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$LiFe^{3+}(Se_2O_5)_2$ and Its Structure Relationships to $Me^{2+}(Se_2O_5)$ Compounds

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Summary. $LiFe^{3+}(Se_2O_5)_2$ was obtained by hydrothermal synthesis and the structure was investigated by single crystal X-ray diffraction methods: $a = 5.987(2)$ Å, $b = 6.760(2)$ Å, $c = 10.295(3)$ Å, $V = 416.66$ Å^3; $Z = 2$, space group Pnc2, $R = 0.028$, $R_w = 0.028$ for 2002 independent reflections ($\sin\theta/\lambda \leqslant 0.90$ Å^{-1}). The crystal structure of $LiFe^{3+}(Se_2O_5)_2$ is closely related with that of $Me^{2+}(Se_2O_5)$ compounds (Me = Mn, Co, Zn).

Keywords. $LiFe^{3+}(Se_2O_5)_2$; Crystal structure; Crystal chemistry; Hydrothermal synthesis.

$LiFe^{3+}(Se_2O_5)_2$ und Strukturbeziehungen zu $Me^{2+}(Se_2O_5)$-Verbindungen

Zusammenfassung. Die hydrothermal dargestellte Verbindung $LiFe^{3+}(Se_2O_5)_2$ wurde mittels Einkristallbeugungsmethoden untersucht: $a = 5.987(2)$ Å, $b = 6.760(2)$ Å, $c = 10.295(3)$ Å, $V = 416.66$ Å^3; $Z = 2$, Raumgruppe Pnc2, $R = 0.028$, $R_w = 0.028$ für 2002 unabhängige Reflexe ($\sin\theta/\lambda \leqslant 0.90$ Å^{-1}). Die Kristallstruktur von $LiFe^{3+}(Se_2O_5)_2$ zeigt eine enge Verwandtschaft mit der von $Me^{2+}(Se_2O_5)$-Verbindungen (Me = Mn, Co, Zn).

Introduction

Recently, a study in systems containing iron and selenium led to the structure investigation of $Fe_2(SeO_4)_3$ [1], $Fe(SeO_2OH)(SeO_4)\cdot H_2O$ [2], $Fe_2(SeO_3)_3\cdot H_2O$ [3], $NaFe(SeO_4)_2$ [4], $KFe(SeO_3)_2$ [5], $RbFe(SeO_4)_2$ [6], $LiFe(SeO_3)_2$ [7] and also of $LiFe(Se_2O_5)_2$: lattice parameters of the title compound resemble those of $Me^{2+}(Se_2O_5)$ (Me = Co, Mn, Zn), but systematic absences indicated a different space group. Nevertheless, the structure determination of $LiFe^{3+}(Se_2O_5)_2$ finally established a strong similarity of the atomic arrangements.

Experimental

Synthesis

$LiFe^{3+}(Se_2O_5)_2$ was hydrothermally grown in "Teflon"-lined steel vessels of ~50 cm^3 capacity: Li_2CO_3, SeO_2, $FeC_2O_4\cdot 2H_2O$ and H_2O were heated to 490 K, kept for a month and subsequently cooled to room temperature (12 hours).

Yellow needles (elongated//[100]) of $LiFe^{3+}(Se_2O_5)_2$ were obtained up to 1 mm in length with predominant orthorhombic crystallographic forms {001}, {011} and {111} (including forms related by centrosymmetry). Additionally, also green crystals of $LiFe(SeO_3)_2$ [7] could be isolated.

Structure Determination

All single crystal measurements were done on a four-circle diffractometer at room temperature. The cell parameters were derived from 48 reflections in the range $31° < 2\theta < 38°$. Table 1 gives a summary of crystal data, X-ray data collection and details of the structure refinement. Intensities were corrected for

Table 1. Summary of crystal data, X-ray measurements and structure refinements for $LiFe(Se_2O_5)_2$

a [Å]	5.987(2)
b [Å]	6.760(2)
c [Å]	10.295(3)
V [Å^3]	416.66

Space group	Pnc2
Formula units per cell	2
ρ_{calc} [g cm^{-3}]	4.293
μ(MoKα) [cm^{-1}]	206.46
Transmission factors	0.11–0.22

Equipment: Stoe four-circle diffractometer AED2; graphite monochromatized MoKα-radiation; programs Multan 90 and Shelx 76.

