New Coordination Polymers Based on Transition Metal Squarates and Pyrazine Ligands

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Three new coordination polymers have been prepared by hydrothermal reaction of squaric acid, pyrazine and the metal halides $FeCl_2 \cdot 4\,H_2O$, $CoBr_2$ and $NiBr_2$. In their crystal structures the metal atoms are coordinated by four water molecules and two pyrazine ligands within slightly distorted octahedra. The pyrazine ligands connect the metal atoms *via* μ-N,N'-coordination to linear chains which are connected via hydrogen bonding. The squarate dianions are not coordinated to the metal atoms and are located between the chains. The thermal behaviour of all compounds was investigated using TG-DTA-MS measurements. A complex behaviour for all compounds is found and the decomposition temperatures increase from Fe to Ni. From these investigations there are no hints for the occurrence of stoichiometric intermediate compounds.

Key words: Coordination Polymers, Transition Metal Squarates, Crystal Structures, Thermoanalysis

Introduction

In recent years the design of new coordination polymers based on transition metals and organic ligands has become of increasing interest [1]. One major goal in this area is the design of new solids with special physical properties [2]. It has been shown that dependent on the coordination behaviour of the metal atoms and the organic ligands, strategies for a more directed construction of crystal structures can be developed [1 – 3].

In our own investigations we are interested in the preparation of new coordination polymers based on transition metal squarates and multidentate N-donor ligands like 4,4'-bipyridine [4, 5] or pyrazine [6]. During these investigations we have obtained several compounds of the composition $[M(H_2O)_2(C_4O_4)(C_{10}H_8N_2) \cdot x\,H_2O]$(M = Mn, Fe, Co, Ni; x = 0 – 3) [4, 5]. In these compounds the metal cations are octahedrally coordinated by two 4,4'-bipyridine ligands, two water molecules and two squarate dianions. The 4,4'-bipyridine ligands connect the metal atoms *via* μ-N,N' coordination to linear chains which are interconnected by the squarate dianions to sheets by μ-O,O' coordination (Fig. 1). The interpenetrating chains forming a threedimensional structure that contains channels in which additional water molecules are embedded.

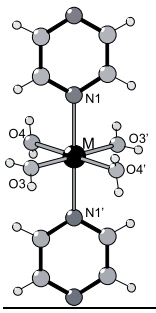
Thermoanalytic, X-ray powder and single crystal structure investigations on the manganese compound poly[diaqua-μ_2-squarato-O,O')-μ_2-4,4'-bipydridine-N,N')-manganese(II)] trihydrate show that the channel water molecules can be reversibly deintercalated and reintercalated in a presumably topotactic reaction, a process which is accompanied by a change of the colour of the material. We have also shown that the two water molecules coordinated to the metal centers can be reversibly removed. Starting from these findings, we have prepared additional metal squarates by hydrothermal reaction using pyrazine as a ligand. However, the structure determination of these compounds has shown that the squarate dianions are not coordinated to the metal atoms and no open structure has been formed.

Results and Discussion

Crystal structures

All compounds crystallize in the centrosymmetric, monoclinic space group $P2_1/n$ with two formula units per cell. The Fe and the Co compound **I** and **II** are isotypic, whereas in the Ni compound **III** the *b*- and the *c*-axis are exchanged. However, all structures

Table 1. Selected bond lengths (Å) and angles (°) for catena[tetra-aqua-(μ_2-pyrazine)metal(II)squarates] (**I**) (M = Fe), (**II**) (M = Co) and (**III**) (M = Ni).



