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Address:-Ashok Yakkaldevi 258/34, Raviwar Peth, Solapur - 413 005 Maharashtra, India
Cell : 9595 359 435, Ph No: 02172372010 Email: ayisrj@yahoo.in Website: www.isrj.net

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ORIGINAL ARTICLE

SPECTROSCOPIC AND BIOLOGICAL STUDIES OF SOME NEW COORDINATION COMPOUNDS OF TIN (II) AND (IV) WITH SEMICARBAZONES AND THIOSEMICARBAZONES.

JITENDRA KUMAR RAWAT , HARI SHANKAR YADAV , A.K. VARSHNEY AND S. VARSHNEY

Department of Chemistry, University of Rajasthan Jaipur, INDIA

Abstract:

The present paper is a report on the synthesis of some new tin (II) and tin (IV) complexes by the reaction of stannous chloride and dimethyltin dichloride with semicarbazones and thiosemicarbazones using tetrahydrofuran(THF) as reaction medium. Semicarbazones and thiosemicarbazones used in these studies are synthesized by the condensation of 1-acetyl-2-naphthol, 2-acetyl-1-naphathol, 2-acetyl-5-methyl furan, 2-acetyl-4-methyl thiophene and 2-acetyl-naphthalene with semicarbazide/ thiosemicarbazide. The bonding pattern and geometry of tin complexes are characterized by spectroscopic evidences. The ligands and their metal complexes have been screened for antitubercular, antibacterial and antifungal activities and are found quite active in this respect. Plant growth activity has also been evaluated and is found negative growth.

KEYWORDS:

Semicarbazones, Thiosemicarbazones, Antibacterial activities, Spectroscopic evidence

INTRODUCTION

Schiff base ligands are able to coordinate metals through imine nitrogen or another group, usually linked to aldehyde or ketone. These ligands represent the most widely utilized classes of ligand in metal coordination chemistry (1-3). Their complexes find many important catalytic applications to various types of polymerization. The real impetus towards developing the coordination chemistry of these potential ligands was probably provided by the remarkable, antitumer, antiviral and antimalarial activity observed for some of these derivatives which have been shown to be related to their complexing ability (4-6). Semicarbazones and thiosemicarbazones are also similar and most important nitrogen oxygen / sulphur donor ligands because of them act as neutral or charged ligand moieties (7-8). Therefore, the present paper is an effort to describe structural characterization of some new compounds tin (II) & (IV) with semicarbazones and thiosemicarbazones.

EXPERIMENTAL

Analytical methods and physical measurements

Tin was estimated gravimetrically as SnO2. Nitrogen and sulphur were estimated by Kjeldahl's method and Messenger's method, respectively. The IR spectra were recorded on FTIR spectrophotometer using a model A-8400 S, Shimadzu in KBr pellets. The electronic spectra were taken with a Toshniwal spectrophotometer. 1H, 13C & 119Sn NMR spectra were recorded on JEOL AL- 300 spectrometer. Molar conductance measurements were made in anhydrous dimethyl formamide at 36±1°C using a model 305

systronics conductivity bridge. Molecular weight determinations were carried out by the Rast Method (9-10).

Synthesis of ligands

Semicarbazones and thiosemicarbazones were synthesized by the condensation of aldehydes/ketones viz. 1-acetyl-2-naphthol, 2-acetyl-1-naphathol, 2-acetyl-5-methyl furan, 2-acetyl-4-methyl thiophene and 2-acetyl-naphthalene with semicarbazide/thiosemicarbazide in 1:1 molar ratio using absolute alcohol as the reaction medium. The mixture was heated on a water bath for about half an hour and then allowed to cool at room temperature. The crystals that separated out were recrystallized from the same solvent (11-13). Their physical properties and analysis have been recorded in Table -1.

Synthesis of Tin (II) and Tin (IV) complexes

Tin (II) complexes were prepared by the reaction of stannous chloride with semicarbazones and thiosemicarbazones in 1:1 molar ratio in dry tetrahydrofuran as reaction medium under an oxygen free nitrogen atmosphere. The resulting solution was stirred on magnetic stirrer for two hours. The solvent was removed and the product was finally dried in vacuo. (14-16).

Tin (IV) complexes were prepared by the reaction of dimethyltin dichloride with above mentioned semicarbazones and thiosemicarbazones in 1:1 molar ratio in dry benzene(17). The mixture was refluxed on refluxing column for one hour. The solvent was removed and the product was finally dried in vacuo at 40-50°C. Their physical properties and analysis have been recorded in Table-2.

