*Asian Journal of Chemistry* Vol. 19, No. 7 (2007), 5775-5777

***NOTE***

# Mass and $^1$H NMR Spectral Characterization of the Reaction Product of $S_4N_3Cl$ and Thiourea

ANJUL SINGH† and S.P.S. JADON*
*Department of Chemistry, S.V. College, Aligarh-202 001, India*
*E-mail: anjul_singh@rediffmail.com*

The reaction of thiotrithiazyl chloride ($S_4N_3Cl$) and thiourea was carried out in DMF. The product, obtained, was characterized on the basis of Mass and $^1$H NMR spectra and is formulated as $(S_4N_3)_2NCSNH_2$.

**Key Words: Thiotrithiazyl chloride, Thiourea, Symmetrical geometry.**

Thiotrithiazyl chloride ($S_4N_3Cl$)[1] is the most stable cyclic derivative of tetrasulfur tetranitride[2,3]. It has the tendency to combine with metal ions as well as organic compounds. The reaction of $S_4N_3Cl$ with various transition metal ions[4-7] and also with triphenyl phosphine have already been studied. The reaction between $S_4N_3Cl$ and $NH_2CSNH_2$ have not been investigated till now. Therefore, product, formed and studied spectrometrically, is being presented herewith.

All the chemicals used, were of AR grade. $S_4N_3Cl$ was prepared by the reaction of $S_4N_4$ with acetyl chloride as reported (Loc.cit.). The product was obtained by the refluxing of $S_4N_3Cl$ and thiourea in DMF for 6 h. The solid obtained was filtered, washed with DMF and ether. Mass and $^1$H NMR spectrum were recorded on a Jeol SX 102 (FAB) spectrometer and Bruker DRX-300, respectively. IR Spectrum was recorded on Shimadzu 8201 P.C. spectrophotometer. Elemental analysis were obtained from Perkin-Elmer CHN microanalyzer. Molecular weight was determined by Rast method using camphor as a solvent.

The product, obtained, after refluxing $S_4N_3Cl$ and thiourea for 6 h, is white in colour and sparingly soluble in DMSO. Analytical data %: found (cal); S 69.62 (69.56); N 27.10 (27.05); C 2.90 (2.89); H 0.50 (0.48) and molecular weight 412.5 (414.0) g/mol assign the product as $(S_4N_3)_2NCSNH_2$.

†Department of Chemistry, D.S. College, Aligarh-202 001, India.

Mass spectrum shows the prominent mass lines at m/z ratio 89, 107, 199, 232, 363 due to $NNHCSNH_2$, $SNNHCSNH_2$, $S_4N_3NHC$, $S_4N_3NHCS$, $(S_4N_3)_2NC$ fragments, respectively along with the other peaks at m/z 91, 107, 171, 352 for the fragments of $S_4N_3Cl$ as presented in Table-1.

TABLE-1
MASS SPECTRAL DATA OF THE ADDUCT

| m/z ratio | Bands assigned |
|---|---|
| 89 | $NNHCSNH_2$ |
| 91 | $S_2N_2$ (M-1) |
| 107 | $S_2N_3$ (M+1) |
| 120 | S-N-$NHCSNH_2$ (M-1) |
| 138 | N-S-$NNHCSNH_2$ (M+3) |
| 171 | $S_4N_3$ (M+1) |
| 199 | $S_4N_3NHC$ (M+2) |
| 232 | $S_4N_3NHC$-S (M+3) |
| 241 | $S_4N_3$-N-CSN (M-1) |
| 274 | $S_4N_3NCS_2N$ |
| 324 | $S_4N_3S_2N$ N-C=S-$NH_2$ (M+2) |
| 352 | $(S_4N_3)_2$ N (M-2) |
| 363 | $(S_4N_3)_2$ NC (M-3) |

The reaction between $S_4N_3Cl$ and thiourea may be expressed as

$$2S_4N_3Cl + NH_2CSNH_2 \rightarrow (S_4N_3)_2NCSNH_2 + 2HCl$$
$$(m/z = 414)$$

The formation of adduct may be proved by the fragments, formed, during the decomposition of $(S_4N_3)_2NCSNH_2$ with the loss of some groups and indicating the prominent mass lines for the various fragments as explained below:

