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# MICROBIOLOGICAL AND SPECTROMETRIC STUDIES OF DICHLORO Ni (II) TETRA SELENIAZIDE COMPLEX

Govind Kumar GUPTA, Ajay SINGH and S.P.S. JADON*

Department of Chemistry, S.V. College, Aligarh (U.P.) 202001, India

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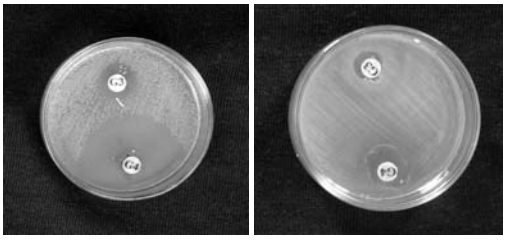
The complex of $Se_4N_3Br$ with Ni(II) compound, synthesized, was analyzed, qualitatively, quantitatively and Mass Spectrometrically. On the basis of chemical data, the complex is assigned as $(Se_4N_3)_4NiCl_2$. The formation and its molecular formula is supported by the prominent mass line m/z 1528 (M+1) for $(Se_4N_3)_4NiCl$ in its mass spectrum 35 less for Cl than mol. wt. and I.R. vibrations. The values of $\Delta Eg$ & $N_c$ indicate that the complex is good conductor. Its E.P.R. spectrum inferred paramagnetic character having two unpaired $e^-$ in Ni - atom for tetrahedral structure while the X-Ray diffraction suggested its hexagonal packing with f.c.c. geometry. The microbiological investigations inferred the activeness of the complex against E.coli (gram -ve) and Staphylococcus aureus (gram +ve) bacteria. Ni (II) tetra seleniazide may be used as medicine for the treatment of skin and other diseases caused by E. coli & S. aureus.



## INTRODUCTION

$Se_4N_4$ as well as its halogenated derivative such as $Se_3N_2Cl_2$ & $Se_4N_3Cl$ have been used as donor.[1-3] The substitution reaction of $Se_4N_3Cl$ with Urea, Thio-urea have also been reported.[4,5] The complex of $Se_4N_3Br$ with Fe(III) & Co(II) compounds synthesized[6,7] have been investigated. Hence the studies of Ni(II) tetra seleniazide synthesized and characterized are being reported herewith.

## RESULTS AND DISCUSSION

The chemical data, % found (cal.) – Se 80.921 (80.89), N 10.755 (10.751), Ni 3.758 (3.756), Cl 4.545 (4.543) and mol. wt. 1562.0 (1562.6) $gmol^{-1}$, assigned it as $(Se_4N_3)_4NiCl_2$ which is supported by the prominent mass line at m/z 1528 (Fig. 1) for $(Se_4N_3)_4NiCl$ fragment having 35 mass unit less for one Cl atom than that of the mol. wt. of complex. The other prominent mass lines in mass pattern (Fig. 1) at m/z 1194, 598, 413, 339, 149 are subsequently for the fragments:

| S. No. | m/z | Fragment |
|---|---|---|
| 1 | 1194 (M–2) | $(Se_4N_3)_3$–NiCl–$N_2$ |
| 2 | 598 (M+3) | $Se_3N_3$–$NiCl_2$– (Se–N)$_2$ |
| 3 | 413 (M–4) | $Se_4N_3$→Ni |
| 4 | 339 (M+1) | $Se_3N_3$→Ni |
| 5 | 149 (M–3) | Se–N→Ni |

