One-Dimensional and Two-Dimensional Coordination Polymers of Copper(II) Nitrobenzoate with Bridging 3-Pyridylmethanol Ligand

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Abstract. Complexes of composition $[Cu(X-NO_2bz)_2(\mu-3PM)_2]_n$ [X-NO₂bz = 2-nitrobenzoate (1), 3-nitrobenzoate (2) or 4-nitrobenzoate (3) and 3PM = 3-pyridylmethanol] were prepared and studied by elemental analysis, UV/Vis, IR and EPR spectroscopy. The molecular structures of two new complexes 1 and 3 were solved. The copper atoms of both complexes exhibit an elongated octahedral coordination environment with the equatorial positions occupied by two monoden-

Introduction

The field of coordination polymers represents growing area of solid-state coordination chemistry and crystal engineering [1, 2]. Metal-organic frameworks with flexible or rigid microporous channels are interesting materials with useful properties as physical adsorption of gas [3], heterogeneous catalysis [4], non-liner optical materials [5], luminescent materials [6], dynamic porous coordination polymers [7] and magnetic materials [8].

The compound 3-pyridylmethanol can be used as flexible bridging ligand [9] for construction of metal-organic frameworks [10]. It is well known that the ligand usually prefers formation of carboxylato copper(II) complexes with $[Cu(RCO_2)_2(\mu-3PM)_2]_n$ stoichiometry. The structures of the complexes are one-dimensional chain-like [10–14], or two-dimensional sheet-like [10, 15–20]. The similar one-dimensional chain-like structures were found for carboxylato zinc(II) [21] and for carboxylato cadmium(II) [22] complexes. On the other hand, only a few dinuclear and mononuclear copper(II) com-

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tate nitrobenzoato anions and two 3-pyridylmethanol nitrogen atoms in *trans* positions. The both axial positions are occupied by oxygen atoms of bridging 3-pyridylmetanol ligands The polymeric structure of complex [Cu(2-NO₂bz)₂(μ -3PM)₂]_n (1) contains two-dimensional layers. The complex **3** exhibits a polymeric chain-like structure [Cu(4-NO₂bz)₂(μ -3PM)₂]_n with copper atoms double-bridged by two 3-pyridylmethanol molecules similarly as it was found for complex **2**.

plexes with 3-pyridylmethanol as terminal ligand exist. For example, the complex [Cu₂(CH₃CO₂)₄(3PM)₂]·CH₂Cl₂ has a paddle-wheel dinuclear molecular structure with two terminal 3-pyridylmethanol ligands [23]. The carboxylato copper(II) complexes [Cu(2-NO₂bz)₂(3PM)₂-(H₂O)₂] [11] and [Cu(3 $pyac_{2}(3PM)_{2}(H_{2}O)$] (3-pyac = 3-pyridylacrylato) [24] exhibit monomeric molecular structures with two terminal 3-pyridylmethanol ligands. Terminal 3-pyridylmethanol ligands were also found in the mononuclear complex [CuCl₂(3PM)₄] [25] and in the oxalato-bridged coordination polymer [Cu(µ- C_2O_4)(3PM)₂]_n [26] as well as in some iron(III) [27], cadmium(II) [28], zinc(II) [29] and platinum(II) [30, 31] com-Two other copper(II) coordination polymers plexes. $[Cu_3(C_2H_5CO_2)_6(\mu-3PM)_2(3PM)_2]_n$ [32] and $[Cu_3(2-Clnic)_6 (\mu$ -3PM)₄(3PM)₂]_n (2-Clnic = 2-chlornicotinato) [10] are known in which the 3-pyridylmethanol molecules act as bridging as well as terminal ligands.

In this report, we describe the synthesis and spectral properties of coordination polymers: $[Cu(2-NO_2bz)_2(\mu-3PM)_2]_n$ (1), $[Cu(3-NO_2bz)_2(\mu-3PM)_2]_n$ (2) and $[Cu(4-NO_2bz)_2(\mu-3PM)_2]_n$ (3), where 2-NO_2bz = 2-nitrobenzoate; 3-NO_2bz = 3-nitrobenzoate; 4-NO_2bz = 4-nitrobenzoate and 3PM = 3-pyridylmethanol. The molecular structure of $[Cu(3-NO_2bz)_2(\mu-3PM)_2]_n$ (2) has been already published [13], but some new aspects of the structure of compound 2 are presented herein together with its spectral properties. Herein, we additionally present the molecular structures of $[Cu(2-NO_2bz)_2(\mu-3PM)_2]_n$ (1) and $[Cu(4-NO_2bz)_2(\mu-3PM)_2]_n$ (3).