		I	II	III	
M - N(1)	-	2.228(1)	2.189(1)	2.126(1)	(2x)
M - O(3)	-	2.068(1)	2.058(1)	2.059(1)	(2x)
M - O(4)	-	2.122(1)	2.078(1)	2.060(1)	(2x)
O3 - Me	- N1	90.08(4)	89.30(5)	87.48(4)	(2x)
O4 - Me	- N1	90.39(4)	90.84(5)	90.30(4)	(2x)
O4 - Me	- N1'	89.61(4)	89.16(5)	89.70(4)	(2x)
O3 - M	- O4	88.95(5)	89.19(5)	89.84(4)	(2x)
O3 - M	- O4'	91.05(5)	90.83(5)	90.16(4)	(2x)
O3 - M	- N1'	89.92(4)	90.70(5)	92.52(4)	(2x)
O3 - M	- O3'	180	180	180	(1x)
O4 - M	- O4'	180	180	180	(1x)
N1 - M	- N1'	180	180	180	(1x)

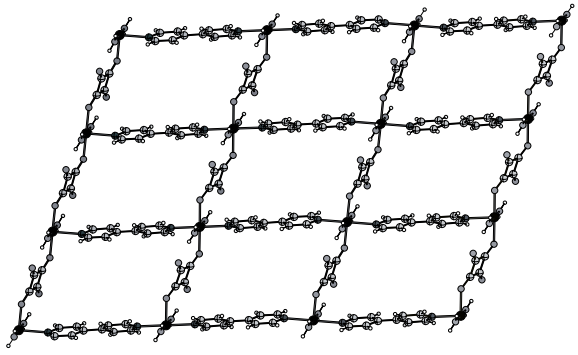


Fig. 1. Crystal structure of poly[diaqua(μ_2-squarato-O,O')-(μ_2-4,4'-bipyridine-N,N')-manganese(II)] tri hydrate with view onto the sheets.

are topologically identical. The asymmetric unit contains one metal atom, one squarate dianion and one pyrazine ligand in special positions as well as two water molecules in general positions. The metal atoms are coordinated by two nitrogen atoms of two symmetry related pyrazine ligands and to four oxygen atoms of two pairs of symmetry equivalent water molecules within slightly distorted octahedra (Table 1). Bond lengths and angles are comparable to those of related compounds retrieved from the Cambridge Structural Database [7]. In contrast to most of the structurally characterized metal squarates, the squarate dianions are not coordinated to the metal atoms.

The pyrazine ligands connect the metal atoms *via* μ-N,N' coordination into linear chains elongated in the direction of the crystallographic *a*-axis (Fig. 2). The metal atoms are located nearly in the plane of the pyrazine rings and in the direction of the N—N vector.

The squarate dianions and the pyrazine ligands are stacked perpendicular to the chains in a way that their

Table 2. Hydrogen bonding parameters (Å and °) for catena[tetra-aqua-(μ_2-pyrazine)metal(II)squarates] (**I**) (M = Fe), (**II**) (M = Co) and (**III**) (M = Ni).

D – H	d (D – H)	d (H···A)	DHA	d (D···A)	A	Symmetry operation
Catena[tetra-aqua-(μ_2-pyrazine)iron(II)squarate] (I)						
O3H1O	0.82	1.86	166.1	2.66	O2	[-*x*+½, *y*+½, -*z*+½]
O3H2O	0.82	1.91	178.6	2.73	O1	[-*x*+1, -*y*+1, -*z*+1]
O4H3O	0.82	1.95	169.9	2.76	O1	[*x*, *y*+1, *z*]
O4H4O	0.82	1.86	177.1	2.68	O2	[-*x*+1, -*y*+1, -*z*+1]
Catena[tetra-aqua-(μ_2-pyrazine)cobalt(II)squarate] (II)						
O3H1O	0.82	1.88	164.9	2.68	O2	[-*x*+½, *y*+½, -*z*+½]
O3H2O	0.82	1.92	177.5	2.74	O1	[-*x*+1, -*y*+1, -*z*+1]
O4H3O	0.82	1.94	170.1	2.76	O1	[*x*, *y*+1, *z*]
O4H4O	0.82	1.86	177.7	2.68	O2	[-*x*+1, -*y*+1, -*z*+1]
Catena[tetra-aqua-(μ_2-pyrazine)nickel(II)squarate] (III)						
O3H1O	0.82	1.90	169.4	2.71	O2	[*x*-½, -*y*+3/2, *z*-½]
O3H2O	0.82	1.94	164.4	2.74	O1	[-*x*+1, -*y*+1, -*z*+1]
O4H3O	0.82	1.92	170.4	2.73	O1	[-*x*+1, -*y*+1, -*z*+2]
O4H4O	0.82	1.87	177.6	2.69	O2	

A = acceptor, D = donator.