RESULTS AND DISCUSSION

The reactions of stannous chloride /dimethyltin dichloride with, these ligands are as follows:

$$SnCl_2 + L^1H \longrightarrow SnCl_2.L^1H$$

$$Me_2SnCl_2 + L^1H \longrightarrow Me_2SnCl_2.L^1H$$

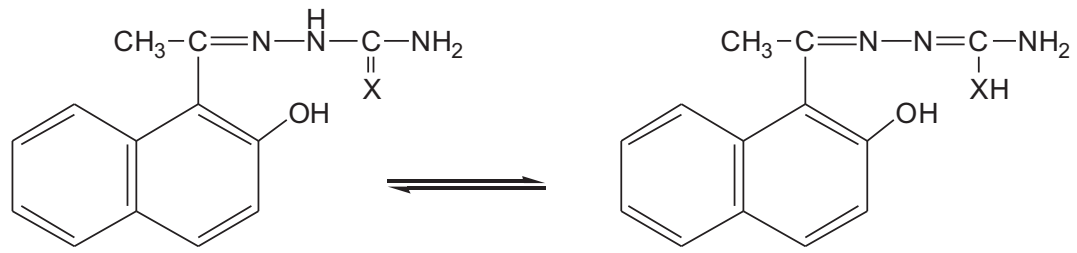
The resulting complexes are obtained as coloured solids which are soluble in DMF and DMSO. These complexes are sensitive to moisture.

Electronic spectra:

In the electronic spectra of the ligands, two bands were observed at ~ 338 nm and ~ 410 nm. The band, at ~ 338 nm was due to the - transition within the aromatic ring and it is shifted to ~ 350 nm in the spectra of tin complexes. Another band at ~ 410 nm was due to n- transition within the azomethine group (>C = N) which is shifted to ~ 415 nm in the spectra of complexes.

Infrared Spectra:

In the IR- spectra of ligands in solution, bands due to $\sqrt{}$ C(=O) or $\sqrt{}$ C(=S) and $\sqrt{}$ N(H), which are observed in the IR spectra in KBr captics, do not appear. This may be attributed to the existence of two tautomeric forms, viz. an amide or thioamide in the solid state and hydroxylimine or thiolimine in solution as shown below:



The ligands show a strong and sharp band at ~ 1620 cm-1 which is assignable to √C=N12. This band shifts to lower frequency and appears at ~ 1630 cm-1 in the spectra of complex. The ligands exhibit NH2 band at ~ 3440 cm-1 which remains unchanged in the spectra of the complex. A band in the region ~ 3350-2850 cm-1 due to ~NH vibration remains unaffected reflecting the non involvement of NH group in coordination. A band at ~ 1700 ±10 cm-1 due to √ C(=O) in the ligands shifts to higher frequency on complex formation. Another band at ~ 1050±15 cm-1 due to √ C(=S) in the ligands shifts to lower frequency in the spectra of complexes which indicate the participation of ketonic oxygen / sulphur in bond formation. Presence for some new bands of √Sn-O, √Sn-N[13], √Sn-S[14] and √Sn-Cl[15] at 550- 525 cm^{-1}, 425-405 cm-1, 325±20 cm-1 and 280±15 cm-1 in the spectra of complex also supports the bonding of oxygen, sulphur and nitrogen to tin atom(18).

1H NMR spectra:

1H NMR spectra of ligands and their complexes have been recorded in d6- DMSO or CDC13 using TMS as internal standard. The proton signals (in ppm) of ligands and their corresponding complexes are as follows:-

S.N.	Ligands/ Complexes	Proton signal (in δ ppm) in ligands	Proton signal (in δ ppm) in complexes
1.	NH	10.09	10.22
2.	HC = N |	8.45	8.55
3.	NH_2	3.50	3.50
4.	Aromatic proton	7.85-6.98	7.85-6.98

In the proton NMR spectra of the ligands , a broad signal at 3.50 ppm due to NH_2 protons remain almost unchanged in the spectra of tin complexes, which clearly indicates the non involvement of this group in complexation. A sharp signal at 8.45 ppm was observed due to H-C=N group[16] and this shifted downfield (8.55 ppm) in the spectra of complexes due to the coordination of azomethine nitrogen to the metal atom. The aromatic protons show signals at 7.85-6.98 ppm in the spectra of ligands which remain unchanged in the spectra of tin complexes. The ligands also exhibited NH proton signal at 10.09 ppm, appeared in the complexes, showing the involvement of adjacent O or S in bonding with the tin atom. As a result of which the NH becomes less shielded.