Results and Discussion

$[Cu(2-NO_2bz)_2(\mu-3PM)_2]_n$ (1)

The molecular structure of compound 1 contains two-dimensional sheets parallel to the ab plane. Each Cu²⁺ cation is lo-



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cated on an inversion center. The coordination environment around the Cu²⁺ cation is square-bipyramidal (Figure 1). The equatorial plane consists of a pair of monodentate 2-nitrobenzoate ligands bound through their carboxylate oxygen atoms [Cu–O1 = 1.965(1) Å] and a pair of neutral 3-pyridylmethanol molecules coordinated through their pyridine nitrogen atoms [Cu–N1 = 2.021(1) Å]. The axial positions are occupied by two hydroxy oxygen atoms [Cu–O5ⁱ = Cu–O5ⁱⁱ = 2.472(1) Å, symmetry code: (i) -x + 3/2, y - 1/2, z; (ii) x - 1/2, -y + 1/2, -z + 1] from two adjacent symmetry-related 3-pyridylmethanol molecules.



Figure 1. Perspective view of $[Cu(2-NO_2bz)_2(\mu-3PM)_2]_n$ (1), with the atom-numbering scheme. Thermal ellipsoids are drawn at the 30 % probability level. [Symmetry code: (i) -x + 3/2, y - 1/2, z; (ii) x - 1/2, -y + 1/2, -z + 1].

The hydroxy hydrogen atoms of 3-pyridylmethanol are "fixed" to the uncoordinated carboxylate oxygen atoms O2 by hydrogen bonds O5–H5O···O2ⁱⁱⁱ [symmetry code: (iii) -x + 3/2, v + 1/2, z] with interatomic O5--O2 distances of 2.7259(17) Å and six-membered metallocycles are created. Details of the hydrogen bonding parameters are given in Table 1. An additional π - π stacking interaction between the molecules of 1 [33] was found between the centroids c_g of two adjacent pyridine rings, N1/C8–C12 with $c_g \cdots c_g^{iv} = 3.78$ Å [symmetry code: (iv) -x + 1, -y + 1, -z + 1]. The distance between parallel planes of stacked pyridine rings is 3.42 Å. Many complexes of [Cu(RCO₂)₂- $(\mu$ -3PM)₂]_n stoichiometry are two-dimensional coordination polymers, but only the complex $[Cu(sal)_2(\mu-3PM)_2]_n$ (sal = salicylato) [18, 19] has shown a crystal structure similar to complex 1 (Figure 2). The crystal system of both complexes is orthorhombic in space group Pbca. The crystal systems of the other two-dimensional coordination polymers $[Cu(RCO_2)_2(\mu-3PM)_2]_n$ (RCO₂ = 2-chlorobenzoato [10], 2,6-dimethoxynicotinato [15], 4-chlorosalicylato [16], flufenamato [17] or clofibrinato [20]) are monoclinic in space group $P2_1/c$.

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Table 1. Selected bond lengths and hydrogen bond parameters /Å and $^\circ$ for 1–3.

	1	2	3
Cu–O1	1.965(1)	1.986(1)	1.973(2)
Cu–N1	2.021(1)	2.037(1)	2.043(2)
Cu–O5 _{ax}	2.472(1)	2.372(1)	2.475(2)
O1-Cu-N1	90.18(5)	89.73(5)	90.13(7)
O1–Cu–O5 _{ax}	87.54(5)	86.47(5)	85.25(7)
N1–Cu–O5 _{ax}	87.21(5)	85.87(5)	84.60(7)
Hydrogen	O5–H5O····O2 ⁱⁱⁱ	O5–H5O····O2 ^{vii}	O5–H5O···O2 ^{vii}
bond			
H····A	1.93	1.81	1.83
D····A	2.726(2)	2.617(2)	2.628(3)
D–H•••A	156	162	165
	[this work]	[13]	[this work]

Symmetry code: (iii) -x + 3/2, y + 1/2, z; (vii) -x + 2, -y + 1, -z + 1.



Figure 2. Crystal packing of two-dimensional coordination polymer $[Cu(2-NO_2bz)_2(\mu-3PM)_2]_n$ (1).

$[Cu(4-NO_2bz)_2(\mu-3PM)_2]_n$ (3)

The molecular structure of compound **3** with atomic-numbering scheme of independent part is shown in Figure 3. The independent part of the molecule consists of the copper atom, which is bonded centrosymmetrically to two monodentate 4nitrobenzoato anions through the oxygen atoms O1 [Cu–O1 = 1.973(2) Å] and two 3-pyridylmethanol molecules bonded through the pyridine nitrogen atoms N1 [Cu–N1 = 2.043(2) Å]. The coordination polyhedron of the copper atom is completed by two oxygen atoms O4 of the neighboring 3pyridylmethanol hydroxy groups [Cu–O5^v = Cu–O5^{vi} = 2.475(2) Å, symmetry code: (v) x - 1, y, z; (vi) -x + 2, -y +1, -z + 1] giving the distorted octahedral arrangement. A pair of 3-pyridylmethanol molecules bridge each pair of adjacent copper atoms (Figure 4, A) and an infinite linear chain of doubly bridged copper atoms is formed.





