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U.V., E.P.R. and X.R.D. Spectral Analysis of Bromo Mn(II) Tetra Seleniazide Complex

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ABSTRACT

The complex of Mn (II) compound with Se_4N_3Br synthesized, was analyzed by U.V., E.P.R. and X.R.D. spectra. From the results, it is evident that the complex is good conductor, having paramagnetic character and orthorhombic geometry.

Key word: Se_4N_3Br, Orthorhombic, Geometry, Magnetic susceptibility.

INTRODUCTION

The complexes of halogenated derivative of Se_4N_4 have been reported [1,2] . The adducts of Se_4N_3Cl with urea, thiourea, hydrazine and phenyl hydrazine have also been synthesized and reported [3,4]. The Mass and I.R. spectral studies Mn (II), Fe(III), Co (II) complex with Se_4N_3Br have been reported by us [5-7]. The present investigations are in continuation of previous work.

EXPERIMENTAL

To synthesis the complex, first of all Se_4N_3Br was prepared by the reaction of dry HBr on Se_4N_4 [8,9] which was prepared by the ammoniation of $SeBr_4$ in benzene. Equimoler ratio of $MnCl_2$ and Se_4N_3Br (1:1) was mixed and refluxed for 6 hrs. in DMF. The grayish product formed, was separated, washed with D.M.F. and alcohol, dried and stored in vacuum desiccators over fused $CaCl_2$.

U.V.,E.P.R, and X.R.D. spectra of complex, were recorded subsequently on Perkin-Elmer-Lambda-15 spectrophotometer (200-800nm) Varian's X-E-4 band spectrometer at room temperature and PW-1710 X-ray power diffractometer using λ =1.5418 Å, CuK_α, as source of radiation in the 2θ range 0^o-80^o.

RESULTS AND DISCUSSION

On the basis of the quantitative ,Mass & I.R. spectral analysis the complex bromo Mn(II) tetra seleniazide has been assigned as $(Se_4N_3Br)_2$ $MnCl_2$. $4H_2O$ (loc. cit). The U.V. spectrum (fig-1) consist three prominent peaks at 200, 222.5, 282.5 nm. Former two bands 200, 222.5, corresponding

6.2, and 5.57ev energy, showing the ionic environment are due to the charge transfer transition in the complex. The last band, 282.5nm is on account of p_π-d_π transition for Se_4N_3 ring present in the complex. This is also confirmed from the frequencies ratios ν_1/ν_2 =1.27 less than 2. The oscillator strength 'f' of the order 10^{-5} (Table-1, Column-3) suggest the low spin Laporte forbidden transition in the complexes which is due to the sharing of electrons in Se_4N_3 ring. The low value of band gape energy, ΔEg (Table-1,Column-4) and high value of number of conducting electrons, N_c of the order of 10^5 expounds the good conductive nature of complex.

A single broad peak of high intensity has occurred in E.P.R. spectrum (fig-2) suggesting the paramagnetic character of complexes which is supported by the low value of magnetic susceptibility, χ_A =1.2352×10^{-3} e.s.u. (Table-1, Column-10). The value of $g_x = g_y$ = 1.9407 (Table-

Table 1: U.V. and E.P.R. Spectral Data of the Complex

U.V. Spectral Data					E.P.R. Spectral Data				
Band Assigned nm (cm^{-1})	Transition	f×10^{-5}	ΔEg (ev)	N_c × 10^5	Magnetic Field H (Gauss)	$g_x = g_y$	g_z	μ_{eff} (B.M.)	χ_A× 10^{-3} (e.s.u.)
1	2	3	4	5	6	7	8	9	10
200 (50,000)	C.T.	3.15659	-	-	3251.90	1.9407	2.0790	1.7215	1.2352
222.5 (44943.82)	C.T.	2.43540	0.3135	0.1299					
282.5 (35398.23)	p_π - d_π	0.46635	0.5920	6.0342					

