CHAPTER-5

OXIDATION OF 4H-1,4 BENZOTHIAZINES AND PHENOTHIAZINES TO THEIR SULFONES
This chapter deals with the oxidation of 4H-1, 4-benzothiazines and phenothiazines to their sulfone derivatives by 30% hydrogen peroxide in glacial acetic acid using ultrasonic radiations.

The purity of synthesized compounds was checked by thin layer chromatography and structure confirmed by spectral studies as well as other analytical data.
The oxidation of sulfide linkage in 4H-1,4-benzothiazines and phenothiazines to dioxide leads to an interesting class of heterocyclic compounds due to their wide spectrum of pharmacological efficacy\textsuperscript{1-8}. Sulfones also exhibit number of applications in photography, industry etc. Diverse application of these compounds have stimulated our interest to convert benzothiazines and phenothiazines to their sulfones. It is considered worthwhile to study the oxidation behaviour of phenothiazines and 4H-1,4-benzothiazine to investigate the changes in IR spectra caused by the conversion of sulfide linkage into sulfone\textsuperscript{9}.

Detailed literature survey reveals that oxidation of phenothiazines and benzothiazines by various oxidizing agents yield sulfoxides and sulfones. Some of them are able to oxidize phenothiazines to their 5-oxide, while some others are capable of oxidizing only a few phenothiazines to their sulfonyl derivatives. Potassium permagnate in acetone with a small amount of sulphuric acid oxidizes to sulfoxide (45\%) along with small amount of sulfone. However, potassium permagnate oxidizes 10-benzylphenothiazine at its sulfone in acetone
and acetic acid. The oxidation of ethyl 10-phenothiazine carboxylate to its sulfone in quantitatively yield have been reported by potassium permagnate in acetic acid\textsuperscript{10-13}.

Hydrogen peroxide has been widely used for affecting oxidation at heterocyclic sulfur. Hydrogen peroxide in ethanol and ethanol-acetone provides phenothiazines sulfoxides. The oxidation with hydrogen peroxide in ethanol containing hydrochloric acid result in both chlorination and oxidation.

The oxidation with two moles of hydrogen peroxide in alcoholic solution and glacial acetic acid containing sulfuric acid produces S,S-dioxides and sulfones respectively. Anderson et al\textsuperscript{14} have used 30% hydrogen peroxide in methanol and acetic acid for selective oxidation of pharmacologically active phenothiazine derivatives to their corresponding sulfones.

Oxidation behavior of phenothiazines and 1,4-benzothiazines has been thoroughly investigated by Gupta et al\textsuperscript{15}. Potassium permagnate in glacial acetic acid oxidizes benzothiazines also to sulfone accompanied by sulfoxides but their separation is difficult. Therefore oxidation of phenothiazine and 1,4-benzothiazine by hydrogen peroxide in glacial acetic acid has been reported to yield sulfone in high yield\textsuperscript{16-21}. 
EXPERIMENTAL

The melting point of synthesized compounds has not been corrected and their purity was checked by TLC (thin layer of silica gel) in various non-aqueous solvent systems. Infrared (IR) spectra of all the synthesized compounds recorded using KBr from Shimadzu FTIR, Affinity-1. Elemental data obtained from all the synthesized compounds found satisfactory.

1. Synthesis of 4H-1,4-benzothiazines and phenothiazines

Synthesis of 4H-1,4-benzothiazines and phenothiazines used as precursor in the preparation of their sulfones has been reported in chapter 3A and 4 respectively.

2. Synthesis of 4H-1,4-benzothiazine and phenothiazine sulfones

For the synthesis of sulfones, 5 ml of 30% hydrogen peroxide was added to substituted-4H-1,4-benzothiazine / phenothiazine 10 mmol in 15 ml of glacial acetic acid, at room temperature with constant stirring. After complete addition, the contents were heated for 15 minutes. When the color of solution changed to yellow, another 5 ml of 30 % hydrogen peroxide was added and the solution refluxed further for one hour in ultrasound bath. After that, the major portion of the solvent evaporated under reduced pressure and the solution poured into beaker containing
crushed ice. The yellow residue separated out collected and recrystallized from ethanol to get the desired sulfone derivatives (scheme 5.1 and 5.2).

