The Crystal Structure of Triclinic Nickelous Ethyl Xanthate, $Ni(S_2COC_2H_5)_2$

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Abstract

Acicular nickelous ethyl xanthate, $Ni(EtX)_2$, crystals often grow from the acetone solution with usual platy square crystals. The crystal structure of orthorhombic form corresponding to the platy square crystal has been determined by Franzini (1963). The acicular one found in the present work is determined to be triclinic by the x-ray method. The crystal structure has been solved by the Patterson method and refined using the 4-circle x-ray diffraction data. Space group: $P\bar{1}$, $a=8.835$, $b=10.299$, $c=8.143$ Å, $\alpha=91.81°$, $\beta=122.33°$, $\gamma=70.52°$; $Z=2$. A residual factor is $R=5.3\%$ for observed 2048 structure factors.

Four strong Ni–S bonds in the molecule and two weak bonds between neighbouring molecules make an octahedral coordination of NiS_6. These octahedra make chain structure sharing edges parallel to the c-axis, which is concordant with elongation habit of this acicular crystal. Crystallographically different two $Ni(EtX)_2$ molecules in the unit cell of the triclinic form and one kind of molecule in the orthorhombic form are very similar with each other. Hydrogen atom positions of ethyl group were determined on the map of difference Fourier synthesis.

Introduction

Crystal structures of metal xanthates (dithiocarbonate) have been analyzed by some workers from the view of collector action of xanthic radicals on sulfide minerals[1]. Those results have been utilized to estimate molecular structure or configurations of the arrangement of xanthic radicals on mineral surfaces, because we have no reliable method to determine the structure of surface radicals.

Stable xanthate salt of Ni^{2+} crystallizes easily by standing acetone solution in beaker for an appropriate duration of evaporating acetone. Two kinds of crystal were obtained as shown in Fig. 1. The one is platy black crystal with square habit which is identified to be the same cell dimensions with the orthorhombic form. Franzini (1963) determined the crystal structure with Buerger's precession and Weissenberg photograph methods. The space group: $Pbca$ with $a=7.57$, $b=7.23$, $c=20.92$ Å[2]. The square coordination of four sulfur atoms around Ni makes an octahedron in cooperation with adjacent two sulfur atoms belonging to neighbouring molecules. These octahedra share corners with each other and construct plane network in the (001) plane, as seen in Fig. 2.

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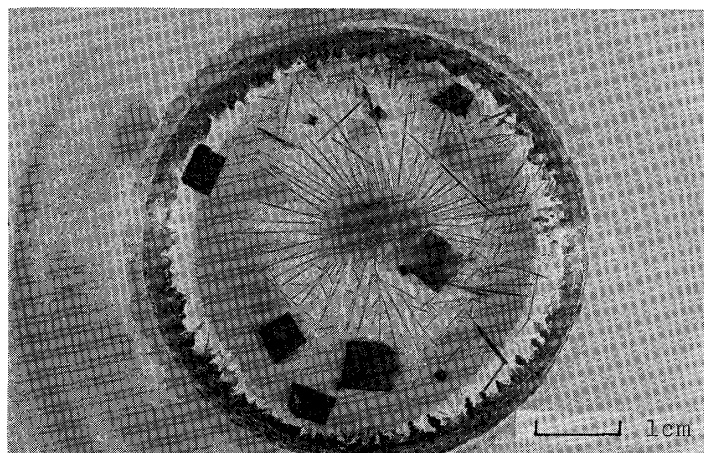** Chugoku Suiko Co.