* Corresponding author: sps_jadon@yahoo.co.in

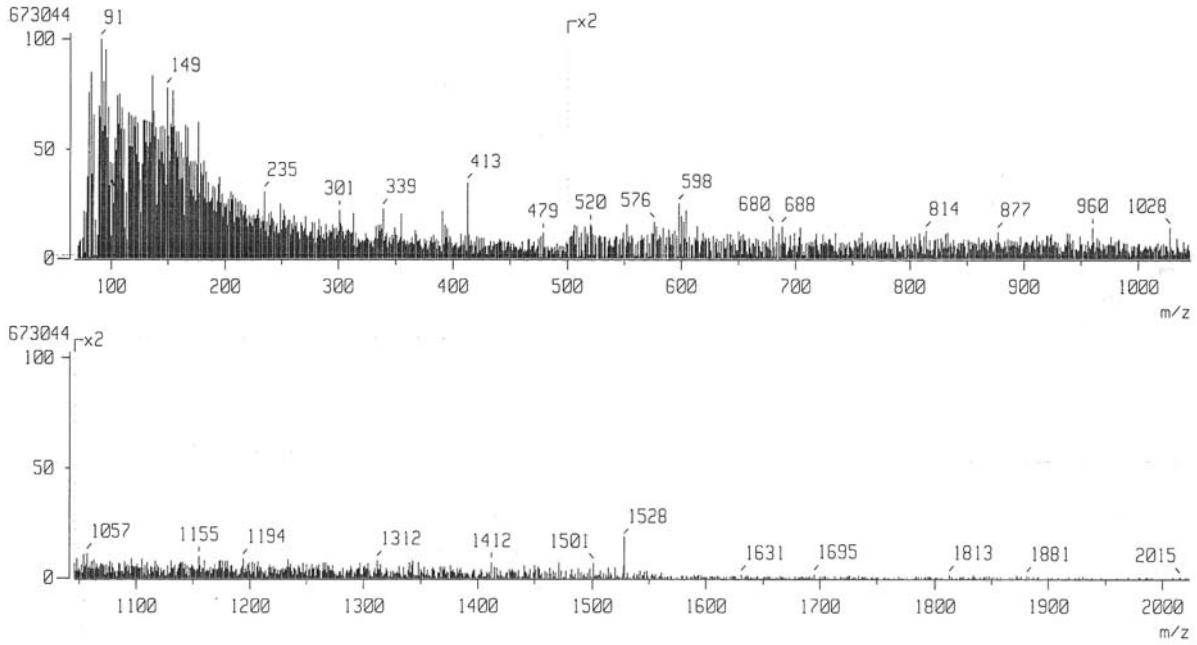


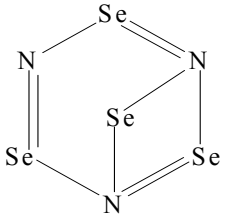

Fig. 1 – Mass spectrum of complex.

Thus the $Se_4N_3Br$ has reacted with $NiCl_2$ (anhydrous) with liberation of $Br_2$ and forming complex $(Se_4N_3)_4NiCl_2$ as below:

$$4Se_4N_3Br + 4NiCl_2 \rightarrow 4(Se_4N_3)_4NiCl_2 + 2Br_2$$

## I.R. and U.V. Spectra

The vibrations in its I.R. spectrum (Table 1) at 670.3(b), 1062.0(trip.,b), 1380.7(d,b), 3414.9(b), are according to Se–N→Ni bands because peaks has broadened & condensed while the other sharp peaks in I.R. spectrum are for the Se-N ring indicating that the $Se_4N_3$ ring, after elimination of bromine, has quadridentatively coordinated to Ni-atom forming a tetrahedral complex. This view is supported by its U.V. spectral data (Table 1) showing the two transitions at 200nm and 275nm, out of which former transition is for the charged transfer transition having the energy 6.2 ev for the ionic environment present in the complex due to $Ni^{2+}$ and $Cl^-$ions. While the later band at 275nm corresponding to 4.5ev energy is due to $p_\pi$–$d_\pi$ transition caused by spin orbital coupling in the complex showing the presence of $Se_4N_3$ ring. This opinion is supported by the value of oscillate strength 'f' being of the order of $10^{-5}$. The low value of band gape energy, $\Delta Eg$ = 0.8455ev & high value of conducting electron, $N_c = 3.2718 \times 10^5$ suggests the good conductive nature of complex. Generally three bands in lower region 8500-30000 $cm^{-1}$ should be found for $d^8$ $Ni^{2+}$ for its square planar geometry. The absence of such bands in lower region indicate that $Ni^{2+}$ complex with $Se_4N_3$ ring is not a square planar but a tetrahedral. During the elimination of bromine $Se_4N_3^+$ has gained one electron from $Br^-$ forming neutral $Se_4N_3$ ring having ring structure as follow:[6]




$Se_4N_3$

*Table 1*

I.R. and Electronic Spectral data of Complex

| I.R. data | | | U.V. data | | | |
|---|---|---|---|---|---|---|
| **Vibrations ($cm^{-1}$)** | **Bands assigned** | **Bands nm ($cm^{-1}$)** | **Transitions** | **f × $10^{-5}$** | **ΔEg (eV)** | **Nc × $10^5$** |
| 670.3 (b) | Se – N →Ni | 200 | C.T. | 2.51608 | 0.8455 | 3.2718 |
| 768.7 | Se – N | (50000) | | | | |
| 1062.0 (trip, b) | Se – N →Ni | 275 | $p_\pi - d_\pi$ | 0.84761 | -- | -- |