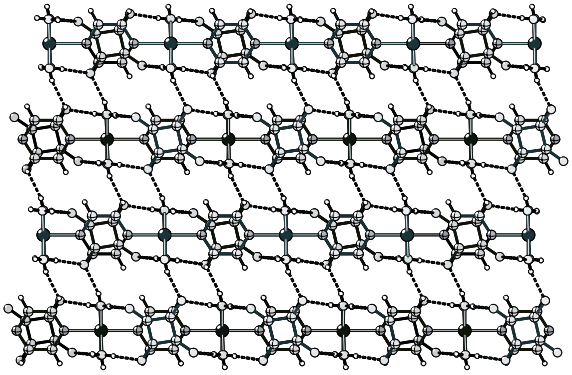


Fig. 2. Crystal structures of catena[tetra-aqua-(μ_2-pyrazine)metal(II)squarates] (**I**) (M = Fe), (**II**) (M = Co) and (**III**) (M = Ni) with view perpendicular to the metal-pyrazine chains (hydrogen bonds are shown as dotted lines; M = ●, O = ○, N = ⊕, C = ⊕, H = ○).

molecular planes are coplanar (Fig. 2). Such packing patterns are well known *e.g.* from several crystals structures of aromatic hydro- carbons [8].

The squarate dianions and the water molecules are connected *via* O—H···O hydrogen bonding between the squarate oxygen atoms and the water molecules (Fig. 2 and Fig. 3). The intermolecular H···O and O···O distances as well as the O—H···O angles of nearly 180 ° show that this must be a strong interaction (Table 2). The intermolecular O···O distances vary only slightly from Fe to Ni and no defined

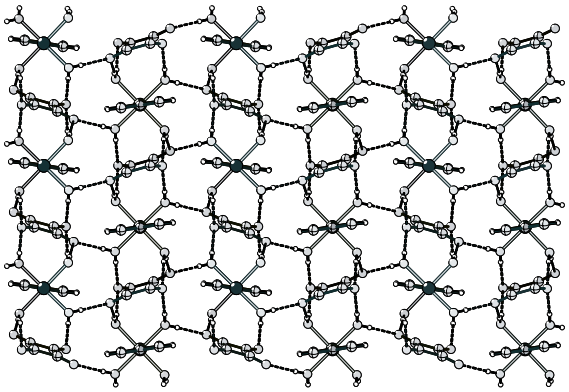


Fig. 3. Crystal structures of catena[tetra-aqua-(μ_2-pyrazine)metal(II)squarates] (**I**) (M = Fe), (**II**) (M = Co) and (**III**) (M = Ni) with view perpendicular to the metal-pyrazine chains (hydrogen bonding is shown as dotted lines; M = ●, O = ○, N = ⊕, C = ⊕, H = ○).

trend can be extracted. Due to the O—H···O hydrogen bonding, a three-dimensional network is formed (Fig. 2 and 3).

Compound **III** is isotypic to the copper compound catena[tetra-aqua-μ_2-pyrazine)copper(II)squarate] [9]. In this compound the Cu—N bond length amounts to 2.057 (3) Å, and the Cu—O distances are 2.320 (2) and 1.996 (2) Å. As expected, the M—N bond lengths decrease from Fe to Cu (Table 1) and the same trend is observed for one of the two M—O distances in compounds **I**, **II** and **III**. For the second, shorter M— O distance practically no alteration is observed. It must be noted that in the copper compound one of the two Cu—O distances is extremely elongated. This is presumably due to Jahn-Teller distortion [9]. The coordination polyhedron around the metal atoms is more strongly distorted for M = Ni or Cu than for M = Fe or Co. This is found especially for the O—M—N angles (Table 1).

