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A chiral mixed carboxylate, $[Nd_4(H_2O)_2(OOC(CH_2)_3COO)_4(C_2O_4)_2]$, exhibiting NLO properties

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Abstract

Reaction of a mixture of neodymium carbonate, HCl, oxamic acid and glutaric acid under hydrothermal conditions gives rise to a new mixed carboxylate of neodymium, $[Nd_4(H_2O)_2(OOC(CH_2)_3COO)_4(C_2O_4)_2]$, **I**. The structure, determined using single crystal X-ray diffraction, comprises a helical column formed by the grafting of the oxalate unit on to helical NdO_9 chains, cross-linked by the glutarate anions. It is noteworthy that the pitch of the helix is equivalent to the length of the oxalate unit. Furthermore, **I** shows about 1.1 times the SHG activity of urea.

Keywords: Hydrothermal; Mixed carboxylate; SHG; Nd

1. Introduction

The variety of inorganic open-framework materials investigated in the last few years has yielded many a fascinating structure [1,2]. Some of them exhibit interesting properties such as porosity and magnetism. Thus, a few open-framework compounds showing ferrimagnetic ordering have been reported [3,4]. Though many new materials with novel frameworks are known today, those with chirality are rather rare. Zeolitic frameworks showing chirality are generated by computational techniques, but their preparation has proved difficult. Amongst the known chiral frameworks, goosecreekite [5], the zinc phosphate, $NaZnPO_4 \cdot H_2O$ [6], the chiral polymorphs of zeolite-β [7–9] and the titanosilicate (ETS-10) [10] are important. Both zeolite-β and ETS-10 occur as intergrown materials with only one of the polymorphs present in the intergrowth being chiral. A chiral tin(II) phosphate has been prepared using an achiral template and both the enantiomers have been characterized [11]. Metal borophosphates [12], zinc and beryllium arsenates [13] and a zinc phosphate [14] with chiral structures and helical channels have also been reported. The motivation to prepare materials with non-centrosymmetric space groups is their potential use in enentioselective separation and in the synthesis of optically pure compounds, besides their second-harmonic generation (SHG) properties.

The use of mixed carboxylic acids for the preparation of new open-framework structures offers immense scope, but has not been investigated systematically. During the course of our synthetic efforts on metal carboxylates with open architectures employing mixed dicarboxates, we have obtained a new oxalate-glutarate of neodymium, $[Nd_4(H_2O)_2(OOC(CH_2)_3COO)_4(C_2O_4)_2]$, **I**, which crystallizes in the polar space group $P2_1$. The structure possesses one-dimensional infinite helical chains of NdO_9 polyhedra and exhibits NLO properties. In this paper we report the synthesis, structure and properties of this novel compound.

2. Experimental

The Nd carboxylate, **I**, was synthesized under mild conditions starting from neodymium carbonate hydrate. In a typical synthesis, about 0.25 g of $Nd_2(CO_3)_3 \cdot 4H_2O$ (0.49 mM) was dissolved in deionized water and methanol mixture (3 + 2 mL). To this 1 mL of concentrated HCl (35%) was added drop-wise until a clear pale pink solution was obtained. The pH of this solution was

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~1.0. The clear solution was treated with 5 mL of 0.1 M NaOH, in order to precipitate the neodymium hydroxide and also to neutralize the excess HCl present in the reaction mixture. The pH of the resulting solution was ~7. To this gelatinous precipitate, 0.1 g of oxamic acid (1.12 mM) and 0.09 g of glutaric acid (0.68 mM) were added under continuous stirring. Finally, 0.06 mL of acetic acid was added to the reaction mixture and the contents were stirred to homogeneity. The pH of the final mixture was ~4. The mixture was heated in a 23 mL PTFE lined autoclave and heated at 150°C for 72 h. The resulting product containing a good quantity of rod-shaped pale pink crystals (yield = 0.32 g, 50% with respect to $Nd_2(CO_3)_3 \cdot 4H_2O$), were washed with a mixture of water and methanol and dried under ambient conditions.

3. Single crystal structure determination

A suitable single crystal of compound **I** was carefully selected under a polarizing microscope and glued to a thin glass fiber. Crystal structure determination by X-ray diffraction was performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å) operating at 40 kV and 40 mA. Pertinent details for the structure determinations are presented in Table 1.

An empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS program [15]. The systematic absences in the reduced data ($0k0$, $k \neq 2n$) indicated space groups $P2_1$ or $P2_1/m$. The direct methods solution in the space group $P2_1$ readily established the heavy atom positions (Nd) and facilitated the identification of most of the other fragments (O, C, N and H) from the difference Fourier maps and the refinements to proceed to $R < 10\%$. All the

Table 1
Crystal data and structure refinement parameters for **I**, $Nd_4(H_2O)_2(OOC(CH_2)_3COO)_4(C_2O_4)_2]$

Empirical formula	$Nd_4O_{26}C_{24}H_{24}$
Formula mass	1305.39
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	9.7280(2)
b (Å)	9.2517(2)
C (Å)	19.7912(5)
β (deg)	97.550(1)
V (Å^3)	1765.78(7)
Z	2
T (K)	293
ρ_{calc} (gcm^{-3})	2.455
μ (mm^{-1})	5.883
Reflections total, observed	7374, 4702
R indexes $[I > 2\sigma(I)]$	$R_1 = 0.0295$[a], w$R_2 = 0.0656$[b]

[a] $R_1 = \sum||F_o| - |F_c||/S|F_o|$.

[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = [\max.(F_o^2, 0) + 2(F_c)^2]/3$, where $a = 0.0399$ and $b = 0.0$ for **I**.

Table 2
Final atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times 10^3$) for **I**, $Nd_4(H_2O)_2(OOC(CH_2)_3COO)_4(C_2O_4)_2]$

Atom	x	y	z	U(eq)[a]
Nd(1)	6303(1)	2337(1)	9156(1)	16(1)
Nd(2)	2611(1)	915(1)	9609(1)	16(1)
Nd(3)	8601(1)	8175(1)	5808(1)	15(1)
Nd(4)	12367(1)	6748(1)	5481(1)	15(1)
O(1)	8552(7)	2918(8)	8863(4)	27(2)
O(2)	2780(7)	−1955(9)	9705(4)	26(2)
O(3)	5520(7)	846(9)	8140(4)	32(2)
O(4)	5588(8)	4155(9)	8268(4)	35(2)
O(5)	4340(7)	3019(8)	9814(4)	23(2)
O(6)	5229(7)	195(8)	9703(4)	23(2)
O(7)	3471(7)	125(9)	10767(3)	22(2)
O(8)	3768(7)	1626(9)	8624(3)	28(2)
O(9)	10726(7)	2137(9)	8987(4)	35(2)
O(10)	1900(9)	−962(10)	8746(4)	45(2)
O(11)	8067(7)	−2088(8)	9680(4)	27(2)
O(12)	563(7)	−107(9)	10056(4)	31(2)
O(13)	12255(8)	3775(10)	5344(4)	31(2)
O(14)	6242(7)	8695(8)	5987(3)	24(2)
O(15)	7154(7)	6019(8)	5594(4)	26(2)
O(16)	9013(9)	10033(9)	6703(4)	36(2)
O(17)	9289(7)	6745(10)	6854(4)	33(2)
O(18)	10609(7)	8810(8)	5177(4)	23(2)
O(19)	9776(7)	5987(8)	5321(3)	21(2)
O(20)	11060(6)	7588(8)	6403(3)	22(2)
O(21)	11604(7)	5954(9)	4305(3)	23(2)
O(22)	14400(7)	5796(9)	5043(4)	32(2)
O(23)	14250(7)	7771(8)	6219(3)	27(2)
O(24)	12646(10)	4786(9)	6328(4)	50(3)
O(25)	6838(7)	3804(8)	5138(4)	27(2)
O(26)	7808(7)	214(8)	9353(4)	29(2)
C(1)	7405(10)	−928(13)	9594(5)	22(3)
C(2)	5961(10)	−913(12)	9849(5)	17(2)
C(3)	7538(10)	4909(13)	5300(5)	20(2)
C(4)	9035(9)	4924(11)	5146(5)	15(2)
C(5)	9574(11)	2388(12)	8622(5)	26(3)
C(6)	9542(14)	2159(18)	7866(7)	57(4)
C(7)	11726(15)	7547(16)	2588(6)	59(4)
C(8)	11617(14)	7553(14)	3343(6)	43(3)
C(9)	11389(10)	6134(12)	3660(5)	22(3)
C(10)	2133(10)	−2071(13)	9104(5)	25(3)
C(11)	1704(13)	−3557(13)	8840(6)	39(3)
C(12)	10748(14)	6441(13)	8166(6)	41(3)
C(13)	11480(10)	6789(14)	7559(5)	28(3)
C(14)	10538(11)	7023(12)	6902(5)	24(3)
C(15)	4257(11)	1134(13)	8104(5)	29(3)
C(16)	3311(12)	928(15)	7457(5)	38(3)
C(17)	13369(16)	2301(14)	7063(7)	62(4)
C(18)	12668(15)	2191(15)	6311(6)	52(4)
C(19)	12528(12)	3678(13)	5988(6)	30(3)
C(20)	15471(10)	8139(11)	6397(5)	21(2)
C(21)	16096(12)	7975(14)	7136(6)	35(3)
C(22)	5695(14)	6666(15)	7484(6)	44(3)
C(23)	6221(14)	6645(16)	8239(6)	44(3)
C(24)	6076(11)	5241(13)	8591(6)	27(3)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected bond distances in **I**, $Nd_4(H_2O)_2(OOC(CH_2)_3COO)_4(C_2O_4)_2]$