*Table 1 (continued)*

| | | |
|---|---|---|
| 1380.7 (d,b) | Se – N →Ni | (36363.63) |
| 1623.3 | Se – N | |
| 2362.0 | Se – N | |
| 2919.3 | Se – N | |
| 3414.9 (b) | Se – N →Ni | |

### E.P.R. and X-Ray spectra

A broad peak of high intensity in E.P.R. spectrum of complex (Fig. 2) indicates its paramagnetic character which is supported by the value of magnetic susceptibility, $\chi_A = 2.6412\times10^{-3}$e.s.u.. The value $g_x=g_y=1.6395 < 2$ shows the presence of vacant 4s and 4p energy shells to accepts the electron pairs from the donor $Se_4N_3$ ring. The value of $g_z= 4.7465 > 2$ explain the presence of the shared electrons for the covalent bonds of $Se_4N_3$ rings. The value of $g_{av} = 3.0498$ & $\mu_{eff} = 2.6412$ are according to the presence of two unpaired electron in '3d' energy shell of Ni-atom inferring divalent nature of Ni. Thus Ni-atom has gained four $e^-$ pairs in 4s-p energy shell from 4 N-atoms of $Se_4N_3$ ring forming the tetrahedral complex due to 4 $sp^3$ hybridization. If complex has octahedral geometry, it must have weak paramagnetism.

Further, to know the geometry, X.R.D. spectrum, recorded in the 2θ range from 0º-80º is interpreted on the basis of available literature. The values of $\sin^2\theta$, miller indices, hkl and inter-planar distance 'd' are calculated (table-2). The value of 'd' closely resembles with the theoretical ones. The axial ratios, calculated as $a_0 = b_0 = 3.9091$ Å & $c_0 = 4.7876$ Å and $\alpha = \beta = 90º$, $\gamma = 120º$ are as $a_0 = b_0 \neq c_0$, $\alpha = \beta = 90º$, $\gamma = 120º$ for hexagonal geometry suggesting that complex has hexagonal geometrical packing with f.c.c. structure.

