Contributions to the stereochemistry of zirconium oxysalts—part III: syntheses and crystal structures of $M^{2+}\text{Zr}(\text{SO}_4)_3$ with $M = \text{Mg}, \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}$ and Cd , and a note on $(\text{Fe}^{3+,2+}, \text{Zr})_2(\text{SO}_4)_3$ and $\text{Fe}_2(\text{SO}_4)_3$

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Received: 18 June 2019 / Accepted: 13 August 2019 / Published online: 27 September 2019
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Abstract

The novel compounds $M^{2+}\text{Zr}(\text{SO}_4)_3$ with $M = \text{Mg}, \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}$, and Cd as well as $(\text{Fe}^{3+,2+}, \text{Zr})_2(\text{SO}_4)_3$ were synthesized at mild hydrothermal conditions (Teflon-lined stainless steel vessels, 220 °C) from the mixtures of $\text{Zr}_2\text{O}_2(\text{CO}_3)(\text{OH})_2$, the respective $M^{2+}(\text{SO}_4) \cdot n\text{H}_2\text{O}$ hydrated salts, H_2SO_4 and a minor amount of water. Crystals up to several tenths of a mm in size were obtained within a few days and studied at 200 K by single-crystal X-ray diffraction techniques. All these compounds belong to the structure type of monoclinic $\text{Fe}_2(\text{SO}_4)_3$; they are either isotypic in space group $P2_1/n$ (No. 14), $Z = 4$, i.e. $M^{2+}\text{Zr}(\text{SO}_4)_3$ with $M = \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}$, and Cd as well as the mixed valence sulfate $(\text{Fe}^{3+,2+}, \text{Zr})_2(\text{SO}_4)_3$ or in the case of $\text{MgZr}(\text{SO}_4)_3$, closely related but with a larger unit cell, in space group Pc and $Z = 8$. The framework of the monoclinic $\text{Fe}_2(\text{SO}_4)_3$ structure is characterized by two types of isolated Fe^{3+}O_6 octahedra, corner-linked with three types of sulfate groups. In the isotypic $M^{2+}\text{Zr}(\text{SO}_4)_3$ series, the Fe^{3+} atom on the Fe(1) position is substituted by Zr^{4+} while M^{2+} ions occupy the Fe(2) site in the ferric sulfate structure type. Mean cation-oxygen bond lengths ($\text{S}^{[4]}$: 1.462–1.472 Å; $\text{Zr}^{[6]}$: 2.053–2.060 Å as well as $M^{2+}\text{—O}$ distances) are generally rather short, but still within the range reported in literature.

Graphic abstract

Environment of the Zr and Cd atoms in the crystal structure of $\text{CdZr}(\text{SO}_4)_3$ in a projection along the a -axis with $[011]$ towards the right. Displacement ellipsoids represent 90% probability.

Keywords Single-crystal X-ray structure determination · Sulfate · Transition metal compounds · Zirconium oxysalts · Ferric sulfate structure type

Introduction

We recently have initiated a study on the crystal chemistry of novel zirconium oxysalts synthesized under mild hydrothermal conditions. In part I the compounds $\text{Zr}(\text{SeO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{Zr}(\text{SeO}_4)_2 \cdot 4\text{H}_2\text{O}$ have been described [1] while part

II characterized $\text{Zr}(\text{SeO}_3)(\text{SeO}_4)$, $\text{Zr}_4(\text{SeO}_3)(\text{SeO}_4)_7$, and $\text{Zr}_3(\text{SeO}_3)(\text{SeO}_4)_5 \cdot 2\text{H}_2\text{O}$ [2].

Part III now deals with a new group of isotypic or closely related sulfates of the general formula $M^{2+}\text{Zr}(\text{SO}_4)_3$ with $M = \text{Mg}, \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}$, and Cd , as well as $(\text{Fe}^{3+,2+}, \text{Zr})_2(\text{SO}_4)_3$. These compounds will be referred to as **MZr** or e.g. abbreviated as **MgZr** for $\text{MgZr}(\text{SO}_4)_3$ throughout the further text. Evaluation of unit cell parameters for $(\text{Fe}^{3+,2+}, \text{Zr})_2(\text{SO}_4)_3$ and **MZr** ($M = \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}, \text{Cd}$) suggested isotopy with monoclinic $\text{Fe}_2(\text{SO}_4)_3$.

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Anhydrous ferric sulfate is known to occur in two modifications, a rhombohedral one (mikasaite) in space group $R\bar{3}$ [3, 4], and a monoclinic one in space group $P2_1/n$ [5–7], the latter being the type structure of a series of compounds. Further representatives described in space group $P2_1/n$ (No. 14) with $Z=4$ are e.g. $\text{In}_2(\text{SO}_4)_3$ [8], $\text{Sc}_2(\text{SeO}_4)_3$ [9], $\text{Yb}_2(\text{SeO}_4)_3$ [10], $\text{Fe}_2(\text{SeO}_4)_3$ [11], $\text{Al}_2(\text{WO}_4)_3$ [12], $\text{Sb}_2(\text{PO}_4)_3$ [13], and $\text{V}_2(\text{PO}_4)_3$ [14].

For the compound **MgZr** a larger monoclinic unit cell with $Z=8$ was obtained. This phase may be derived from the $\text{AlFe}(\text{MoO}_4)_3$ structure type (space group $P2_1/a$ (No. 14) with $Z=8$ [15]), but with reduced symmetry (space group Pc (No. 7)). Several other molybdates belong to the $\text{AlFe}(\text{MoO}_4)_3$ type, among them $\text{In}_2(\text{MoO}_4)_3$ [16], $\text{Cr}_2(\text{MoO}_4)_3$ [17], $\text{Fe}_2(\text{MoO}_4)_3$ [18], and $\text{Al}_2(\text{MoO}_4)_3$ [19], further also $\text{In}_2(\text{WO}_4)_3$ [20].

The present paper aims to elucidate the new class of **MZr** compounds, especially their structure relationships to $\text{Fe}_2(\text{SO}_4)_3$ and $\text{AlFe}(\text{MoO}_4)_3$. Our report on zirconium

oxysalts will be continued (part IV), describing $\text{Zr}(\text{SeO}_3)_2$ as well as structure refinements of $\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3 \cdot 4\text{H}_2\text{O}$ ($X=\text{S}, \text{Se}$) and a new modification of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$.

Results and discussion

All compounds presented belong or are related to the structure type of monoclinic $\text{Fe}_2(\text{SO}_4)_3$; they are either isotypic in space group $P2_1/n$ (No. 14), $Z=4$, i.e. **MZr** with $M=\text{Mn}, \text{Co}, \text{Ni}, \text{Zn}$, and Cd as well as the mixed valence sulfate ($\text{Fe}^{3+,2+}, \text{Zr}$) $_2(\text{SO}_4)_3$, or, in the case of **MgZr**, closely related but with a larger unit cell and space group Pc , $Z=8$.

Selected individual and mean bond lengths and bond valence strengths for the **MZr** compounds as well as for ($\text{Fe}^{3+,2+}, \text{Zr}$) $_2(\text{SO}_4)_3$ and $\text{Fe}_2(\text{SO}_4)_3$ are listed in Tables 1, 2 (all measurements at 200 K).

Structure details for $\text{Fe}_2(\text{SO}_4)_3$, i.e. bond lengths, polyhedral distortion and the specific arrangement of the

Table 1 Selected interatomic bond distances /Å and bond valence strengths ν /v.u. [22] for **MgZr**

ν			ν			ν			ν		
Zr11–O092	2.044 (5)	0.75	Zr12–O094	2.049 (5)	0.74	Mg13–O122	2.042 (5)	0.39	Mg14–O093	2.035 (6)	0.40
–O073	2.053 (5)	0.73	–O033	2.053 (4)	0.73	–O091	2.043 (6)	0.39	–O061	2.045 (5)	0.39
–O064	2.056 (4)	0.72	–O071	2.058 (5)	0.72	–O034	2.050 (5)	0.38	–O072	2.051 (6)	0.38
–O042	2.060 (4)	0.72	–O044	2.070 (4)	0.70	–O063	2.051 (5)	0.38	–O041	2.053 (5)	0.38
–O031	2.063 (4)	0.71	–O062	2.077 (4)	0.68	–O074	2.056 (6)	0.37	–O124	2.056 (5)	0.37
–O121	2.081 (4)	0.68	–O123	2.084 (5)	0.67	–O043	2.059 (5)	0.37	–O032	2.063 (5)	0.37
<Zr11–O>/$\Sigma\nu$	2.060	4.31	<Zr12–O>/$\Sigma\nu$	2.065	4.25	<Mg13–O>/$\Sigma\nu$	2.050	2.29	<Mg14–O>/$\Sigma\nu$	2.051	2.28
Zr21–O054	2.041 (5)	0.75	Zr22–O011	2.034 (4)	0.77	Mg23–O012	2.042 (5)	0.39	Mg24–O014	2.032 (5)	0.40
–O013	2.042 (4)	0.75	–O101	2.047 (5)	0.74	–O053	2.050 (6)	0.38	–O051	2.035 (6)	0.40
–O103	2.043 (5)	0.75	–O112	2.052 (4)	0.73	–O104	2.059 (6)	0.37	–O102	2.039 (6)	0.39
–O081	2.054 (4)	0.73	–O052	2.056 (5)	0.72	–O113	2.077 (5)	0.35	–O111	2.059 (5)	0.37
–O114	2.058 (4)	0.72	–O083	2.065 (4)	0.71	–O082	2.080 (5)	0.35	–O023	2.070 (5)	0.36
–O024	2.082 (4)	0.68	–O022	2.081 (4)	0.68	–O021	2.083 (5)	0.35	–O084	2.080 (5)	0.35
<Zr21–O>/$\Sigma\nu$	2.053	4.38	<Zr22–O>/$\Sigma\nu$	2.056	4.36	<Mg23–O>/$\Sigma\nu$	2.065	2.20	<Mg24–O>/$\Sigma\nu$	2.053	2.27
S11–O041	1.437 (4)	1.66	S12–O012	1.432 (4)	1.68	S13–O023	1.439 (5)	1.65	S14–O014	1.429 (4)	1.69
–O021	1.441 (5)	1.64	–O032	1.440 (4)	1.64	–O043	1.446 (5)	1.62	–O034	1.449 (4)	1.60
–O031	1.493 (4)	1.42	–O042	1.497 (4)	1.41	–O033	1.478 (4)	1.48	–O024	1.492 (5)	1.43
–O011	1.506 (4)	1.38	–O022	1.501 (4)	1.39	–O013	1.494 (4)	1.42	–O044	1.496 (5)	1.41
<S11–O>/$\Sigma\nu$	1.469	6.10	<S12–O>/$\Sigma\nu$	1.468	6.13	<S13–O>/$\Sigma\nu$	1.464	6.17	<S14–O>/$\Sigma\nu$	1.467	6.14
S21–O051	1.433 (5)	1.68	S22–O082	1.428 (5)	1.70	S23–O053	1.435 (5)	1.67	S24–O084	1.418 (5)	1.75
–O061	1.434 (4)	1.67	–O072	1.441 (5)	1.64	–O063	1.441 (4)	1.64	–O074	1.443 (5)	1.63
–O071	1.497 (5)	1.41	–O062	1.498 (4)	1.41	–O073	1.499 (5)	1.40	–O064	1.489 (4)	1.44
–O081	1.512 (4)	1.35	–O052	1.500 (5)	1.40	–O083	1.513 (4)	1.35	–O054	1.497 (5)	1.41
<S21–O>/$\Sigma\nu$	1.469	6.11	<S22–O>/$\Sigma\nu$	1.467	6.14	<S23–O>/$\Sigma\nu$	1.472	6.06	<S24–O>/$\Sigma\nu$	1.462	6.23
S31–O111	1.436 (4)	1.66	S32–O102	1.431 (5)	1.68	S33–O113	1.442 (4)	1.64	S34–O104	1.429 (5)	1.69
–O091	1.444 (5)	1.63	–O122	1.458 (5)	1.57	–O093	1.445 (5)	1.62	–O124	1.453 (5)	1.59
–O121	1.488 (4)	1.44	–O092	1.490 (5)	1.44	–O123	1.482 (5)	1.47	–O114	1.492 (4)	1.43
–O101	1.501 (5)	1.39	–O112	1.498 (4)	1.41	–O103	1.493 (5)	1.42	–O094	1.495 (5)	1.42
<S31–O>/$\Sigma\nu$	1.467	6.13	<S32–O>/$\Sigma\nu$	1.469	6.09	<S33–O>/$\Sigma\nu$	1.466	6.15	<S34–O>/$\Sigma\nu$	1.467	6.13