Bond	Distance (Å)	Bond	Distance (Å)
Nd(1)–O(1)	2.396(7)	Nd(3)–O(13)#3	2.388(8)
Nd(1)–O(2)#1	2.405(7)	Nd(3)–O(14)	2.416(6)
Nd(1)–O(3)	2.474(7)	Nd(3)–O(15)	2.445(7)
Nd(1)–O(4)	2.466(7)	Nd(3)–O(16)	2.463(8)
Nd(1)–O(5)	2.529(7)	Nd(3)–O(17)	2.474(7)
Nd(1)–O(6)	2.548(7)	Nd(3)–O(18)	2.523(7)
Nd(1)–O(7)#1	2.592(9)	Nd(3)–O(19)	2.573(7)
Nd(1)–O(8)	2.634(7)	Nd(3)–O(20)	2.581(6)
Nd(1)–O(26)	2.451(8)	Nd(3)–O(21)#3	2.587(9)
Nd(2)–O(2)	2.666(9)	Nd(4)–O(13)	2.764(10)
Nd(2)–O(5)	2.569(7)	Nd(4)–O(18)	2.580(7)
Nd(2)–O(6)	2.615(7)	Nd(4)–O(19)	2.596(6)
Nd(2)–O(7)	2.446(7)	Nd(4)–O(20)	2.482(6)
Nd(2)–O(8)	2.465(7)	Nd(4)–O(21)	2.460(7)
Nd(2)–O(9)#2	2.358(7)	Nd(4)–O(22)	2.427(7)
Nd(2)–O(10)	2.470(8)	Nd(4)–O(23)	2.384(7)
Nd(2)–O(11)#1	2.464(7)	Nd(4)–O(24)	2.461(8)
Nd(2)–O(12)	2.471(7)	Nd(4)–O(25)#3	2.443(7)
O(1)–C(5)	1.257(12)	O(14)–C(20)#2	1.283(12)
O(2)–C(10)	1.275(12)	O(15)–C(3)	1.261(13)
O(3)–C(15)	1.250(12)	O(16)–C(9)#3	1.278(13)
O(4)–C(24)	1.251(14)	O(17)–C(14)	1.234(12)
O(5)–C(2)#1	1.248(13)	O(18)–C(4)#3	1.284(12)
O(6)–C(2)	1.261(12)	O(19)–C(4)	1.241(12)
O(7)–C(24)#4	1.294(13)	O(20)–C(14)	1.280(12)
O(8)–C(15)	1.274(12)	O(21)–C(9)	1.278(12)
O(9)–C(5)	1.272(12)	O(23)–C(20)	1.241(11)
O(10)–C(10)	1.250(14)	O(24)–C(19)	1.224(14)
O(11)–C(1)	1.252(13)	O(25)–C(3)	1.246(13)
O(13)–C(19)	1.270(12)	O(26)–C(1)	1.243(13)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1,\ y+\frac{1}{2},\frac{1}{2}\ -z+2$; #2 $x-1,\ y,\ z$; #3 $-x+2,\ y+\frac{1}{2},\ -z+1$; #4 $-x+1,\ y-\frac{1}{2},\ -z+2$.