Figure 3. Perspective view of $[Cu(4-NO_2bz)_2(\mu-3PM)_2]_n$ (3), with the atom numbering scheme. Thermal ellipsoids are drawn at the 30 % probability level. [Symmetry code: (v) x - 1, y, z; (vi) -x + 2, -y + 1, -z + 1].



Figure 4. Crystal packing of one-dimensional coordination polymer: A) $[Cu(4-NO_2bz)_2(\mu-3PM)_2]_n$ (**3**) and B) $[Cu(3-NO_2bz)_2(\mu-3PM)_2]_n$ (**2**).

The strong hydrogen bonds between each 3-pyridylmethanol hydroxy group and the oxygen O5 atom of the coordinated carboxylate group of the 4-nitrobenzoate anions (O2) by hydrogen bonds O5–H5O···O2^{vii} [symmetry code: (vii) -x + 2, -y + 1, -z + 1] with interatomic distances O5···O2 of 2.628(2) Å are formed and six-membered metallacyclic rings are created. Details of the hydrogen-bonding parameters are given in Table 1. The infinite chains of **3** are collinear to the

a axis (Figure 4A). The angle between the plane of the major part of the disordered nitro group and the plane of the benzene ring of 4-nitrobenzoate is 9.3°. It is close to planarity and concurs that two 4-nitrobenzoate anions are stacked (see Supporting Information, Figure S1) by their 4-nitrophenyl groups. The distance between two planes of stacked benzene rings of 4-nitrobenzoate anions [C2–C7] amounts 3.53 Å and the $c_g \cdots c_g$ distance is 3.93 Å. The stacked 4-nitrobenzoate anions are linking the infinite by 3-pyridylmethanol doubly bridged chains into two-dimensional supramolecular layers and the copper atoms and stacked 4-nitrobenzoate anions are in linear arrangement (Figure S1).

The molecular structure of complex 2 is similar to that of complex 3 [13]; selected bond lengths and angles for comparison are given in Table 1. The crystal structure of 2 creates infinite chains, which are collinear to the *a* axis (Figure 4, B). The benzene rings together with nitro-groups of 3-nitrobenzoate anions are stacked too (see supplementary Figure S1) and layers create two-dimensional supramolecular frameworks. The angle between the nitro group and the benzene ring of 3nitrobenzoate anion is 8.5°. The distance between the two planes of benzene rings of 3-nitrobenzoate anions [C2-C7] amounts 3.55 Å and the c_{g} distance is 4.08 Å. The stacked 3-nitrobenzoate anions are linking the infinite chains to twodimensional supramolecular layers, but the copper atoms and stacked 3-nitrobenzoate anions are in zigzag arrangement (Figure S2). Similar stacked nitro-groups and benzene rings are known for the crystal structure of [Cu(3,5-(NO₂)₂bz)₂(µ- $3PM_{2}_{n}$ (3,5-(NO₂)₂bz = 3,5-dinitrobenzoate) [11], but in the crystal structure of $[Cu(2-MeSnic)_2(\mu-3PM)_2]_n$ (2-MeSnic = 2methytionicotinate) only π - π stacking interaction between pyridine rings of 2-methyltionicotinate anions is observed [10].

Supramolecular Structure Comparison

As it was mentioned above, complex 1 builds up a two-dimensional coordination polymer whereas the other two "isomeric" complexes 2 and 3 construct one-dimensional polymers. Moreover, another one-dimensional polymer [Cu(3,5- $(NO_2)_2 bz)_2 (\mu - 3PM)_2]_n$ has been already published [11] together with complex the monomeric [Cu(2- $NO_2bz_2(3PM)_2(H_2O)_2$]. An interesting feature of the last mentioned complex is that taking into account the orientation of the 3PM ligands the structure could be explained as one-dimensional doubly bridged chain (Figure S3) with methanol···water O-H···Ow hydrogen bridges. The insertion of water molecules into the bridges increased the Cu--Cu distance to 9.312 Å, whereas the O-H···O hydrogen bond parameters $[O \cdot \cdot \cdot O_W \text{ distance } 2.723(2) \text{ Å and } O - H \cdot \cdot \cdot O_W \text{ angle } 157^\circ]$ are very similar to those of 2 or 3. The comparison of the Cu-Cu distance within the group of 1D complexes (6.878(1) Å for **3**, 6.692(1) Å for **2** and 7.618(2) Å for $[Cu(3,5-(NO_2)bz)_2(\mu 3PM_{2}_{n}$ shows great variation for complexes with the same ligand 3PM. It is unexpectedly wide in comparison to the according Cu-N or plane-to-plane distances between the pyridine ring pairs (2.648 Å for 3, 2.667 Å for 2 and 2.642 Å for $[Cu(3,5-(NO_2)_2bz)_2(\mu-3PM)_2]_n)$ and is caused by free rotation