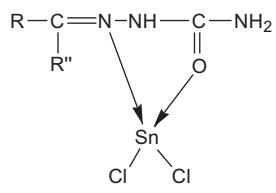
^{13}C NMR spectra:

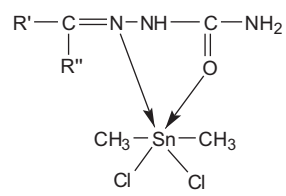
The ^{13}C NMR spectra of ligands and their corresponding tin complexes have been recorded. The signals due to carbon atoms attached to azomethine groups in the ligands appear at 178.0 and 172.2 ppm. However, in the spectra of the corresponding tin complexes, these signals appear at 168.6 and 165.7 ppm. The shifting of azomethine (>C=N) carbon signal in the spectra of complexes as compared to the ligands clearly indicated that the azomethine moiety has been involved in coordination with the tin atom.

^{119}Sn NMR spectra:

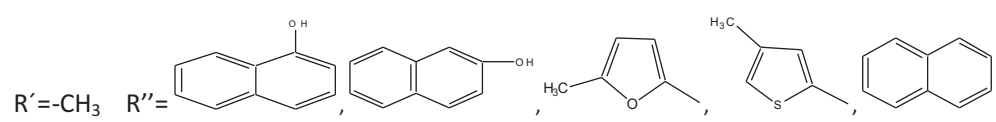
^{119}Sn NMR spectra of Tin (IV) complexes also gave sharp signals at -250 ppm & -252 ppm which can be attributed to an octahedral six coordinated geometry shown in Fig. B (19-21).The complexes give a sharp signal at δ-5.78 ppm in ^{119}Sn NMR spectra, which is below the reported values for tricoordinated hydrated tin (II) chloride. Threfere, four coordinate environment around tin atom can be proposed for the

resulting complexes.





(A) (B)



Antibacterial Activity:

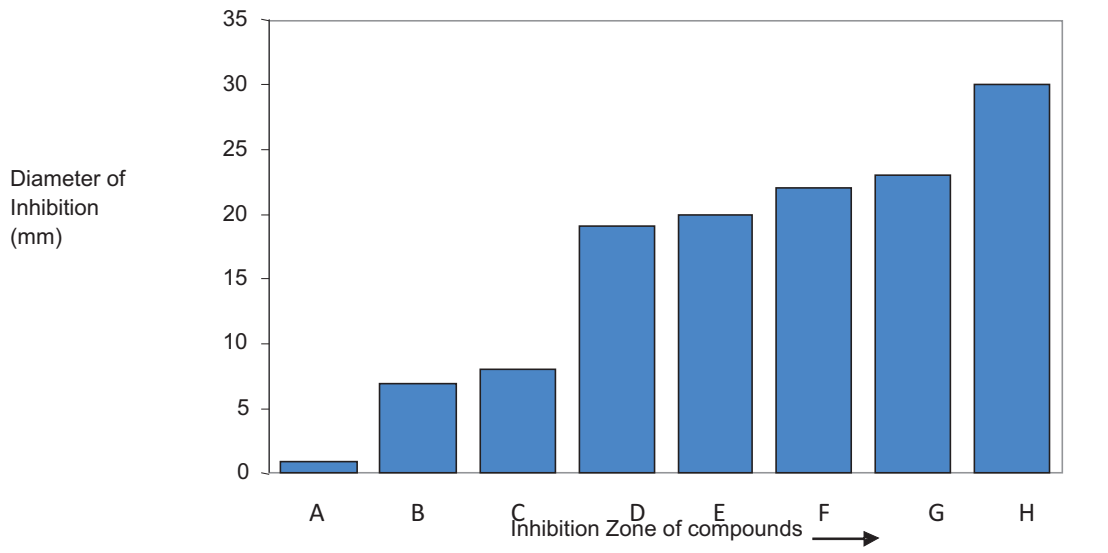
All the synthesized ligand and their correspond Tin (II) and Tin (iv) complexes were screened in vitro for their antibacterial activity against Gram-negative (E.Coli and P. Milamilis) and Gram-positive (B.Thuringiensis and S.Aureus) bacterial strains using paper disc plate method. The nutrient agar medium (peptone, beef extract, NaCl and agar-agar) and 5mm diameter papar disc of Whatman filter paper No.1 were used. The compounds under investigation were dissolved in methanol to give concentration of 500 and 1,000 ppm. The plates were incubated for 48 h at 28±2°c and inhibition zone around each disc was measured (22-23). The antibacterial activity displayed by various compound is shown in Table-3.