hydrogen atoms were initially located in the difference Fourier maps and the hydrogen atoms were placed geometrically ideal positions and held in the riding model. A refined Flack parameter [16] of −0.00(2) clearly indicates that the material is homochiral [17]. Final R values of $R_1 = 0.0295$ and $wR_2 = 0.0656$ resulted by this refinement. By setting Flack parameters to 1.00 and repeating the refinement resulted in R values of $R_1 = 0.0347$ and $wR_2 = 0.0811$. Final refinements varying atomic positions for all the atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms have been performed using full-matrix least-squares refinement against $|F^2|$ using the SHELXTL-PLUS suite of programs [18]. Details of the final refinements for **I** are given in Table 1. The final atomic coordinates and selected bond distances are listed in Tables 2 and 3.

4. Results and discussion

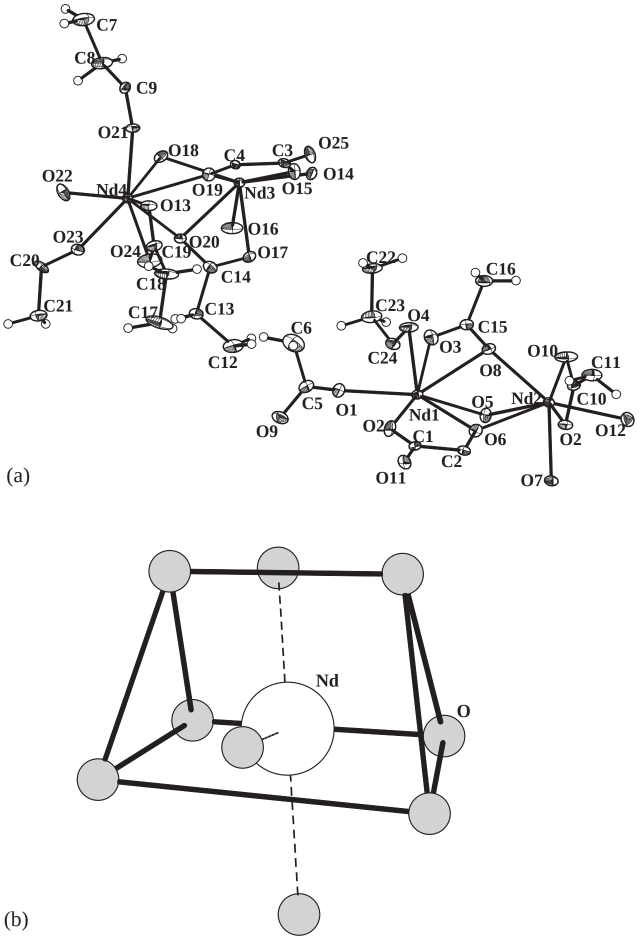

Fig. 1. (a) ORTEP diagram of **I** showing the asymmetric unit. Thermal ellipsoids are given at 50% probability. (b) The coordination environment around the Nd atoms, forming the triply capped trigonal prism.

The asymmetric unit of **I** contains 54 non-hydrogen atoms (Fig. 1a), of which four Nd atoms are crystallographically independent. All the Nd atoms have nine nearest neighbor oxygen atoms with the Nd–O distances in the range 2.358(2)–2.764(2) Å (av. 2.502 Å). The coordination geometry around the Nd atoms is a distorted triply capped trigonal prism (Fig. 1b). Two Nd atoms, Nd(2) and Nd(4), each have one terminal Nd–O bond, formed with a water molecule. The oxygen atoms, O(2), O(5), O(6), O(7) and O(8) are three-coordinated connecting Nd(1) and Nd(2) besides bonding with the carbon atoms. Similarly, the oxygen atoms, O(13), O(18), O(19), O(20) and O(21) link Nd(3) and Nd(4) through three-coordinated bonds. The presence of three-coordination oxygen atoms gives rise to Nd–O–Nd linkages and to infinite one-dimensional chains of NdO_9 polyhedra. The O–Nd–O bond angles are in the 48.1(3)–161.9(3)° range. The C–O and O–C–O bond distances as well as the angles of the oxalate and the glutarate anions are in the ranges expected for this type of connectivity. The oxalate anions, found in **I**, could have resulted from the hydrolysis of oxamic acid used in