Table 2 Selected interatomic bond distances /Å and bond valence strengths ν /v.u. [22] for **MZr** compounds with $M = \text{Mn, Co, Ni, Zn and Cd}$ as well as for $(\text{Fe}^{3+}, \text{Zr})_2(\text{SO}_4)_3$ and $\text{Fe}_2(\text{SO}_4)_3$

Compound	MnZr		CoZr		NiZr		ZnZr	
	ν		ν		ν		ν	
Zr1–O3	2.0742 (8)	0.69	2.0730 (11)	0.69	2.0710 (11)	0.70	2.0689 (7)	0.70
–O4	2.0401 (8)	0.76	2.0365 (10)	0.76	2.0364 (10)	0.76	2.0341 (7)	0.77
–O6	2.0579 (8)	0.72	2.0600 (10)	0.72	2.0623 (10)	0.71	2.0608 (7)	0.72
–O7	2.0644 (8)	0.71	2.0619 (11)	0.71	2.0586 (11)	0.72	2.0597 (7)	0.72
–O9	2.0421 (8)	0.75	2.0455 (11)	0.75	2.0460 (11)	0.74	2.0413 (7)	0.75
–O12	2.0804 (8)	0.68	2.0796 (11)	0.68	2.0777 (11)	0.68	2.0751 (7)	0.69
<Zr1–O>/ $\Sigma\nu$	2.060	4.31	2.059	4.31	2.059	4.32	2.057	4.35
M2–O1	2.1196 (8)	0.41	2.0549 (11)	0.38	2.0277 (11)	0.36	2.0408 (7)	0.40
–O2	2.2165 (8)	0.32	2.1317 (11)	0.30	2.0956 (11)	0.30	2.1369 (7)	0.31
–O5	2.1503 (9)	0.38	2.0858 (11)	0.34	2.0608 (11)	0.33	2.0652 (7)	0.38
–O8	2.1423 (8)	0.39	2.0719 (11)	0.36	2.0483 (11)	0.34	2.0578 (7)	0.38
–O10	2.1523 (9)	0.38	2.0652 (12)	0.36	2.0335 (11)	0.36	2.0663 (8)	0.38
–O11	2.1889 (9)	0.34	2.1215 (11)	0.31	2.0923 (11)	0.31	2.1090 (7)	0.33
<M2–O>/ $\Sigma\nu$	2.162	2.21	2.089	2.06	2.060	2.01	2.079	2.18
S1–O1	1.4385 (8)	1.65	1.4376 (11)	1.65	1.4400 (11)	1.64	1.4386 (7)	1.65
–O2	1.4452 (9)	1.62	1.4473 (11)	1.61	1.4510 (11)	1.60	1.4452 (7)	1.62
–O3	1.4946 (8)	1.42	1.4925 (10)	1.43	1.4877 (10)	1.45	1.4904 (7)	1.43
–O4	1.4999 (8)	1.40	1.4992 (11)	1.40	1.4962 (10)	1.41	1.4970 (7)	1.41
<S1–O>/ $\Sigma\nu$	1.470	6.09	1.469	6.10	1.469	6.10	1.468	6.12
S2–O5	1.4429 (8)	1.63	1.4446 (11)	1.62	1.4497 (11)	1.60	1.4445 (7)	1.62
–O6	1.4937 (8)	1.42	1.4948 (11)	1.42	1.4905 (10)	1.43	1.4902 (7)	1.44
–O7	1.4963 (8)	1.41	1.4956 (11)	1.41	1.4942 (10)	1.42	1.4932 (7)	1.42
–O8	1.4431 (8)	1.63	1.4466 (11)	1.62	1.4451 (11)	1.62	1.4427 (7)	1.63
<S2–O>/ $\Sigma\nu$	1.469	6.10	1.470	6.07	1.470	6.08	1.468	6.12
S3–O9	1.4962 (8)	1.41	1.4923 (11)	1.43	1.4879 (10)	1.44	1.4912 (7)	1.43
–O10	1.4418 (9)	1.64	1.4444 (11)	1.62	1.4472 (12)	1.61	1.4423 (8)	1.63
–O11	1.4403 (9)	1.64	1.4417 (11)	1.64	1.4436 (11)	1.63	1.4399 (7)	1.64
–O12	1.4975 (8)	1.41	1.4966 (11)	1.41	1.4936 (11)	1.42	1.4944 (7)	1.42
<S3–O>/ $\Sigma\nu$	1.469	6.10	1.469	6.10	1.468	6.11	1.467	6.13
Compound	CdZr		$\text{Fe}^{3+}\text{Fe}^{2+}\text{Zr}$		$\text{Fe}^{3+}\text{Fe}^{3+}$			
	ν		ν		ν			
Zr1(M1)–O3			2.0812 (9)	0.68	2.0115 (10)	0.55	1.9955 (7)	0.53
–O4			2.0305 (9)	0.78	1.9676 (10)	0.61	1.9546 (7)	0.59
–O6			2.0514 (8)	0.73	1.9901 (10)	0.58	1.9759 (6)	0.56
–O7			2.0653 (9)	0.71	1.9934 (10)	0.57	1.9782 (7)	0.55
–O9			2.0349 (9)	0.77	1.9715 (10)	0.61	1.9611 (7)	0.58
–O12			2.0788 (9)	0.68	2.0126 (10)	0.54	2.0020 (7)	0.52
<Zr1(M1)–O>/ $\Sigma\nu$			2.057	4.34	1.991	3.47	1.978	3.32
M2–O1			2.2081 (9)	0.44	1.9835 (10)	0.55	1.9543 (6)	0.59
–O2			2.3165 (9)	0.33	2.0696 (10)	0.44	2.0392 (7)	0.47
–O5			2.2463 (10)	0.40	2.0227 (11)	0.50	1.9975 (7)	0.52
–O8			2.2231 (9)	0.42	1.9973 (10)	0.53	1.9709 (7)	0.56
–O10			2.2554 (11)	0.39	2.0063 (11)	0.52	1.9754 (7)	0.56
–O11			2.2863 (10)	0.36	2.0485 (11)	0.46	2.0190 (7)	0.50
<M2–O>/ $\Sigma\nu$			2.256	2.33	2.021	3.00	1.993	3.20

Table 2 (continued)

Compound	CdZr		Fe ³⁺ Fe ²⁺ Zr		Fe ³⁺ Fe ³⁺	
	ν		ν		ν	
S1–O1	1.4356 (9)	1.66	1.4617 (10)	1.55	1.4663 (7)	1.53
–O2	1.4429 (9)	1.63	1.4660 (10)	1.53	1.4694 (7)	1.52
–O3	1.4934 (8)	1.42	1.4680 (10)	1.52	1.4656 (7)	1.53
–O4	1.4996 (8)	1.40	1.4698 (10)	1.52	1.4648 (7)	1.54
<S1–O>/ $\Sigma\nu$	1.468	6.12	1.466	6.12	1.467	6.12
S2–O5	1.4415 (9)	1.64	1.4659 (11)	1.53	1.4696 (7)	1.52
–O6	1.4885 (9)	1.44	1.4668 (10)	1.53	1.4643 (7)	1.54
–O7	1.4916 (9)	1.43	1.4660 (10)	1.53	1.4620 (7)	1.55
–O8	1.4429 (9)	1.63	1.4661 (10)	1.53	1.4711 (7)	1.51
<S2–O>/ $\Sigma\nu$	1.466	6.14	1.466	6.13	1.467	6.12
S3–O9	1.4949 (8)	1.42	1.4678 (10)	1.53	1.4627 (7)	1.55
–O10	1.4420 (10)	1.64	1.4640 (11)	1.54	1.4672 (7)	1.53
–O11	1.4357 (10)	1.66	1.4652 (11)	1.54	1.4702 (7)	1.52
–O12	1.4948 (9)	1.42	1.4691 (10)	1.52	1.4660 (7)	1.53
<S3–O>/ $\Sigma\nu$	1.467	6.13	1.467	6.12	1.467	6.12

Fig. 1 Comparison of the crystal structures of **a** Fe₂(SO₄)₃ and **b** NiZr(SO₄)₃ (as representative of the P2₁/n-type **MZr** compounds) in projections along the crystallographic *b*-axis

framework show no significant differences with the earlier results obtained at room temperature. The cell volume given in [7] is 823.6 Å³, as compared to our data 819.4(1) Å³, measured at 200 K. A study at ~4 K by neutron diffraction techniques [21] reports a cell volume of 788.8 Å³.

