termine the conditions appropriate for the necessary uptake of nutrients by plants. Various factors such as soil bulk density, soil moisture content, pH and CaCO₃ content have been found to affect the diffusion of metallic ions in soils.²⁴

Rowell et al. studied self-diffusion of sodium in soil and found an increase in the diffusion coefficient of ²²Na with an increase in moisture content. Recently Staunton and Nye reported that the ²²Na diffusion was independent of moisture content and bulk density. The present study was conducted to test the effect of soil bulk density and moisture content on ²²Na self-diffusion in silt loam soil of pH 8.5.

The diffusion coefficient (D) was measured by the method of Rowell et al. using the following equation of Schofield and Graham-Bryce for the analysis:

\[ Q_s / Q_w = 1 / 4L (D.t/\pi)^{1/2} \]

where \( Q_s \) is the amount of ions which had diffused from active to non-active soil of the two half cells \( Q_w \) is one half of the total ²²Na in soil system, \( L \) is the length of cell in cm and \( t \) is the diffusion time (sec).

The results presented in Table 1 indicate significant relationship between soil bulk density and moisture content. At 10% moisture level, as the bulk density increased from 1.25 to 1.6 g/cm³, due to compaction the pores were probably filled giving continuous liquid phase by bringing water films into close contact. On further increasing bulk density to 1.75 g/cm³ the soil particles were pushed much closer together. Hence the diffusing ions were forced to move around the particles which increased the tortuosity of diffusion path, resulting in decrease in diffusion coefficient at 1.75 g/cm³. The ²²Na ion-soil particle interaction was minimum at soil bulk density of 1.6 g/cm³.

Further, the value of ²²Na self-diffusion coefficient increased with increase in the moisture from 10% to 20% (Table 1). When moisture increases, the thickness of water films around soil particles increases reducing the chemical interaction of ²²Na ions with soil particles. Due to higher moisture content, the continuity of liquid phase increases resulting in increased diffusion coefficient.

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### Table 1 ²²Na self-diffusion coefficients.

<table>
<thead>
<tr>
<th>Effect of bulk density at 10% moisture</th>
<th>Effect of moisture content at 1.75 g/cm³ soil bulk density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil bulk density (g/cm³)</td>
<td>D x 10⁷(cm²/sec)</td>
</tr>
<tr>
<td>-------------------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>1.25</td>
<td>3.4 ± 0.3</td>
</tr>
<tr>
<td>1.45</td>
<td>12.1 ± 0.9</td>
</tr>
<tr>
<td>1.60</td>
<td>19.7 ± 1.3</td>
</tr>
<tr>
<td>1.75</td>
<td>17.8 ± 1.2</td>
</tr>
</tbody>
</table>

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**Catalytic decomposition of N₂O on La₂MnMO₆**

(M = Ni, Cu and Zn)

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The structure of a double perovskite allows stabilization of transition metal ions in their unusual oxidation states. This has stimulated considerable interest in identifying oxide systems crystallizing in this structure to understand the relation between solid state properties and catalytic behaviour. The activity of La₂MnNiO₆ in the catalytic decomposition of 2-propanol has been reported earlier. The catalytic activity of the compounds La₂MnMO₆ (M = Ni, Cu and Zn) towards the decomposition of N₂O is briefly discussed in this note.

The compounds have been synthesized by the solid state reaction between the component oxalate mixtures, by heating them in appropriate proportions in a Pt crucible, in air, at 960°C for 28 hr, with intermittent grindings. The compounds have been characterized by x-ray analysis, conductivity measurements using a two
probe cell and magnetic measurements on a Guoy balance. The decomposition has been carried-out on an all-glass static reactor provided with a recirculation assembly. The temperature range employed is 350–480°C at initial pressures of 50 and 200 Torr of N₂O. The kinetic parameters have been evaluated using the corresponding no/strong inhibition rate equations, as shown below respectively.

\[-dP_{N_2O}/dt = k_1 P_{N_2O} \quad (1 - NI)\]
\[-dP_{N_2O}/dt = k_2 P_{N_2O}/(P_{O_2})^{1/2} \quad (2 - SI)\]

The results are reported in table 1 along with the solid state properties.