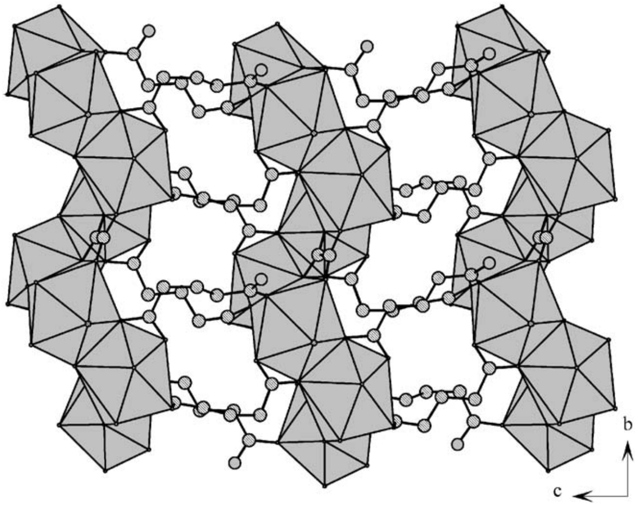

Fig. 2. Structure of **I** in the *bc* plane showing the entire connectivity. Hydrogen atoms of the glutarate anions have been omitted for clarity.

the synthesis mixture, under solvothermal conditions. Transformations of reactants under hydro/solvothermal conditions have been known before [19].

The structure of **I** contains four independent Nd atoms, each of which is bound to nine oxygens from the oxalate and glutarate anions (Fig. 2). The complex three-dimensional structure of **I** can be understood by considering the smaller fragments of the structure. Thus, the connectivity between the Nd atoms, through the three-coordinated oxygen atoms, gives rise to one-dimensional helical chains of [NdO_9] as shown in Fig. 3a. The NdO_9 helical chains are at a 2-fold screw axis with the oxalate units grafting on to the chain to form a helical column. The pitch of the helix is equivalent to the length of the oxalate anion as demonstrated in Fig. 3a. The one-dimensional helical columns are connected through the glutarate units giving rise to the three-dimensional structure (Fig. 3b). A view down the helical columns in this unique arrangement is shown in Fig. 4.

Since the compound crystallizes in the space group ($P2_1$) and is homochiral [17], we have investigated its non-linear optical characteristics. The measurements were made on powdered sample (~200 μm thick) by using the method of Kurtz and Perry [20], and employing urea (150–180 μm) as the reference standard material [21]. Employing a Nd-YAG laser emitting at 1.06 μm, the frequency-doubled green beam at 532 nm was observed through the band-pass filters. The relative magnitude of the SHG for compound **I** was found to be about 1.1, compared to the values for urea. The commonly used optical material, KDP, shows a SHG activity of ~50% relative to urea. In this respect, the present material, **I**, appears to have a superior frequency doubling property. The SHG would be expected to be even higher if measured on single crystals.

