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Synthesis, spectroscopic, and antimicrobial studies on bivalent Nickel(II) and Copper(II)complexes with 2,6-diacetyl pyridine bisthiosemicarbazone

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ABSTRACT

A series of metal complexes of Cu(II) and Ni(II) having the general composition [M(L)X_2] with2,6-diacetyl pyridine bisthiosemicarbazonehas been prepared and characterized by elemental chemical analysis,molar conductance,magnetic susceptibilitymeasurements, andspectral (electronic, IR, EPR, mass) studies. The IR spectral data suggest the involvement of sulphur and azomethane nitrogen incoordination to the central metal ion. On the basis of spectral studies, an octahedral geometry has been assigned for Ni(II) complexesbut a tetragonal geometry for Cu(II) complexes. The free ligand and its metal complexes have been tested in vitro against anumber of microorganisms in order to assess their antimicrobial properties.

Keywords: 2,6diacetyl pyridine bisthiosemicarbazone, azomethanes, antifungal activities, antimicrobial activities.

INTRODUCTION

The chemistry of thiosemicarbazones has received considerableattention in view of their variable bonding modes,promising biological implications, structural diversity, andion-sensing ability [1–3]. They have been used as drugs andare reported to possess a wide variety of biological activitiesagainst bacteria, fungi, and certain type of tumors andthey are also a usefulmodel for bioinorganic processes [4, 5].As regards biological implications,thiosemicarbazone complexeshave been intensively investigated for antiviral, anticancer,antitumoral, antimicrobial, antiamoebic, and anti-inflammatory activities. The inhibitory action is attributeddue to their chelating properties [6–16]. The activity of thesecompounds is strongly dependent upon the nature of theheteroatomic ring and the position of attachment to the ringas well as the form of thiosemicarbazone moiety [17]. Theseare studied extensively due to their flexibility, their selectivityand sensitivity towards the central metal atom, structuraland similarities withnatural biological substances, due to thepresence of imine group (−N=CH−) which imparts the biologicalactivity [18].In view of the above applications, the present workrelates to the synthesis, spectroscopic, and antimicrobialstudies of Cu(II) and Ni(II) complexes with 2,6 diacetyl pyridine bisthiosemicarbazone.

EXPERIMENTALSECTION

Materials

All the chemicals used were of Anala R grade and procuredfrom Sigma-Aldrich and Fluka. Metal salts were purchasedfrom E. Merck and used as received.

Synthesis of ligand(L)

Hot ethanolic solution of thiosemicarbazide (1.82 g,0.02mol) and ethanolic solution of2,6diacetylpyridine (2.1 g, 0.01mol)were mixed in the presence of few drops of conc.HCl withconstant stirring. This mixture was refluxed at 60–70^{0}Cfor 3 hours. The completion of the reaction was confirmedby the TLC. The reaction mass was degassed on a rotatory evaporator, over a water bath. The degassed reaction masson cooling gives cream-colored crystals. It was filtered,washed with cold EtOH, and dried under vacuum overP_4O_{10}, (yield 65%, mp 164◦C) [found: C 42.7; H 4.91; N 31.37; S 20.5, $C_{11}H_{15}N_7S_2$(For atomic mass calcd. 309; C 2.75; H 4.87; N 31.7%)].