The framework of the monoclinic type structure Fe₂(SO₄)₃ (Fig. 1a) is characterized by two sites of isolated Fe³⁺O₆ octahedra, corner-linked with three types of sulfate groups. The mean Fe–O bond lengths of the Fe(1) site are somewhat shorter (1.978 Å) than those of the Fe(2) position (1.993 Å). In the isotypic **MZr** series (Fig. 1b), M²⁺ and Zr⁴⁺ were found to be strictly ordered (within the limits of error), with Zr⁴⁺ occupying the Fe(1) and M²⁺ the Fe(2) position of the ferric sulfate structure type for **MZr** members

with M²⁺ = Mn, Co, Ni, Zn and Cd. The mean [6]Zr–O distance is generally shorter (~2.06 Å), as compared to the respective [6]M–O bond lengths, which range from 2.06 Å (Ni) up to 2.26 Å (Cd).

Partial cation disorder was found in the mixed-valence sulfate (Fe^{3+,2+},Zr)₂(SO₄)₃, which can be expressed as (Fe_{2–2x}³⁺, Fe_x²⁺, Zr_x)(SO₄)₃ with *x* ~ 0.21, assuming full site occupancies. Also in this case, zirconium is preferentially substituting the Fe(1) site with 16% while the Fe(2) position shows 5% Zr. A representative with *x* = 1, i.e. an ordered **FeZr** phase containing only ferrous iron, could not be synthesized up to now.

In monoclinic Fe₂(SO₄)₃, each oxygen atom is bound to one S⁶⁺ and one Fe³⁺ cation. Individual S–O distances

Fig. 2 Comparison of corresponding sections of the crystal structures of **a** $\text{NiZr}(\text{SO}_4)_3$ (as representative of the $P2_1/n$ -type MZr compounds), **b** $\text{MgZr}(\text{SO}_4)_3$, and **c** $\text{AlFe}(\text{MoO}_4)_3$ in projections along the

crystallographic b -axes. Note the different distribution of M^{2+} vs. Zr in the Ni- compared to the Mg-compound, whereas in $\text{AlFe}(\text{MoO}_4)_3$, all octahedra are equally occupied by $\text{Al}_{0.5}\text{Fe}_{0.5}$ [8]

Fig. 3 Unit cell relationships for MgZr (black, Pc), MZr (blue, $P2_1/n$), $\text{AlFe}(\text{MoO}_4)_3$ (green, $P2_1/a$; black, $P2_1/c$), and pseudo-orthorhombic C -centered setting of MgZr (red)

for the three different sulfate groups show minor bond length distortions only. Contrary, in MZr compounds with $M = \text{Mn}, \text{Co}, \text{Ni}, \text{Zn},$ and Cd the S–O distances are clearly separated into two groups: oxygen atoms shared with ZrO_6 octahedra have S–O distances of about 1.49 Å, while those belonging to $M^{2+}\text{O}_6$ polyhedra show considerably shorter S–O bond lengths (~ 1.44 Å). This can be explained by the bond strength contributions of the tetravalent zirconium in comparison to the respective divalent M cation. In the more complex structure type of MgZr discussed later, an even more pronounced splitting of the corresponding S–O distances is evident. Comparable bond length distortions of sulfate groups are commonly observed, e.g. in ZnSO_4 [23] or $\alpha\text{-MgSO}_4$ [24].

The S–O–Fe $^{3+}$ bond angles in $\text{Fe}_2(\text{SO}_4)_3$ vary between 135 and 160°. In general, the respective values for MZr compounds exhibit similar trends even though they are

Table 3 Crystal data and details of the intensity measurements and structure refinements for $M^{2+}\text{Zr}(\text{SO}_4)_3$ compounds with $M = \text{Mg}, \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}$ and Cd as well as $(\text{Fe}^{3+}, \text{Zr})_2(\text{SO}_4)_3$ and $\text{Fe}_2(\text{SO}_4)_3$

Crystal data	MgZr	MnZr	CoZr	NiZr
Space group	Pc	$P2_1/n$	$P2_1/n$	$P2_1/n$
$a/\text{\AA}$	14.902 (2)	8.706 (1)	8.580 (1)	8.537 (2)
$b/\text{\AA}$	8.759 (1)	8.911 (1)	8.824 (1)	8.782 (2)
$c/\text{\AA}$	14.896 (2)	12.219 (2)	12.030 (2)	11.964 (3)
$\beta/^\circ$	108.70 (1)	90.61 (1)	90.32 (1)	90.45 (1)
$V/\text{\AA}^3$	1841.7 (5)	947.9 (2)	910.7 (3)	896.9 (3)
Z	8	4	4	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	2.912	3.043	3.197	3.244
$\mu/\text{MoK}\alpha$ (mm^{-1})	2.01	3.15	3.72	4.03
Crystal size/ μm^3	$100 \times 50 \times 25$	$200 \times 175 \times 150$	$175 \times 100 \times 75$	$300 \times 175 \times 125$
<i>Data and refinement</i>				
Unique data	22677	5847	5617	5531
Data with $F_o > 4\sigma/F_o$	19890	5220	4463	4790
Variables	623	155	155	155
$R1$ [for $F_o > 4\sigma/F_o$] ¹	0.0360	0.0193	0.0248	0.0250
$wR2$ [for all F_o^2] ¹	0.0727	0.0481	0.0583	0.0667
a, b^2	0.028, 0.0	0.017, 0.69	0.022, 0.62	0.031, 0.74
$\Delta\rho_{\text{min/max}}/\text{e}^- \text{\AA}^{-3}$	−1.03/0.90	−0.54/0.70	−0.75/0.88	−0.99/1.30
Crystal data	ZnZr	CdZr	$\text{Fe}^{3+}\text{Fe}^{2+}\text{Zr}$	FeFe
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
$a/\text{\AA}$	8.556 (1)	8.710 (2)	8.341 (1)	8.279 (1)
$b/\text{\AA}$	8.796 (1)	9.002 (2)	8.599 (1)	8.530 (2)
$c/\text{\AA}$	11.997 (2)	12.312 (3)	11.702 (2)	11.604 (2)
$\beta/^\circ$	90.39 (1)	91.09 (1)	90.79 (1)	90.78 (1)
$V/\text{\AA}^3$	902.8 (1)	965.2 (4)	839.2 (1)	819.4 (1)
Z	4	4	4	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	3.272	3.385	3.225	3.242
$\mu/\text{MoK}\alpha$ (mm^{-1})	4.57	3.99	4.17	4.38
Crystal size/ μm^3	$200 \times 200 \times 100$	$250 \times 200 \times 100$	$250 \times 175 \times 150$	$200 \times 200 \times 100$
<i>Data and refinement</i>				
Unique data	5594	5981	5144	5065
Data with $F_o > 4\sigma/F_o$	5313	5739	4245	4837
Variables	155	155	159	155
$R1$ [for $F_o > 4\sigma/F_o$] ¹	0.0164	0.0162	0.0266	0.0186
$wR2$ [for all F_o^2] ¹	0.0403	0.0421	0.0513	0.0481
a, b^2	0.013, 0.59	0.015, 0.90	0.012, 1.22	0.018, 0.56
$\Delta\rho_{\text{min/max}}/\text{e}^- \text{\AA}^{-3}$	−0.52/0.64	−0.73/0.70	−0.71/0.77	−0.82/0.60

¹ $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$ ² $w = 1/[\sigma^2(F_o^2) + (a \times P)^2 + b \times P]$; $P = \{[\max \text{ of } (0 \text{ or } F_o^2)] + 2F_c^2\}/3$

somewhat modified by the individual substitution of ferric iron by M^{2+} and Zr^{4+} , respectively.

The crystal structure of **MgZr** (Fig. 2b) is closely related with that of the other **MZr** members (Fig. 2a), as well as with compounds which belong to the $\text{AlFe}(\text{MoO}_4)_3$ type (Fig. 2c). This is evident from the unit cell transformations, illustrated in Fig. 3.

By the transformation $(\frac{1}{2} \ 0 \ \frac{1}{2} \ 0 \ 1 \ 0 / -\frac{1}{2} \ 0 \ \frac{1}{2})$, the lattice parameters of **MgZr** [$a = 14.902 \text{ \AA}$, $b = 8.759 \text{ \AA}$, $c = 14.896 \text{ \AA}$, $\beta = 108.70^\circ$, $V = 1841.7 \text{ \AA}^3$, $Z = 8$, space group Pc] change to a monoclinic subcell with $a = 8.684 \text{ \AA}$, $b = 8.759 \text{ \AA}$, $c = 12.107 \text{ \AA}$, $\beta = 90.024^\circ$, $V = 920.84 \text{ \AA}^3$, $Z = 4$, resembling the unit cells of the other **MZr** compounds (see Table 3). By transformation via $(-1 \ 0 \ -1/0$

Fig. 4 Behaviour of **a** the lattice parameters (with second order regression lines), and **b** the overall mean $M-O$ bond lengths with increasing $r(M)$ [29] along the MZr series. Note: $Fe^* = Fe_{0.21}^{2+}Fe_{0.74}^{3+}Zr_{0.05}$

1 0/1 0 0), the unit cell of $AlFe(MoO_4)_3$ [$a = 15.509$ Å, $b = 9.132$ Å, $c = 18.021$ Å, $\beta = 125.31^\circ$, $V = 2082.9$ Å³, $Z = 8$, space group $P2_1/a$] turns into [$a = 15.564$ Å,

$b = 9.132$ Å, $c = 15.509$ Å, $\beta = 109.104^\circ$, $V = 2082.9$ Å³, $Z = 8$, space group setting $P2_1/c$] revealing its relationship to $MgZr$. The unit cell parameters of $MgZr$ can also be transformed to a close to orthorhombic C -centred cell [$a = 17.367$ Å, $b = 24.214$ Å, $c = 8.759$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 90.024^\circ$, $V = 3683.3$ Å³, $Z = 16$] by the transformation (1 0 1/− 1 0 1/0 1 0), but no reliable orthorhombic structure model could be refined.