In all structures presented the squarate dianions are not coordinated to the metal centers. This is in contrast to that what is frequently found in the structures of transition metal squarates. It appears that the coordination by water molecules is preferred. This idea is supported by the observations made on the corresponding 4,4'-bipyridine compounds described in the introduction [4,5]. In these compounds the two water molecules coordinated to the metal atoms can be removed by heating but the coordination is regenerated if the dehydrated samples are exposed to a humid atmosphere. However, in these compounds the metal atoms are actually connected to two squarate dianions. Assuming

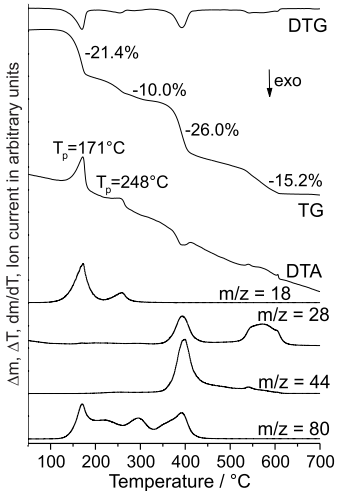


Fig. 4. DTA, TG, DTG and MS trend scan curve for compound (**I**) (simultaneous measurement; powder; weight: 52.14 mg; heating rate: 4 °C/min.; dynamic helium atmosphere; flow rate: 75 ml/min; $m/z = 18$ (H_2O); $m/z = 28$ (CO from C_4O_4); $m/z = 44$ (CO_2 from C_4O_4); $m/z = 80$ (pyrazine); Al_2O_3-crucible).

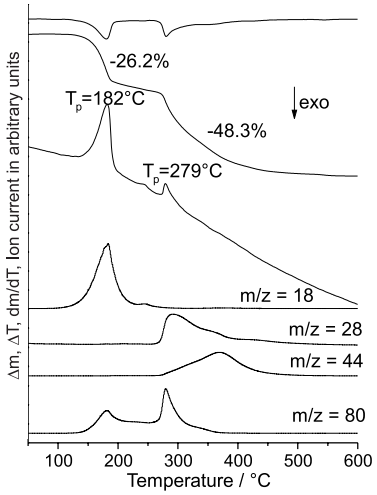


Fig. 5. DTA, TG, DTG and MS trend scan curve for compound **II** (simultaneous measurement; powder; weight: 44.71 mg; conditions as for **I** in Fig. 4).

a structure for the pyrazine compounds that is similar to that of the 4,4'-bipyridine compounds, the pores shown in Fig. 1 must be smaller and therefore interpenetration of metal squarate pyrazine sheets is more difficult to achieve. All attempts to obtain additional metal squarates for M = Fe, Co, or Ni and with pyrazine as ligand with a different metal coordination failed, ex-

Table 3. Selected crystal data and details of the structure determination for catena[tetra-aqua-(μ_2-pyrazine)metal(II)squarates] (**I**) (M = Fe), (**II**) (M = Co) and (**III**) (M = Ni).