Table 2: X-ray Diffraction pattern of complex

S. No.	2θ(°)	$Sin^2\theta$	$(h^2 + k^2 + l^2)Q$	hkl	d(A°) Obs (theo)		d_{hkl} (Å)
	1	2	3	4	5		6
1	10.48	0.00834	1×(0.00834)	(100)	8.4408	(8.4339)	8.4404
2	13.81	0.01445	2(0.00725)	(110)	6.4124	(6.4022)	5.9682
3	23.00	0.03974	5(0.007948)	(210)	3.8668	(3.8635)	3.7746
4	27.29	0.05565	6(0.009275)	(211)	3.2679	(3.2663)	3.4457
5	29.21	0.06358	8(0.007947)	(220)	3.0573	(3.0557)	2.9841
6	31.61	0.07418	9(0.008242)	(221)	2.8304	(2.8289)	2.8135
7	40.86	0.12184	14(0.00870)	(321)	2.2085	(2.2066)	2.2557
8	43.11	0.13948	17(0.008204)	(322)	2.06415	(2.0970)	2.04711
9	44.83	0.14539	18(0.008077)	(330)	2.0217	(2.0204)	1.9894
10	51.21	0.18670	22(0.008486)	(332)	1.7838	(1.7826)	1.7995
11	55.57	0.21730	25(0.00869)	(430)	1.6537	(1.6526)	1.6881
12	66.18	0.25897	30(0.00863)	(521)	1.5148	(1.5136)	1.5410
13	64.56	0.28521	34(0.008388)	(530)	1.4434	(1.4423)	1.4475
14	69.62	0.32587	38(0.00857)	(532)	1.3504	(1.3493)	1.3692
15	70.88	0.33622	40(0.008405)	(620)	1.3294	(1.3284)	1.3345

Q_{av} = 0.008343

a_0 = 8.4399Å, b_0 = 18.8723Å, c_0 = 9.2454 Å and $\alpha = \beta = \gamma = 90$

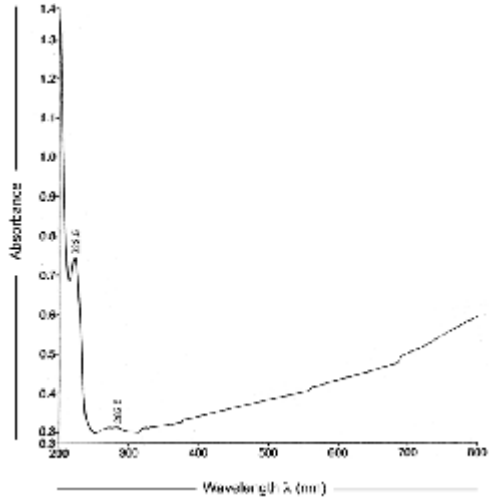

Fig. 1: U.V. spectrum of the Complex

1,Column-7) less than two explore the presence of vacant 3d energy shells in Mn atom to accept the electron pairs form N atom of Se_4N_3 ring, forming coordinate bond. The value of g_z =2.0790 (Table-1,Column-8) greater than two indicate the sharing of electrons i.e. covalent bonding in Se_4N_3 ring of the complex.

Thus bromo Mn(II) tetra seleniazide, $(Se_4N_3Br)_2MnCl_24H_2O$ possess ionic bond due to Mn^{2+} and $2Cl^-$, coordinate bond, Se-N→Mn and Se-N, Se-Br covalent linkage with the $3d^5$ configuration of Mn^{2+} because the value of μ_{eff}=1.7215 is according to the presence of one unpaired electron. Thus the complex formed having quadridentated, coordinated linkage with square planar structure as reported (loc. cit) fig. 4.