N₂O adsorption [corresponding to (1)] is found to be rate limiting on La₂MnNiO₆ at both the pressures whereas on La₂MnZnO₆, oxygen desorption is the slowest step. The compound La₂MnCuO₆ exhibited strong and no inhibition by oxygen at 200 and 50 Torr respectively, portraying the effect of pressure on the rate limiting step.

High magnetic moment on the catalyst (as in La₂MnNiO₆) facilitates the decoupling of the spins of the O⁺ ion in the oxygen desorption step, whereas the increases in Eₐ for conduction and lattice parameters along a series (table 1) decelerate the diffusion of O⁻ ions on the surface. Based on these grounds, the applicability of different rate equations on these catalysts could be well understood.

Table 1 Physicochemical Properties of La₂MnMO₆

<table>
<thead>
<tr>
<th>Property</th>
<th>La₂MnNiO₆</th>
<th>La₂MnCuO₆</th>
<th>La₂MnZnO₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetry</td>
<td>Cubic</td>
<td>Cubic</td>
<td>Cubic</td>
</tr>
<tr>
<td>Cell Parameter, a (Å)</td>
<td>7.76</td>
<td>7.80</td>
<td>7.81</td>
</tr>
<tr>
<td>Eₐ for conduction (eV)</td>
<td>0.26</td>
<td>0.30</td>
<td>High</td>
</tr>
<tr>
<td>µeff (BM)</td>
<td>2.813</td>
<td>2.047</td>
<td>1.391</td>
</tr>
<tr>
<td>Sign of Seebeck Potential</td>
<td>+ve</td>
<td>+ve</td>
<td>-ve</td>
</tr>
<tr>
<td>Binding Energies (kcal/mole)</td>
<td>59.34</td>
<td>55.98</td>
<td>55.90</td>
</tr>
<tr>
<td>Rate Equation obeyed at 50 Torr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eₐ for reaction at 200 Torr (kcal/mole)</td>
<td>16.3</td>
<td>4.2</td>
<td>5.3</td>
</tr>
<tr>
<td>lnA for reaction at 50 Torr</td>
<td>4.6</td>
<td>-3.0</td>
<td>5.3</td>
</tr>
<tr>
<td>lnA for reaction at 200 Torr</td>
<td>2.6</td>
<td>4.2</td>
<td>3.7</td>
</tr>
</tbody>
</table>

At 50 Torr, the order of activities based on percentage conversions (table 1), for the three catalysts, in the temperature range 350–450°C, is

La₂MnZnO₆ > La₂MnCuO₆ > La₂MnNiO₆

In nitrous oxide decomposition reaction, n-type oxides are generally much less reactive than P-type oxides. But in the present investigation, La₂MnZnO₆, even though it is an n-type oxide, exhibited highest percentage conversions at all temperatures. This may partly be due to the highly isolated Mn³⁺ ions present in the inert oxide matrix, which are the result of slight non-stoichiometry of the compound.

When the present series of compounds is compared with the series La₂TiMO₆ (M = Ni, Cu and Zn) for N₂O decomposition at 200 Torr (table 2), the very low Eₐ for reaction and lnA values suggest a larger multipoint-mode of adsorption on the series La₂MnMO₆. One can visualize different types of clusters on mixed oxides of the type discussed here. Clusters of the type Mn-O-M are probably the active sites in the series La₂MnMO₆, owing to the availability of d electrons on the Mn ion. The lower lattice parameters for the Mn-substituted series also favour multipoint-adsorption. The lower M-O binding energies in the series La₂MnMO₆ as compared to La₂TiMO₆ may reduce the Eₐ for reaction to certain extent.

One of the authors (NK) acknowledges the Department of Atomic Energy, Government of India for the award of fellowship.

