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# Synthesis, Structure and Non-linear Optical Properties of Manganese Mercury Tetrathiocyanate

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**Abstract :** The title copound Manganese Mercury Tetrathiocyanate ($MnHg(SCN)_4$) has been synthesized and its structure has been determined. It belongs to tetragonal system, $I\bar{4}$ space group. The cell dimensions are: a = 1.1324 (3) nm, c = 0.4270 (2) nm, V = 0.5475 (3) $nm^3$, Z = 2, $D_c$ = 2.959 $g/cm^3$, R = 0.028, $R_w$ = 0.037. The structure feature of the crystal is the Hg-S-C≡N-Mn bridge which leads to the formation of an infinite three dimensional network. Irradiated by a 1064 nm Nd:YAG laser beam, $MnHg(SCN)_4$ shows a 532 nm second harmonic intensity which is 18 times as that of organic nonlinear optical crystal urea, and therefore shows a quite promising application value as a useful nonliear optical material.

**Keywords:** $MnHg(SCN)_4$, synthesis; structure, nonlinear optical property.

## Introduction

Recently, our research interests have focused on $MHg(SCN)_4$ series of crystalline complexes because of their striking nonlinear optical properties. In the previous paper[1,2], we have repored the synthesis, structure and nonlinear optical (NLO) properties of $CdHg(SCN)_4$ and $FeHg(SCN)_4$. Here, we will report $MnHg(SCN)_4$ as another new member of $MHg(SCN)_4$ family. Compared with $FeHg(SCN)_4$ and $CdHg(SCN)_4$, their crystal structures are similar, but the second harmonic intensity of $MnHg(SCN)_4$ was measured to be much stronger than $FeHg(SCN)_4$, even stronger than $CdHg(SCN)_4$.

## Synthesis

0.03 mol $MnCl_2 \cdot 4H_2O$ was dissolved in 30 mL distilled water at room temperature. This pink colored solution was added into a colorless 30 mL water solution containing 0.03 mol

$HgCl_2$ and 0.12 mol KSCN. Then this solution was evaporated slowly in atmosphere. Three days later, the pale yellow-green colored tetrahedral shaped crystals were obtained. The crystal used for structural determination had been recrystallized from water. Calcd for MnHg $(SCN)_4$: C, 9.84%; N, 11.48%; Found: C, 9.89%; N, 11.50%. Thermal analysis shows that it is stable up to its decomposition temperature of 612 K without showing melting process. A strong UV absorption peak is at 240.5 nm ($\varepsilon = 2.0 \times 10^4$ L/cm·mol) . The IR spectrum of MnHg $(SCN)_4$/KBr shows a unique strong peak of C≡N at 2131.93 $cm^{-1}$.

**Structure**

A MnHg $(SCN)_4$ crystal with a dimension of 0.2×0.2×0.2 mm was mounted on a Siemens P4 four circle diffractometer. Irradiated by MoKa ( $\lambda = 0.071073$ nm ), in the range of $3° \leq 2\theta \leq 60°$, 703 reflections were collected, of which 592 ($F > 4.0\ \sigma(F)$) were used in the structure determination and refinement. The crystal belongs to tetragonal system, $I\bar{4}$ space group. The unit cell parameters are as follows: a = 1.1324 (3) nm, c = 0.4270 (2) nm, V = 0.5475 (3) $nm^3$, Z = 2, $D_c = 2.959$ g/$cm^3$, R = 0.028, $R_w = 0.037$. The crystal consists of two kinds of slightly flattened coordinate tetrahedrons with the local symmetry of $D_{2d}$. One is $MnN_4$ and the other is $HgS_4$. The Hg-S-C≡N-Mn bridge leads to an infinite three dimensional network. This structural characteristic accounts for a quite high physico-chemical stability of the crystal.

**Table 1.** The bond parameters and SHG intensity of MnHg $(SCN)_4$ and similar compounds.

| | CdHg $(SCN)_4$ | CoHg $(SCN)_4$[3] | FeHg $(SCN)_4$[2] | MnHg $(SCN)_4$ |
|---|---|---|---|---|
| S—C (nm) | 0.1655 (8) | 0.1635 (14) | 0.1659 (11) | 0.1659 (8) |
| C—N (nm) | 0.1148 (11) | 0.1199 (21) | 0.115 (2) | 0.1140 (14) |
| M—N (nm) | 0.2174 (8) | 0.1921 (16) | 0.201 (2) | 0.2070 (13) |
| Hg—S (nm) | 0.2574 (2) | 0.2558 (4) | 0.2568 (2) | 0.2565 (2) |
| S—C—N | 178 (1)° | 178 (2)° | 177 (2)° | 178 (1)° |
| SHG intensity/urea | 13 | | 0.6 | 18 |

From **Table 1**, one can see that all S—C bond lengths are considerably shorter than the typical single S—C bond length of 0.181 nm. C—N and Hg—S bond lengths have no significant difference. S—C—N bond angles are very close to 180◦, *i.e.*, SCN group is almost perfectly linear. Therefore, the bond parameters of M (II)Hg $(SCN)_4$ series are quite similar. It is no strange that all of them belong to tetragonal system, $I\bar{4}$ space group.