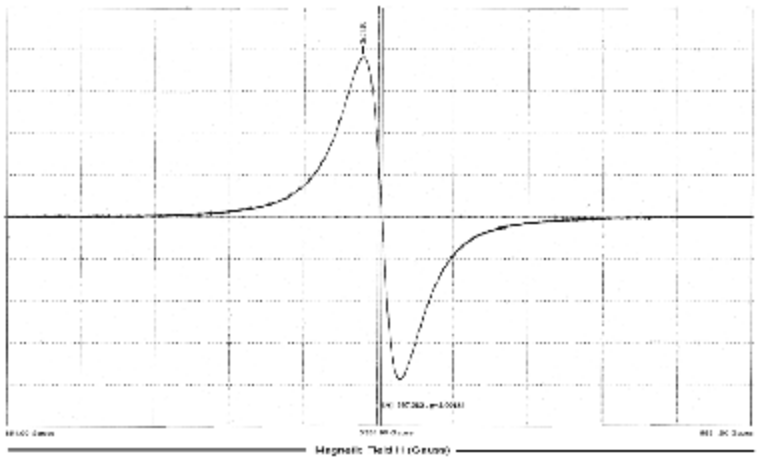

Fig. 2: E.P.R. spectrum of the Complex

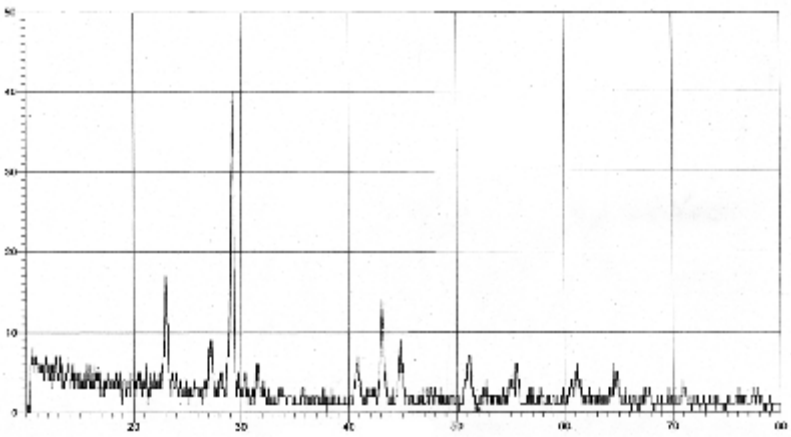

Fig. 3: X.R.D. Pattern of the Complex

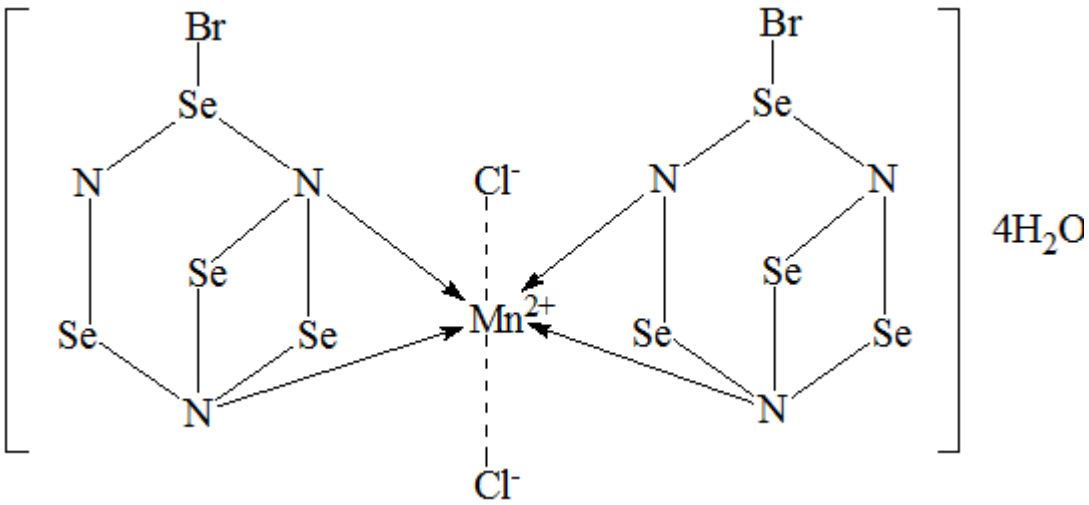

Fig. 4: Proposed Geometrical Structure of Complex, $(Se_4N_3Br)_2MnCl_2.4H_2O$

The X.R.D. pattern of complex recorded in 2θ range 0°-80° (fig-3) possesses a strong and intense peak at 29.21° for the Se_4N_3 ring. From the X-ray pattern the values of $\sin^2\theta$, miller indices, hkl, and inter planar distances 'd', calculated, resembles to the theoretical values (Table-2). From these X.R.D. data, the values of axial ratio and axial angles (Table-2) calculated are corresponding $a_0 \neq b_0 \neq c_0$ and $\alpha=\beta=\gamma=90°$ for the orthorhombohedral geometrical packing of the molecule in the complex.

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