$(S_4N_3)_2NCSNH_2 \rightarrow S_4N_3$ m/z = 171 (M+1)

$(S_4N_3)_2NCSNH_2 \rightarrow S_4N_3NHC$ m/z = 199 (M+2)

$(S_4N_3)_2NCSNH_2 \rightarrow S_4N_3NHCS$ m/z = 232 (M+2)

$(S_4N_3)_2NCSNH_2 \rightarrow (S_4N_3)_2NC$ m/z = 363 (M-3)

Above fragmentation process supports the molecular formula $(S_4N_3)_2NCSNH_2$

The formation of $(S_4N_3)_2NCSNH_2$ is also supported by IR spectrum[8]. IR spectrum shows vibrations at 619, 735, 1110, 1404, 1464, 1591, 2067 $cm^{-1}$ corresponding to S-S band in $S_4N_3$ ring, C=S str., S-N band of $S_4N_3$ ring, SNH band, N-C-N str, C=N str and NCS str, respectively, confirming the presence of these groups in the adduct.

For confirm the geometrical structure of the reaction product of $S_4N_3Cl$ and thiourea its $^1H$ NMR spectrum is recorded. It has two signals at chemical shift δ - 0.001 and 1.238 ppm for the NH group of thiourea. The other signals in the range of δ 2:284-3.370 and δ 6.613-7.488 ppm are due to N atom present in the two $S_4N_3^-$; ion. These two groups has been separated by other N-atom of thioureate group which shows a signals at δ 5.415 ppm inferring that two $S_4N_3^-$ ion has separately reacted with H-atoms of terminal N-atoms of thiourea. A signal near to δ 5.415 ppm has faded due to other H-atoms attached to N-atoms of thiourea. $^1H$ NMR has two symmetrical groups of signals suggesting a symmetrical geometry of this product as shown in Fig. 1.

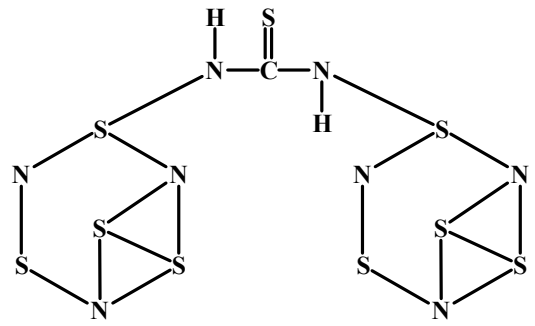

Fig. 1. Structure of $(S_4N_3)_2NCSNH_2$

## ACKNOWLEDGEMENTS

The authors are grateful to Dr. K.P. Madhusudan, Director, C.D.R.I. Lucknow and Head, Department of Chemistry, G.N.D. University, Amritsar for providing instrumental facilities.

## REFERENCES

1. W.L. Jolly, K.D. Maguir and D. Robinovich, *Inorg. Chem.*, **2**, 1304 (1963).
2. M.B. Goehring, *Progr. Inorg. Chem.*, **1**, 207 (1959).
3. M.B. Goehring and H.P. Latscha, *Z. Naturforsch*, **17B**, 125 (1962).
4. S.S. Yadav and S.P.S. Jadon, *J. Indian Chem. Soc*., **79**, 751 (2002).
5. S.S. Yadav and S.P.S. Jadon, *Ultra Sci.*, **15**, 143 (2003).
6. S. Upadhyay and S.P.S. Jadon, *Asian J. Chem.*, **15**, 1181 (2003).
7. S. Upadhyay and S.P.S. Jadon, *Asian J. Chem.*, **15**, 1065 (2003).
8. K. Nakamoto, The Infrared and Raman spectra of Inorganic and Coordination Compunds, John Wiley & Sons, Inc., New York (1978).

(*Received*: 11 September 2006; *Accepted*: 22 June 2007) AJC-5771