of–CH₂OH arm. Positioning of –CH₂OH relative to the pyridine ring plane becomes obvious on the angle between the Cu– O_{3PM} bond and the pyridine ring plane (61° for **3** Å, 64° for **2** and only 32° for [Cu(3,5-(NO₂)₂bz)₂(μ -3PM)₂]_n). Similar trends could be seen in the D···A–H bond parameters, where A is carboxylate anion oxygen atom {e.g. 2.628(3) Å for **3**, 2.617(2) Å for **2** and 2.753(2) Å for [Cu(3,5-(NO₂)₂bz)₂(μ -3PM)₂]_n}, which suggest a relation of these geometrical parameters to the basicity of nitrobenzoato anions (pK_a = 3.43 for 4-nitrobenzoic [34, 3.46 for 3-nitrobenzoic 34] and 2.79 for the 3,5-dinitrobenzoic acid [35]).

Finally, it should be pointed out that formation of the *quasi* one-dimensional [Cu(2-NO₂bz)₂(μ -3PM)₂(H₂O)₂] diaqua complex in comparison to two-dimensional [Cu(2-NO₂bz)₂(μ -3PM)₂] could be related to non-planarity because of the bulkiness of the 2-nitrobenzoate anion, whereas the other three nitrobenzoate anions are nearly planar. This deviation from planarity could be expressed by the angles φ_{rot} (angle between –CO₂ and phenyl ring planes) [36] and φ'_{rot} (the angle between –NO₂ and ring planes), which amount 44.0 and 43.7° for complex **1**, and 28.9 and 54.5° for [Cu(2-NO₂bz)₂(μ -3PM)₂(H₂O)₂]. In spite of the insertion of water molecules into both bridges, the hydrogen atom H7 of the pyridine ring forms C–H··· π interaction [37] with 2-nitrobenzoate phenyl [C2–C7] ring (H7··· c_g distance 2.9 Å).

Preparation and Spectral Properties

The preparations of complexes 1–3 reveal some interesting features. The best soluble complex 1 was obtained in a smaller yield under the reaction conditions given in Experimental Section and the crystals obtained from mother liquid were not suitable for X-ray analysis. However, greater dilution (over 50 mL with the same amount of reactants) of reaction mixture gave clear solution from which the crystals of $[Cu(2-NO_2bz)_2(3PM)_2(H_2O)_2]$ were obtained [11]. Moreover, the less soluble complex 3 was obtained in highest yield and good crystals were obtained from the light blue mother liquid. All experiments performed with diluted reaction mixtures yielded products 2 or 3 in unchanged fashion and we were not able to obtain a diaqua complex similar to mentioned $[Cu(2-NO_2bz)_2(3PM)_2(H_2O)_2]$ [11].

In the IR spectrum of complex **1**, the bands corresponding to $v_{as}(COO^{-})$ and $v_{s}(COO^{-})$ are present at 1602 cm⁻¹ and 1371 cm⁻¹, respectively. The value of $\Delta v (\Delta v = v_{as} - v_s)$ amounts 231 cm⁻¹ and is greater than Δv for the ionic form of the 2nitrobenzoate salt (211 cm⁻¹). It corresponds to a monodentate coordination mode. For complexes **2** and **3**, the corresponding bands are found at 1598 cm⁻¹ and 1376 cm⁻¹ for **2**, and at 1578 cm⁻¹ and 1382 cm⁻¹ for **3**, respectively. The Δv values are 222 cm⁻¹ and 196 cm⁻¹, respectively and confirm in both cases monodentate coordination mode. The monodentate bonding mode of carboxylate anions is typical for complexes with the 3PM ligand. Nitrobenzoatocopper(II) complexes with other nitrogen donor ligands (e.g. 2PM, nicotinamide, or diethylnicotinamide) exhibit greater variability in composition, structure and spectral properties. The hydrogen bond vibrations in the spectra of all three complexes show broad signals between 2530 and 2910 cm⁻¹, which can be attributed to a system of intramolecular and/or intermolecular hydrogen bonds (see hydrogen bonds formation above). The electronic spectra of the three complexes are very similar and exhibit broad asymmetric absorption bands attributed to d←d transitions with a maximum positioned at 610 nm for 1, 650 nm for 2, and at 656 nm for 3.

