Askarov, A. B. Khudoyarov, *Zh. Neorg. Khim.(Russ.) (Russ. J. Inorg. Chem.)* **1991**, *36*, 1722 – 1724.

[19] A. Vegas, A. Perez-Salazar, F. Silio, *Acta Crystallogr.* **1981**, *B37*, 1916 – 1918.

[20] M. I. Matsaberidze, A. S. Batsanov, R. G. Gerr, Yu. T. Struchkov, G. V. Tsintsadze, *Koord. Khim. (Russ.) (Coord. Chem.)* **1985**, *11*, 411.

[21] E. E. Castellano, O. E. Piro, B. S. Parajon-Costa, E. J. Baran, *Z. Naturforsch.* **2002**, *57b*, 657 – 660.

[22] S. Cakir, I. Bulut, K. Aoki, *J. Chem. Cryst.* **2003**, *33*, 875 – 884.

[23] Y. Miwa, T. Mizuno, K. Tsuchida, T. Tagaa, Y. Iwata, *Acta Crystallogr.* **1999**, *B55*, 78 – 84.

[24] M. Kurmoo, *Chem. Soc. Rev.* **2009**, *38*, 1353 – 1379.

[25] F. S. Delgado, M. H. Molina, J. Sanchiz, C. R. Perez, Y. R., Martin, T. Lopez, F. Lloret, M. Julve, *CrystEngComm* **2004**, *6*, 106 – 111.

[26] G. M. Sheldrick, SHELXS/L-97, Programs for Crystal Structure Determination, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467 – 473; *ibid.* **2008**, *A64*, 112 – 122.