Compound	**I**	**II**	**III**
Formula	$C_8H_{12}N_2O_8Fe$	$C_8H_{12}N_2O_8Co$	$C_8H_{12}N_2O_8Ni$
MG [g/mol]	320.039	323.125	322.882
Crystal colour [shape]	light orange-red needle	light orange needle	light green plate
Crystal size [mm]	$0.2 \times 0.05 \times 0.05$	$0.25 \times 0.06 \times 0.06$	$0.2 \times 0.2 \times 0.05$
a [Å]	7.247(1)	7.174(1)	7.042(1)
b [Å]	7.206(1)	7.208(1)	11.247(1)
c [Å]	11.366(1)	11.332(2)	7.290(1)
β [Å^3]	92.39 (1)	91.83(1)	90.69 (1)
V [Å^3]	593.1(1)	585.7(2)	577.3(1)
Temperature	room-temperature	room-temperature	room-temperature
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Z	2	2	2
Diffractometer	Nonius CAD-4	Phillips PW-1100	STOE AED-II
Scan range	$3^\circ \leq 2\Theta \leq 60^\circ$	$3^\circ \leq 2\Theta \leq 60^\circ$	$3^\circ \leq 2\Theta \leq 60^\circ$
$d_{calc.}$ [g cm^3]	1.792	1.832	1.858
μ [mm^{-1}]	1.31	1.51	1.72
Index range	$-1 \leq h \leq 10$ $-10 \leq k \leq 7$ $-15 \leq l \leq 15$	$0 \leq h \leq 10$ $-10 \leq k \leq 4$ $-15 \leq l \leq 15$	$0 \leq h \leq 9$ $-15 \leq k \leq 11$ $-10 \leq l \leq 10$
Refl. collected	3832	2831	3406
Independent refl.	1727	1706	1690
Refl. $F_o < 4\sigma(F_o)$	1356	1187	1313
R_{int} [%]	0.0159	0.0167	0.0181
Parameters	88	88	88
$R1(F_o < 4\sigma(F_o))$	0.0257	0.0248	0.0239
$wR2$ (all refl.)	0.0710	0.0680	0.0637
GOOF	1.057	1.015	1.018
δF [eÅ^{-3}]	0.39/−0.23	0.32/−0.38	0.39/−0.28

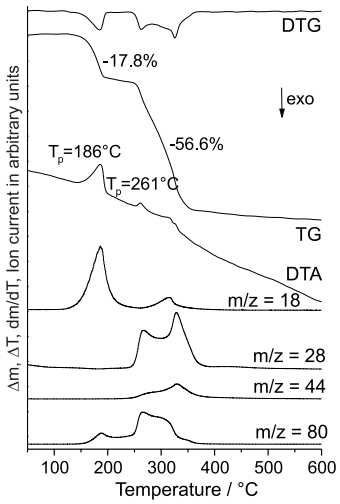


Fig. 6. DTA, TG, DTG and MS trend scan curve for compound **III** (simultaneous measurement; powder; weight: 37.14 mg; conditions as for **I** in Fig. 4).

cept for poly[μ_3-squarato)(μ_2-pyrazine) a compound which we published recently [6]. Interestingly this compound was prepared by hydrothermal reaction of copper(I) oxide with squaric acid and pyrazine. It contains no water molecules. As in the title compounds linear metal pyrazine chains are found but in this structure the chains are connected by the squarate dianions. The copper atoms are only 5-coordinated and the coordination polyhedra are completed by one additional, very long contact to a squarate oxygen atom.

Thermoanalytic investigations

The thermal behaviour of all compounds was investigated using differential thermoanalysis and thermogravimetry coupled with mass spectrometry (Figs. 4 – 6). When the compounds were heated in a thermobalance, a very complex behaviour was found. The decomposition of the iron compound starts at a peak temperature of about 171 °C, whereas 182 and 186 °C were measured for the Co and Ni compound. This shows that the thermal stability of the compound increases from Fe to Ni, which is in agreement with the decrease of the M—N and M—O bond lengths. Four mass steps could be observed up to 700 ° in the DTG curve for the iron compound (**I**) (Fig. 4). The first

Table 4. Atomic coordinates [$\cdot 10^4$] and isotropic displacement parameters [$Å^2 \cdot 10^3$] for catena[tetra-aqua-(μ_2-pyrazine)metal(II)squarates] (**I**) (M = Fe), (**II**) (M = Co) and (**III**) (M = Ni).