The EPR spectra (measured at room temperature) are very similar and exhibit axial type with spectroscopic splitting factors $g_{\perp} = 2.078$ and $g_{\parallel} = 2.280$ for 1, $g_{\perp} = 2.060$ and $g_{\parallel} = 2.280$ for 2, and $g_{\perp} = 2.080$ and $g_{\parallel} = 2.285$ for 3. It is interesting that well resolved parallel hyperfine splitting $A_{\parallel} = 160$ Gauss, resulting from the interaction of the unpaired electron of the copper atom with the spin of copper nucleus I = 3/2 was observed only for complex 3. It is worth to mention, that this hyperfine splitting was not observed for complex 2, which is of very similar molecular structure (Table 1).

Conclusions

Three coordination polymers with copper(II) nitrobenzoate and the ligand 3-pyridylmethanol were prepared and characterized. The crystal structure of 1 consists of 2D sheets. On the other hand, the crystal structures of 2 and 3 consist of 1D chains (Table 2), which are linked by face-to-face π - π stacking interactions. This study has shown that 3-pyridylmethanol is a suitable bridging ligand for the construction of one- or two-

 Table 2. Crystal data and structure refinement parameters for complexes 1 and 3.

Compound	1	3
Chemical formula	C ₂₆ H ₂₂ CuN ₄ O ₁₀	C ₂₆ H ₂₂ CuN ₄ O ₁₀
$M_{\rm r}$ /g·mol ⁻¹	614.03	614.03
Crystal system	orthorhombic	triclinic
Space group	Pbca	$P\overline{1}$
T/K	100(2)	293(2)
a /Å	13.031(4)	6.878(1)
b /Å	9.196(3)	7.897(1)
c /Å	21.758(7)	12.145(1)
α /°	90	86.65(1)
β /°	90	83.87(1)
γ /°	90	78.42(1)
$V/Å^3$	2607.3(14)	642.08(13)
Ζ	4	1
$\rho_{\rm calcd.}$ /g·cm ⁻³	1.564	1.588
Radiation type	$Cu-K_{\alpha}$	Mo- K_{α}
μ / mm^{-1}	1.773	0.918
Crystal size /mm	$0.20\times0.20\times0.30$	$0.22 \times 0.34 \times 0.35$
<i>F</i> (000)	1260	315
$\theta_{\rm max}/^{\circ}$	72.45	26.37
Reflections collect.	20465	3265
$R_1 (2\sigma) / wR_2$ (all data)	0.034/0.096	0.039/0.103
Data/restrains/	2535/0/188	2603/18/202
parameters		
S	1.04	1.03
$\Delta_{ m m pmax}$ / $\Delta_{ m m pmin}$ /e·Å ⁻³	0.35/-0.66	0.30/-0.27

dimensional coordination polymers. Our failed attempt to prepare diaqua complexes with 4-, or 3-nitrobenzoate anions could be related to a coplanar orientation of the NO₂ substituents and phenyl rings that allow additional structure stabilization by π --- π stacking interactions of anionic ligands.

Experimental Section

Physical Measurements

Carbon, hydrogen and nitrogen analyses were carried out with a CHNSO FlashEATM 1112 automatic elemental analyzer. The copper content was determined by electrolysis of water solution obtained by the sample mineralization with a mixture of sulfuric acid and potassium peroxodisulfate.

The electronic spectra (190–1100 nm) of the complexes were measured in nujol suspension with a SPECORD 200 (Carl Zeiss Jena) spectrophotometer at room temperature. The infrared spectra (4000–100 cm⁻¹) were recorded with a MAGNA 750 IR (Nicolet) and Nicolet 5700 FT-IR spectrophotometers at room temperature. EPR spectra of the powdered samples were recorded with a spectrometer Bruker ER 200-SRC operating at X-band.

Preparation of the Complexes

The blue complexes were prepared by similar reactions of aqueous solutions of copper(II) acetate (1 mmol in 10 mL) with 3-pyridylmethanol (ronicol, 2 mmol). 2-Nitrobenzoic acid (2 mmol for 1), 3-nitrobenzoic (2 mmol for 2) or 4-nitrobenzoic acid (2 mmnol for 3) was added with water (10 mL), and the reaction mixtures were stirred until blue powders formed. The products were filtered off (0.10 mmol of 1, 0.28 mmol of 2 and 0.57 mmol of 3), washed with a small amount of cold water and dried at room temperature. Blue crystals suitable for X-ray analysis of 2 and 3 were obtained from the aqueous mother liquids after one week at room temperature. The crystals obtained for 1 were not good enough for X-ray analysis, suitable single crystals were obtained by the same procedure using ethanol instead of water as solvent (0.80 mmol of 1).

