Crystal Structure of Robidium Nickel Thiocyanate Tetrahyderate $Rb_4Ni(SCN)_6 \cdot 4H_2O$

Dr. Bertha Abdu

***Abstract*—**In this research, $Rb_4Ni(SCN)_6.4H_2O$ was prepared by reaction of equimolar solution of Rb_2CO_3 with $NiCl_2$ and NH_4SCN at room temperature. The single crystal measurement was done using the image plate Diffractometer, from the company STOE (Darmstadt). The radiation source was graphite monochromatic MoK α radition (λ= 71.069pm) with a detector image plate ($BaClF:Eu^{2+}$) and a resolution of $0.0225mm^2$. $Rb_4Ni(SCN)_6 \cdot 4H_2O$ crystallizes in a monoclinic crystal system with the space group $P2_1/m$ and 4 formula units per elementary cell.

***Keywords*—**Thiocyanates, Crystal measurement, Elemental cell, lumniscence.

I. Introduction

Thiocyanates have been investigated in different aspects of this research (Danja et al)[1 & 2]), It is a pseudo-halogen, due to it similarity with halogen ions, for example it is a monovalent anion. The nature of these compounds makes them to be of great interest as host lattice in lumniscence science. For luminescence to occur an activator and a host lattice are needed. Host lattice consist of cations combined with one of several different anions, hence have closed electron shells, and therefore are optically inactive. It is important that the host is optically transparent, for the absorption- excitation process to take place at the activator site. The nature of Thiocyanates makes them to fulfil these conditions, therefore the interest in them as host lattice. Since a few of the divalent have been investigated (Danja, Wickleder(1&3), effort was made in this work to prepare a little more complex one, i.e. the trivalent one with the aim of using them as host lattice.

II. Experimental

- Preparation of $Rb_4Ni(SCN)_6.4H_2O$

$Rb_4Ni(SCN)_6.4H_2O$ was prepared by the reaction of equimolar solutions of Rb_2CO_3 with $NiCl_2$ and NH_4SCN at room temperature. The mixed solution was allowed to stand for 24hours to allow the new compound to crystallise out.

- Single Crystal Analysis.

The single crystal measurement was done using the image plate Diffractometer, from the company STOE (Darmstadt Germany). The radiation source is graphite monochromatic MoK α radition (λ= 71.069pm) with a detector image plate ($BaClF:Eu^{2+}$) and a resolution of $0.0225mm^2$. The single crystal was first picked, fixed at the top of a capillary and sealed inside of the capillary, which was then put on a goniometer head, and mounted on a horizontal rotation axis, which is perpendicular to the X-ray beam. The reflections and intensities were then measured. The structure was solved using computer program given in Table 1 below.

TABLE I
COMPUTER PROGRAM USED

Computer program	Application
SHELXS-97	Structure solution
SHELXL-97	Structure refinement
PLATON	Space group and symmetry analysis
Diamond	Graphical description for crystal structure
STOE Window	Program for table calculation
Window Formula editor	Program for chemical formula

III. Results And Discussion

Blue crystals of $Rb_4Ni(SCN)_6 \cdot 4H_2O$ were formed alongside white crystals of NH_4Cl. The blue crystals of $Rb_4Ni(SCN)_6 \cdot 4H_2O$ were mechanically separated from the NH_4Cl. After which a good single crystal was selected using a polarization microscope, the picked crystal was used to measure the complete intensity data set using Imaging Plate-Diffractometer (STOE IPDSI). $Rb_4Ni(SCN)_6 \cdot 4H_2O$ crystallizes in a monoclinic crystal system with the space group $P2_1/m$ and 4 formula units per elementary cell (figure 1). The crystallographic data are given in table 2. The positional and isotropic atomic displacement data are given in table 3, with the Anisotropic atomic displacement parameters in table 4. Some selected angles and bond lengths are given in table 5**.** This information was used to generate the crystal structure of the compound synthesised.