Fig. 1   Two kinds of Ni(EtX)$_2$ crystal. Square and acicular crystals correspond to orthorhombic and triclinic forms, respectively. Evaporation rate of acetone is 2 g/h at 30°C.
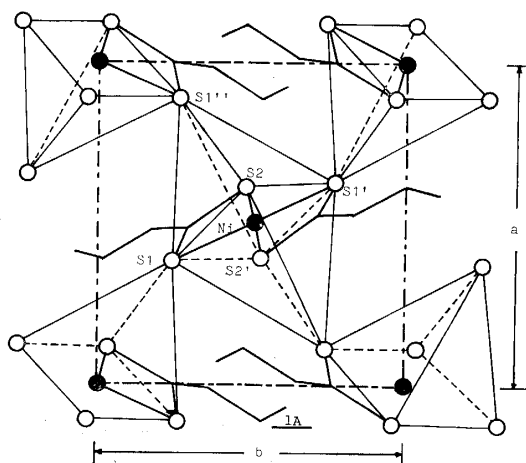

Fig. 2   Crystal structure of orthorhombic Ni(EtX)$_2$ after Franzini (1963). Solid and dashed lines represent the NiS$_6$ octahedra.

However, the acicular crystal picked out of the solution showed triclinic symmetry by the x-ray precession photograph method different from that of the orthorhombic one. The unit cell dimensions obtained from the 4-circle x-ray diffractometer are $a = 8.835$, $b = 10.299$, $c = 8.143$ Å, $\alpha = 91.81°$, $\beta = 122.33°$, $\gamma = 70.52°$ as standard setting ($b > a > c$, α, $\beta > 90°$).

Our aim is mainly to clarify the nature of the interatomic bonding between xanthate molecules by comparing these two structures and contribute to understand the collector action of xanthic radicals in mineral flotation.

Experimental

An acicular crystal cutted to suitable size for the x-ray work is 0.05 × 0.09 × 0.28 mm,

elongating to the c-axis. No systematic extinction rule was found on the x-ray preces-sion photographs on the triclinic unit cell. Diffraction intensities were collected in a $\omega - 2\theta$ mode up to $2\theta = 60°$ using a 4-circle diffractometer (Philips PW 1100) with graphite monochromatized Mo Kα radiation ($=0.71069$ Å). Three standard reflec-tions were measured after every 180 minutes and weak reflections followed by $I_{top} - 2\sqrt{I_{top}} < I_{back}$ were skipped for the data collection. Number of independent reflections observed and used in this analysis is 2048. Correction for Lorentz-polarization was adopted.

Specific gravity of the orthorhombic and the triclinic crystals measured by the picnometer method were 1.71 and 1.73 g/cm³, respectively.

The computations were carried out by FACOM M-200 using UNICS-II library programs[3] of Computer Center of the Kyushu University written by Sakurai $et\ al.$ (1974)[4] and revised by Kawano (1980)[5].

Structure determination and refinement

Three dimensional Patterson map showed the strongest peak at (0, 0, 1/2) and secondary strong peaks near to the origin and (0, 0, 1/2). The strongest peak at (0, 0, 1/2) was assigned Ni–Ni interatomic vector and the secondary peaks were cor-related to those of Ni–S. The specific gravity and the cell volume indicate that the triclinic form contains two Ni(EtX)₂ molecules in a unit cell. The IR spectra of the orthorhombic and triclinic forms give very similar patterns and indicate that the molecules in these crystals are fundamentally isostructural. Thus, Ni atoms were located at (0, 0, 0) and (0, 0, 1/2) and the sulfur coordinates around Ni atoms were easily determined by the Patterson map. By the successive Fourier syntheses, oxygen and carbon-atom coordinates of xanthic radicals were found. Using these atomic parameters and nonionized scattering factors of Ni, S, O, and C[3], the residual factor;