Within the investigated series, the lattice parameters shown in Fig. 4a (including the transformed values for $MgZr$) seem to deviate from a linear relationship with the M^{2+} cationic radii, whereas the mean $M-O$ bond lengths (Fig. 4b) obviously behave according to Vegard's rule. This might be explained by the flexibility of this structure type in terms of angular variation at the bridging polyhedral oxygen corners, thus enabling a partial compensation of the MO_6 polyhedral volume increase.

On the other hand, the $Fe_2(SO_4)_3$ structure type does not seem to be flexible enough to allow the accommodation of Mg at the M site. Investigations of kieselite-, blödite-, and Tutton-type sulfates [25–28] indicate that the absence of $3d$ orbitals in Mg compared to the M^{2+} transition metal cations strongly influences its crystal chemical behaviour, especially concerning a tendency towards comparatively larger $Mg-O-S$ angles at the bridging oxygen atoms. As a consequence, the octahedral Mg/Zr distribution and the structure type changes. In fact, the overall mean $M-O-S$ and $Zr-O-S$ angles in the MZr compounds (without Mg) are 142.5° and 149.7° , respectively, whereas respective angles in the $MgZr$ compound are 150.5° and 154.2° .

Conclusion

A series of novel $M^{2+}Zr(SO_4)_3$ compounds with $M = Mg$, Mn , Co , Ni , Zn , and Cd as well as $(Fe^{3+,2+},Zr)_2(SO_4)_3$ were obtained at mild hydrothermal conditions by the reaction of $Zr_2O_2(CO_3)(OH)_2$ with $M^{2+}(SO_4) \cdot nH_2O$, H_2SO_4 and H_2O . All these compounds are either isotypic or at least related to the structure type of monoclinic $Fe_2(SO_4)_3$ in space group $P2_1/n$, $Z = 4$, where two types of isolated $Fe^{3+}O_6$ octahedra occur, corner-linked with three types of sulfate groups to a framework structure. In the isotypic series $M^{2+}Zr(SO_4)_3$ with $M = Mn$, Co , Ni , Zn , and Cd , Zr^{4+} substitutes Fe^{3+} on the $Fe(1)$ position, while M^{2+} ions occupy the $Fe(2)$ site of the ferric sulfate structure type. In the mixed valence sulfate $(Fe_{2-2x}^{3+}, Fe_x^{2+}, Zr_x)(SO_4)_3$ with $x \sim 0.21$, zirconium is also preferentially incorporated in the $Fe(1)$ position. The structure of $MgZr(SO_4)_3$ is closely related, but with a larger unit cell and space group Pc , $Z = 8$. Compared to the $M^{2+}Zr$ transition metal compounds,

Table 4 Atomic coordinates and displacement parameters with e.s.d.'s in parentheses for $\text{MgZr}(\text{SO}_4)_3$

	x	y	z	$U_{\text{iso/eq}}$
Zr11	0.63278 (5)	0.21541 (7)	0.36884 (5)	0.00609 (8)
Zr12	0.13714 (5)	0.78904 (7)	0.37235 (5)	0.00619 (8)
Mg13	0.5000 (2)	0.7114 (3)	0.5000 (2)	0.0056 (3)
Mg14	−0.0002 (2)	0.2838 (3)	0.5033 (2)	0.0059 (3)
Zr21	0.24139 (5)	0.22037 (7)	0.25102 (5)	0.00722 (12)
Zr22	0.76140 (4)	0.79177 (7)	0.25761 (4)	0.00654 (12)
Mg23	0.87283 (18)	0.7089 (2)	0.6156 (2)	0.0063 (4)
Mg24	0.39218 (19)	0.2785 (2)	0.6217 (2)	0.0057 (4)
S11	0.80006 (12)	0.4939 (2)	0.42160 (11)	0.00754 (18)
S12	0.83882 (11)	1.0026 (2)	0.46037 (11)	0.00722 (17)
S13	0.30572 (12)	0.4966 (2)	0.42537 (11)	0.00762 (16)
S14	0.33894 (11)	0.0034 (2)	0.45330 (11)	0.00776 (19)
S21	0.19776 (10)	0.14453 (17)	0.66378 (11)	0.0076 (2)
S22	0.94796 (10)	0.37474 (17)	0.70896 (10)	0.0069 (2)
S23	0.68741 (10)	0.86249 (17)	0.65887 (11)	0.0071 (2)
S24	0.43498 (10)	0.36473 (17)	0.20050 (10)	0.0074 (2)
S31	0.55236 (10)	0.85235 (17)	0.31778 (11)	0.0074 (2)
S32	0.59462 (10)	0.37309 (17)	0.56747 (10)	0.0074 (2)
S33	0.03298 (10)	0.13390 (17)	0.30552 (11)	0.0075 (2)
S34	0.07414 (10)	0.63668 (17)	0.55280 (10)	0.0076 (2)
O011	0.8035 (3)	0.6219 (4)	0.3552 (3)	0.0137 (7)
O012	0.8261 (3)	0.8796 (4)	0.5184 (3)	0.0141 (7)
O013	0.2657 (3)	0.4106 (5)	0.3346 (3)	0.0168 (8)
O014	0.3715 (3)	0.0879 (5)	0.5397 (3)	0.0167 (8)
O021	0.8002 (3)	0.5537 (5)	0.5118 (3)	0.0130 (8)
O022	0.8325 (3)	0.9440 (5)	0.3638 (3)	0.0118 (7)
O023	0.3104 (3)	0.3985 (5)	0.5042 (3)	0.0175 (9)
O024	0.3270 (3)	0.1044 (5)	0.3696 (3)	0.0143 (8)
O031	0.7076 (2)	0.4158 (4)	0.3761 (3)	0.0121 (7)
O032	0.9271 (3)	1.0825 (5)	0.5005 (3)	0.0133 (7)
O033	0.2362 (3)	0.6195 (5)	0.4199 (3)	0.0149 (8)
O034	0.4017 (3)	−0.1200 (5)	0.4476 (4)	0.0169 (8)
O041	0.8768 (3)	0.3914 (5)	0.4264 (3)	0.0130 (8)
O042	0.7583 (3)	1.1124 (5)	0.4452 (3)	0.0131 (8)
O043	0.3959 (3)	0.5605 (5)	0.4277 (4)	0.0142 (8)
O044	0.2424 (3)	−0.0583 (5)	0.4424 (3)	0.0136 (8)
O051	0.2793 (3)	0.2333 (6)	0.6661 (3)	0.0165 (9)
O052	0.8776 (3)	0.2572 (6)	0.7167 (3)	0.0133 (8)
O053	0.7589 (3)	0.7517 (5)	0.6607 (3)	0.0132 (8)
O054	0.3527 (3)	0.2699 (6)	0.2042 (3)	0.0169 (9)
O061	0.1183 (3)	0.1664 (5)	0.5797 (3)	0.0149 (9)
O062	1.0307 (3)	0.3597 (5)	0.7978 (3)	0.0112 (7)
O063	0.6052 (3)	0.8568 (5)	0.5752 (3)	0.0137 (8)
O064	0.5119 (3)	0.3272 (5)	0.2899 (3)	0.0162 (9)
O071	0.1715 (4)	0.1820 (6)	0.7502 (3)	0.0157 (9)
O072	0.9772 (3)	0.3414 (5)	0.6277 (3)	0.0132 (8)
O073	0.6572 (3)	0.8394 (5)	0.7447 (3)	0.0125 (8)
O074	0.4609 (4)	0.3176 (6)	0.1193 (3)	0.0174 (10)
O081	0.2234 (4)	−0.0231 (5)	0.6727 (4)	0.0133 (8)
O082	0.9091 (3)	0.5240 (5)	0.7079 (3)	0.0120 (8)

Table 4 (continued)