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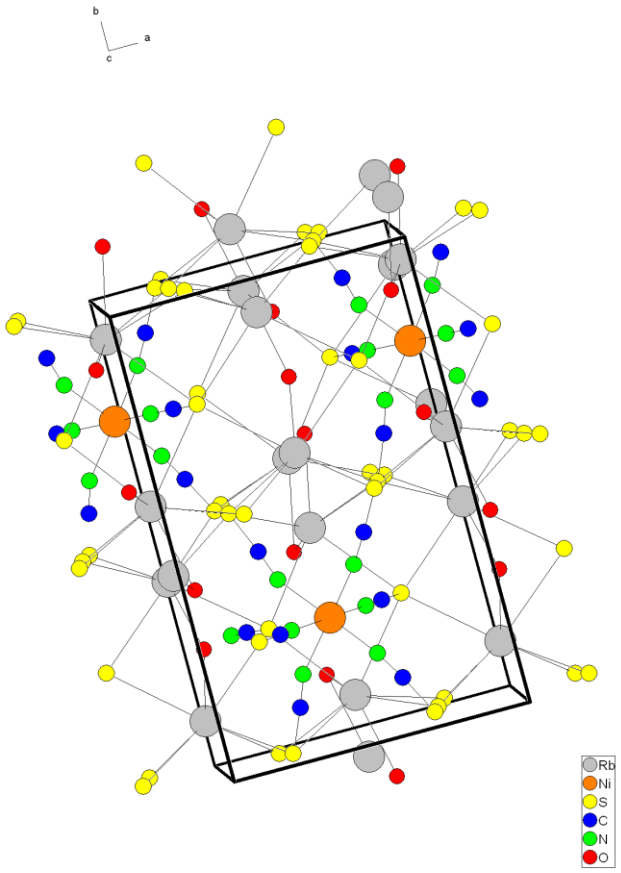

Fig. 1: Elemental cell in the structure of $Rb_4Ni(SCN)_6 \bullet 4H_{2O}$

TABLE II

CRYSTALLOGRAPHIC DATA OF $Rb_4Ni(SCN)_6 \bullet 4H_{2O}$

Lattice constants (pm)	a = 9.6294(17), b = 15.129(3), c =16.932(3),
Cell Volume (10^6 $pm^{3)}$	2466.7(7)
Formula Units (Z)	4
Mole Volume (cm^3/mol)	371.0
Calculated density (ρ) in g•cm^{-3}	1.887
Crystal system, Space group	Monoclinic p , $P2_1/m$ (No11)
Radiation	Mo-Kα(Graphite-Monochromatic., λ = 71,07 pm)
Temperature (K)	293(2)
Diffractomer	STOE IPDS I
Irradiation time (min)	23
Detector distance (mm)	50
Absorption coefficient (mm^{-1})	5.975
F (000)	1344
Measuring range (θ) in °	2.78 – 30.75
Measuring range (h, k, l)	-13 ≤ h ≤13, -21 ≤ k ≤1, -19 ≤ l ≤24
Collected reflections	7774
Unique reflections	599
Reflection with $I_0 > 2\sigma(I)$	272
Solution and Refinement method	SHELXS – 97 and SHELXL – 97 [17,18]
Absorption correction	Numerical [60,61]
R, wR2(measured)	0.1148, 0.5437
R, wR2[$I_0 > 2\sigma(I)$]	0.2251, 0.3689
Goodness of fit	0.633
Extinction coefficient	0.00115(17)

TABLE III

SELECTED ANGLES AND BOND LENGTHS IN RB_4 $Ni(SCN)_6$ •$4H_2O$

Angle Between	Angle(°)	Distances between	Distances(pm)
N2-Ni1-N1	93(11),	Ni-N	202,217,219,207,218,220.
N1-Ni1-N1	90.5(13)		
O3-Rb1-O3	92.2(7)	Rb-S	348.2,353.5, 342.4,
O3-Rb1-S7	148.2(6),		
S3-Rb1-S5	76.2(5)	Rb-O	349.3,349.7,302
Rb1-S2-Rb1	133.9(4)		
S1-Rb2-S8	100.6(4)	S2-C2	160
O5-Rb2-S1	141.8(3)		
Rb2-S1-Rb2	70.7(6)	S5-C5	163
S8-Rb3-S6	76.4(3)		
Rb4-O6-Rb4	148.4(4)	C-N	119, 125,109, 120, 108.
	99.4(14)		
C7-S7-Rb3	93.6(14)		
C8-S8-Rb4	93.8(10)		