 $[Cu(2-NO_2bz)_2(\mu\mathcal{3}PM)_2]_n$ (1): calcd. C 50.86, H 3.61, N 9.13, Cu 10.35; found C 50.92, H 3.60, N 9.17, Cu 10.44.

 $[Cu(3-NO_2bz)_2(\mu-3PM)_2]_n$ (2): calcd. C 50.86, H 3.61, N 9.13 Cu 10.35; found C 50.97 H 3.65 N 9.14 Cu 10.35.

 $[Cu(4-NO_2bz)_2(\mu-3PM)_2]_n$ (3): calcd. C 50.86, H 3.61, N 9.13, Cu 10.35; found C 50.86, H 3.82, N 8.79, Cu 10.00 %.

X-ray Crystallography

The crystal data and details of data collections for all structures are given in Table 2. Intensity data for **1** were collected with a Xcalibur PX κ -diffractometer [38] with graphite-monochromated Cu- K_{α} radiation and CCD detector at 100 K. Data for **3** were collected with a diffractometer Siemens P4 [39] with graphite-monochromated Mo- K_{α} radiation at 293 K. The diffraction intensities were corrected for Lorentz and polarization effects. Absorption corrections were applied using the programs CrysAlis-RED [38] for **1** and XEMP [39] for **3**. The structures were solved by direct methods using the programs SIR-97 [40] (for **1**) or SHELXS-97 [41] (for **3**) and refined by the full-matrix least-squares method on all F^2 data using the program SHELXL-97 [41]. Geometrical analyses were performed using SHELXL-97. The structures were drawn by XP in SHELXTL [41].

The nitro group of complex **3** is orientationally disordered and the refined site-occupancy factors of the three disordered parts are 0.66, 0.11 and 0.23, respectively. The N–O, O···O and C···O distances were restrained by SADI instructions of SHELXL-97. Thermal ellipsoids of disordered nitro-groups were constrained by EADP instructions of SHELXL-97.

Crystallographic data for the structural analysis were deposited with the Cambridge Crystallographic Data Centre CCDC-741830 (1), and -741831 (3). Further details of the crystal structures investigations are available free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; +44-1223-336033; E-Mail: deposit@ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): The supplementary figures S1–S3.

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References

- a) C. Janiak, *Dalton Trans.* 2003, 2781–2804; b) C. N. R. Rao, S. Natarajan, R. Vaidhyanathan, *Angew. Chem. Int. Ed.* 2004, 43, 1466–1496; c) S. L. James, *Chem. Soc. Rev.* 2003, 32, 276–288.
- a) S. Taheri, F. Marandi, H.-K. Fun, R. Kia, Z. Anorg. Allg. Chem. [2] 2009, 635, 1352-1354; b) S. K. Henninger, H. A. Habib, C. Janiak, J. Am. Chem. Soc. 2009, 131, 2776-2777; c) H. A. Habib, J. Sanchiz, C. Janiak, Dalton Trans. 2008, 4877-4884; d) J. L. Xiel, Z. Anorg. Allg. Chem. 2009, 635, 384-388; e) I. Stein, U. Ruschewitz, Z. Anorg. Allg. Chem. 2009, 635, 914-919; f) M. Bröring, S. Prikhodovski, Z. Anorg. Allg. Chem. 2008, 634, 2451-2458; g) F. Marandi, M. Khosravi, H. K. Fun, Z. Anorg. Allg. Chem. 2008, 634, 2617-2628; h) A. Kromm, Y. Geldmacher, W. S. Sheldrick, Z. Anorg. Allg. Chem. 2008, 634, 2191-2198; i) K. Müller-Buschbaum, Y. Mokaddem, Z. Anorg. Allg. Chem. 2008, 634, 2360-2366; j) R. Koferstein, C. Robl, Z. Anorg. Allg. Chem. 2007, 633, 1127-1130; k) J.-P. Zou, G.-S. Zeng, Z.-H. Wen, Q. Peng, Q.-J. Xing, M.-H. Chen, G.-C. Guo, J.-S. Huang, Inorg. Chim. Acta 2009, 362, 4843-4848; 1) M. Wriedt, C. Nather, Z. Anorg. Allg. Chem. 2009, 635, 1115-1122; m) W.-W. Sun, X.-B. Qian, C.-Y. Tian, E.-Q. Gao, Inorg. Chim. Acta 2009, 362, 2744-2748; n) D. P. Martin, R. M. Supkowski, R. L. LaDuca, Cryst. Growth Des. 2008, 8, 3518-3520; o) B. Xiao, P. J. Byrne, P. S. Wheatley, D. S. Wragg, X.-B. Zhao, A. J. Fletcher, K. M. Thomas, L. Peters, J. S. O. Evans, J. E. Warren, W. Z. Zhou, R. E. Morris, Nat. Chem. 2009, 1, 289-294.
- [3] J.-R. Li, R. J. Kuppler, H.-C. Zhou, Chem. Soc. Rev. 2009, 38, 1477–1504.
- [4] J.-Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nquyen, J. T. Hupp, *Chem. Soc. Rev.* **2009**, *38*, 1450–1459.
- [5] O. R. Evans, W. B. Lin, Acc. Chem. Res. 2002, 35, 511-522.
- [6] M. D. Allendorf, C. A. Bauer, R. K. Bhakta, R. J. T. Houk, *Chem. Soc. Rev.* 2009, 38, 1330–1352.
- [7] S. Kitagawa, K. Uemura, Chem. Soc. Rev. 2005, 34, 109–119.
- [8] D. Maspoch, D. Ruiz-Molina, J. Veciana, J. Mater. Chem. 2004, 14, 2713–2723; M. Kurmoo, Chem. Soc. Rev. 2009, 38, 1353– 1379.