$$R = \Sigma ||F_O| - |F_c|| / \Sigma |F_O|$$

was 13%. After several cycles of the full-matrix least squares refinement using atomic scattering factors[3] of Ni²⁺, S²⁻, O⁻ and C with anisotropic temperature factors, the R value dropped to 5.8% excluding hydrogen atoms of the ethyl group. Schematic view of Ni(EtX)₂ molecules in triclinic form is shown in Fig. 3. c^* projection of molecules in a unit cell is illustrated in Fig. 4. Difference Fourier synthesis on the final stage at $R = 5.3\%$ revealed hydrogen atoms and electron density around Ni atoms. Final atomic coordinates and anisotropic temperature factors are listed in Table 1. Interatomic distances and bond angles are shown in Table 2 with those of orthorhombic form by Franzini for comparison.
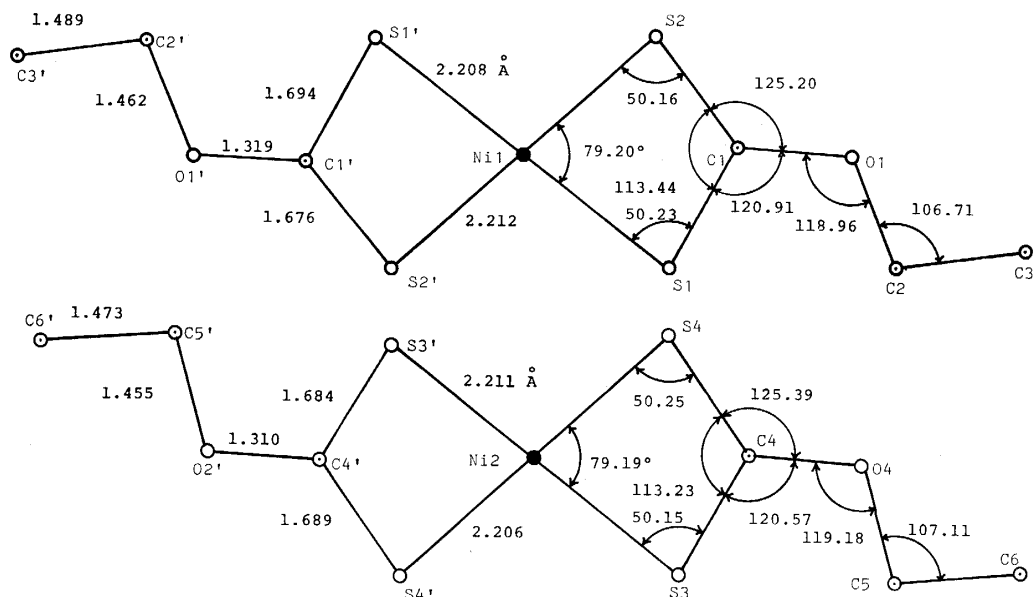
Fig. 3   Molecular structure of Ni(EtX)₂ in the triclinic form.   Crystallographically different two molecules are very similar in the structure.
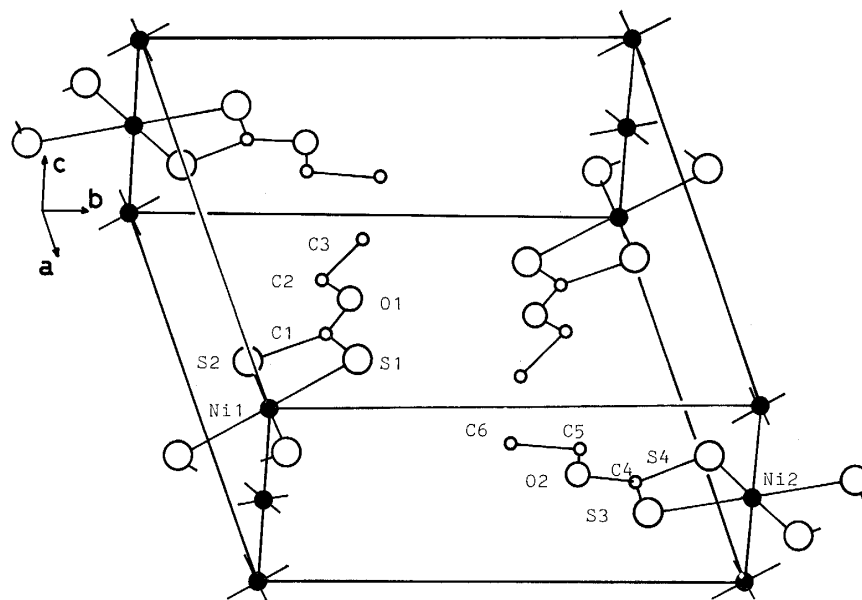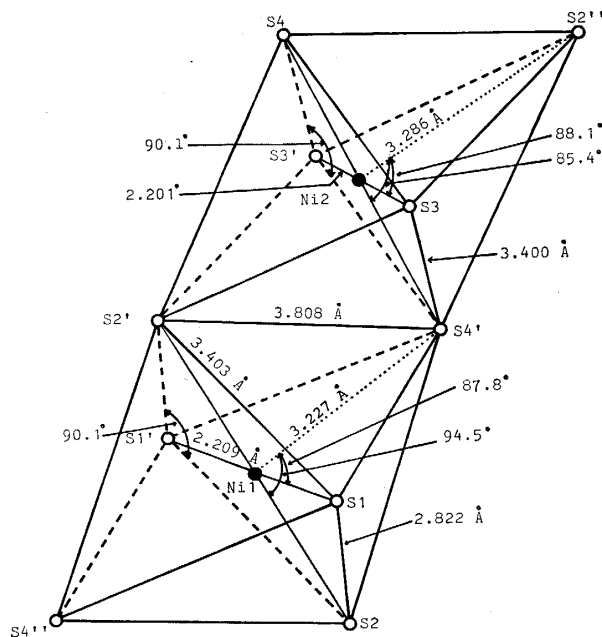