Antifungal Activity:

The antifungal activity was evaluated against A .flavus, F.oxysporum, A.niger and R.phaseoli by the agar palate technique. Solutions of the compounds in different concentrations in DMF were then mixed with the medium (24). The linear growth of the fungus was recorded by measuring the diameters of the fungus colony in the control and test plates, respectively as shown inTable-4(25-26).

Antitubercular Activity:

The YT agar medium was prepared using 1% yeast extract, 2% trypton, 1.5% agar, 1% NaC1 in 250 mL distilled water by maintaining the pH of the medium at 7 using 10% NaOH solution This medium was then sterilized by autoclaving at 120°C for 15 mm. After cooling to 50°C the medium was poured into 85 mm diameter Petri dishes (approx. 25 mL each) and setting aside at 37°C. After a few hours, Petri dishes were stored in the cold room at 4°C. Freshly prepared 100 mL of inoculum of Micobacterium smegmatis was spread in each dish and 20 mL (100 mg) solution of the test compound was poured in each well. 20 mL DMSO was used as negative control. The plates were kept at 37°C for 24 h after which the diameter of the inhibition zones was measured (Bar diagram). Ciprofloxacin was used as a standard reference drug for comparison (27-28).



Plant Growth Activity:

Tin (II) and Tin (IV) complexes were tested for their plant growth regulating activity against gram plant. The observations for percent germination and normal seedling were recorded on the 4th and 8th days. The seedlings, which possessed the ability to develop into fully normal and healthy plants, were considered as normal seedlings.

The seeds were treated with physiologically active concentration of the plant growth regulators solution for six h at room temperature and drying them to the original moisture level by a hot air circulating oven. After that, uniform size seeds were placed on Whatman no. 1 filter paper lying in the glass petri plates. Each petri plate has 15 seeds placed at equidistance. The filter papers were moistened with fresh solutions of required concentrations. The concentrations of the plant growth regulators used were 1,5,10, and 25 ppm (29-31).

Table. Effect of ligands and tin (IV) complexes on the concentrations of the plant growth regulators used was 1, 5, 10, 20 and 25 ppm.

Group	Treatment	Plant Graowth Regulators (ppm)	PGIZ(mm)		PGAI(mm)		Plant Graowth %
A	Control	0	0	0	0	0	0
B	L^1H	1	0.0	0.0	0.00	0.0	00
C	L^2H	5	42	0.0	0.72	0.0	58 (-)
D	L^3H	10	41	0.0	0.68	0.0	56 (-)
E	L^4H	20	39	0.0	0.60	0.0	54 (-)
F	L^5H	25	28	0.0	0.42	0.0	47 (-)
A	Control	0	0	0	0	0	0
B	$Me_2Sn(L^1)Cl_2$	1	13	0.0	0.81	0.0	90 (-)
C	$Me_2Sn(L^1)_2$	5	19	0.0	0.87	0.0	94 (-)
D	$Me_2Sn(L^2)Cl_2$	10	15	0.0	0.79	0.0	80 (-)
E	$Me_2Sn(L^3)Cl_2$	20	21	0.0	0.95	0.0	96 (-)
F	$Me_2Sn(L^4)Cl_2$	25	18	0.0	0.78	0.0	86 (-)

Dose.1, 5,10,20,25 ppm

PGIZ= Plant Growth Inhibition Zone (diameter in mm)

PGAI= Plant Growth Activity Index (diameter in mm)

CONCLUSION:

The synthesized derivatives were characterized and identified on the basis of physical and spectral data. These play a vital role as bioligands in biological systems. Nitrogen and sulfur/oxygen containing azomethine compounds are well recognized bioligands. It has been found that the activity of the metals is attained through the formation of complexes with different bioligands and the thermodynamic and kinetic properties of the complexes govern the mode of biological action. Antibacterial Activity, Antifungal Activity and Antitubercular Activity were found that metal complexes are much more active than the ligands. Plant growth Activity found negative because complex behave like toxin.