(Scheme: 5.1)

(Scheme: 5.2)

In present investigation following 4H-1,4-benzothiazine/phenothiazine sulfones have been synthesized:

(1). 7-Ethoxy-2-ethoxycarbonyl-3-methyl-4H-1,4-benzothiazine sulfone.

(2). 2-Ethoxycarbonyl-7-methoxy-3-methyl-4H-1,4-benzothiazine sulfone.

(3). 2-Benzoyl-7-methoxy-3-phenyl-4H-1,4-benzothiazine sulfone.
(4).  2- Ethoxycarbonyl-3,7-dimethyl-4H-1,4-benzothiazine sulfone.

(5).  2- Benzoyl-7-methyl-3-phenyl-4H-1,4-benzothiazine sulfone.

(6).  7-Chloro-2-ethoxycarbonyl-3-methyl-4H-1,4-benzothiazine sulfone.

(7).  7-Bromo-1-methylphenothiazine sulfone.

(8).  7-Carboxy-1-methylphenothiazine sulfone.

(9).  1-Methyl-7-nitrophenothiazine sulfone.

(10).  7-Trifluomethyl-1-methylphenothiazine sulfone.

(11).  1-Chloro-7-nitrophenothiazine sulfone.

(12).  7-Carboxy-1-chlorophenothiazine sulfone

Physical and spectral data of the synthesized 4H-1,4-benzothiazine/phenothiazine sulfones:

(1).  **7-Ethoxy-2-ethoxycarbonyl-3-methyl-4H-1,4-benzothiazine sulfone.**

Molecular Formula: $C_{14}H_{17}O_5NS$

Yield: 65%, M.P. 198$^\circ$C
IR (KBr, $\nu_{\text{max}}$, cm$^{-1}$): 3425 (N-H), 1690 (>C=O), 1462, 1350 (C-CH$_3$), 1235, 1030 (C-O-C), 3000 (C-H, aliph.), 1335, 1280, 1245 ($\nu_{\text{asym}}$, SO$_2$), 1164, 1155 ($\nu_{\text{sym}}$, SO$_2$), 555, 525 ($\nu_{\text{bend}}$, SO$_2$).

Anal. Calculated (%) for C$_{14}$H$_{17}$O$_5$NS: C, 54.01; H, 5.46; N, 4.50.
Found (%): C, 54.05; H, 5.45; N, 4.55.

(2) 2- Ethoxycarbonyl-7-methoxy-3- methyl-4H-1,4-benzothiazine sulfone.

Molecular Formula : C$_{13}$H$_{15}$O$_5$N

Yield: 60%, M.P. 169$^\circ$C

IR (KBr, $\nu_{\text{max}}$, cm$^{-1}$): 3338 (N-H), 1692 (>C=O), 1470, 1345 (C-CH$_3$), 1245, 1040 (C-O-C), 1338, 1285, 1249 ($\nu_{\text{asym}}$, SO$_2$), 1166, 1157 ($\nu_{\text{sym}}$, SO$_2$), 560, 530 ($\nu_{\text{bend}}$, SO$_2$).

Anal. Calculated (%) for C$_{13}$H$_{15}$O$_5$NS: C, 52.52; H, 5.05; N, 4.71.
Found (%): C, 52.50; H, 5.10; N, 4.75.
(3) 2-Benzoyl-7-methoxy-3-phenyl-4H-1,4-benzothiazine sulfone.

Molecular Formula: $\text{C}_{22}\text{H}_{17}\text{O}_{4}\text{NS}$

Yield: 78%, M.P. 242\(^\circ\)C

IR (KBr, $\nu_{\text{max}}, \text{cm}^{-1}$): 3390 (N-H), 1670 (>C=O), 1232, 1050 (C-O-C), 860, 822 (adj. 2H in ring), 2930 (C-H, aliph.); 1348, 1295, 1270 ($\nu_{\text{asy}}$, SO$_2$), 1180, 1155 ($\nu_{\text{sym}}$, SO$_2$), 570, 565 ($\nu_{\text{bend}}$, SO$_2$).

Anal. Calculated (%) for $\text{C}_{22}\text{H}_{17}\text{O}_{4}\text{NS}$: C, 64.45; H, 4.34; N, 3.58.

Found (%): C, 64.00; H, 4.32; N, 3.55.