Fig. 4   Molecular arrangement in the triclinic unit cell.

Fig. 5 NiS_6 octahedra and their edge sharing in the triclinic structure.

Table 1.   Atomic coordinates and temperature factors of triclinic $Ni(EtX)_2$.

Atom	X	Y	Z	B11	B22	B33	−B12	−B13	B23
Ni1	0.0	0.0	0.0	0.0186	0.0074	0.0257	0.0035	0.0120	0.0008
Ni2	0.0	0.0	0.5	0.0178	0.0076	0.0276	0.0042	0.0136	0.0026
S1	0.1538	0.7705	0.0936	0.0236	0.0081	0.0305	0.0041	0.0157	0.0006
S2	0.2506	0.9721	0.0835	0.0213	0.0092	0.0277	0.0050	0.0139	0.0014
S3	0.9236	0.2291	0.4768	0.0216	0.0085	0.0326	0.0045	0.0174	0.0033
S4	0.7762	0.9771	0.5305	0.0195	0.0087	0.0293	0.0042	0.0149	0.0027
C1	0.3100	0.8006	0.0577	0.0186	0.0088	0.0189	0.0040	0.0091	0.0015
C2	0.5920	0.7274	0.0477	0.0207	0.0145	0.0294	0.0040	0.0155	0.0026
C3	0.7595	0.5935	0.1124	0.0254	0.0161	0.0383	0.0016	0.0194	0.0034
C4	0.8875	0.8051	0.5436	0.0157	0.0083	0.0202	0.0048	0.0087	0.0020
C5	0.3205	0.2628	0.4068	0.0231	0.0128	0.0299	0.0082	0.0166	0.0028
C6	0.6452	0.6071	0.5970	0.0302	0.0141	0.0354	0.0102	0.0188	0.0017
O1	0.4621	0.6964	0.0850	0.0228	0.0094	0.0308	0.0018	0.0149	0.0001
O2	0.8398	0.7038	0.5700	0.0230	0.0091	0.0304	0.0061	0.0153	0.0028
H2′	0.3564	0.2411	0.8780						
H2″	0.4561	0.2644	0.0688						
H3′	0.2016	0.4266	0.7913						
H3″	0.1848	0.3973	0.9058						
H3‴	0.2903	0.4553	0.9558			B(iso.)=6.0 fixed			
H5′	0.6071	0.7740	0.5153						
H5″	0.7159	0.7529	0.7041						
H6′	0.6267	0.5776	0.5055						
H6″	0.7255	0.5637	0.6864						
H6‴	0.5765	0.6142	0.6023						

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Table 2.   Interatomic distances and angles in the triclinic Ni(EtX)$_2$.