	x	y	z	U _{iso/eq}		
O083	0.7286 (3)	1.0218 (5)	0.6681 (3)	0.0106 (8)		
O084	0.4118 (4)	0.5216 (5)	0.2011 (4)	0.0171 (9)		
O091	0.5467 (3)	0.7391 (5)	0.3862 (3)	0.0139 (8)		
O092	0.6051 (3)	0.2740 (6)	0.4902 (3)	0.0153 (8)		
O093	0.0250 (3)	0.2327 (6)	0.3803 (3)	0.0174 (9)		
O094	0.0937 (3)	0.7529 (5)	0.4879 (3)	0.0125 (8)		
O101	0.6419 (3)	0.8254 (6)	0.2946 (4)	0.0153 (9)		
O102	0.5133 (3)	0.3244 (6)	0.5911 (4)	0.0157 (9)		
O103	0.1229 (3)	0.1703 (6)	0.2861 (4)	0.0168 (10)		
O104	−0.0115 (3)	0.6776 (5)	0.5705 (4)	0.0162 (9)		
O111	0.4727 (3)	0.8544 (5)	0.2322 (3)	0.0143 (9)		
O112	0.6822 (3)	0.3466 (5)	0.6502 (3)	0.0141 (8)		
O113	−0.0465 (3)	0.1437 (5)	0.2195 (3)	0.0142 (8)		
O114	0.1555 (3)	0.6490 (5)	0.6425 (3)	0.0153 (9)		
O121	0.5634 (3)	1.0072 (5)	0.3610 (3)	0.0125 (8)		
O122	0.5924 (3)	0.5327 (5)	0.5390 (4)	0.0124 (8)		
O123	0.0433 (3)	−0.0275 (5)	0.3369 (4)	0.0129 (8)		
O124	0.0731 (3)	0.4852 (5)	0.5126 (3)	0.0137 (9)		
	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Zr11	0.0064 (2)	0.0064 (2)	0.0064 (2)	0.0064 (2)	0.0064 (2)	0.0064 (2)
Zr12	0.0068 (2)	0.0068 (2)	0.0068 (2)	0.0068 (2)	0.0068 (2)	0.0068 (2)
Mg13	0.0052 (7)	0.0052 (7)	0.0052 (7)	0.0052 (7)	0.0052 (7)	0.0052 (7)
Mg14	0.0062 (8)	0.0062 (8)	0.0062 (8)	0.0062 (8)	0.0062 (8)	0.0062 (8)
Zr21	0.0074 (3)	0.0074 (3)	0.0074 (3)	0.0074 (3)	0.0074 (3)	0.0074 (3)
Zr22	0.0067 (3)	0.0067 (3)	0.0067 (3)	0.0067 (3)	0.0067 (3)	0.0067 (3)
Mg23	0.0058 (11)	0.0058 (11)	0.0058 (11)	0.0058 (11)	0.0058 (11)	0.0058 (11)
Mg24	0.0049 (10)	0.0049 (10)	0.0049 (10)	0.0049 (10)	0.0049 (10)	0.0049 (10)
S11	0.0078 (6)	0.0078 (6)	0.0078 (6)	0.0078 (6)	0.0078 (6)	0.0078 (6)
S12	0.0075 (6)	0.0075 (6)	0.0075 (6)	0.0075 (6)	0.0075 (6)	0.0075 (6)
S13	0.0081 (6)	0.0081 (6)	0.0081 (6)	0.0081 (6)	0.0081 (6)	0.0081 (6)
S14	0.0083 (6)	0.0083 (6)	0.0083 (6)	0.0083 (6)	0.0083 (6)	0.0083 (6)
S21	0.0076 (5)	0.0076 (5)	0.0076 (5)	0.0076 (5)	0.0076 (5)	0.0076 (5)
S22	0.0070 (5)	0.0070 (5)	0.0070 (5)	0.0070 (5)	0.0070 (5)	0.0070 (5)
S23	0.0089 (5)	0.0089 (5)	0.0089 (5)	0.0089 (5)	0.0089 (5)	0.0089 (5)
S24	0.0066 (5)	0.0066 (5)	0.0066 (5)	0.0066 (5)	0.0066 (5)	0.0066 (5)
S31	0.0077 (5)	0.0077 (5)	0.0077 (5)	0.0077 (5)	0.0077 (5)	0.0077 (5)
S32	0.0078 (5)	0.0078 (5)	0.0078 (5)	0.0078 (5)	0.0078 (5)	0.0078 (5)
S33	0.0078 (5)	0.0078 (5)	0.0078 (5)	0.0078 (5)	0.0078 (5)	0.0078 (5)
S34	0.0086 (5)	0.0086 (5)	0.0086 (5)	0.0086 (5)	0.0086 (5)	0.0086 (5)
O011	0.0166 (19)	0.0166 (19)	0.0166 (19)	0.0166 (19)	0.0166 (19)	0.0166 (19)
O012	0.0154 (18)	0.0154 (18)	0.0154 (18)	0.0154 (18)	0.0154 (18)	0.0154 (18)
O013	0.0207 (19)	0.0207 (19)	0.0207 (19)	0.0207 (19)	0.0207 (19)	0.0207 (19)
O014	0.023 (2)	0.023 (2)	0.023 (2)	0.023 (2)	0.023 (2)	0.023 (2)
O021	0.0165 (18)	0.0165 (18)	0.0165 (18)	0.0165 (18)	0.0165 (18)	0.0165 (18)
O022	0.0126 (17)	0.0126 (17)	0.0126 (17)	0.0126 (17)	0.0126 (17)	0.0126 (17)
O023	0.0168 (19)	0.0168 (19)	0.0168 (19)	0.0168 (19)	0.0168 (19)	0.0168 (19)
O024	0.0128 (17)	0.0128 (17)	0.0128 (17)	0.0128 (17)	0.0128 (17)	0.0128 (17)
O031	0.0102 (15)	0.0102 (15)	0.0102 (15)	0.0102 (15)	0.0102 (15)	0.0102 (15)
O032	0.0100 (15)	0.0100 (15)	0.0100 (15)	0.0100 (15)	0.0100 (15)	0.0100 (15)

Table 4 (continued)

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
O033	0.0157 (18)	0.0157 (18)	0.0157 (18)	0.0157 (18)	0.0157 (18)	0.0157 (18)
O034	0.0123 (18)	0.0123 (18)	0.0123 (18)	0.0123 (18)	0.0123 (18)	0.0123 (18)
O041	0.0127 (17)	0.0127 (17)	0.0127 (17)	0.0127 (17)	0.0127 (17)	0.0127 (17)
O042	0.0106 (16)	0.0106 (16)	0.0106 (16)	0.0106 (16)	0.0106 (16)	0.0106 (16)
O043	0.0120 (17)	0.0120 (17)	0.0120 (17)	0.0120 (17)	0.0120 (17)	0.0120 (17)
O044	0.0091 (16)	0.0091 (16)	0.0091 (16)	0.0091 (16)	0.0091 (16)	0.0091 (16)
O051	0.0138 (18)	0.0138 (18)	0.0138 (18)	0.0138 (18)	0.0138 (18)	0.0138 (18)
O052	0.0118 (17)	0.0118 (17)	0.0118 (17)	0.0118 (17)	0.0118 (17)	0.0118 (17)
O053	0.0128 (17)	0.0128 (17)	0.0128 (17)	0.0128 (17)	0.0128 (17)	0.0128 (17)
O054	0.0127 (18)	0.0127 (18)	0.0127 (18)	0.0127 (18)	0.0127 (18)	0.0127 (18)
O061	0.0120 (17)	0.0120 (17)	0.0120 (17)	0.0120 (17)	0.0120 (17)	0.0120 (17)
O062	0.0109 (17)	0.0109 (17)	0.0109 (17)	0.0109 (17)	0.0109 (17)	0.0109 (17)
O063	0.0133 (19)	0.0133 (19)	0.0133 (19)	0.0133 (19)	0.0133 (19)	0.0133 (19)
O064	0.0129 (18)	0.0129 (18)	0.0129 (18)	0.0129 (18)	0.0129 (18)	0.0129 (18)
O071	0.025 (2)	0.025 (2)	0.025 (2)	0.025 (2)	0.025 (2)	0.025 (2)
O072	0.0172 (19)	0.0172 (19)	0.0172 (19)	0.0172 (19)	0.0172 (19)	0.0172 (19)
O073	0.0178 (19)	0.0178 (19)	0.0178 (19)	0.0178 (19)	0.0178 (19)	0.0178 (19)
O074	0.018 (2)	0.018 (2)	0.018 (2)	0.018 (2)	0.018 (2)	0.018 (2)
O081	0.022 (2)	0.022 (2)	0.022 (2)	0.022 (2)	0.022 (2)	0.022 (2)
O082	0.0159 (19)	0.0159 (19)	0.0159 (19)	0.0159 (19)	0.0159 (19)	0.0159 (19)
O083	0.0146 (18)	0.0146 (18)	0.0146 (18)	0.0146 (18)	0.0146 (18)	0.0146 (18)
O084	0.024 (2)	0.024 (2)	0.024 (2)	0.024 (2)	0.024 (2)	0.024 (2)
O091	0.021 (2)	0.021 (2)	0.021 (2)	0.021 (2)	0.021 (2)	0.021 (2)
O092	0.024 (2)	0.024 (2)	0.024 (2)	0.024 (2)	0.024 (2)	0.024 (2)
O093	0.028 (2)	0.028 (2)	0.028 (2)	0.028 (2)	0.028 (2)	0.028 (2)
O094	0.0197 (19)	0.0197 (19)	0.0197 (19)	0.0197 (19)	0.0197 (19)	0.0197 (19)
O101	0.0114 (18)	0.0114 (18)	0.0114 (18)	0.0114 (18)	0.0114 (18)	0.0114 (18)
O102	0.0118 (18)	0.0118 (18)	0.0118 (18)	0.0118 (18)	0.0118 (18)	0.0118 (18)
O103	0.0128 (19)	0.0128 (19)	0.0128 (19)	0.0128 (19)	0.0128 (19)	0.0128 (19)
O104	0.0130 (18)	0.0130 (18)	0.0130 (18)	0.0130 (18)	0.0130 (18)	0.0130 (18)
O111	0.0152 (19)	0.0152 (19)	0.0152 (19)	0.0152 (19)	0.0152 (19)	0.0152 (19)
O112	0.016 (2)	0.016 (2)	0.016 (2)	0.016 (2)	0.016 (2)	0.016 (2)
O113	0.0140 (18)	0.0140 (18)	0.0140 (18)	0.0140 (18)	0.0140 (18)	0.0140 (18)
O114	0.0134 (18)	0.0134 (18)	0.0134 (18)	0.0134 (18)	0.0134 (18)	0.0134 (18)
O121	0.017 (2)	0.017 (2)	0.017 (2)	0.017 (2)	0.017 (2)	0.017 (2)
O122	0.0121 (18)	0.0121 (18)	0.0121 (18)	0.0121 (18)	0.0121 (18)	0.0121 (18)
O123	0.0132 (19)	0.0132 (19)	0.0132 (19)	0.0132 (19)	0.0132 (19)	0.0132 (19)
O124	0.0160 (19)	0.0160 (19)	0.0160 (19)	0.0160 (19)	0.0160 (19)	0.0160 (19)

the absence of 3d orbitals in case of the Mg cation seems to play a decisive role for its differing structural behaviour.

Experimental

Synthesis

The investigated zirconium sulfates were obtained by mild hydrothermal synthesis from mixtures of ~0.03 g

Zr₂O₂(CO₃)(OH)₂, 0.08 g of the respective M²⁺(SO₄)·nH₂O hydrated salts, 0.1 g 93% H₂SO₄, and minor contents of water (0.5–1 cm³). These reagents were filled in Teflon-lined steel vessels with a capacity of a few cm³, heated up to 220 °C within several hours, kept at this temperature for a period of one week, and finally cooled down to room temperature within 24 h. Various crystals of up to 0.4 mm had formed, which were separated from the remaining liquid, washed in water and ethanol, dried, and embedded in silicone grease.