(4) 2-Ethoxycarbonyl-3,7-dimethyl-4H-1,4-benzothiazine sulfone.

Molecular Formula: $\text{C}_{13}\text{H}_{15}\text{O}_{4}\text{NS}$

Yield: 60%, M.P. 240\(^\circ\)C
IR (KBr, $\nu_{\text{max}}$, cm$^{-1}$): 3465 (N-H), 1690 (>C=O), 1470, 1350 (C-CH$_3$), 1240, 1030 (C-O-C), 850, 830 (adj. 2H in ring), 2985 (C-H, aliph.); 1380, 1278, 1260 ($\nu_{\text{asym}}$, SO$_2$), 1155, 1140 ($\nu_{\text{sym}}$, SO$_2$), 560, 535 ($\nu_{\text{bend}}$, SO$_2$).

Anal. Calculated (%) for C$_{13}$H$_{15}$O$_4$NS: C, 55.51; H, 5.33; N, 4.98.
Found (%): C, 55.45; H, 5.35; N, 4.95.

(5) 2- Benzoyl-7-methyl-3-phenyl-4H-1,4-benzothiazine sulfone.

Molecular Formula : C$_{22}$H$_{17}$O$_3$NS

Yield: 60%, M.P. 265$^\circ$C

IR (KBr, $\nu_{\text{max}}$, cm$^{-1}$): 3340 (N-H), 1690 (>C=O), 1475, 1340 (C-CH$_3$), 870, 825 (adj. 2H in ring), 3060 (C-H, Ar); 1350, 1300, 1260 ($\nu_{\text{asym}}$, SO$_2$), 1180, 1152 ($\nu_{\text{sym}}$, SO$_2$), 568, 560 ($\nu_{\text{bend}}$, SO$_2$).

Anal. Calculated (%) for C$_{22}$H$_{17}$O$_3$NS: C, 70.4; H, 4.53; N, 3.73.
Found (%): C, 70.00; H, 4.48; N, 3.70.
(6) **7-Chloro-2-ethoxycarbonyl-3-methyl-4H-1,4-benzothiazine sulfone.**

Molecular Formula : $C_{12}H_{12}O_{4}NSCl$

Yield: 45%, M.P. 260° C

IR (KBr, $\nu_{\text{max}}$, cm$^{-1}$): 3395 (N-H), 1670 (>C=O), 1470, 1350 (C-CH$_3$), 745 (C-Cl), 1250, 1050 (C-O-C), 870, 830 (adj. 2H in ring), 3000 (C-H, aliph.); 1340, 1290, 1260 ($\nu_{\text{asym}, \ SO_2}$), 1178, 1152 ($\nu_{\text{sym}, \ SO_2}$), 568, 562 ($\nu_{\text{bend}, \ SO_2}$).

Anal. Calculated (%) for $C_{12}H_{12}O_{4}NSCl$: C, 47.76; H, 3.98; N, 4.64.

Found (%): C, 47.70; H, 3.90; N, 4.60.

(7) **7-Bromo-1-methylphenothiazine sulfone.**

Molecular Formula : $C_{13}H_{10}NSBrO_{2}$

Yield : 69%, M.P. 250° C
IR (KBr, $\nu_{\text{max}}, \text{cm}^{-1}$): 3400 (N-H), 1495, 1385 (C-H), 770 (C-Br); 1350, 1285, 1265 ($\nu_{\text{asym}, \text{SO}_2}$), 1180, 1152 ($\nu_{\text{sym}, \text{SO}_2}$), 565, 560 ($\nu_{\text{bend}, \text{SO}_2}$).


(8) **7-Carboxy-1-methylphenothiazine sulfone.**

Molecular Formula : $\text{C}_{14}\text{H}_{11}\text{NSO}_4$

![Chemical Structure](image)

Yield : 65%, M.P. 187°C

IR (KBr, $\nu_{\text{max}}, \text{cm}^{-1}$): 3385 (N-H), 1465, 1380 (C-H), 1695 (C=O); 1345, 1290, 1240 ($\nu_{\text{asym}, \text{SO}_2}$), 1180, 1150 ($\nu_{\text{sym}, \text{SO}_2}$), 570, 545 ($\nu_{\text{bend}, \text{SO}_2}$).