Triclinic				Orthorhombic	
Ni1–S1	2.208 Å	Ni2–S3	2.211 Å	Ni –S1	2.24 Å
Ni1–S2	2.212	Ni2–S4	2.206	Ni –S2	2.23
C1 –S1	1.676	C4 –S3	1.684	C1 –S1	1.73
C1 –S2	1.694	C4 –S4	1.689	C1 –S2	1.65
C1 –O1	1.319	C4 –O2	1.310	C1 –O	1.38
C2 –O1	1.462	C5 –O2	1.455	C2 –O	1.38
C2 –C3	1.489	C5 –C6	1.473	C2 –C3	1.48
C2 –H2′	0.686	C5 –H5′	0.612	Franzini (1963)	
C2 –H2″	0.798	C5 –H5″	0.813		
C3 –H3′	0.672	C6 –H6′	0.749		
C3 –H3″	0.619	C6 –H6″	0.700		
C3 –H3‴	0.789	C6 –H6‴	0.613		
S1 –S2	2.822	S3 –S4	2.819		
S1 –S2′	3.404	S3 –S4′	3.400		

Bond length to other molecule					
O1 –H6′	3.015	O2 –H3′	3.114		
O1 –H5′	3.204	O2 –H3′*	3.085		
		O2 –H2′*	3.056		

Bond angles					
S1–Ni–S2	79.20°	S3–Ni–S4	79.19°	S1–Ni–S2	79.5°
–S2*	100.39	–S4*	100.40		
S1–C1–S2	113.44	S3–C4–S4	113.23	S1–C1–S2	116
–O1	120.91	–O2	120.57	–O	119.5
S2–C1–O1	125.20	S4–C4–O2	125.39	S2–C1–O	124.5
C1–O1–C2	118.96	C4–O2–C5	119.18	C1–O–C2	123
O1–C2–C3	106.71	O2–C5–C6	107.11	O–C2–C3	108.5
O1–C2–H2′	108.2	O2–C5–H5′	106.3	Franzini (1963)	
–H2″	106.5	–H5″	108.2		
H2′–C2′–H2″	136.3	H5′–C5–H5″	127.1		
C2–C3–H3′	105.3	C5–C5–H6′	110.4		
–H3″	109.3	–H6″	105.2		
–H3‴	102.2	–H6‴	114.1		
H3′–C3–H3″	114.3	H6′–C6–H6″	115.5		
–H3‴	110.0	–H6‴	104.1		
S1–S2–S1*	89.53	S3–S4–S3*	89.68		

Discussion

Obviously, the structural difference between orthorhombic and triclinic forms is in the way of arrangement of the molecules.   In triclinic structure, four S atoms surrounding a Ni atom in each molecule and other two atoms belonging to neighbouring molecules make elongated octahedral coordination (Fig. 5).   Similar octahedra are also found in orthorhombic structure.   In the orthorhombic form, these octahedra share corners with each other and make plane networks parallel to the (001) plane (Fig. 2).   The Ni–S bond length in a molecule is 2.23–2.24 Å.   Franzini (1963) explained these bondings due to the four strong d–s–p bonds of a Ni atom directed to the corners of a NiS$_4$ square in a molecule, and a fifth weak p bond which leaves the pos-