**Figure 1.** The projection of unit cell along c direction

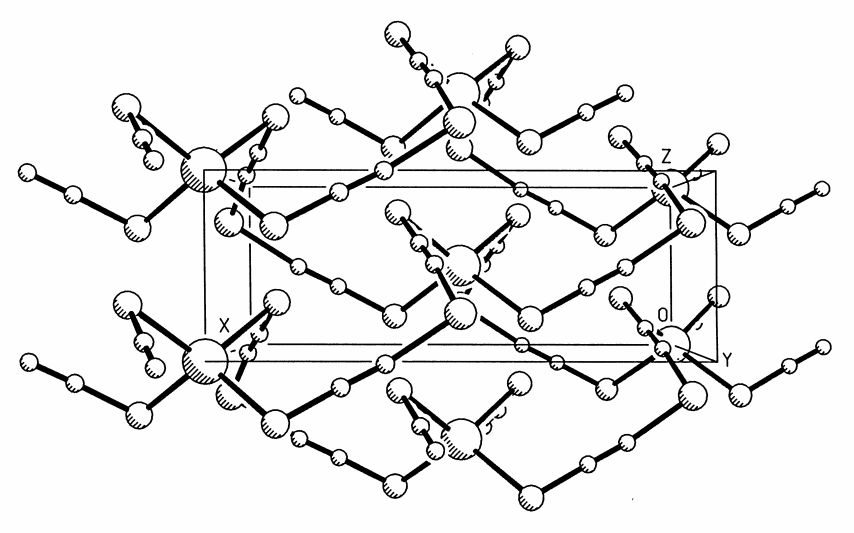
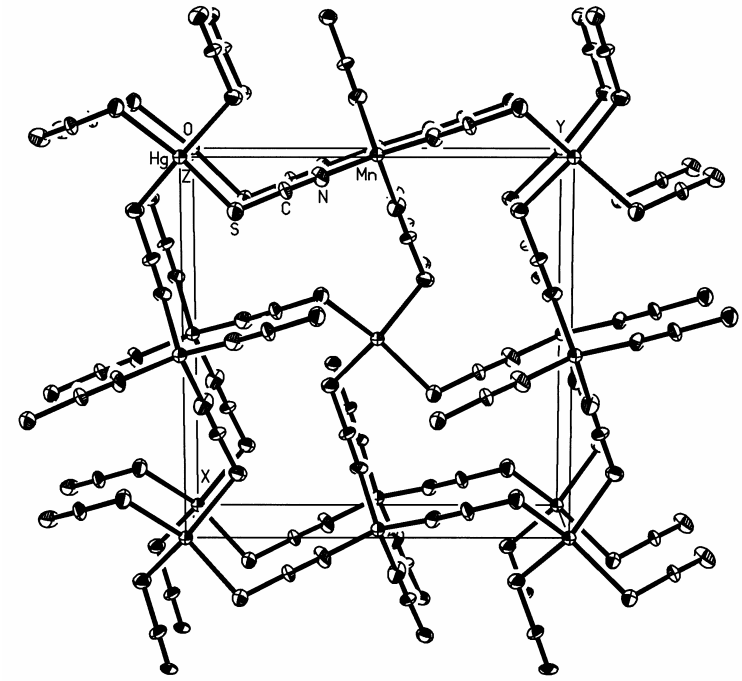



**Figure 2.** The projection of unit cell along a direction



## Nonlinear Optical Test

The second order NLO tests were carried out by the power second harmonic generation (SHG) method. Irradiated by a 1064 nm passive mode-locked Nd:YAG laser beam, $MnHg(SCN)_4$ showed a 532 nm second harmonic intensity of 18 times as that of organic NLO crystal urea, By comparison, $CdHg(SCN)_4$ showed a second harmonic intensity of 13 times as that of urea, but $FeHg(SCN)_4$ only 0.6 times. Therefore, $MnHg(SCN)_4$ is a quite promising SHG materials. From **Table 1**, one can see that the S—C—N bond angle of $FeHg(SCN)_4$ has a little more deviation from 180°, but such a tiny geometrical structure difference can not well explain the NLO difference. On the other hand, The d-shell of Fe in $FeHg(SCN)_4$ is open, while d-shell of Mn in $MnHg(SCN)_4$ is half –filled and that of Cd in $CdHg(SCN)_4$ is fully filled. So the NLO difference may more reasonably come from the difference in electronic structure rather than geometrical structure.

The same as $FeHg(SCN)_4$, the NLO properties of $MnHg(SCN)_4$ may not be limited to SHG effect only. Because Mn (II) may be changed to Mn (III) and meanwhile Hg (II) to Hg (I), we believe that a charge transfer between the two coordination centers may take place under certain conditions and electro-optic effect may exist, and the enhanced photoconductivity effect may become operative. Further studies are under way.

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