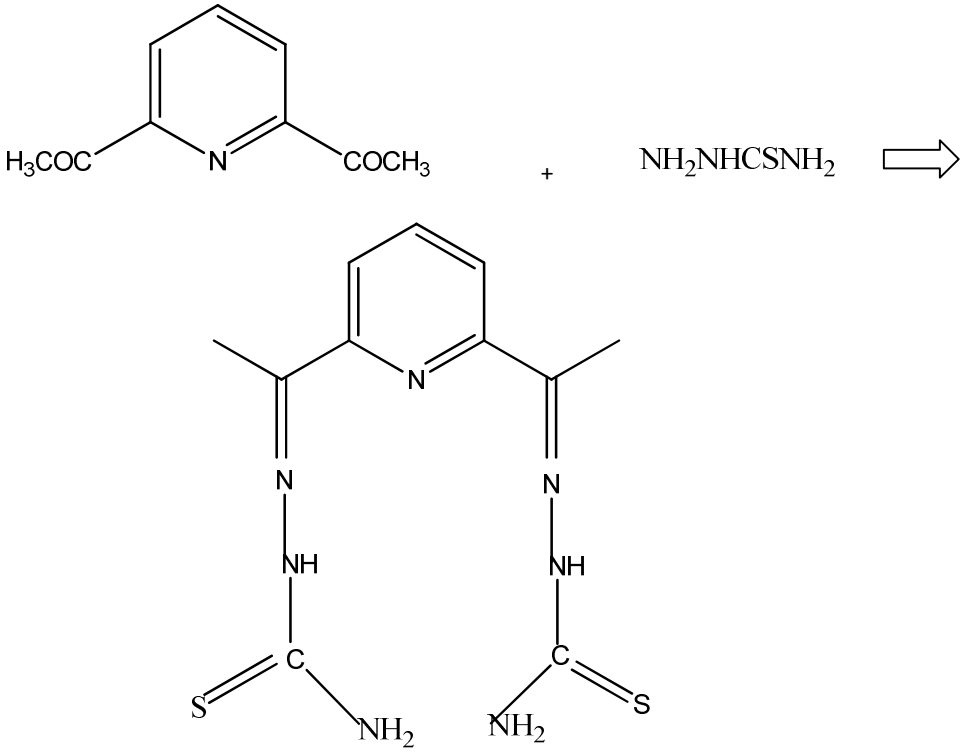

Figure 1: Synthesis and structure of ligand

Synthesis of complexes

20 ml of hot ethanolicsolution of corresponding metal salts(0.01mol) was mixed with hot ethanolic solution of the ligand (0.01mol). The mixture was refluxed for3-4 hours at 50–60◦C. On cooling the contents, thecoloredcomplex separated out in each case. It was filtered andwashed with 50% ethanol and dried under vacuum over P_4O_{10}. Purity of the complexes was checked by TLC.

Analysis

The C and H were analyzed on Carlo-Erba 1106 elementalanalyzer. The Nitrogen content of the complexes was determinedusing Kjeldahl's method. Molar conductance wasmeasured on the ELICO (CM82T) conductivity bridge.Magneticsusceptibilities were measured at room temperature ona Gouy balance using $CuSO_4 \cdot 5H_2O$ as callibrant. Diamagneticcorrections were made by using Pascal's constants. Electronicimpact mass spectrum was recorded on Jeol, JMS-DX-303 mass spectrometer. IR spectra (KBr) were recordedon FTIR spectrum BX-II spectrophotometer. The electronicspectra were recorded in DMSO on Shimadzu UVmini-1240spectrophotometer. EPR spectra of the Cu(II) complexeswere recorded as polycrystalline sample at room temperatureE4-EPR spectrometer using the DPPH as the g-marker. Themolecular weights of complexes were determined cryoscopicallyin benzene.

RESULTS AND DISCUSSION

The complexes were synthesized by reacting ligand with themetal ions in 1:1 molar ratio in ethanolic medium. Theligand behaves as tetradentate coordinate through sulphurand nitrogen donor atoms (Figure 2). All the Nickel(II) andcopper(II) complexes are paramagnetic in nature. The analyticaldata, magnetic susceptibility, and spectral analysisagree well with the proposed composition of formed complexes.All the complexes have shown good solubility in allthe common organic solvents, but they were found insolublein ether, water, acetone, and benzene. The molar conductanceof the complexes in DMF lies in the range of 10–20$\Omega^{-1}cm^2mol^{-1}$ indicating their nonelectrolytic behavior.Thus, the complexes may be formulated as $[M(L)X_2]$ (whereM = Ni(II), Cu(II); L =2,6diacetyl pyridinethiosemicarbazone; X =Cl^-, NO_3^- , and CH_3COO^-).