	x	*y*	*z*	U_{eq}
Catena[tetra-aqua(μ_2-pyrazine)iron(II)squarate]				
O(1)	2677(2)	66(1)	6147(1)	30(1)
O(2)	1516(2)	1194(2)	3445(1)	32(1)
C(1)	1220(2)	34(2)	5517(1)	23(1)
C(2)	686(2)	539(2)	4297(1)	23(1)
Fe	5000	5000	5000	19(1)
O(3)	4963(1)	6981(2)	3683(1)	31(1)
O(4)	5173(1)	7165(1)	6265(1)	30(1)
N(1)	1927(2)	5087(2)	5010(1)	22(1)
C(3)	1025(2)	4783(2)	5993(1)	26(1)
C(4)	885(2)	4695(2)	5982(1)	27(1)
Catena[tetra-aqua(μ_2-pyrazine)cobalt(II)squarate]				
O(1)	2694(2)	28(2)	6147(1)	29(1)
O(2)	1554(2)	1214(2)	3441(1)	30(1)
C(1)	1224(2)	15(2)	5516(1)	22(1)
C(2)	703(2)	546(2)	4298(1)	23(1)
Co	5000	5000	5000	18(1)
O(3)	4936(2)	7002(2)	3704(1)	30(1)
O(4)	5145(2)	7084(2)	6267(1)	27(1)
N(1)	1950(2)	5056(2)	5000(1)	21(1)
C(3)	1028(2)	4788(2)	5994(1)	24(1)
C(4)	904(2)	4725(2)	5993(1)	25(1)
Catena[tetra-aqua(μ_2-pyrazine)nickel(II)squarate]				
O(1)	7222(2)	3941(1)	10057(2)	29(1)
O(2)	8445(2)	6584(1)	8709(2)	29(1)
C(1)	8741(2)	4523(2)	10026(2)	21(1)
C(2)	9294(2)	5715(1)	9415(2)	21(1)
Ni	5000	5000	5000	16(1)
O(3)	5066(2)	6284(1)	2988(1)	23(1)
O(4)	5083(2)	6308(1)	6978(1)	24(1)
N(1)	8017(2)	4983(1)	4922(2)	19(1)
C(3)	8997(2)	5992(1)	4724(2)	23(1)
C(4)	10967(2)	6009(1)	4802(2)	23(1)

The temperature factor exponent has the form:
$-2\pi^2(h^2 \cdot a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$.

step is somewhat smaller than expected for the removal of the four water molecules ($\Delta m_{theo} - 4H_2O = 25\%$). However, it is obvious from the diagram that in the first two steps the coordinated water molecules as well as parts of the pyrazine ligands are emitted. Therefore, the dehydrated phase could not be obtained pure. In the third step the squarate dianions decompose predominantly and the remaining pyrazine ligands are emitted. No stoichiometric intermediate compound can be expected from the observed mass loss of these steps. If the reactions were stopped at different temperatures the residues were of low crystallinity and the compounds could not be identified. The residue of this reaction consisted of a mixture of elemental iron and a second phase which could not be identified.

On heating the Co compound (**II**) only two mass steps were observed (Fig. 5). The mass loss observed in the first step corresponds roughly to the removal of all water molecules. However, similar to the iron compound in the first step, water and pyrazine were emitted simultaneously. In the second step the remaining ligands were emitted and the squarate dianions decompose. The residue of this reaction consists of a mixture of elemental Co and Co_3O_4.

For the Ni compound (**III**) a behaviour is found that is similar to that of compound **II**. Two mass steps were observed, the first of them corresponding to the emission of water and pyrazine and the second to the emission of the remaining ligands and decomposition of the squarate dianions. The residue consists predominantly of elemental Ni. When the measurements were performed in air, a similar behaviour was found. These investigations have shown a complex thermal behaviour, which differs from the Mn compound with 4,4'-bipyridine where even the coordinated water can be reversibly removed and all intermediate phases can be obtained pure [5].