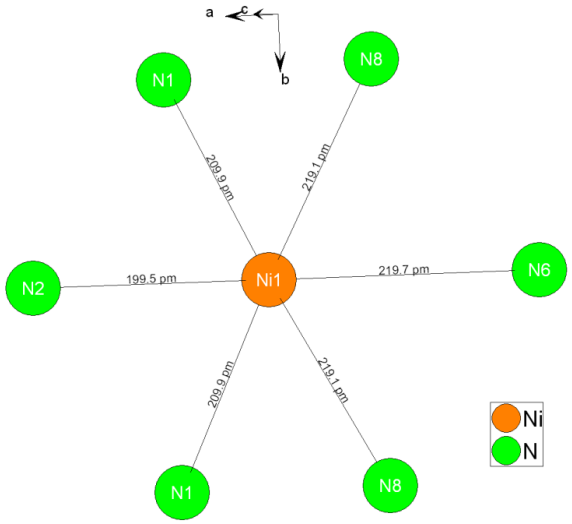

Fig. 2: Coordination spheres of Ni1

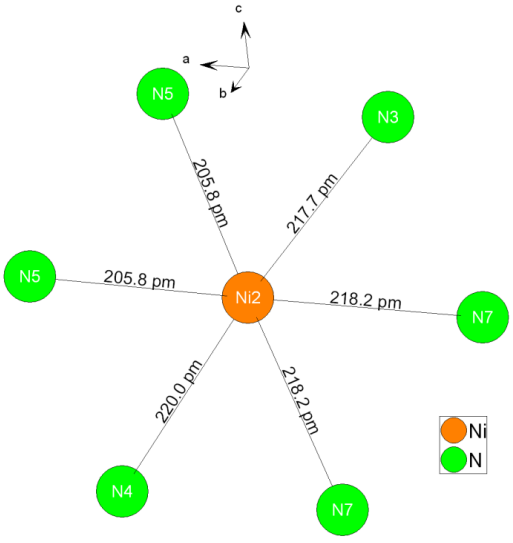

Fig. 3: Coordination spheres of Ni2.

There are two crystallographically independent Ni ions which are coordinated by six SCN^- ions through Nitrogen atoms each, to form an octahedral structure around the Ni ion. The SCN are coordinated by the Ni^{2+} and Rb^+ ions such that

they are almost linear with an angle of ~ 180°. **Figure** 2 and 3 are the coordination spheres of these two crystallographically different Ni^{2+} ions, the bond length do not differ very much from each other; they are within 205-220pm.

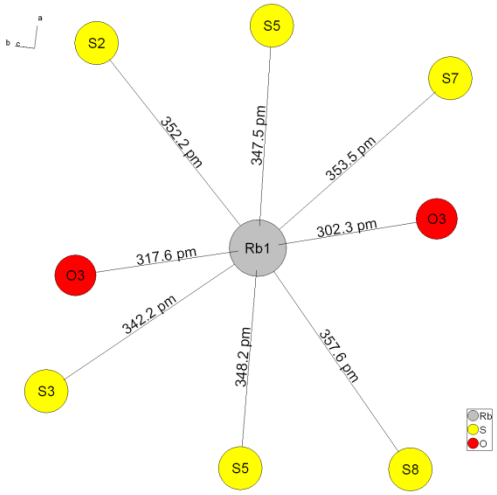

Fig. 4 a and b. Coordination spheres of Rb1 and Rb2.