sibility of a weak interaction with a S atom belonging to an other molecule. Same considerations are also applicable to the triclinic structure, because of the close similarity of the NiS_6 octahedrons in these structure. Crystallographically different two kinds of $Ni(EtX)_2$ molecule exist in the triclinic form and Ni atoms in them are located at the positions of the center of symmetry. The differences between the Ni–S bond lengths in the two molecules are only 0.003 Å for Ni1–S1 and Ni1–S2, 0.005 Å for Ni2–S3 and Ni2–S4. The close equidistant character between each Ni–S bond length (Table 2) is explained by a resonance structure of the following schema;
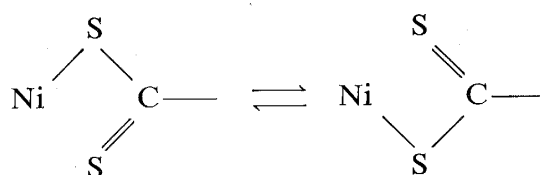
As seen in Fig. 5, the bond distances and angles show rectangular coordination of four sulfurs. S–S–S angles are almost 90° within a deviation of ±0.1°. The distances S1–C1 and S2–C1 are 1.674 and 1.694 Å, respectively, which shows higher double bond character of S1–C1 than that of S2–C1. The difference in length between S1–C1 and S2–C1, 0.020 Å, is smaller than the value of 0.08 Å, reported on the orthorhombic crystal by Franzini[1]. The value on the other molecule belonging to Ni2 is extremely small, that is 0.005 Å (see Table 2 on S3–C4 and S4–C4 bonds). We have concluded that the triclinic $Ni(EtX)_2$ has more resonant structure than the orthorhombic form, although the comparison should be made on the same order of precision. In terms of chain structure, S2 and S4 atoms are clearly distinguished by their bridging nature from nonbridging S1 and S3 atoms (see Fig. 6). Acicular habit of the triclinic $Ni(EtX)_2$ has been explained by the chain structure of edge sharing NiS_6 octahedron, as well as the platy habit of the orthorhombic $Ni(EtX)_2$ has been recognized with the corner sharing network. Thus, one dimensional interaction among molecules is explained by a concept of the octahedral connection in which the weak Ni^{2+}–S bond has a most important role.

On the other hand, interchain structure is well expressed in Fig. 6. Three sulfur atoms, S1, S2, and S4' on one and the same chain and a sulfur, S4 on neighbouring chain make a tetrahedral arrangement. Such tetrahedra lie along the c-axis as line. The arrangement may be seen as indicating interchain bonding between S and S. But the minimum bond length between these sulfurs is 4.066 Å which is too large to recognize the interatomic bonding, as the twice value of the ionic radius of S^{2-} is 3.68 Å. While, bond length between a hydrogen atom of an ethyl group and an oxygen of the other molecule is 3.1 Å, that is, H3'–O2=3.1 Å and also H2''–O2=3.1 Å. The position of hydrogen atom could not be determined so clearly by the x-ray method that the distances should be inaccurate. Usually, C–H bond length determined by the x-ray method is apt to become shorter than the actual length because of the low electron density of the hydrogen atom. Electron density around hydrogen atoms was observed by the difference Fourier synthesis between observed structure factors and
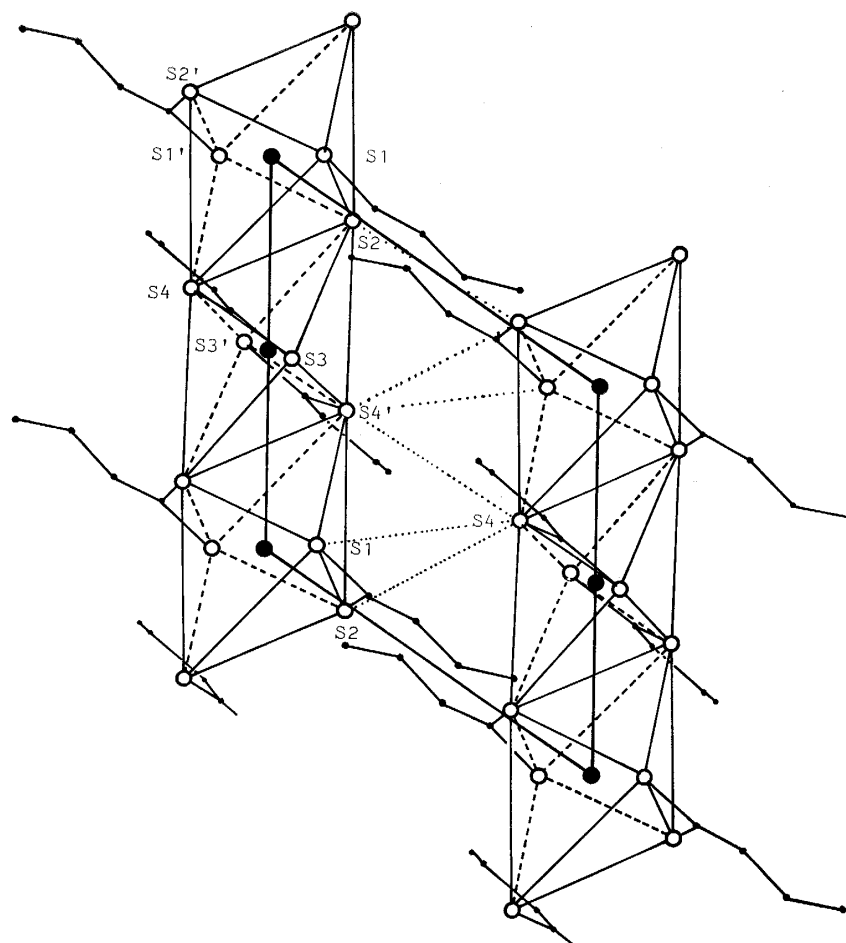
Fig. 6   Chain structure of NiS_6 octahedra along the c-axis.