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Table -1: Analytical and physical properties of l igands

Ligands	Colour & State	M.P.	Analysis (%)			M.Wt. Found (Calcd.)
			C Found (Calcd.)	N Found (Calcd.)	S Found (Calcd.)	
l-Acetyl-2-naphthol semicarbazone (L'H) ($C_{13}H_{13}N_3O_2$)	Yellow Solid	192	64.19 (64.38)	17.27 (17.91)	-	243.26 (245.71)
l-Acetyl-2-naphthol thiosemicarbazone (L^2H) ($C_{13}H_{13}N_3OS$)	White Solid	205	60.21 (61.19)	16.20 (16.82)	12.36 (12.71)	259.32 (260.91)
2-Acetyl-l-naphthol semicarbazone (L^3H) ($C_{13}H_{13}N_3O_2$)	Pale Yellow Shiny	192	64.19 (64.38)	17.27 (17.91)	-	242.6 (243.71)
2-Acetyl-l-naphthol thiosemicarbazone (L^4H) ($C_{13}H_{13}N_3OS$)	Yellow P owder	205	60.21 (61.19)	16.20 (16.82)	12.36 (12.71)	259.32 (260.91)
2-Acetyl-5-methyl furan semicarbazone (L^5H) ($C_8H_{13}N_3O_2$)	Orange Shiny	182	53.03 (53.78)	23.19 (23.42)	-	181.19 (182.12)
2-Acetyl-5-methyl furan thiocarbazone (L^6H) ($C_8H_{13}N_3OS$)	Yellowish O range	190	48.71 (49.02)	21.30 (21.42)	16.26 (16.79)	197.26 (198.81)
2-Acetyl-4-methyi thiophene semi carbazone (L^7H) ($C_7H_nN_3OS$)	Orange	178	48.71 (49.91)	21.30 (21.42)	16.26 (16.79)	197.26 (198.71)
2-Acetyl-4-methyl thiophene thiosemi carbazone (L^8H) ($C_7HuN_3S_2$)	Yellow	191	45.04 (45.68)	19.70 (19.98)	21.02 (21.81)	213.33 (214.66)
2-Acetyl-naphtalene semicarbazone (L^9H) ($Ci_3H_{23}N_3O$)	White	188	69.29 (69.92)	18.49 (18.91)		227.26 (229.16)
2-Acetyl-naphtalene thiosemicarbazone ($L^{10}H$) ($C_{13}H_{23}N_3S$)	White Crystal	196	65.58 (66.12)	18.21	18.21 (8.52)	243.33 (245.71)

Table 2: Some new coordination compounds of Stannous chloride and dimethyltin with semicarbazones and thiosemicarbazones.

Reactant	Ligand	Molar ratio	Yield %	Product	Colour and State	M.P. C°	Mol. wt. found (Calcd.)	% Analysis found (Calcd.)		
								Sn Found (Calcd.)	N Found (Calcd.)	S Found (Calcd.)
$SnCl_2$	$C_{13}H_{13}N_3O_2$	1:1	78	$C_{13}H_{13}N_3O_2\ SnCl_2$	Yellow	290	484.95	12.16 (12.28)	3.11 (3.27)	-
$SnCl_2$	$C_{13}H_{13}N_3OS$	1:1	74	$C_{13}H_{13}N_3OS\ SnCl_2$	Cream	200	468.89	10.06 (10.29)	3.08 (3.31)	5.27 (5.71)
$SnCl_2$	$C_{13}H_{13}N_3O_2$	1:1	72	$C_{13}H_{13}N_3O_2\ SnCl_2$	Brown	240	484.95	12.08 (12.96)	3.01 (3.13)	-
$SnCl_2$	$C_{13}H_{13}N_3OS$	1:1	76	$C_{13}H_{13}N_3OS\ SnCl_2$	Yellow	170	468.89	10.08 (10.32)	3.14 (3.37)	5.26 (5.41)
$SnCl_2$	$C_8H_{11}N_3O_2$	1:1	74	$C_8H_{11}N_3O_2\ SnCl_2$	Orange	240	406.82	05.04 (05.18)	3.16 (3.41)	-
$SnCl_2$	$C_8H_{11}N_3OS$	1:1	73	$C_8H_{11}N_3OS\ SnCl_2$	Yellowish orange	160	422.89	04.26 (04.57)	3.08 (3.22)	5.39 (5.52)
$(CH_3)_2SnCl_2$	$C_8H_{11}N_3OS$	1:1	77	$C_8H_{11}N_3OS(CH_3)_2SnCl_2$	Yellow	250	416.94	4.92 (5.09)	2.14 (2.47)	5.42 (5.91)
$(CH_3)_2SnCl_2$	$C_8H_{11}N3S_2$	1:1	71	$C_8H_{11}N3S_2(CH_3)_2SnCl_2$	Orange	150	433.01	4.83 (5.02)	2.09 (2.14)	6.15 (6.88)
$(CH_3)_2SnCl_2$	$C_{13}H_{13}N_3S$	1:1	79	$C_{13}H_{13}N_3S(CH_3)_2SnCl_2$	White	210	463.01	4.11 (4.39)	2.18 (2.71)	4.18 (4.56)
$(CH_3)_2SnCl_2$	$C_{13}H_{13}N_3O$	1:1	73	$C_{13}H_{13}N_3O(CH_3)_2SnCl_2$	White	150	445.94	4.19 (4.33)	2.01 (2.34)	-