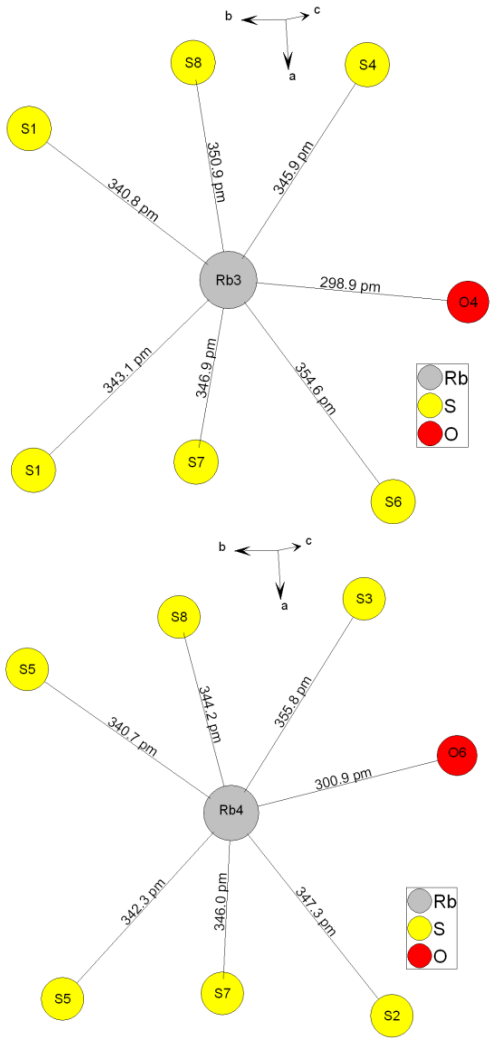

Fig. 5 a and b. Coordination spheres of Rb3 and Rb4**.**

The Rb polyhedral are mutually linked by S-Rb bonds to form rings built up from one kind of edge sharing and face sharing to form the crystal structure, the coordination spheres of these Rb ions are shown in Fig 4 a & b and Fig 5 a & b above. There are two kinds of rings as shown in figures 6 and 7. The polyhedral as mentioned above are connected in two ways to each other, one by edge connections of the Rb^+ ions through S atoms and the other by face connections of Rb^+ ions also through sulphur atoms. It can be seen that at the corners of the Rb the S atoms are connected to another set of polyhedral. In these rings, one contain four Rb^+ ions that are 8-fold coordinated and two that are seven fold coordinated, in the other ring the reverse is the case, i.e. it contain four 7-fold coordinated Rb^+ and two 8-fold coordinated Rb^+. The most striking features of the crystal is the –N=C=S- bridges. The ambidentate SCN ion, usually s-bonded to a soft ion centre and N-bonded to a hard ion centre [6,7] act here as bridging bidentate ligand to satisfy the coordination number of Ni and Rb metals.

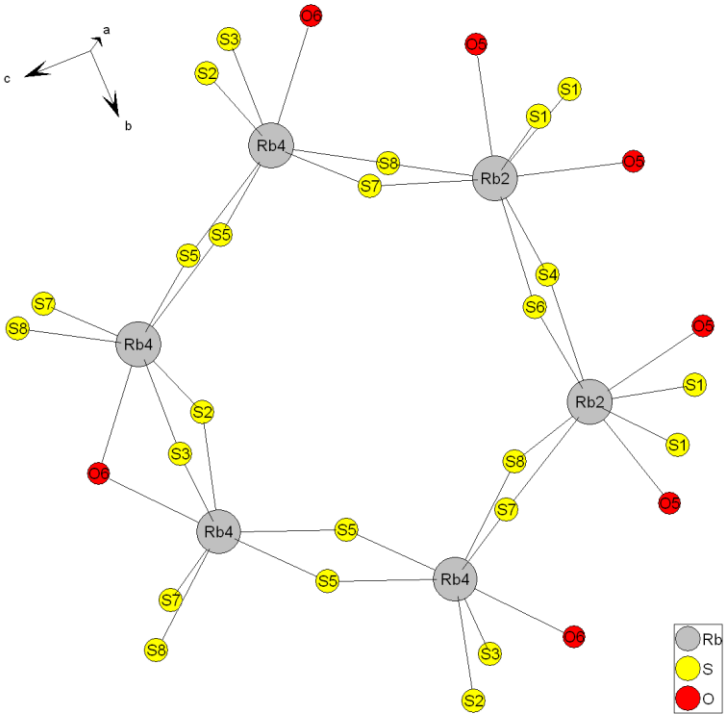

Fig. 6: Ring 1 in the structure of $Rb_4Ni(SCN)_6 \bullet 4H_{2O}$

The water molecules coordinate with Rb through the oxygen atoms. They connect to the Rb^+ ions in two ways, one forming a bridge across two Rb^+ ions and occupying the centre of the ring, second type connect to Rb^+ ion without forming a bridge. In ring 1 above and 2 below, it can be seen that Ring one is empty which is normally occupied by a Ni^{2+} ion, while in the other ring, three of the oxygen atoms form a chain in the centre of the ring. The first two Rb^+ ions have two oxygen in the coordination sphere and the last two have only one each. This also relate to how they form the rings around Ni^{2+} ions.

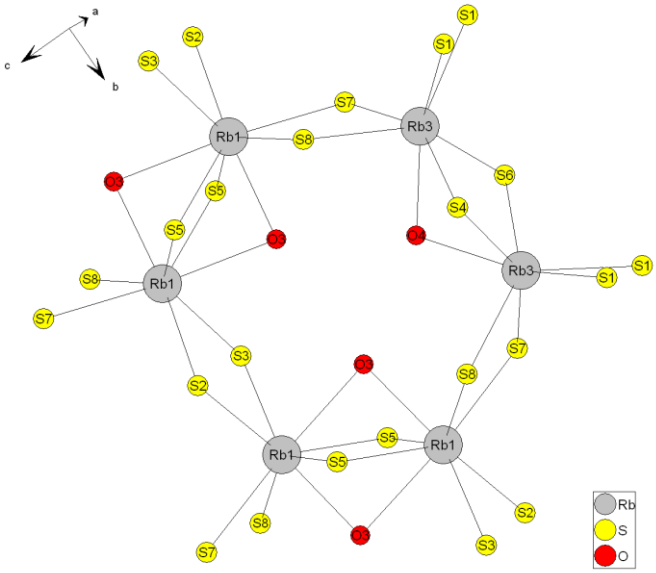

Fig. 7 Ring 2 in the structure of $Rb_4(SCN)_6 \bullet 4H_{2O}$

In the structured viewed along (100) shown in figure 8 below, nickel alternate with oxygen in the centre of these rings. This alternation of the nickel oxygen and the rings connection can be seen in the view along (001) shown in figure 8 below