Table 1: Analytical data for the ligand and its Ni(II) and Cu(II) complexes

CompoundsAtomic mass Yield Color Mp (^{0}C)Analysisfound(calcd.)μeff found (calcd)(%) (BM) C H N M
$C_{11}H_{15}N_7S_2$ ligand (L)308(309) 65 cream 165 42.7 4.87 31.7 - - (42.8)(4.85)(31.37)
$[Ni(L)Cl_2]$ 438(439) 66 brown 282 30.01 3.4 22.2 13.4 2.82 (30.01)(3.42)(22.42)(13.43)
[Ni(L)(NO3)2] 492(493) 70 Dark 290 26.75 3.01 25.52 12.14 2.94 brown(26.77)(3.03)(25.55)(12.17)
[Ni(L)(CH3COO)2] 489(487) 67 brown 28436.94 4.2920.10 12.34 2.93 (36.96)(4.31) (20.12)(12.32)
[Cu(L)Cl2] 442(444) 72 Green 177 29.71 3.39 22.0514.40 1.93 (29.73) (3.37)(22.07) (14.41)
[Cu(L)(NO3)2] 496(497) 66 Green181 26.51 3.00 25.3112.831.96 (26.55) (3.01) (25.35) (12.87)
[Cu(L)(CH3COO)2]] 442(443) 63light 185 40.62 4.7122.1014.40 1.99 Green (40.63) (4.74)(22.12) (14.44)

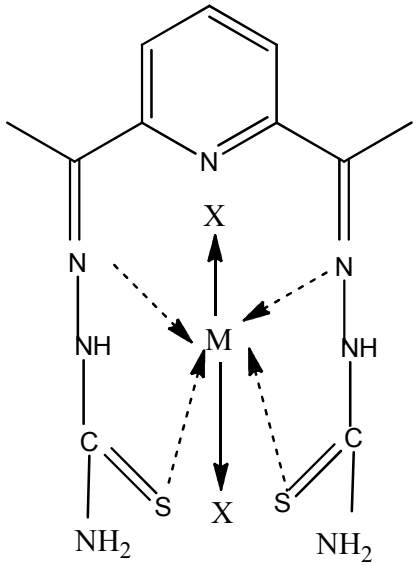

Figure: suggested structure of the complexes

Mass spectrum

The electronic impact mass spectrum of the ligand shows a molecular ion (M^+) peak at m/z = 309 amu corresponding to species $[C_{11}H_{15}N_7S_2]^+$, which confirms the proposed formula. It also shows series of peaks at 16, 60, 76, 89, 116, 179, 216, 245, 273, and 309 amu, corresponding to various fragments. The intensities of these peaks give the idea of the stabilities of the fragments.

Magnetic susceptibility

The observed magnetic moments of Ni(II) and Cu(II) complexes are given in Table 1. The best summary of the results on the magnetic behavior of nickel and copper compounds was given by Figgis and Nyholm [24]. The observed values of magnetic moment for complexes are generally diagnostic of the coordination geometry about the metal ion. Ni(II) has the electronic configuration $3d^8$ and should exhibit a magnetic moment higher than that expected for two unpaired electrons in octahedral (2.8–3.2 BM) and tetrahedral (3.4–4.2 BM) complexes, whereas its square planar complexes would be diamagnetic. The magnetic moment observed for the Ni(II) complexes lies in the range of 2.89– 2.95BM which is consistent with the octahedral stereochemistry of the complexes. Roomtemperature magnetic moment of the Cu(II) complexes lies in the range of 1.92–1.98 BM, corresponding to one unpaired electron. Whatsoever the geometry of Cu(II) is, its complexes always showmagneticmomentcorresponding to one unpaired electron.

Infrared spectra

The assignments of the significant IR spectral bands of ligand and itsmetal complexes are presented in Table 2. In principle, the ligand can exhibit thione-thioltautomerism since it contains a thioamide−NH−C=S functional group.ν(S−H) band at 2565 cm^{-1} is absent in the IR spectrum of ligand but ν(N−H) band at ca.3237 $cm^{-1}$is present, indicating that in the solid state, the ligand remains as the thione tautomer. The position of ν(C=N) band of the thiosemicarbazone appeared at 1608 $cm^{-1}$is shifted towards lower wave number in the complexes indicating coordination via the azomethane nitrogen [25, 26]. This is also confirmed by the appearance of bands in the range of 459–485 cm^{-1}, this has been assigned to the ν(M−N) [27]. A strong band found at 1106 cm^{-1} is due to the ν(N−N) group of the thiosemicarbazone. The position of this band is shifted towards higher wave number in the spectra of complexes. It is due to the increase in the bond strength, which again confirms the coordination via the azomethane nitrogen. The band appearing at ca. 837 $cm^{-1}$$\nu$(C=S) in the IR spectrum of ligand is shifted towards lower wave number. It indicates that thionesulphur coordinates to the metal ion [28]. Thus, it may be concluded that the ligand behaves as tetradentate chelating agent coordinating through azomethane nitrogen and thiolatesulphur [29].