calculated structure factors omitting hydrogen atoms. The electron density of them drawn in three dimensions by a contour line of 0.4 e/$\mathring{A}^3$ and atomic positions of ethyl radicals are shown in Fig. 7 and 8, respectively. The C–H length determined by the present work is 0.7 $\mathring{A}$ which is shorter than the actual length of about 1 $\mathring{A}$[6,7].

For an example, the hydrogen bond length of N–H$\cdots$O in $(NH_2)_2CO$ is reported to be 3.034 $\mathring{A}$[8]. Thus, the intermolecular O$\cdots$H interaction plays important role in forming structure of xanthate crystals.

NiS_6 octahedra, in this structure, share edges with each other and make chains parallel to the c-axis. This structure provides short distances between molecules. The shortest Ni to Ni distance, which is suitable as an indicator of intermolecule distance, in orthorhombic form, is 5.23 $\mathring{A}$ from Ni(0, 0, 0) to Ni (1/2, 1/2, 0), while in triclinic form, the distance from Ni1 (0, 0, 0) to Ni2 (0, 0, 1/2) is 4.070 $\mathring{A}$. This suggests the possibility that xanthic radicals adsorbed on a mineral surface approach to 4 $\mathring{A}$.
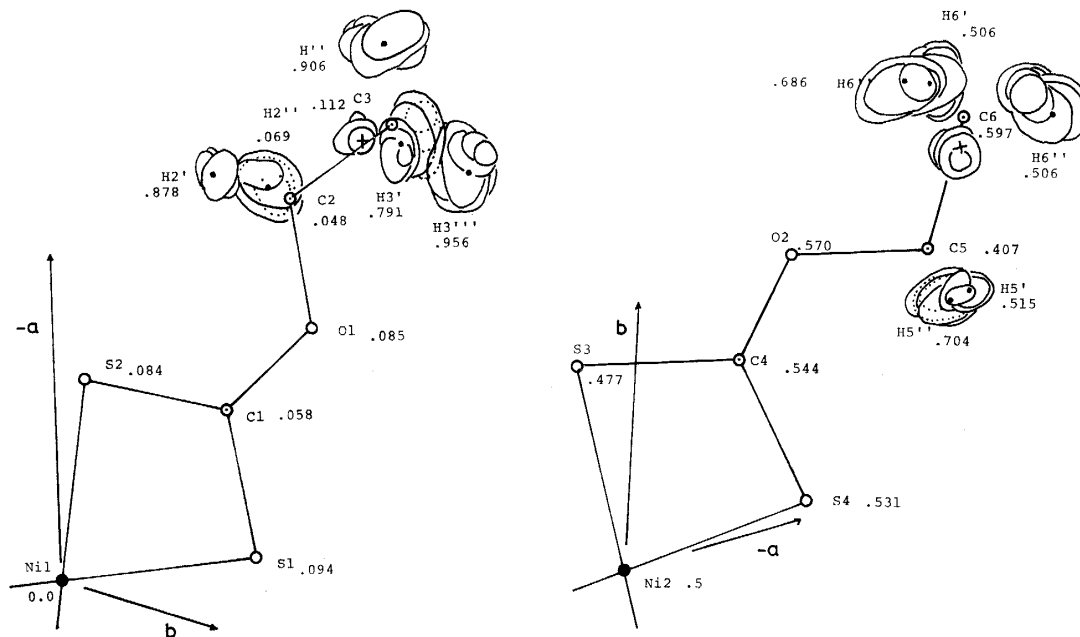
Fig. 7   Three dimensional electron density around hydrogen atoms. The contour of 0.4 e$Å^{-3}$ on each c section of $c/50$ interval is projected on the (001) plane. Cross marked electron densities do not correspond to those of hydrogen atoms. Figures represent z-coordinates in each atom.
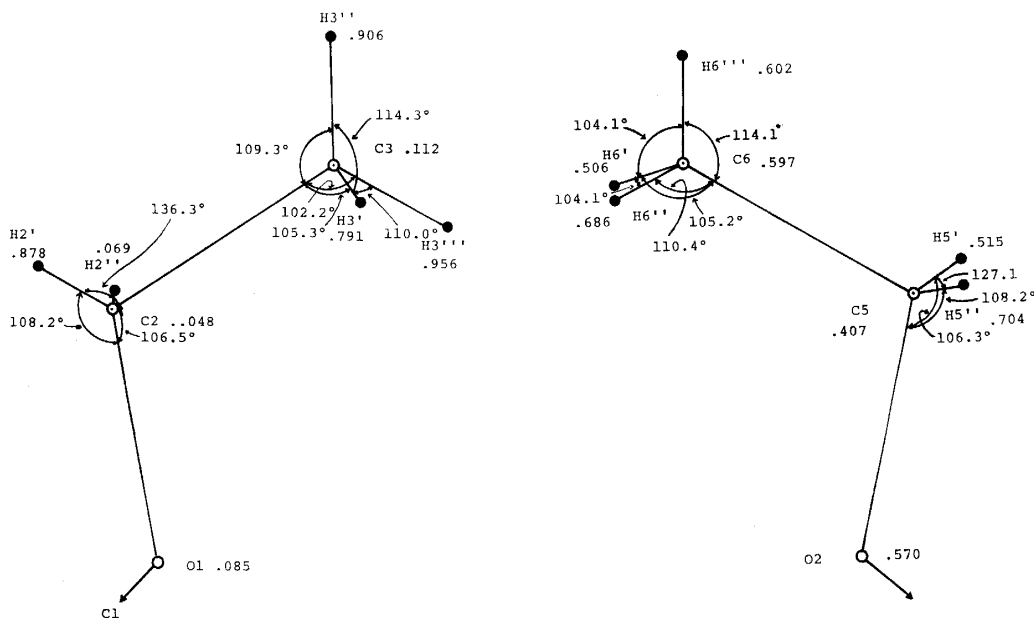

Fig. 8   Detail structure of ethyl radicals in triclinic $Ni(EtX)_2$.

Acknowledgement

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