Data collection: 2θ-ω scans; 37 steps/reflection, increased for α_1-α_2 splitting; 0.03° and 0.5–2.0 s/step; 2 × 6 steps for background measurement; 3 standard reflections each 120 min; $2\theta_{max} = 80°$

Crystal dimensions [mm]	0.63 × 0.054 × 0.035
Extinction coefficient $g \times 10^3$	6.2
Measured reflections	3018 $h\,k \pm l$
Unique data set	2514
Data with $F_0 > 3\sigma(F_0)$	2002
Number of variables	75
R	0.028
$R_w (w = 0.339/[\sigma(F_0)]^2$	0.028

Table 2. Structural parameters of $LiFe(Se_2O_5)_2$ with e.s.d.'s in parentheses. U_{ij} are given in pm^2. The anisotropic displacement factor is defined as $\exp[-2\pi^2\Sigma_i\Sigma_j U_{ij} h_i h_j a_i^* a_j^*]$

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Li	0.5	0	0.7776(15)	329(72)	172(54)	155(56)	83(52)	0	0
Fe	0	0	0.8997(1)	102(3)	114(3)	75(3)	11(3)	0	0
Se1	0.72086(9)	0.12914(7)	0.5	115(2)	105(2)	95(2)	−8(1)	0(2)	3(1)
Se2	0.22250(8)	0.36529(7)	0.68961(4)	119(2)	103(2)	84(2)	2(1)	−10(2)	4(1)
O1	0.5884(6)	0.2037(5)	0.6305(4)	181(16)	192(16)	110(14)	10(10)	7(9)	1(8)
O2	0.7237(6)	0.3341(6)	0.4064(4)	181(15)	129(12)	158(15)	−29(8)	−30(10)	40(8)
O3	0.5	0	0.4121(5)	195(20)	205(19)	100(20)	−93(19)	0	0
O4	0.1048(6)	0.3158(5)	0.5459(3)	222(17)	140(13)	72(12)	11(9)	−25(9)	−1(7)
O5	0.1852(7)	0.1509(6)	0.7693(4)	197(17)	123(13)	163(17)	25(9)	37(10)	35(8)
O6	0	0.5	0.7705(5)	196(22)	203(21)	97(20)	60(19)	0	0