Table 5 Atomic coordinates and displacement parameters with e.s.d.'s in parentheses for $M^{2+}\text{Zr}(\text{SO}_4)_3$ compounds with $M = \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}$ and Cd as well as $(\text{Fe}^{3+,2+})_2(\text{SO}_4)_3$ and $\text{Fe}_2(\text{SO}_4)_3$

	x	y	z	$U_{\text{iso/eq}}$
Zr1	0.75106 (2)	0.46527 (2)	0.61508 (2)	0.00527 (3)
Mn2	0.75130 (2)	0.03276 (2)	0.38166 (2)	0.00746 (3)
S1	0.03598 (3)	0.24921 (2)	0.49572 (2)	0.00681 (4)
S2	0.60794 (3)	0.38241 (2)	0.35120 (2)	0.00636 (4)
S3	0.61068 (3)	0.11330 (3)	0.64343 (2)	0.00712 (4)
O1	0.09136 (10)	0.13761 (9)	0.57148 (7)	0.01395 (13)
O2	−0.05509 (10)	0.19131 (10)	0.40561 (7)	0.01450 (14)
O3	0.16844 (9)	0.33583 (8)	0.45128 (7)	0.01147 (12)
O4	−0.05677 (9)	0.36032 (9)	0.55933 (7)	0.01236 (13)
O5	0.70460 (10)	0.47875 (10)	0.28661 (7)	0.01548 (15)
O6	0.44342 (9)	0.42474 (9)	0.33412 (6)	0.01156 (12)
O7	0.64158 (9)	0.41094 (9)	0.46972 (6)	0.01152 (12)
O8	0.62269 (10)	0.22440 (9)	0.32769 (7)	0.01440 (14)
O9	0.64332 (10)	0.01287 (9)	0.73900 (6)	0.01203 (12)
O10	0.70107 (12)	0.06280 (11)	0.55235 (7)	0.01929 (16)
O11	0.44756 (10)	0.11751 (10)	0.62272 (8)	0.01682 (15)
O12	0.66508 (10)	0.26566 (8)	0.67804 (6)	0.01184 (12)
Zr1	0.74913 (2)	0.46483 (2)	0.61621 (2)	0.00550 (3)
Co2	0.75293 (2)	0.03495 (2)	0.38407 (2)	0.00690 (4)
S1	0.03729 (3)	0.24440 (3)	0.49442 (3)	0.00683 (5)
S2	0.61137 (3)	0.37996 (4)	0.34724 (3)	0.00661 (5)
S3	0.60759 (4)	0.11103 (4)	0.64101 (3)	0.00720 (5)
O1	0.09306 (12)	0.13372 (12)	0.57280 (9)	0.01283 (18)
O2	−0.05354 (12)	0.18447 (12)	0.40271 (9)	0.01322 (18)
O3	0.17119 (11)	0.33191 (12)	0.44856 (9)	0.01129 (17)
O4	−0.05800 (12)	0.35690 (12)	0.55809 (9)	0.01202 (18)
O5	0.71190 (13)	0.47580 (13)	0.28178 (9)	0.01392 (19)
O6	0.44481 (11)	0.42200 (12)	0.32708 (9)	0.01104 (17)
O7	0.64127 (12)	0.41259 (12)	0.46748 (8)	0.01138 (17)
O8	0.62696 (13)	0.21930 (12)	0.32608 (9)	0.01325 (18)
O9	0.63781 (12)	0.00777 (12)	0.73698 (9)	0.01169 (17)
O10	0.70844 (14)	0.06629 (14)	0.55104 (10)	0.0172 (2)
O11	0.44354 (12)	0.11102 (13)	0.61436 (10)	0.0150 (2)
O12	0.65527 (12)	0.26560 (11)	0.67948 (9)	0.01156 (17)
Zr1	0.74898 (2)	0.46439 (2)	0.61682 (2)	0.00687 (3)
Ni2	0.75298 (2)	0.03579 (2)	0.38479 (2)	0.00741 (4)
S1	0.03744 (3)	0.24325 (3)	0.49348 (2)	0.00821 (5)
S2	0.61141 (3)	0.37991 (4)	0.34609 (2)	0.00812 (5)
S3	0.60542 (3)	0.11108 (4)	0.64055 (2)	0.00844 (5)
O1	0.09436 (12)	0.13135 (12)	0.57185 (9)	0.01448 (17)
O2	−0.05477 (12)	0.18268 (13)	0.40129 (9)	0.01421 (17)
O3	0.17098 (11)	0.33081 (12)	0.44678 (9)	0.01287 (16)
O4	−0.05798 (12)	0.35495 (12)	0.55836 (9)	0.01362 (16)
O5	0.71199 (12)	0.47695 (14)	0.27988 (9)	0.01574 (19)
O6	0.44412 (11)	0.41993 (12)	0.32493 (8)	0.01196 (16)
O7	0.64144 (12)	0.41395 (13)	0.46673 (8)	0.01311 (16)
O8	0.62886 (13)	0.21869 (12)	0.32541 (9)	0.01492 (17)
O9	0.63601 (12)	0.00559 (12)	0.73556 (8)	0.01333 (16)
O10	0.70745 (14)	0.06910 (15)	0.54956 (9)	0.0185 (2)
O11	0.44054 (12)	0.11034 (13)	0.61281 (10)	0.01669 (19)
O12	0.65159 (12)	0.26598 (12)	0.68044 (8)	0.01300 (16)

Table 5 (continued)

	x	y	z	U _{iso/eq}
Zr1	0.74946 (2)	0.46554 (2)	0.61637 (2)	0.00488 (2)
Zn2	0.75245 (2)	0.03401 (2)	0.38307 (2)	0.00736 (2)
S1	0.03714 (2)	0.24410 (2)	0.49477 (2)	0.00587 (3)
S2	0.61164 (2)	0.37934 (2)	0.34705 (2)	0.00548 (3)
S3	0.60690 (2)	0.11157 (2)	0.64056 (2)	0.00621 (3)
O1	0.09200 (9)	0.13168 (8)	0.57286 (6)	0.01169 (12)
O2	−0.05420 (9)	0.18572 (9)	0.40248 (6)	0.01202 (12)
O3	0.17201 (8)	0.33119 (8)	0.44953 (6)	0.01034 (11)
O4	−0.05710 (8)	0.35728 (8)	0.55887 (6)	0.01129 (11)
O5	0.71193 (9)	0.4762 1 (9)	0.28167 (6)	0.01277 (12)
O6	0.44494 (8)	0.42074 (9)	0.32685 (6)	0.00995 (11)
O7	0.64165 (9)	0.41192 (9)	0.46745 (6)	0.01055 (11)
O8	0.62826 (9)	0.21877 (8)	0.32565 (6)	0.01206 (12)
O9	0.63674 (9)	0.00804 (8)	0.73681 (6)	0.01083 (11)
O10	0.70738 (10)	0.06630 (10)	0.55040 (7)	0.01609 (14)
O11	0.44258 (8)	0.11252 (9)	0.61386 (7)	0.01407 (13)
O12	0.65531 (9)	0.26610 (8)	0.67940 (6)	0.01081 (11)
Zr1	0.75245 (2)	0.46494 (2)	0.61341 (2)	0.00506 (2)
Cd2	0.74910 (2)	0.03295 (2)	0.38097 (2)	0.00831 (2)
S1	0.03759 (3)	0.25415 (3)	0.49593 (2)	0.00693 (4)
S2	0.60575 (3)	0.38432 (3)	0.35335 (2)	0.00657 (4)
S3	0.61639 (3)	0.11580 (3)	0.64623 (2)	0.00758 (4)
O1	0.08499 (10)	0.14250 (10)	0.57278 (8)	0.01523 (15)
O2	−0.04975 (11)	0.19910 (11)	0.40367 (7)	0.01572 (15)
O3	0.17380 (9)	0.33771 (9)	0.45656 (7)	0.01072 (12)
O4	−0.05586 (9)	0.36599 (9)	0.55616 (7)	0.01261 (13)
O5	0.70759 (11)	0.47940 (12)	0.29400 (7)	0.01740 (16)
O6	0.44402 (9)	0.43322 (10)	0.33532 (7)	0.01197 (13)
O7	0.63799 (10)	0.40384 (10)	0.47191 (6)	0.01165 (12)
O8	0.61384 (11)	0.2289 7 (10)	0.32517 (8)	0.01667 (16)
O9	0.63900 (10)	0.01997 (9)	0.74440 (7)	0.01147 (12)
O10	0.70895 (13)	0.05648 (12)	0.5605 8 (8)	0.02111 (18)
O11	0.45530 (10)	0.12643 (11)	0.62054 (9)	0.01885 (17)
O12	0.67614 (10)	0.26551 (9)	0.67822 (7)	0.01203 (13)
Fe/Zr1	0.74936 (2)	0.46533 (2)	0.61653 (2)	0.00616 (4)
Fe2	0.75250 (2)	0.03466 (2)	0.38371 (2)	0.00703 (4)
S1	0.03845 (4)	0.25196 (3)	0.49499 (3)	0.00705 (5)
S2	0.60489 (4)	0.38158 (4)	0.34937 (3)	0.00742 (5)
S3	0.60869 (4)	0.11548 (4)	0.64550 (3)	0.00781 (5)
O1	0.09043 (13)	0.12923 (12)	0.57359 (9)	0.01132 (17)
O2	−0.05862 (13)	0.18945 (12)	0.40024 (9)	0.01183 (17)
O3	0.18018 (12)	0.3297 6 (11)	0.44879 (9)	0.01088 (17)
O4	−0.05449 (13)	0.36460 (12)	0.56145 (9)	0.01207 (17)
O5	0.71252 (14)	0.47908 (14)	0.28205 (9)	0.0157 (2)
O6	0.43756 (12)	0.42003 (12)	0.32146 (8)	0.01036 (16)
O7	0.63536 (13)	0.41051 (12)	0.47121 (8)	0.01243 (17)
O8	0.62720 (13)	0.21602 (12)	0.32421 (9)	0.01367 (19)
O9	0.63301 (13)	0.00369 (12)	0.73893 (9)	0.01211 (17)
O10	0.71050 (14)	0.07084 (14)	0.55001 (9)	0.0158 (2)
O11	0.43883 (13)	0.11448 (13)	0.61191 (10)	0.01469 (19)
O12	0.65567 (13)	0.27137 (11)	0.68495 (8)	0.01207 (17)