(9) **1-Methyl-7-nitrophenothiazine sulfone.**

Molecular Formula : $\text{C}_{13}\text{H}_{10}\text{N}_2\text{SO}_4$

![Chemical Structure](image)
Yield : 67%, M.P. 176°C

IR (KBr, ν_{max}, cm^{-1}): 3350 (N-H), 1540, 1530 (NO_{2}), 1490, 1385 (C-H); 1350, 1295, 1245 (ν_{asym}, SO_{2}), 1177, 1145 (ν_{sym}, SO_{2}), 575, 565 (ν_{bend}, SO_{2}).

Anal. Calculated (%) for: C_{13}H_{10}N_{2}SO_{4}: C, 53.79; H, 3.44; N, 9.65.

Found (%): C, 53.89; H, 3.45; N, 9.68.

(10) **7-Trifluromethyl-1-methylphenothiazine sulfone.**

Molecular Formula : C_{14}H_{10}NSF_{3}O_{2}

Yield : 60%, M.P. 202°C

IR (KBr, ν_{max}, cm^{-1}): 3375 (N-H), 1465, 1375 (C-H), 1335, 1120 (C-F); 1347, 1280, 1240 (ν_{asym}, SO_{2}), 1177, 1145 (ν_{sym}, SO_{2}), 562, 565 (ν_{bend}, SO_{2}).

Anal. Calculated (%) for:C_{14}H_{10}NSF_{3}O_{2}: C, 53.67; H, 3.19; N, 4.47.

Found (%): C, 53.62; H, 3.15; N, 4.45.
(11) 1-Chloro-7-nitrophenothiazine sulfone.

Molecular Formula : \(\text{C}_{12}\text{H}_7\text{N}_2\text{SClO}_4\)

\[
\begin{array}{c}
\text{Cl} \\
\text{H} \\
\text{N} \\
\text{S} \\
\text{O} \\
\text{O} \\
\text{NO}_2
\end{array}
\]

Yield : 71%, M.P. 200\(^0\)C

IR1 (KBr, \(\nu_{\text{max}}, \text{cm}^{-1}\)): 3355 (N-H), 1535, 1530 (NO\(_2\)), 740 (C-Cl); 1348, 1298, 1248 (\(\nu_{\text{asym}}, \text{SO}_2\)), 1175, 1155 (\(\nu_{\text{sym}}, \text{SO}_2\)), 565, 545 (\(\nu_{\text{bend}}, \text{SO}_2\)).

Anal. Calculated (\%) for: \(\text{C}_{12}\text{H}_7\text{N}_2\text{SClO}_4\): C, 46.37; H, 2.25; N, 9.01.

Found (\%): C, 46.80; H, 2.24; N, 8.93.

(12) 7-Carboxy-1-chlorophenothiazine sulfone.

Molecular Formula : \(\text{C}_{13}\text{H}_8\text{NSClO}_4\)

\[
\begin{array}{c}
\text{Cl} \\
\text{H} \\
\text{N} \\
\text{S} \\
\text{O} \\
\text{O} \\
\text{COOH}
\end{array}
\]

Yield : 65%, M.P. 280\(^0\)C
IR (KBr, \( \nu_{\text{max}}, \text{cm}^{-1} \)): 3375 (N-H), 1680 (C=O), 740 (C-Cl); 1348, 1295, 1260 (\( \nu_{\text{asym}} \), SO\(_2\)), 1178, 1152 (\( \nu_{\text{sym}} \), SO\(_2\)), 570, 562 (\( \nu_{\text{bend}} \), SO\(_2\)).

Anal. Calculated (%) for: C\(_{13}\)H\(_8\)NSClO\(_4\): C, 50.40; H, 2.58; N, 4.52.

Found (%): C, 50.35; H, 2.50; N, 4.55.

**SPECTRAL ANALYSIS:**

The oxidation behaviour of benzothiazines and phenothiazines involves the conversion of sulfide linkage into sulfone and provides an opportunity to study the effect of this conversion in infrared spectra.