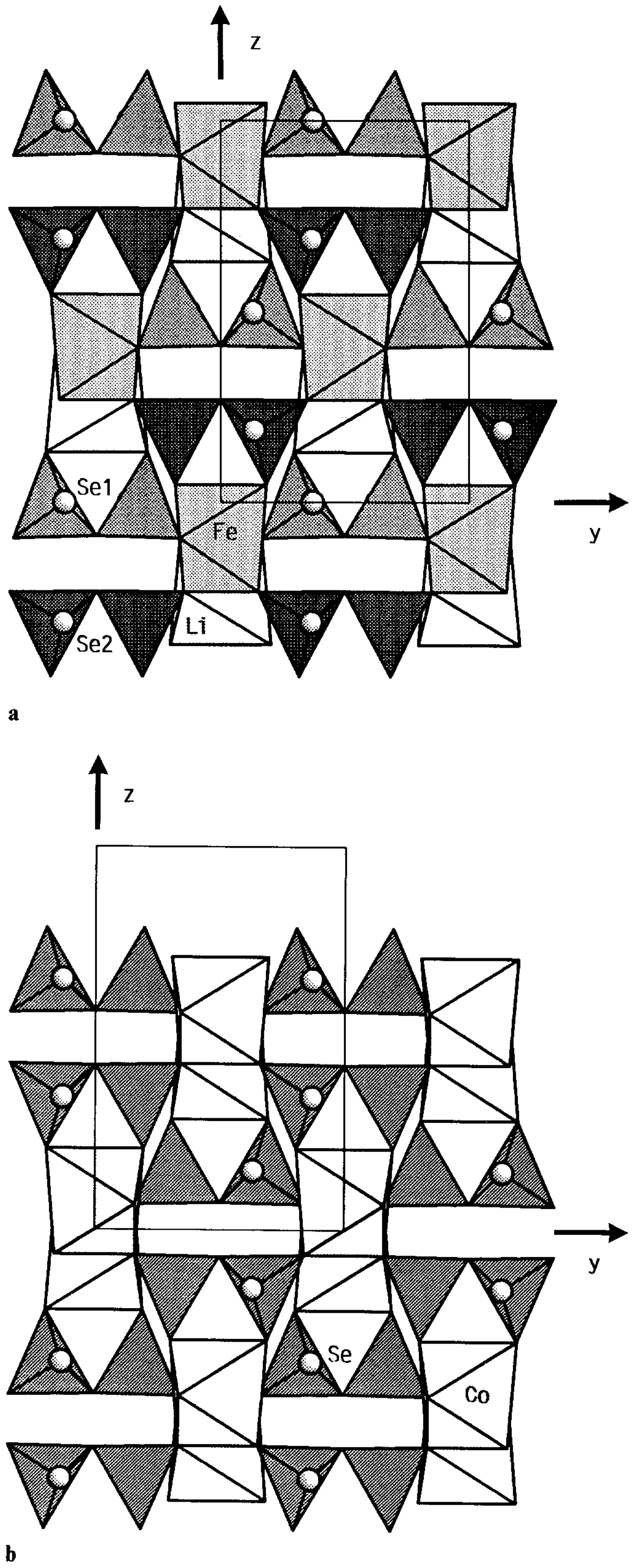

Fig. 1. Comparable sections of the crystal structures of **a**: $LiFe^{3+}(Se_2O_5)_2$ and **b**: $Co(Se_2O_5)$ in a projection parallel to [100]. The selenium atoms of the diselenite groups are indicated as circles