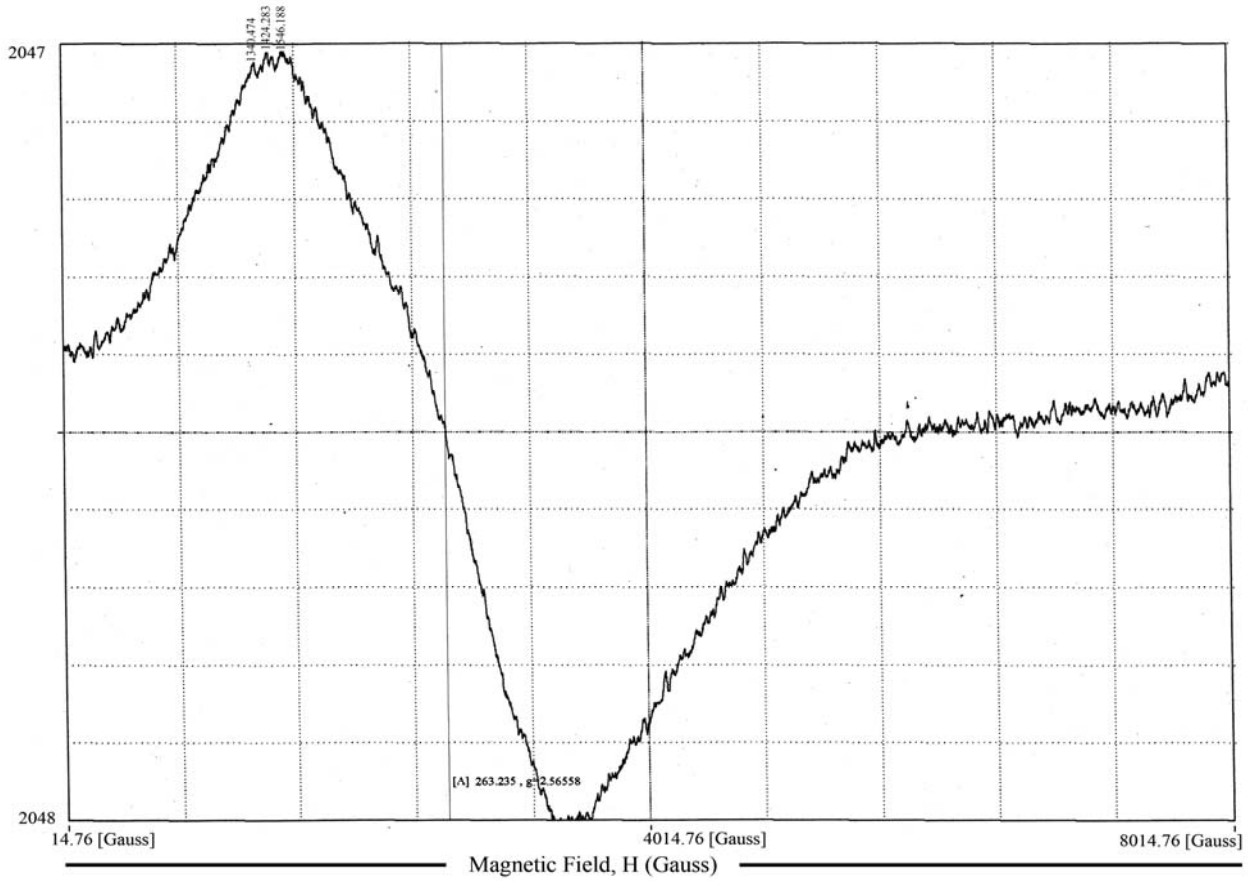



Fig. 2 – E.P.R. Spectrum of complex.

*Table 2*

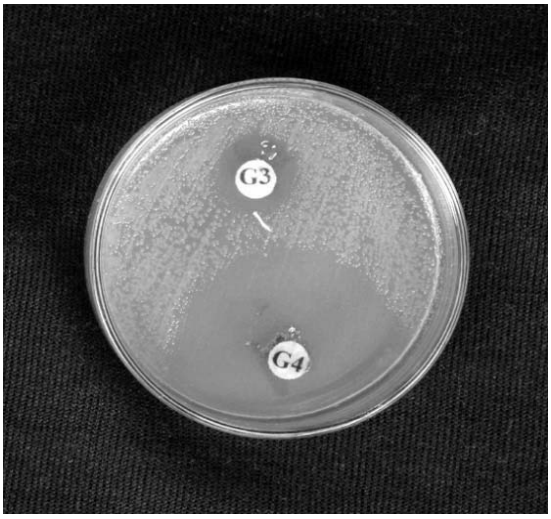
X-ray Diffraction pattern of complex

| S. No. | 2θ (°) | Sin θ | $Sin^2$ θ | $(h^2+k^2+l^2)$ Q | (hkl) | d (Å) obs (theo.) | $d_{hkl}$ |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 1 | 23.18 | 0.20090 | 0.04036 | 1×(0.04036) | (100) | 3.8372 (3.8339) | 3.9091 |
| 2 | 29.32 | 0.25308 | 0.06405 | 2× (0.03202) | (110) | 3.0460 (3.0435) | 2.7641 |
| 3 | 42.99 | 0.36642 | 0.13426 | 3× (0.04475) | (111) | 2.1038 (2.1026) | 2.2569 |
| 4 | 44.80 | 0.38107 | 0.14521 | 4× (0.03630) | (200) | 2.0229 (2.0213) | 1.9545 |
| 5 | 51.09 | 0.43121 | 0.18595 | 5× (0.03719) | (210) | 1.7877 (1.7865) | 1.7482 |
| 6 | 61.26 | 0.50949 | 0.25958 | 6× (0.04326) | (211) | 1.5130 (1.5118) | 1.5959 |
| 7 | 67.65 | 0.55665 | 0.30986 | 8× (0.03873) | (220) | 1.3848 (1.3839) | 1.3820 |
| 8 | 71.93 | 0.58729 | 0.34491 | 9× (0.03832) | (221) | 1.3126 (1.3117) | 1.3030 |
| 9 | 77.48 | 0.62578 | 0.39160 | 10×(0.01031) | (310) | 1.2319 (1.2308) | 1.2361 |