Table 2: Important infrared spectral bands (cm^{-1}) and their assignments

Compounds	ASSIGNMENT				
	ν(N−H)	ν(N−N)	*N*(C=N)	ν(C=S)	ν(M−N)
Ligand (L)	3237	1106	1608	837	—
$[Ni(L)Cl_2]$	3260	1125	1570	816	479
[Ni(L)(NO	3272	1128	1595	825	465
$[Ni(L)(CH_3COO)_2]$	3255	1123	1585	815	459
$[Cu(L)_2Cl_2]$	3250	1124	1560	810	485
$[Cu(L)(NO_3)_2]$	3261	1123	1596	818	460
$[Cu(L)_2(CH_3COO)_2$	3264	1125	1590	820	475

Anions

The presence of bands at 1457-1412, 1320-1299, and 1078-1012 cm^{-1}, in the IR spectra of the metal complexes of Ni(II)and Cu(II), suggests that both nitrate groups are coordinatedto the central metal ion in a unidentate fashion. Inthe IR spectra of chloro complexes, bands corresponding toν(M−Cl) are observed at 345-320 cm^{-1}indicating the presenceof M−Cl bond. The IR spectra of Ni(II) and Cu(II)of acetato complexes show the medium intensity bands at1620-1619 and 1332-1321 cm^{-1}, assigned to νa(C−O) andνs(C−O), respectively. The difference between these two frequenciesis 287 cm^{-1}, which is greater than that for uncoordinatedacetate ion by 143 $cm^{-1}$and that for bidentateacetate ion by 217 cm^{-1}. It is strongly supported that bothacetate ions are coordinated to the metal ion in a unidentatefashion [30–32].

Electronic spectra

Nickel(II) complexes

The electronic spectra of Ni(II) complexes display three absorption bands (Table 3) in the ranges of 9870-9337 cm^{-1}, 14577-14124 cm^{-1}, and 25700-24100 cm^{-1}. The ground state nickel(II) in an octahedral coordination is ^3A_2g. Thus, these bands may be assigned to three spin-allowed transitions: $^3A_2g(F) \rightarrow {}^3T_2g(F)(\nu_1)$, $^3A_2g(F) \rightarrow {}^3T_1(F)(\nu_2)$ and $^3A_2g\ (F) \rightarrow {}^3T_1g(P)\ (\nu_3)$, respectively. The position of bands indicates that the complexes have six coordinated octahedral geometries [33]. Various ligand field parameters were calculated for the Ni(II) complexes and listed in Table 3. The values of Dq and B were calculated by using Orgel diagram. The ratio ν_1/ν_2 was considered for the calculation of B. The Nephelauxetic parameter β was readily obtained by using the relation: β = B(complex)/B(free

ion), where B(free ion) for Ni(II) is 1041 cm^{-1}. The β values lying in the range of 0.58– 0.61 indicate the appreciable covalent character of metal ligand "σ" bond [34].

Copper(II) complexes

The electronic spectra of Cu(II) complexes display bands in the ranges of 15432-14727 cm^{-1} and 25575-25380 cm^{-1} (Table 3). These bands correspond to the transitions $2B_1g \rightarrow 2A_1g(dx_2-y_2 \rightarrow dz_2)v_1$ and $2B_1g \rightarrow 2B_2g(dx_2y_2 \rightarrow dzy)v_2$,respectively. The third band in the range of 33670- 32570 cm^{-1}may be due to charge transfer. Therefore, the complexes may be considered to possess a tetragonal geometry [35, 36].