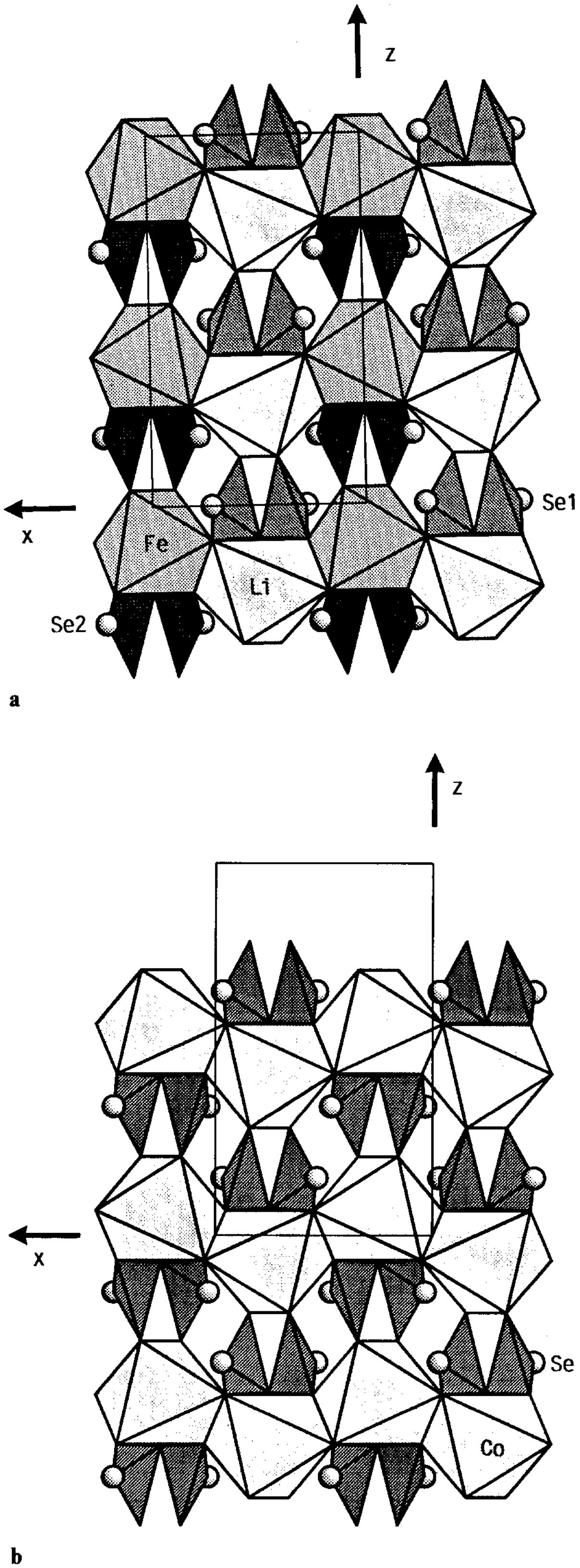

Fig. 2. Crystal structures of **a**: $LiFe^{3+}(Se_2O_5)_2$ and **b**: $Co(Se_2O_5)$ in projection parallel to [010]. Both figures were drawn with the program ATOMS. The data for $Co(Se_2O_5)$ are taken from [10]

Lorentz and polarization effects and an empirical absorption correction was applied. Complex scattering curves for neutral atoms were used [8] and the data were corrected for secondary isotropic extinction. Systematic absences indicated the space groups Pncm or Pnc2 and the structure could be solved by direct methods (Multan 90) in the acentric space group. Final structure parameters obtained by full-matrix least-squares techniques are listed in Table 2. In a difference Fourier synthesis the residual electron densities were $< 1.4\,e\text{Å}^{-3}$. A refinement with atomic parameters $-x$, $-y$, $-z$ resulted in R-values insignificantly larger.

Figures 1a and 2a show the crystal structure of LiFe^{3+}(Se$_2$O$_5$)$_2$ in projections parallel to [100] and [010].

Table 3. Interatomic bond lengths [Å], bond angles [°] (with e.s.d.'s in parentheses) and intrapolyhedral O–O distances (given in brackets) in LiFe(Se$_2$O$_5$)$_2$

			[Å]				[Å]
Li–O1	2x		2.114(11)	Fe–O2	2x		1.999(4)
Li–O5	2x		2.145(4)	Fe–O5	2x		2.018(4)
Li–O2	2x		2.193(10)	Fe–O4	2x		2.051(4)
⟨Li–O⟩			⟨2.151⟩	⟨Fe–O⟩			⟨2.023⟩
		[°]	[Å]			[°]	[Å]
O5–Li–O2	2x	108.5(3)	[3.521(5)]	O2–Fe–O5	2x	101.2(2)	[3.104(6)]
O5–Li–O2	2x	74.4(2)	[2.622(6)]	O2–Fe–O5	2x	81.5(2)	[2.622(6)]
O5–Li–O1	2x	93.5(4)	[3.102(5)]	O2–Fe–O4	2x	93.6(2)	[2.953(5)]
O5–Li–O1	2x	83.2(3)	[2.828(5)]	O2–Fe–O4	2x	83.6(2)	[2.699(5)]
O1–Li–O2	2x	87.0(2)	[2.964(6)]	O5–Fe–O4	2x	90.8(2)	[2.897(5)]
O2–Li–O2	1x	105.6(6)	[3.494(5)]	O5–Fe–O5	1x	96.6(2)	[3.013(6)]
O1–Li–O1	1x	88.5(6)	[2.951(5)]	O4–Fe–O4	1x	85.6(2)	[2.788(5)]
			⟨3.043⟩				⟨2.863⟩
	[Å]				[Å]		
Se1–O1	1x		1.640(4)	Se2–O4	1x		1.672(4)
Se1–O2	1x		1.688(4)	Se2–O5	1x		1.681(4)
Se1–O3	1x		1.824(3)	Se2–O6	1x		1.816(2)
⟨Se1–O⟩			⟨1.717⟩	⟨Se2–O⟩			⟨1.723⟩
		[°]	[Å]			[°]	[Å]
O1–Se1–O2		102.7(2)	[2.600(6)]	O4–Se2–O5		101.7(2)	[2.601(5)]
O1–Se1–O3		101.7(2)	[2.689(6)]	O4–Se2–O6		101.4(2)	[2.700(6)]
O2–Se1–O3		96.7(2)	[2.627(4)]	O5–Se2–O6		96.4(2)	[2.608(4)]
⟨O–Se1–O⟩		⟨100.4⟩	⟨2.639⟩	⟨O–Se2–O⟩		⟨99.8⟩	⟨2.636⟩
Se1–O3–Se1		120.6(3)		Se2–O6–Se2		125.4(3)	