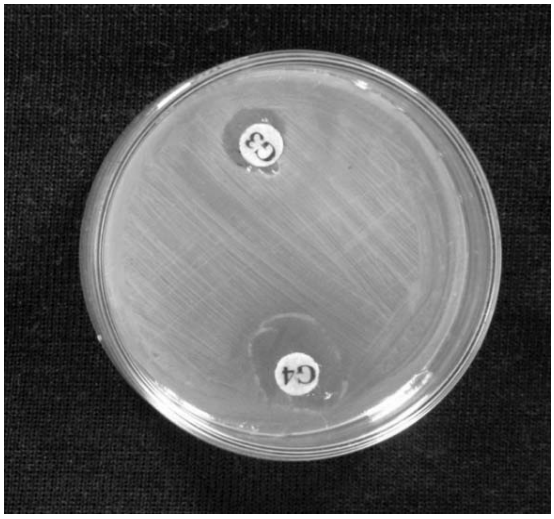
$Q_{av}$ = 0.03889
$a_0 = b_0$ = 3.9091, $c_0$ = 4.7876, α = β = 90°, γ = 120°

## Antibacterial

The complex was treated against E. coli (gram-ve) and S.aureus (gram+ve) bacteria by using in vitro technique. The bloody diarrhea, sever anemia, kidney failure & urinary tract infection are caused by E.coli which entered into human body from the unpasteurized milk. Similarly S. aureus causes mastitis, swelling, skin disease, pneumonia and destroy the cell membrane & tissue. Both bacteria are affected (killed) on treating by the complex (G-4), dichloro Nickel (II) tetra seleniazide up to +14 mm (E. coli) and +36 mm (S. aureus) (Fig. 3). From these results, it is inferred that dichloro Nickel (II) tetra seleniazide may be used as medicine for the disease caused by E. coli & S. aureus.




**S. Aureus (gm +ve) bacteria effect of complex G-4 – Ni(II)**




**E. Coli (gm –ve) bacteria effect of complex G-4 – Ni(II)**

Fig. 3 – Zone inhibition of complexes against S. aureus and E. coli.

## EXPERIMENTAL

Throughout the work, doubly distilled, A.R. grade chemicals were used to prepare $Se_4N_3Br$. $Se_4N_4$ which was prepared by the ammoniation of $SeBr_4$ in benzene, was treated with HBr gas (dry) using $CCl_4$ as a media. To synthesize the complex, $NiCl_2$ and $Se_4N_3Br$ were taken in equimolar ratio and refluxed for 6hr in D.M.F. The grayish black product, formed, was separated, washed subsequently with D.M.F. alcohol and ether, dried and stored in a vacuum desiccators. The qualitative and quantitative analyses were done for the constituents elements. Test for Se, N, Ni & $Cl^-$ was found positive while bromide ($Br^-$) was found absent.

The Mass, I.R., U.V., E.P.R. and X.R.D. spectra were recorded respectively on Jeol SX- 102 (FAB), Shimadzu 8201 PC (4000-400 $cm^{-1}$), Perkin-Elmer-Lambda-15 (200-800 nm), Varian's XE-4 band (at R.T.) Spectrometers and PW 1710, X-Ray Powder diffractometer (Cu $K_\alpha$ as source, $\lambda = 1.5418$ Å).

## CONCLUSIONS

The complex, Dichloro Nickel (II) tetra seleniazide formulated as $(Se_4N_3)_4NiCl_2$ on the basis of the qualitative & quantitative analysis and supported by its mass spectrum consists $Ni^{2+}$ having paramagnetic character with a good conductive nature. The $Se_4N_3$ ring has co-ordinated to Ni-atom through its N-atom possessing tetrahedral structure (Fig. 4) completing quadridantative co-ordination of $Ni^{2+}$ packed in hexagonal geometry. The complex has too much effectiveness to E.coli (gram-ve) & S.aureus (gram+ve) bacteria and may be used as a drug.

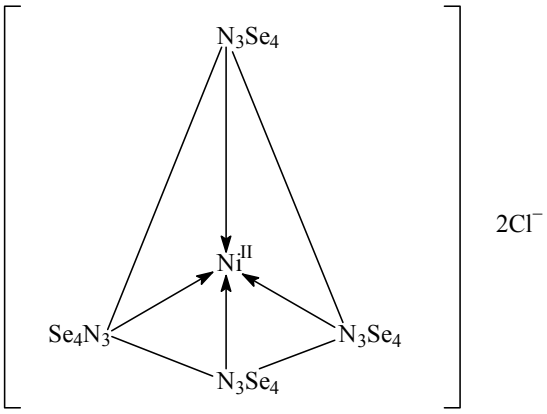



Fig. 4 – Structure of $(Se_4N_3)_4$ $NiCl_2$.

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