Table 2 Results of N₂O decomposition at 200 Torr on La₂TiMO₆

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rate Eqn. obeyed</th>
<th>Eₐ (kcal/mole)</th>
<th>lnA</th>
<th>Binding Energy (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La₂TiNiO₆</td>
<td>SI</td>
<td>3.6</td>
<td>-3.0</td>
<td>71.21</td>
</tr>
<tr>
<td>La₂TiCuO₆</td>
<td>SI</td>
<td>21.5</td>
<td>10.1</td>
<td>67.89</td>
</tr>
<tr>
<td>La₂TiZnO₆</td>
<td>SI</td>
<td>40.7</td>
<td>19.0</td>
<td>67.81</td>
</tr>
</tbody>
</table>

4 August 1984

The IR spectrum of the compound showed no absorptions either due to -SH group near 2850 cm\(^{-1}\) or amide carbonyl around 1620-1650 cm\(^{-1}\) region. It displayed a weak but broad absorption at 3400 cm\(^{-1}\) assignable to an enolic hydroxyl, a strong peak for lactonic carbonyl function at 1750 cm\(^{-1}\) and a peak at 1580 cm\(^{-1}\) due to C= N-stretching.

The PMR spectrum showed only two signals, one a cluster of complex multiplets in the region 7.4–8.5 ppm (1H) due to aromatic protons and a neat singlet at 13.6 ppm for enolic hydroxyl proton which was D\(_2\)O exchangeable.

High resolution mass spectrum of the compound confirmed the proposed structure. While the M\(^+\) ion at m/z 397 corresponding to a formula C\(_9\)H\(_{10}\)O\(_3\)NS was the second most intense peak, a signal at m/z 252 appeared to be the base peak. This M-145 fragment was formed by eliminating a neutral moiety which was characteristic of the compounds containing 4-ylidene tetronic acid skeleton. The other prominent peaks with sizeable intensity were at m/z 224 and 223 the first of which was formed from m/z 252 ion due to the loss of CO and the latter losing a hydrogen from the daughter ion. Other spectral fragmentations with their elemental analyses supported by the spectrum are shown in chart I.

Antibacterial Activity:

Antibacterial activity was studied in vitro using the cup plate method\(^5\). The bacteria employed were Bacillus Polymin, Bacillus pumilus and Streptococcus albus (all gram positive) and Proteus vulgaris, Pseudomonas ovalis and Acetobacter aerogenes (all gram-negative). While the compound showed no activity against gram-positive bacteria it was moderately active against the gram-negative ones.

Antifungal activity:

The fungicidal activity\(^6\) of the compound (II) was assayed against two phytopathogenic fungi \textit{viz.}

\textit{Drechslera rostrata} and \textit{Alternaria alternata} by spore germination method in acetone. The compound exhibited strong fungicidal activity against both the organisms inhibiting the growth completely at 200 µg/ml concentration. The \(\log \text{ED}_{50}\) values for \textit{D. rostrata} and \textit{A. alternata} were 2.2 and 2.08 respectively.

Melting point determined in an open capillary was uncorrected. Homogeneity of the compound was checked by TLC on plate coated (0.25 mm) with

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**CHEMISTRY OF LICHEN PRODUCTS—PART III: SYNTHESIS OF A NEW BENZOTHIAZOLE DERIVATIVE FROM PULVINIC DIACETONE AND ITS PHYSIOLOGICAL ACTIVITY EVALUATION**

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Pulvinic diaceton\(^1\), a lichen metabolite, possesses the tetronic acid ring system which is the essential feature of some biologically active natural products \textit{viz.} vitamin C and the cardenolide, digitoxigenin. Antibiotic activity of variabilin, strobilin and tetrenolin which contain 4-ylidene tetronic acid system is well known. 2-substituted benzothiazoles are shown to be active against dermatophytes, protozoans, gram-positive bacteria and even against the bacterial strains which are resistant to penicillin and viruses\(^2\). Fungicidal activity of 2-amino derivatives is also well known\(^3\). With a view to synthesize new derivatives using lichen metabolites and to screen them for their antimicrobial activity, the present investigation was taken up. Pulvinic anhydride, which was prepared synthetically according to the procedure by Volhard\(^4\), was condensed with \(\alpha\)-aminothiophenol in acid medium to yield the compound (II) (scheme I). An excess of \(\alpha\)-amino thiophenol did not alter the reaction from being equimolar suggesting the stability of the second lactone ring in the compound (I).

![Scheme-1](image)

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