Table 4. Bond distances and angles within the Se_2O_5 groups in $Me^{2+}(Se_2O_5)$ (Me = Mn, Co, Zn) compounds as listed in the literature [9–11]

	$Mn(Se_2O_5)$	$Co(Se_2O_5)$	$Zn(Se_2O_5)$
$Se-O^a$	1.644 Å	1.644 Å	1.658 Å
$Se-O^b$	1.675 Å	1.688 Å	1.693 Å
$Se-O^c$	1.830 Å	1.815 Å	1.827 Å
⟨Se–O⟩	⟨1.716 Å⟩	⟨1.716 Å⟩	⟨1.726 Å⟩
O^a-Se-O^b	102.9°	102.3°	102.1°
O^a-Se-O^c	102.6°	101.4°	102.4°
O^b-Se-O^c	95.8°	96.5°	96.3°
⟨O–Se–O⟩	⟨100.4°⟩	⟨100.1°⟩	⟨100.3°⟩
$Se-O^c-Se$	121.6°	122.9°	121.6°

Results and Discussion

The isostructural compounds $Me^{2+}(Se_2O_5)$ (Me = Mn, Co, Zn) were determined by Koskenlinna et al. (1976) (Mn) [9], Hawthorne et al. (1987) (Co) [10] and Meunier and Bertaud (1974) (Zn) [11]. Harrison et al. (1992) [12] determined the crystal structure of $Co(Se_2O_5)$ again, having obviously overlooked the previous paper. The more it seems astonishing that Harrison et al. cite Hawthorne's paper for other reasons – may be they did not read it carefully.

Figures 1b and 2b show the crystal structure of $Co(Se_2O_5)$, described in space group Pnca as given by Hawthorne et al.: chains of edgesharing CoO_6 octahedra run parallel [100] sharing corners with Se_2O_5 groups. The atomic arrangement in $LiFe^{3+}(Se_2O_5)_2$ can be derived from the $Me^{2+}(Se_2O_5)$ structure type by a substitution of half the divalent cobalt atoms by lithium, the other half by ferric iron – this alternating order leads to the acentric space group Pnc2. Nevertheless, a refinement in Pnca (with a statistical distribution of Li and Fe) gives R values of about 0.08 indicating the close structure relationships.

Distortions of FeO_6 and LiO_6 octahedra correspond to those of the $Me^{2+}O_6$ polyhedra in the $Me^{2+}(Se_2O_5)$ compounds, the short distance O5–O2 belongs to the common edge of these polyhedra. The mean Fe–O bond length (2.023 Å) and the Li–O bond length (2.151 Å) for octahedral coordination comply with common experience (2.011 Å [13] and 2.14 Å [14], respectively (Table 3)).

The diselenite groups $Se1_2O_5$ and $Se2_2O_5$ with the bridging oxygen atoms (on a twofold axis) are in accordance with those in $Me^{2+}(Se_2O_5)$ in respect of bond lengths and bond angle distortions (Table 4).

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