ARTICLE

- [9] a) J. E. Beves, E. C. Constable, C. E. Housecroff, M. Neuburger, S. Schaffner, Inorg. Chem. Commun. 2009, 12, 898-901; b) M. G. Amiri, A. Morsali, M. Zeller, Z. Anorg. Allg. Chem. 2009, 635, 1673-1677; c) N. Lah, R. Clerac, Polyhedron 2009, 28, 2466-2472; d) H. A. Habib, J. Sanchiz, C. Janiak, Inorg. Chim. Acta 2009, 362, 2452-2460; e) M. C. Das, P. K. Bharadwaj, J. Am. Chem. Soc. 2009, 131, 10942-10949; f) H. A. Habib, A. Hoffmann, H. A. Höppe, G. Steinfeld, C. Janiak, Inorg. Chem. 2009. 48, 2166-2180; g) H. A. Habib, A. Hoffmann, H. A. Höppe, C. Janiak, Dalton Trans. 2009, 1742-1751; h) J. Yang, J.-F. Ma, Y.-Y. Liu, S. R. Batten, CrystEngComm 2009, 11, 151-159; i) H. A. Habib, J. Sanchiz, C. Janiak, Dalton Trans. 2008, 1734-1744; j) M. Du, Z.-H. Zhang, X.-G. Wang, L.-F. Tang, X.-J. Zhao, CrystEngComm 2008, 10, 1855-1865; k) P. P. Yang, B. Li, Y. H. Wang, W. Gu, X. Liu, Z. Anorg. Allg. Chem. 2008, 634, 1210-1214; 1) Y.-Q. Lan, S.-L. Li, Y.-M. Fu, Y.-H. Xu, L. Li, Z.-M. Su, Q. Fu, Dalton Trans. 2008, 6796-6807; m) W. Yu, T. L. Zhang, J. G. Zhan, L. Yang, S. Z. Wang, R. F. Wu, Z. Anorg. Allg. Chem. 2008, 634, 754-757; n) Q. Y. Wen, J. Q. Chen, H. C. Fang, L. Chen, Z. Y. Zhou, Z. J. Hu, Y. P. Cai, Z. Anorg. Allg. Chem. 2008, 634, 567-571; o) C. Y. Sun, X. X. Li, S. F.Wang, W. J. Li, X. J. Zheng, Z. Anorg. Allg. Chem. 2008, 634, 950-955; p) P. Ren, M.-L. Liu, J. Zhang, W. Shi, P. Cheng, D.-Z. Liao, S.-P. Yan, Dalton Trans. 2008, 4711-4713.
- [10] J. Moncol, P. Segla, D. Miklos, M. Mazur, M. Melnik, T. Głowiak, M. Valko, M. Koman, *Polyhedron* **2006**, *25*, 1561–1566.
- [11] P. Stachová, M. Korabik, M. Koman, M. Melník, J. Mrozinski, T. Głowiak, M. Mazúr, D. Valigura, *Inorg. Chim. Acta* 2006, 359, 1275–1281.
- [12] M. Mudra, J. Moncol, J. Svorec, M. Melnik, P. Lönnecke, T. Głowiak, R. Kirmse, *Inorg. Chem. Commun.* 2003, 6, 1259–1265.
- [13] P. Stachova, D. Valigura, M. Koman, T. Głowiak, Acta Crystallogr., Sect. E 2005, 61, m994mm996.
- [14] F. Valach, M. Tokarcik, P. Kubinec, M. Melnik, L. Macaskova, *Polyhedron* **1997**, *16*, 1461–1464.
- [15] V. Jorík, E. Scholtzová, P. Segla, Z. Kristallogr. 2008, 223, 524– 529.
- [16] J. Maroszova, L. Martiska, D. Valigura, M. Koman, T. Głowiak, Acta Crystallogr., Sect. E 2006, 62, m1164–m1166.
- [17] S. Lörinc, M. Koman, M. Melnik, J. Moncol, D. Ondrusova, Acta Crystallogr., Sect. E 2004, 60, m590–0592.
- [18] N. N. Hoang, F. Valach, L. Macaskova, M. Melnik, Acta Crystallogr., Sect. C 1992, 48, 1933–1936.
- [19] J. Maroszova, J. Moncol, M. Koman, M. Melnik, T. Głowiak, Acta Crystallogr, Sect. E 2006, 62, m3385–m3387.
- [20] J. Moncol, M. Koman, M. Melnik, T. Głowiak, *CrystEngComm* 2001, 3, 262–264.