Infrared spectra of both phenothiazines and benzothiazines sulfones have been investigated both in crystalline state and in carbon tetrachloride solution. Oxidation of phenothiazines and benzothiazines leads to the formation of sulfones and the sulfonyl group itself produce considerable change in the infrared spectrum of the parent compound. The effect of sulfonyl group could be highlighted through spectral studies\(^{22-26}\).
All the synthesized 4H-1,4-benzothiazine sulfone and phenothiazine sulfones exhibit a sharp intense peak in the region 1390-1360 cm\(^{-1}\), 1380-1330 cm\(^{-1}\) in chloroform which can be assigned to the asymmetric stretching mode of the sulfonyl group, while in solid state this absorption band splits into three bands which appear in the region 1375-1340 cm\(^{-1}\), 1320-1295 cm\(^{-1}\) and 1275-1210 cm\(^{-1}\) for the 4H-1,4 benzothiazine sulfone and in phenothiazine sulfones they appear in the region 1395-1360 cm\(^{-1}\) 1360-1280 cm\(^{-1}\) and 1295-1260 cm\(^{-1}\). The asymmetric stretching vibrations in the sulfones are strongly affected on passing from the solution to the crystalline state. The symmetrical stretching vibration \(\nu_{\text{sym}}\) of benzothiazine and phenothiazine sulfones give rise to high intensity doublet and in some cases a broad signal is obtained in potassium bromide disc in the region 1168-1105 cm\(^{-1}\) and 1185-1110 cm\(^{-1}\), whereas in solution it appears at 1165-1105 cm\(^{-1}\) and 1180-1105 cm\(^{-1}\). Hence, these frequencies are slightly affected by the aggregation. The banding vibrations \(\nu_{\text{bend}}\) in sulfur dioxide exhibit medium absorption bands in low frequencies region 576-510 cm\(^{-1}\). These absorption bands appear either as a doublet or as a singlet bands with an inflection, which have been compared to fundamental vibrations in sulfuryl chloride appearing below 600 cm\(^{-1}\). Analogously, the band in the region 585-510 cm\(^{-1}\) and 595-520 cm\(^{-1}\) in 4H-1,4- benzothiazine and phenothiazine
sulfones can be ascribed to sulfur dioxide scissoring (A) and rocking (B) vibrations\textsuperscript{27-33}.

\begin{center}
\begin{tikzpicture}
  \node (A) at (0,0) {S \hspace{1cm} O \hspace{1cm} O \hspace{1cm} S};
  \node (B) at (2.5,0) {S \hspace{1cm} O \hspace{1cm} O \hspace{1cm} S};

  \draw [->] (A) -- (O);
  \draw [->] (O) -- (B);

  \node (A) at (1.25,0.5) {(A)};
  \node (B) at (3.75,0.5) {(B)};
\end{tikzpicture}
\end{center}

The vibrations belonging to substituent’s can provide information about the electron donor and electron acceptor abilities of the heteroaromatic rings. In the present investigation these vibrations, both in sulfones and in their parent benzothiazines and phenothiazines, have been examined. The vibrational frequency corresponding to each substituent is shifted to higher frequency in both types of sulfones.

A sharp band due to C=O stretching vibrations in 4H-1,4-benzothiazine has shifted to higher frequencies in the corresponding sulfones. This shifting to higher frequency is assigned due to an increased electron accepting ability of sulfones as compared to the parent nucleus.

The lone pair of electrons at nitrogen have withdrawn more effectively towards the ring, it conjugates less effectively with carbonyl group and results in higher carbonyl frequencies. The -I effect of the
SO$_2$ group combines with mesomeric effect which operates in the same direction, and hinders the conjugation of lone pair of electrons at nitrogen with carbonyl group.

A sharp intense band appearing in the region 3450-3380 cm$^{-1}$ in 4H-1,4 benzothiazines due to free N-H stretching vibrations is shifted to higher frequency region 3460-3425 cm$^{-1}$ in the corresponding sulfones. In the spectra of phenothiazine sulfones, the absorption band due to N-H stretching vibrations appears at the same frequency region 3460-3350 cm$^{-1}$ as in phenothiazines.