Table 5 (continued)

	x	y	z	U _{iso/eq}		
Fe1	0.74887 (2)	0.46579 (2)	0.61657 (2)	0.00400 (3)		
Fe2	0.75308 (2)	0.03465 (2)	0.38435 (2)	0.00432 (3)		
S1	0.03838 (2)	0.25227 (2)	0.49479 (2)	0.00393 (3)		
S2	0.60402 (2)	0.38086 (2)	0.34889 (2)	0.00373 (3)		
S3	0.60824 (2)	0.11554 (2)	0.64566 (2)	0.00405 (3)		
O1	0.08953 (8)	0.12705 (8)	0.57379 (6)	0.00775 (10)		
O2	−0.05997 (8)	0.18931 (8)	0.39913 (6)	0.00804 (10)		
O3	0.18208 (8)	0.32846 (8)	0.44815 (6)	0.00751 (10)		
O4	−0.05409 (8)	0.36536 (8)	0.56224 (6)	0.00863 (10)		
O5	0.71344 (8)	0.47851 (8)	0.28072 (6)	0.00877 (10)		
O6	0.43595 (8)	0.41837 (8)	0.31920 (6)	0.00753 (10)		
O7	0.63466 (8)	0.41050 (8)	0.47134 (6)	0.00826 (10)		
O8	0.62745 (8)	0.21345 (8)	0.32363 (6)	0.00828 (10)		
O9	0.63199 (8)	0.00168 (8)	0.73862 (6)	0.00823 (10)		
O10	0.71249 (9)	0.07296 (9)	0.54933 (6)	0.01030 (11)		
O11	0.43731 (8)	0.11289 (8)	0.60967 (6)	0.00937 (11)		
O12	0.65269 (8)	0.27284 (8)	0.68593 (6)	0.00776 (10)		
	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Zr1	0.00515 (4)	0.00514 (4)	0.00552 (4)	−0.00055 (2)	0.00010 (2)	0.00000 (2)
Mn2	0.00777 (6)	0.00715 (6)	0.00746 (6)	−0.00044 (4)	−0.00006 (4)	0.00116 (4)
S1	0.00633 (8)	0.00524 (7)	0.00888 (8)	0.00071 (6)	0.00104 (6)	0.00033 (6)
S2	0.00633 (8)	0.00737 (8)	0.00537 (8)	−0.00028 (6)	0.00000 (6)	0.00087 (6)
S3	0.00814 (9)	0.00748 (8)	0.00573 (8)	0.00088 (6)	−0.00098 (6)	−0.00138 (6)
O1	0.0142 (3)	0.0112 (3)	0.0165 (3)	0.0066 (2)	0.0015 (3)	0.0047 (2)
O2	0.0143 (3)	0.0160 (3)	0.0131 (3)	−0.0017 (3)	−0.0020 (2)	−0.0056 (3)
O3	0.008 7 (3)	0.0088 (3)	0.0170 (3)	0.0015 (2)	0.0042 (2)	−0.0018 (2)
O4	0.0107 (3)	0.0102 (3)	0.0162 (3)	−0.0017 (2)	0.0040 (2)	0.0039 (2)
O5	0.0155 (3)	0.0213 (4)	0.0096 (3)	0.0027 (3)	0.0027 (3)	−0.0070 (3)
O6	0.0074 (3)	0.0151 (3)	0.0122 (3)	−0.0024 (2)	−0.0009 (2)	0.0046 (2)
O7	0.0138 (3)	0.0151 (3)	0.0056 (2)	−0.0014 (2)	−0.0017 (2)	0.0000 (2)
O8	0.0176 (4)	0.0087 (3)	0.0168 (3)	−0.0034 (2)	−0.0054 (3)	0.0056 (3)
O9	0.0156 (3)	0.0106 (3)	0.0097 (3)	0.0044 (2)	−0.0043 (2)	−0.0022 (2)
O10	0.0263 (4)	0.0210 (4)	0.0107 (3)	−0.0032 (3)	0.0075 (3)	0.0012 (3)
O11	0.0097 (3)	0.0156 (3)	0.0251 (4)	0.0057 (3)	−0.0071 (3)	−0.0030 (3)
O12	0.0158 (3)	0.0082 (3)	0.0115 (3)	0.0008 (2)	−0.0009 (2)	−0.0049 (2)
Zr1	0.00532 (5)	0.00538 (5)	0.00580 (5)	−0.00055 (3)	0.00008 (3)	0.00002 (3)
Co2	0.00687 (7)	0.00675 (7)	0.00707 (8)	−0.00030 (5)	−0.00017 (5)	0.00086 (5)
S1	0.00606 (11)	0.00538 (11)	0.00907 (13)	0.00049 (9)	0.00078 (9)	0.00023 (8)
S2	0.00663 (11)	0.00741 (12)	0.00578 (12)	−0.00010 (9)	−0.00012 (9)	0.00068 (9)
S3	0.00769 (11)	0.00783 (12)	0.00607 (12)	0.00074 (9)	−0.00086 (9)	−0.00142 (9)
O1	0.0135 (4)	0.0107 (4)	0.0144 (5)	0.0050 (3)	0.0008 (3)	0.0044 (3)
O2	0.0132 (4)	0.0150 (4)	0.0114 (4)	−0.0013 (4)	−0.0018 (3)	−0.0051 (3)
O3	0.0084 (4)	0.0098 (4)	0.0157 (5)	0.0017 (3)	0.0033 (3)	−0.0022 (3)
O4	0.0105 (4)	0.0101 (4)	0.0155 (5)	−0.0023 (3)	0.0038 (3)	0.0032 (3)
O5	0.0138 (4)	0.0186 (5)	0.0093 (4)	0.0031 (4)	0.0014 (3)	−0.0060 (4)
O6	0.0072 (4)	0.0143 (4)	0.0116 (4)	−0.0018 (3)	−0.0004 (3)	0.0040 (3)
O7	0.0143 (4)	0.0146 (4)	0.0052 (4)	−0.0014 (3)	−0.0019 (3)	0.0000 (3)
O8	0.0159 (4)	0.0083 (4)	0.0156 (5)	−0.0024 (3)	−0.0044 (4)	0.0043 (3)
O9	0.0149 (4)	0.0105 (4)	0.0096 (4)	0.0044 (3)	−0.0043 (3)	−0.0020 (3)
O10	0.0204 (5)	0.0206 (5)	0.0107 (5)	−0.0041 (4)	0.0059 (4)	0.0003 (4)
O11	0.0089 (4)	0.0147 (5)	0.0213 (5)	0.0053 (4)	−0.0062 (4)	−0.0035 (3)
O12	0.0167 (4)	0.0075 (4)	0.0104 (4)	−0.0003 (3)	0.0001 (3)	−0.0043 (3)

Table 5 (continued)

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Zr1	0.00671 (5)	0.00724 (5)	−0.00062 (3)	−0.00009 (3)	0.00003 (3)	0.00671 (5)
Ni2	0.00728 (7)	0.00791 (6)	−0.00030 (4)	−0.00045 (5)	0.00096 (4)	0.00728 (7)
S1	0.00653 (11)	0.01123 (11)	0.00108 (9)	0.00092 (8)	0.00049 (8)	0.00653 (11)
S2	0.00938 (12)	0.00701 (10)	−0.00040 (8)	−0.00046 (8)	0.00128 (8)	0.00938 (12)
S3	0.00936 (12)	0.00700 (10)	0.00087 (8)	−0.00112 (8)	−0.00212 (8)	0.00936 (12)
O1	0.0123 (4)	0.0167 (4)	0.0058 (3)	0.0001 (3)	0.0044 (3)	0.0123 (4)
O2	0.0156 (4)	0.0131 (4)	−0.0006 (3)	−0.0020 (3)	−0.0052 (3)	0.0156 (4)
O3	0.0100 (4)	0.0185 (4)	0.0018 (3)	0.0039 (3)	−0.0028 (3)	0.0100 (4)
O4	0.0116 (4)	0.0185 (4)	−0.0020 (3)	0.0038 (3)	0.0046 (3)	0.0116 (4)
O5	0.0211 (5)	0.0110 (4)	0.0026 (3)	0.0020 (3)	−0.0063 (4)	0.0211 (5)
O6	0.0151 (4)	0.0127 (4)	−0.0022 (3)	−0.0010 (3)	0.0045 (3)	0.0151 (4)
O7	0.0166 (4)	0.0070 (3)	−0.0019 (3)	−0.0026 (3)	0.0007 (3)	0.0166 (4)
O8	0.0095 (4)	0.0176 (4)	−0.0033 (3)	−0.0061 (3)	0.0053 (3)	0.0095 (4)
O9	0.0115 (4)	0.0120 (4)	0.0049 (3)	−0.0052 (3)	−0.0026 (3)	0.0115 (4)
O10	0.0224 (5)	0.0112 (4)	−0.0041 (4)	0.0054 (3)	−0.0002 (4)	0.0224 (5)
O11	0.0168 (5)	0.0237 (5)	0.0052 (4)	−0.0059 (3)	−0.0032 (3)	0.0168 (5)
O12	0.0093 (4)	0.0118 (4)	−0.0006 (3)	0.0005 (3)	−0.0050 (3)	0.0093 (4)
Zr1	0.00461 (3)	0.00469 (3)	0.00534 (3)	−0.00055 (2)	0.00017 (2)	−0.00001 (2)
Zn2	0.00743 (4)	0.00706 (4)	0.00758 (4)	−0.00016 (3)	−0.00010 (3)	0.00143 (3)
S1	0.00520 (7)	0.00437 (7)	0.00803 (7)	0.00068 (6)	0.00085 (6)	0.00032 (5)
S2	0.00547 (7)	0.00607 (7)	0.00490 (7)	−0.00016 (6)	−0.00006 (5)	0.00065 (6)
S3	0.00664 (7)	0.00670 (8)	0.00528 (7)	0.00069 (6)	−0.00083 (6)	−0.00142 (6)
O1	0.0121 (3)	0.0094 (3)	0.0137 (3)	0.0052 (2)	0.0006 (2)	0.0039 (2)
O2	0.0121 (3)	0.0134 (3)	0.0105 (3)	−0.0010 (2)	−0.0017 (2)	−0.0048 (2)
O3	0.0077 (2)	0.0078 (2)	0.0156 (3)	0.0016 (2)	0.0033 (2)	−0.0021 (2)
O4	0.0093 (3)	0.0091 (3)	0.0155 (3)	−0.0021 (2)	0.0038 (2)	0.0036 (2)
O5	0.0128 (3)	0.0167 (3)	0.0088 (3)	0.0027 (2)	0.0018 (2)	−0.0063 (2)
O6	0.0062 (2)	0.0131 (3)	0.0106 (3)	−0.0021 (2)	−0.0006 (2)	0.0040 (2)
O7	0.0127 (3)	0.0135 (3)	0.0054 (2)	−0.0016 (2)	−0.0019 (2)	−0.0004 (2)
O8	0.0146 (3)	0.0065 (2)	0.0150 (3)	−0.0023 (2)	−0.0048 (2)	0.0040 (2)
O9	0.0137 (3)	0.0094 (3)	0.0093 (3)	0.0041 (2)	−0.0048 (2)	−0.0023 (2)
O10	0.0197 (3)	0.0190 (3)	0.0097 (3)	−0.0034 (3)	0.0056 (2)	0.0002 (3)
O11	0.0080 (3)	0.0135 (3)	0.0206 (3)	0.0051 (3)	−0.0060 (2)	−0.0029 (2)
O12	0.0152 (3)	0.0069 (3)	0.0104 (3)	0.0001 (2)	0.0003 (2)	−0.0045 (2)
Zr1	0.00507 (3)	0.00490 (4)	0.00522 (4)	−0.00053 (2)	0.00012 (2)	0.00011 (2)
Cd2	0.00883 (3)	0.00779 (3)	0.00828 (3)	−0.00033 (2)	−0.00018 (2)	0.00140 (2)
S1	0.00675 (8)	0.00503 (8)	0.00905 (9)	0.00085 (6)	0.00126 (6)	0.00050 (6)
S2	0.00653 (8)	0.00773 (8)	0.00545 (8)	−0.00050 (6)	−0.00001 (6)	0.00120 (6)
S3	0.00902 (8)	0.00770 (8)	0.00597 (8)	0.00110 (6)	−0.00146 (6)	−0.00162 (6)
O1	0.0151 (3)	0.0120 (3)	0.0187 (4)	0.0082 (3)	0.0033 (3)	0.0053 (3)
O2	0.0160 (3)	0.0175 (4)	0.0135 (3)	−0.0022 (3)	−0.0016 (3)	−0.0070 (3)
O3	0.0084 (3)	0.0080 (3)	0.0159 (3)	0.0017 (2)	0.0036 (2)	−0.0012 (2)
O4	0.0107 (3)	0.0099 (3)	0.0174 (3)	−0.0008 (2)	0.0049 (3)	0.0038 (2)
O5	0.0162 (4)	0.0260 (4)	0.0100 (3)	0.0033 (3)	0.0025 (3)	−0.0086 (3)
O6	0.0077 (3)	0.0161 (3)	0.0120 (3)	−0.0029 (3)	−0.001 1(2)	0.0052 (2)
O7	0.0141 (3)	0.0152 (3)	0.0056 (3)	−0.001 1(2)	−0.002 2 (2)	−0.0010 (2)
O8	0.0216 (4)	0.0095 (3)	0.0185 (4)	−0.0050 (3)	−0.0085 (3)	0.0072 (3)
O9	0.0148 (3)	0.0104 (3)	0.0090 (3)	0.0042 (2)	−0.0037 (2)	−0.0021 (2)
O10	0.0302 (5)	0.0224 (4)	0.0110 (3)	−0.0037 (3)	0.0072(3)	0.0023 (4)
O11	0.0110 (3)	0.0175 (4)	0.0277 (5)	0.0087 (3)	−0.0097 (3)	−0.0044 (3)
O12	0.0157 (3)	0.0083 (3)	0.0121 (3)	0.0013 (2)	−0.0012 (2)	−0.0052 (2)