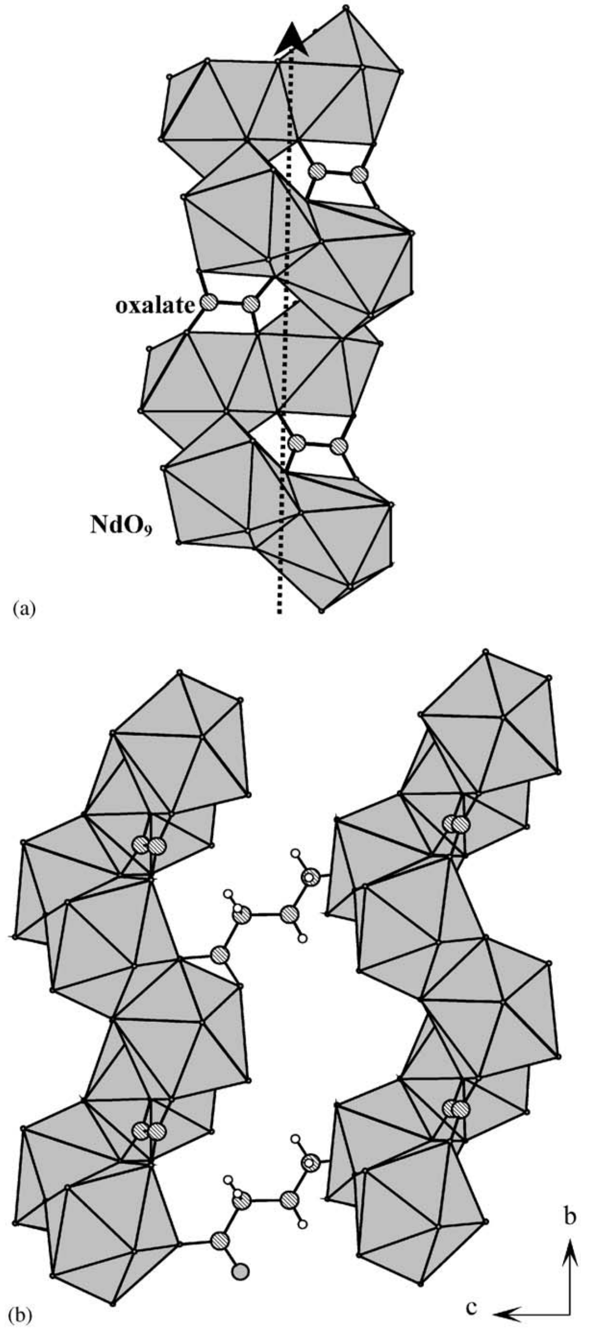

Fig. 3. (a) Structure of **I** showing the helical arrangement of NdO_9 polyhedra. Note that the pitch of the helix is same as the length of the oxalate anion. The arrow shows the direction of the 2-fold screw axis. (b) The figure shows the connectivity between the two helical columns. Only few of the connecting glutarate anions are shown, for purpose of clarity. Hydrogen atoms have been omitted.

In conclusion, the synthesis and structure of a new mixed carboxylate of neodymium, [$Nd_4(H_2O)_2(OOC(CH_2)_3COO)_4(C_2O_4)_2$], **I**, has been accomplished. The presence of helical NdO_9 chains and the associated SHG activity makes this a unique metal carboxylate. Since the use of mixed carboxylates is in its infancy, it is likely that

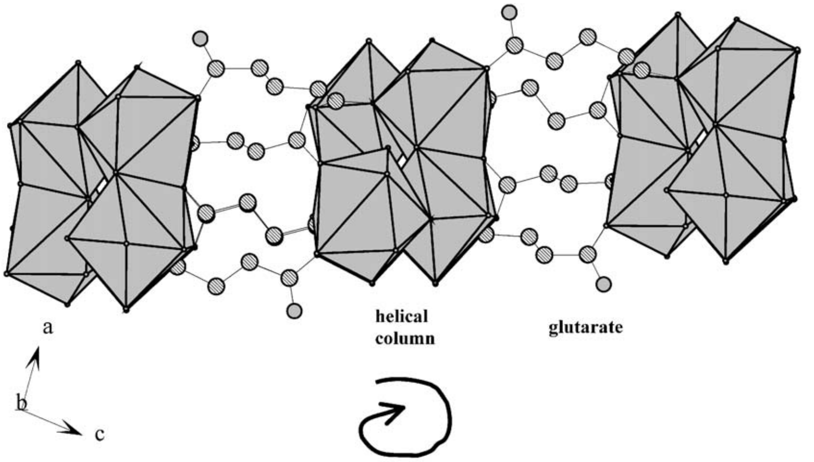

Fig. 4. Structure of **I** in the *ac* plane showing the view along the helical column. The connecting oxalate units and hydrogen atoms are not shown. Arrow indicates the direction of helices.

many new materials will be prepared by employing suitable experimental conditions.

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