**THIN LAYER CHROMATOGRAPHIC STUDIES OF 4H-1,4-BENZOTHIAZINE / PHENOTHIAZINE SULFONES**

Only a few references deals with TLC of 4H-1,4-benzothiazine / phenothiazine sulfones. In the present investigation we have developed a procedure for identification and separation of sulfone derivatives even in micro-grms by thin layer chromatographic method using various non-aqueous solvent systems. Relative and absolute Rf values have been determined which may provide a tool for the separation and detection of sulphone derivatives. A very small quantity i.e. 0.1 ug of sulfone in 100 ug phenothiazines can be detected when chromatographed together.
Experimental

Standard thin layer chromatographic equipment (plates, atomizer, fixed thickness applicators with and developing tanks) obtained from M/s Adair Dutt and Co., New Delhi have been used.

Petroleum ether (m.p. 40-60°C), carbon tetrachloride and acetone of analytical grade and benzene dried over sodium wire have been used. Silica gel G was Merck material.

Chromatographic Procedure

The same procedure has been adopted as successes in chapter 3A.

Results and Discussion

Those developing solvents are considered best which gave the best shaped and tailless spots with remarkable resolution. For this purpose many solvent combinations were examined to developed the chromatogram on silica gel G and the best combinations obtained are:

System $S_1 = \text{Acetone: petroleum ether (40-60°C)} \ (30:70 \ V/V)$

System $S_2 = \text{Acetone: Carbon tetrachloride (30-70°C)} \ V/V$

System $S_3 = \text{Acetone: Benzene (25:75 \ V/V)}$
Benzene, acetone and carbon tetrachloride with or without water were unable to yield good separation. This could be ascribed either to tailing of the spots or the too lowering of Rf values in particular solvent.

It has been concluded from Rf values given in tables 5 and 6 that the 4H-1,4-benzothiazine and phenothiazine sulfones have lower Rf values than their corresponding precursor 4H-1,4-benzothiazine and phenothiazine in all solvent systems. When working with activated layer and non-aqueous solvent system, it was observed that thin layer chromatography Rf values are not reproducible. Therefore 4H-1,4-benzo-thiazine and phenothiazine were selected as standard and spotted along with the other compounds which are under investigation, on all plates of a series. The mean Rf value for 4H-1,4-benzothiazine and phenothiazine was calculated from the value obtained from many different plates and mean value for 4H-1,4-benzothiazine and phenothiazine was regarded as fixed one. To get corrected Rf values of the sulfone, the difference between Rf values of 4H-1,4-benzothiazine and phenothiazine observed on an arbitrary plate and the fixed value was used as correction factor and then correction factor which could be either positive or negative was added to Rf value of the sulfone of that plate.
It had been noted that the Rf values were lower on subsequent plates in all developing solvents. Therefore, all the solvents had to be changed after every two plates development. The lowering in Rf Values on subsequent plates is attributed to the selective evaporation of acetone from the developing tanks. The reproducibility in Rf values is the essential factor in the identification of samples by Rf values and the most crucial factor in attaining reproducibility was securing a constant degree of saturation prior to inserting the plates. The developed in unsaturated 4H-1,4-benzothiazine and phenothiazine developing tanks did not give reproducible Rf values, but on the other hand, plates developed in saturated tanks provided Rf values with normal accepted tolerance (±0.05 Rf units).

It has been concluded from various attempts made that the plates stored in the laboratory instead on calcium chloride and development at room temperature did not give reproducible Rf values. Therefore, the chromatogram must be developed under standard conditions in order to get reproducibility. All the Rf values reported in table 3 and 4 were obtained under condition described in the procedure.
Thin layer Chromatographic data for benzothiazine sulfones

![Chemical structure of benzothiazine sulfone](image)

Table No. 5

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<th>Spot Colour</th>
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Thin layer Chromatographic data for Phenothiazine sulfones

![Chemical Structure](image)

**Table No. 6**

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<td>CF₃</td>
<td>202</td>
<td>58 (39)</td>
</tr>
<tr>
<td>5</td>
<td>Cl</td>
<td>NO₂</td>
<td>200</td>
<td>75 (56)</td>
</tr>
<tr>
<td>6</td>
<td>Cl</td>
<td>COOH</td>
<td>280</td>
<td>61 (49)</td>
</tr>
</tbody>
</table>

*The values given in brackets refer to sulfones.*
REFERENCES


LIST OF PUBLICATIONS

FROM THESIS


OTHERS


2. Synthesis, Characterization and Antimicrobial Activity of 1,2,4-Triazole/Isatin Schiff Bases and There Mn(II), Co (II) Complexes (Communicated).
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