Table 5 (continued)

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Fe/Zr1	0.75106 (2)	0.00600 (7)	0.00608 (6)	0.00640 (7)	−0.00079 (5)	0.00018 (5)
Fe2	0.75130 (2)	0.00667 (8)	0.00657 (7)	0.00786 (7)	−0.00004 (5)	0.00014 (5)
S1	0.03598 (3)	0.00719 (12)	0.00560 (10)	0.00834 (11)	0.00047 (8)	−0.00010 (9)
S2	0.60794 (3)	0.00722 (12)	0.00715 (11)	0.00790 (11)	−0.00110 (9)	0.00025 (9)
S3	0.61068 (3)	0.00732 (13)	0.00945 (11)	0.00665 (11)	−0.00082 (9)	−0.00006 (9)
O1	0.09136 (10)	0.0122 (4)	0.0098 (4)	0.0119 (4)	0.0042 (3)	−0.0006 (3)
O2	−0.05509 (10)	0.0127 (4)	0.0129 (4)	0.0099 (4)	−0.0004 (3)	−0.0026 (3)
O3	0.16844 (9)	0.0091 (4)	0.0082 (4)	0.0154 (4)	0.0020 (3)	0.0043 (3)
O4	−0.05677 (9)	0.0100 (4)	0.0097 (4)	0.0166 (4)	−0.0030 (3)	0.0036 (3)
O5	0.70460 (10)	0.0142 (5)	0.0203 (5)	0.0129 (4)	−0.0015 (4)	0.0038 (3)
O6	0.44342 (9)	0.0077 (4)	0.0132 (4)	0.0102 (4)	−0.0019 (3)	−0.0015 (3)
O7	0.64158 (9)	0.0141 (5)	0.0149 (4)	0.0082 (4)	−0.0031 (3)	−0.0035 (3)
O8	0.62269 (10)	0.0142 (5)	0.0090 (4)	0.0176 (5)	−0.0049 (3)	−0.0055 (4)
O9	0.64332 (10)	0.0141 (5)	0.0110 (4)	0.0111 (4)	0.0034 (3)	−0.0050 (3)
O10	0.70107 (12)	0.0187 (5)	0.0180 (5)	0.0108 (4)	−0.0048 (3)	0.0054 (4)
O11	0.44756 (10)	0.0085 (4)	0.0164 (4)	0.0190 (5)	0.0030 (4)	−0.0047 (3)
O12	0.66508 (10)	0.0185 (5)	0.0082 (4)	0.0096 (4)	−0.0008 (3)	0.0013 (3)
Fe1	0.00377 (5)	0.00379 (5)	0.00442 (5)	−0.00038 (3)	−0.00023 (3)	0.00003 (3)
Fe2	0.00420 (5)	0.00393 (5)	0.00482 (5)	−0.00018 (3)	−0.00035 (3)	0.00059 (3)
S1	0.00337 (6)	0.00312 (7)	0.00530 (7)	0.00036 (5)	0.00005 (5)	0.00017 (5)
S2	0.00363 (7)	0.00382 (7)	0.00373 (7)	0.00012 (5)	−0.00038 (5)	0.00036 (5)
S3	0.00427 (7)	0.00411 (7)	0.00377 (7)	0.00032 (5)	−0.00060 (5)	−0.00084 (5)
O1	0.0076 (2)	0.0066 (2)	0.0090 (2)	0.00360 (18)	−0.00001 (18)	0.00255 (18)
O2	0.0081 (2)	0.0091 (2)	0.0069 (2)	−0.00004 (19)	−0.00203 (18)	−0.00343 (19)
O3	0.0053 (2)	0.0058 (2)	0.0114 (3)	0.00137 (19)	0.00214 (18)	−0.00136 (17)
O4	0.0074 (2)	0.0067 (2)	0.0119 (3)	−0.00205 (19)	0.00247 (19)	0.00258 (18)
O5	0.0090 (2)	0.0111 (3)	0.0063 (2)	0.00232 (19)	0.00058 (18)	−0.00412 (19)
O6	0.0047 (2)	0.0096 (2)	0.0084 (2)	−0.00154 (19)	−0.00135 (17)	0.00323 (18)
O7	0.0102 (2)	0.0108 (3)	0.0036 (2)	−0.00102 (18)	−0.00181 (18)	−0.0006 (2)
O8	0.0099 (2)	0.0041 (2)	0.0107 (3)	−0.00135 (18)	−0.00326 (19)	0.00241 (18)
O9	0.0104 (2)	0.0070 (2)	0.0072 (2)	0.00352 (19)	−0.00369 (19)	−0.00222 (19)
O10	0.0116 (3)	0.0127 (3)	0.0068 (2)	−0.0028 (2)	0.003 (2)	0.0000 (2)
O11	0.0049 (2)	0.0092 (2)	0.0140 (3)	0.0035 (2)	−0.00342 (19)	−0.00191 (18)
O12	0.0115 (2)	0.0046 (2)	0.0071 (2)	−0.00055 (17)	0.00052 (19)	−0.00311 (18)

All atoms occupy general sites

X-ray diffraction data and crystal structure determination

Small fragments of the title compounds with homogeneous extinction under crossed polars were used for single crystal X-ray data collections at 200 K. **MgZr**, **MnZr**, **CoZr**, and **NiZr** were measured on an Enraf–Nonius Kappa CCD diffractometer (sealed tube, equipped with a graphite monochromator + monocapillary optics using Mo-K α radiation and an Oxford Cryosystems Cryostream 600 device). The other compounds were investigated on a Bruker APEXII diffractometer equipped with a CCD area detector, an Incoatec Microfocus Source I μ S (30 W, multilayer mirror, Mo-K α),

and an Oxford Cryosystems Cryostream 800 Plus LT device. Several sets of phi- and omega-scans with 2° scan width were measured at a crystal-to-detector distance of 30 or 35 mm, respectively, up to 80° 2 θ full sphere. The absorption was corrected by the evaluation of multi-scans.

The crystal structure of **MgZr** was solved by direct methods (Shelxs-97 [30]). For all other compounds, the atomic coordinates of monoclinic ferric sulfate given in [7] were used as starting parameters and refined by full-matrix least-squares techniques (Shelxl-97 [30]). The distribution of M²⁺ and Zr⁴⁺ over the two cation sites Fe(1) and Fe(2), as labelled in the type structure of Fe₂(SO₄)₃, was checked by site-occupancy refinement. In (Fe^{3+,2+},Zr)₂(SO₄)₃ minor

amounts of zirconium were refined at the Fe(1) and Fe(2) sites with contents of 16% and 5%, respectively. Selected crystal parameters as well as a summary on the data collections and structure refinements are given in Table 3.

Final atomic positions and important interatomic bond distances are listed in Tables 1, 2, 4, 5. Crystallographic data have also been deposited and may be obtained at <https://icsd.fiz-karlsruhe.de> by referencing the CSD-numbers for $M^{2+}\text{Zr}(\text{SO}_4)_3$ compounds with $M = \text{Mg}$: 1939563, Mn : 1939562, Co : 1939565, Ni : 1939564, Zn : 1939566, and Cd : 1939560, as well as for $(\text{Fe}^{3+,2+},\text{Zr})_2(\text{SO}_4)_3$: 1939567 and $\text{Fe}_2(\text{SO}_4)_3$: 1939561.

Acknowledgements Open access funding provided by University of Vienna. This study was financially supported by grants IS526001 and IP532010 of the University of Vienna. We are grateful to Prof. H. Effenberger for helpful discussions.

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