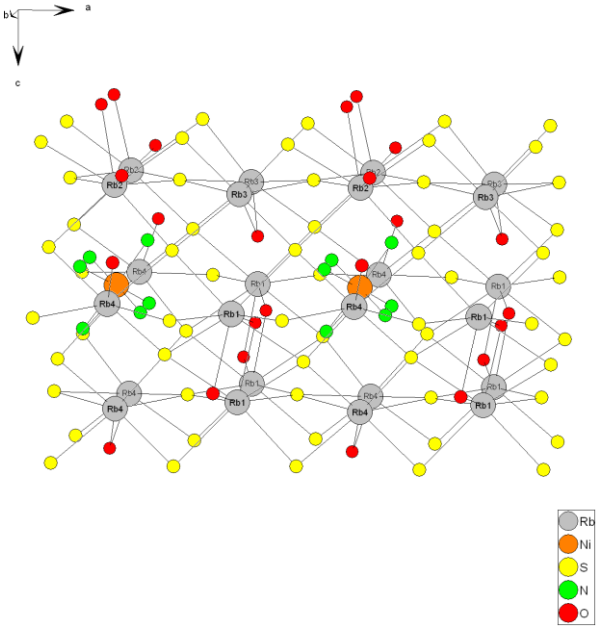

Fig. 8: The Ni-(SCN)-Rb chains along (001).

Fleck [4] has solved a similar structure of a ternary thiocyanate containing Ni ions and observed that the Ni-N bonds (~ 205pm) are covalent. Considering the sum of the covalent and ionic radii of the atoms, the same conclusion can be made about the Ni-N bonds (~ 206pm) obtained in this work. Unlike in his work where the Ni coordinated to both N and S of the thiocyanates, in this work Ni coordinates only to N. From the forgoing and considering the sum of their ionic and covalent radii, it can be said that Rb-S bond (~ 350pm) is more ionic than covalent. The angles C-S-Rb as given in Table 5 are in good agreements with Fleck [4] who observed that SCN groups S-bonded to metal atoms tend to form M-S-C angles of about 90-100^o.

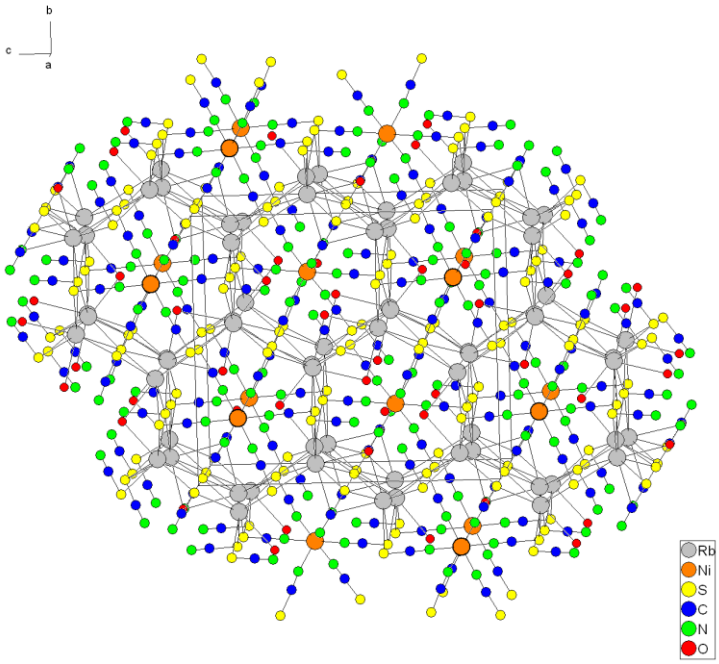

Fig. 3.24 A view of the Rings of $Rb_4Ni(SCN)_6 \bullet 4H_{2O}$ along (100)

IV. CONCLUSION

$Rb_4Ni(SCN)_6 \cdot 4H_2O$ was synthesised for the first time and the structure was solved. It crystallizes in a monoclinic crystal system with the space group $P2_1/m$ and 4 formula units per elementary cell. The net work around the central Ni ion forms an octahedral structure with edge, face and corner connections of the Rb^+ ions by the S atoms of the thiocyanate. The position of the Nickel metal ion makes it in principle easy to replace it with other metals. This will help in future work to synthesis some ternary thiocyanates by replacing the Ni with some metals suitable as host lattice.

LITERATURE

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