C and H analysis are found satisfactory

Table 3: Antibacterial activity screening data of azomethine derivatives of ligand and their tin (II) & tin (IV) complexes. Inhibition (%) after 48h (conc. in ppm)

Compounds	*Staphylococcus aureus* (+)		*Proteus milamilis* (-)		*Escherichia coli* (-)		*Bacillus thuringiensis* (+)	
	50 ppm	100 ppm	50 ppm	100 ppm	50 ppm	100 ppm	50 ppm	100 ppm
$C_{13}H_{13}N_3O_2$	8	9	7	10	6	8	7	12
$C_{13}H_{13}N_3OS$	10	12	10	14	7	9	8	10
$C_8H_{11}N_3O_2$	8	11	9	12	9	10	9	10
$C_8H_{11}N_3S_3$	11	12	12	14	10	12	11	14
$C_{13}H_{13}N_3S_3$	14	16	9	11	8	11	12	13
$SnCl_2$. $C_{13}H_{13}N_3O_2$	12	14	11	13	7	10	14	15
$SnCl_2$. $C_{13}H_{13}N_3OS$	15	17	13	16	11	14	15	17
$SnCl_2$ $C_8H_{11}N_3O_2$	9	12	9	10	12	14	17	18
$(CH_3)_2$ $SnCl_2$. $C_{13}H_{13}N_3O_2$	15	19	15	17	16	18	14	16
$(CH_3)_2$ $SnCl_2$. $C_{13}H_{13}N_3OS$	16	18	14	16	18	19	17	19

Table 4: Antifungal screening data of azomethine derivatives of ligand and their tin (II) & tin (IV) complexes. Inhibition (%) after 72h concentration 50,100 and 200 ppm at 25±2°C

Compounds	Diameter of Inhibition Zone (mm)											
	Organism *Aspergillus flavus*			Organism *Fusarium oxysporum*			Organism *Aspergillus niger*			Organism *Rhizopus phaseoli*		
	50 ppm	**100 ppm**	**200 ppm**	**50 ppm**	**100 ppm**	**200 ppm**	**50 ppm**	**100 ppm**	**200 ppm**	**50 ppm**	**100 ppm**	**200 ppm**
$C_{13}H_{13}N_3O_2$	49	54	60	56	61	71	43	62	77	87	62	82
$C_{13}H_{13}N_3OS$	52	58	61	57	60	72	44	81	81	79	61	56
$C_8H_{11}N_3O_2$	54	64	66	61	71	82	60	78	75	61	76	92
$C_8H_{11}N_3S_3$	29	60	58	39	58	67	61	78	91	67	56	90
$C_{13}H_{13}N_3S_3$	51	62	57	55	59	76	69	82	81	72	63	78
$SnCl_2$. $C_{13}H_{13}N_3O_2$	54	59	63	53	68	69	61	76	71	61	72	74
$SnCl_2$. $C_{13}H_{13}N_3OS$	59	66	71	61	61	81	71	88	74	68	71	68
$SnCl_2$ $C_8H_{11}N_3O_2$	61	71	79	74	69	83	75	90	98	75	74	75
$(CH_3)_2$ $SnCl_2$. $C_{13}H_{13}N_3O_2$	68	89	94	69	79	93	76	94	99	69	96	98
$CH_3)_2$ $SnCl_2$. $C_{13}H_{13}N_3OS$	61	56	75	53	63	74	89	99	91	78	69	91

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