- [21] V. Zelenak, I. Cisarova, M. Sabo, P. Llewellyn, K. Gyoryova, J. Coord. Chem. 2004, 57, 87–96.
- [22] J. Moncol, D. Miklos, P. Segla, M. Koman, T. Lis, Acta Crystallogr, Sect. E 2008, 64, m440–m441.
- [23] M. Melnik, K. Smolander, P. Sharrock, *Inorg. Chim. Acta* 1985, 103, 187–194.
- [24] J. Moncol, P. Segla, J. Jaskova, A. Fischer, M. Melnik, Acta Crystallogr., Sect. E 2007, 63, m698–m700.
- [25] J. Moncol, M. Mudra, P. Lönnecke, M. Koman, M. Melnik, J. Chem. Crystallogr: 2004, 34, 423–431.
- [26] J. Jaskova, D. Miklos, P. Segla, R. Sillanpää, J. Moncol, Acta Crystallogr., Sect. E 2007, 63, m910–m912.
- [27] S. Stefanikova, I. Ondrejkovicova, M. Koman, T. Lis, J. Mrozinski, M. Wrzecion, J. Coord. Chem. 2008, 61, 3895–3903.
- [28] M. A. S. Goher, F. A. Mautner, K. Gatter, M. A. M. Abu-Youssef, A. M. A. Badr, B. Sodin, C. Gspan, *J. Mol. Struct.* 2008, 876, 199–205.
- [29] R. P. Feazell, C. E. Carson, K. K. Klausmeyer, *Inorg. Chem. Commun.* 2007, 10, 873–875.
- [30] F. J. Ramos-Lima, O. Vrana, A. G. Quiroga, C. Navarro-Ranninger, A. Halamikova, H. Rybnickova, L. Hejmalova, V. Brabec, *J. Med. Chem.* 2006, 49, 2640–2651.
- [31] A. Martinez, J. Lorenzo, M. J. Prieto, M. Font-Bardia, X. Solans, F. X. Aviles, V. Moreno, *Bioorg. Med. Chem.* 2007, 15, 969–979.
- [32] J. Moncol, J. Maroszova, M. Melnik, M. Koman, Acta Crystallogr., Sect. C 2007, 63, m114–m116.
- [33] C. Janiak, Chem. Soc., Dalton Trans. 2000, 3885-3896.
- [34] P. D. Bolton, K. A. Fleming, F. M. Hall, J. Am. Chem. Soc. 1972, 94, 1033–1034.
- [35] S. L. Gupta, R. N. Soni, J. Indian Chem. Soc. 1965, 42, 377-378.
- [36] T. Kawata, H. Uekusa, S. Ohba, T. Furukawa, T. Tokii, Y. Muto, M. Kato, *Acta Crystallogr., Sect. B* **1992**, *48*, 253–261.
- [37] H. Suezawa, T. Yoshida, Y. Umezawa, S. Tsuboyama, M. Nishio, *Eur. J. Inorg. Chem.* 2002, 3148–3155.
- [38] Oxford Diffaraction, CrysAlis CCD and CrysAlis RED, Oxford Diffraction Ltd, Abingdon, England, 2006.
- [39] Siemens, XSCANS and XEMP, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1994.
- [40] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 1999, 32, 115–119.
- [41] G. M. Sheldrick, Acta Crystallogr., Sect. A 2008, 64, 112-122.

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