Table 3: Electronic spectral bands (cm^{-1}) and ligand field parameters of the complexes

Complex	γmax (cm^{-1})	ε(Lmol^{-1}cm^{-1})	v_2/v_1Dq (cm^{-1})	B(cm^{-1})	β
$[Ni(L)Cl_2]$	9337, 14124, 24100	30, 48, 60	1.5 1018	599	0.58
$[Ni(L)(NO_3)_2]$	9670, 14388, 24570	32, 50, 61	1.5 1054	620	0.60
$[Ni(L)(CH_3COO)_2]$	9870, 14577, 25700	32, 52, 63	1.5 1076	632	0.61
$[Cu(L)Cl_2]$	14727, 25380, 33445	54, 69, 130	— —	—	—
$[Cu(L)(NO_3)_2]$	15432, 25575, 33670	55, 71, 135	— —	—	—
$[Cu(L)(CH_3COO)_2]$	15290, 25380, 32570	53, 67, 130	— —	—	—

Electronic paramagnetic spectra

Room-temperature EPR spectra of Cu(II) complexes wererecorded as polycrystalline sample, on X band at frequencyof 9.1GHz under the magnetic-field strength of 3000G. Theanalysis of spectra gives $g_{\|} = -2.25-2.10$, $g\perp = 2.14-2.03$(Table 4). The observed $g_{\|}$values for the complexes are lessthan 2.3 in agreement with the covalent character of themetal ligand bond. The trend $g_{\|} > g| > 2.0023$ observed forthe complexes indicates that unpaired electron is localized indx_2-y_2 orbital of the Cu(II) ion and the spectral features are acharacteristic of axial symmetry. Thus, a tetragonal geometryis confirmed for the aforesaid complexes [37].$G = (g_{\|} - 2)/(g\perp - 2)$, which measures the exchange interactionbetween the metal centers in a polycrystalline solid,has been calculated. According toHathaway [38] if G >4, theexchange interaction is negligible, but G <4 indicates considerableexchange interaction in the solid complexes. Thecomplexes reported in this paper, given the "G" value, are <4 indicating the exchange interaction in solid complexes.

Table 4: EPR spectral data of the Cu(II) complexes

Complexes	$g_{\|}$	$g\perp$	g_{iso}	G
$[Cu(L)Cl_2]$	2.10	2.03	2.05	3.34
$[Cu(L)(NO_3)_2]$	2.25	2.14	2.17	1.79
$[Cu(L)(CH_3COO)_2)]$	2.23	2.12	2.16	1.92

Table 5: Antibacterial screening data of the ligand and its Ni(II) and Cu(II) complexes

Compounds	Diameter of inhibition zone (mm) (conc. in $\mu$$gml^{-1}$)					
	Bacillus macerans			*Pseudomonas striata*		
	250	125	63.5	250	125	63.5
Ligand($C_{11}H_{15}N_7S_2$)	16	11	—	10	—	—
$[Ni(L)Cl_2]$	22	16	—	20	14	8
$[Ni(L)(NO_3)_2]$	25	19	10	16	12	7
$[Ni(L)(CH_3COO)_2]$	18	10	—	15	9	—
$[Cu(L)Cl_2]$	32	25	11	16	8	—
$[Cu(L)(NO_3)_2]$	28	16	10	18	12	9
$[Cu(L)(CH_3COO)_2]$	28	19	12	15	8	—
Streptomycin(standard)	35	26	14	28	20	12

Antibacterial screening

The antibacterial activity of the ligand and its metal complexes were tested by using paper disc diffusion method [19–21] against *Bacillus macerans*(gram-positive) and *Pseudomonas striata*(gram-negative). Nutrient agar medium was prepared by using peptone, beef extract, NaCl, agar-agar, and distilled water. The test compounds in measured quantities were dissolved in DMF to get concentrations of 250, 125, and 63.5 ppm of compounds. Twenty five milliliter nutrient agar media (NA) was poured in each Petri plates. After solidification, 0.1mL of test bacteria spread over the medium using a spreader. The discs of Whatmann no. 1 filter paper having the diameter 5.00 mm, each containing 1.5mg cm−1 of compounds, were placed at four equidistant places at a distance of 2 cm from the

center in the inoculated Petri plates. Filter paper disc treated with DMF served as control and Streptomycin used as a standard drug. All determination was made in duplicate for each of the compounds. An average of two independent readings for each compound was recorded. These Petri plates were kept in refrigerator for 24 hours for prediffusion. Finally, Petri plates were incubated for 26–30 hours 28 ± 2◦C. The zone of inhibition was calculated in millimeters carefully.