Experimental Section

Synthesis of catena[tetra-aqua-(μ_2-pyrazine)M(II)squarates] (M = Fe, Co, Ni): 0.5 mmol of MX_2($FeCl_2 \cdot 4\ H_2O$, $CoBr_2$, $NiBr_2$, 0.5 of mmol squaric acid and 0.75 mmol of pyrazine were reacted in 10 ml of water at 150 °C in a teflon-lined steel autoclave under hydrothermal conditions. After 3 d, the reaction mixtures were cooled with 3 °C/h and the residues filtered off and washed with water. The products consisted of an orange-red (Fe), an orange (Co) or a green (Ni) microcrystalline powder. Yields based on the metal halides: 78% (Fe), 82% (Co), 85% (Ni). The homogeneity of all products was checked by X-ray powder diffraction and elemental analysis. Elemental analysis (%): (Fe(**I**)) calcd. C 30.02, H 3.78, N 8.75; found C 30.82, H 4.03, N 8.96. (Co (**II**)) calcd. C 29.74, H 3.74, N 8.67; found C 29.68, H 3.93, N 9.03. (Ni (**III**) calcd. C 29.76, H 3.75, N 8.68; found C 29.93, H 3.81, N 8.76. Single crystals were prepared using the reaction conditions described with stoichiometric amounts of pyrazine (0.5 mmol), 5 ml of water and 6 d reaction time. In this case large single crystals of the title compounds could be isolated, which contained small crystals of the metal squarate dihydrates as a second phase (Fe [10a, b], Co [10a, c], Ni [10d, e]). Obviously, the excess of pyrazine was necessary for the preparation of pure samples, presumably for the neutralisation of the squaric acid used in the synthesis.

Single crystal structure analysis: The structure solution was performed with direct methods using SHELXS-97 [11]. Structure refinement was performed against F^2 using SHELXL-97 [12]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The C—H hydrogen atoms were positioned with idealised geometry ($d_{C—H}$ = 0.93 Å) and were refined with fixed isotropic displacement parameters ($U_{eq}(H) = 1.2 \cdot U_{eq}(C)$) using the riding model. The O—H hydrogen atoms were located from a difference map, the O—H bond lengths were set to idealised values of 0.82 Å and were refined with fixed isotropic displacement parameters ($U_{eq}(H) = 1.5 \cdot U_{eq}(O)$) using the riding model. Details of the structure determination, atomic coordinates and isotropic displacement parameters are given in Table 3 and 4.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 194771 (Fe (**I**)), CCDC 194772 (Co (**II**)) and CCDC 194773 (Ni (**III**)). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK. (fax: +44-(0)1223-336033 or email: deposit@ccdc.ca.ac.uk).

X-ray powder diffraction: Powder diffraction experiments were performed using a STOE STADI P transmission powder diffractometer and a Siemens D-5000 diffractometer both with Cu K_α-radiation ($\lambda = 154.0598$ pm).

Differential thermal analysis, thermogravimetry and mass spectroscopy: DTA-TG measurements were performed in Al_2O_3 crucibles simultaneously using a STA-429 balance from Netzsch. Several measurements under argon and in air atmosphere with heating rates of 1 and 4 °C/min were performed. DTA-TG-MS measurements were performed using the STA-409CD instrument with Skimmer coupling from Netzsch, which is equipped with a quadrupole mass spectrometer QMA 400 (max. 512 amu) from Balzers. The MS measurements were performed in analog and trend scan mode, in Al_2O_3 crucibles under a dynamic helium atmosphere (purity: 4.6) using heating rates of 4 °C/min. All measurements were performed with a flow rate of 75 l/min and were corrected for buoyancy and current effects.

CHN analysis: CHN-O-RAPID combustion analyser from Heraeus.

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