Antifungal screening

The preliminary fungitoxicity screening of the compounds at different concentrations was performed in vitro against the test fungi, *R.bataticola*, *A.alternata*and *F.Odum*by the food poison technique [22, 23]. Stock solutions of compounds were prepared by dissolving the compounds in DMF. Chlorothalonil was used as a commercial fungicide and DMF served as a means of control. Potato dextrose agar medium was prepared by using potato, dextrose, agar-agar, and distilled water. Appropriate quantities of the compounds in DMF were added to potato dextrose agar medium in order to get concentrations of 250, 125, 62.5 ppm of compound in the medium. The medium was poured into a set of two Petri plates under aseptic conditions in a laminar flow hood. When the medium in the plates was solidified, mycelial discs of 0.5 cm in diameter-cut from the periphery of the 7-day old culture and were aseptically inoculated upside down in the centre of the Petri plates. These treated Petri plates were incubated at 26 ± 1◦C until fungal growth in the control Petri plates was almost complete. Themycelial growth of fungi (mm) in each petriplate was measured diametrically and growth inhibition (I) was calculated using the formula:

$$I(\%) = (C-T)/C \times 100, IC = (I-CF)/100CF \times 100, \quad (1)$$

where CF = (90-Co)/x 100, 90 is the diameter (mm) of the petri plates, and Co is the growth of the fungus (mm) in control.

Table 6: Antifungal screening data of the ligand and its Ni(II) and Cu(II) complexes

Compounds Fungal inhibition (%) (conc. Inμgml^{-1})									
RhizoctoniabatatiolaAlternaria alternate						*Fusariumodum*			
250	125	63.5	250	125	63.5	250	125	63.5	
Ligand($C_{11}H_{15}N_7S_2$)	50.2	29.3	11.2	56.2	30.2	11.2	48.2	22.0	—
[Ni(L)Cl_2]	58.0	40.3	14.0	61.2	36.1	15.0	49.2	28.0	—
[Ni(L)$(NO_3)_2$]	52.2	32.1	12.2	57.0	34.2	12.0	51.0	23.4	11.2
[Ni(L)$(CH_3COO)_2$]	61.0	35.0	17.3	63.2	45.2	18.4	54.3	28.0	12.3
[Cu(L)Cl_2]	76.3	48.0	35.0	79.0	48.0	22.0	65.0	32.0	14.0
[Cu(L)$(NO_3)_2$	67.0	49.2	26.0	64.2	38.0	18.0	62.0	34.2	16.2
[Cu(L)$(CH_3COO)_2$]	70.1	45.3	28.0	59.3	33.0	12.0	62.2	30.0	12.2
Chlorothalonil (standard)	90.0	76.6	49.0	98.0	80.0	46.0	89.0	74.0	42.2

Antimicrobial screening

The antimicrobial screening data show that the compoundsexhibit antimicrobial properties, and it is important to notethat the metal chelates exhibit more inhibitory effects thanthe parent ligands. From Table 5 it is clear that the zoneof inhibition is much larger for metal complexes againstthe gram-positive bacteria (*Bacillus macerans*) and gramnegativebacteria (*Pseudomonas striata*). The increased activityof the metal chelates can be explained on the basis ofchelation theory [39]. It is known that chelation tends tomake the ligand act as more powerful and potent bactericidalagents, thus killing more of the bacteria than the ligand.It is observed that, in a complex, the positive charge of themetal is partially shared with the donor atoms present in theligands, and there may be π-electron delocalization over thewhole chelating [39]. This increases the lipophilic characterof the metal chelate and favours its permeation through thelipoid layer of the bacterial membranes.There are other factorswhich also increase the activity, which are solubility, conductivity and bond length between the metal and the ligand.The results of fungicidal screening (Table 6) show thatCu(II) and Ni(II) complexes were highly active than the freeligand against phytopathogenic fungi, *Rhizoctonia bataticola*,6 Bioinorganic Chemistry and Applications*Alternariaalternata*, and *Fusariumodum*. The mode of action may involve the formation of a hydrogen bond throughthe azomethane nitrogen atom with the active centers ofthe cell constituents, resulting in interference with the normalcell process. The variation in the effectiveness of differentcompounds against different organisms depends eitheron the impermeability of the cells of the microbes or the differencein ribosomes of microbial cells [40,41,42]. It has also beenproposed that concentration plays a vital role in increasingthe degree of inhibition; as the concentration increases, theactivity increases.

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