Synthesis and Characterization of a Molybdenum(VI) Complex containing Diazenido(1-) and Hydrazido(2-) Ligands. X-ray Crystal Structure of ([Mo(C₆H₅CON=N)(C₆H₅C(O)-NH-N=)(C₁₀H₅OCH=N-N=COC₆H₅)])

The reaction of the complex [(µ₂-O₂)(MoO₂)(H₄NSH)₂]·2C₂H₅OH (3.1) with benzoyl hydrazine in 1:3 molar ratio has been studied in ethanol. The resultant product has been characterized by IR, ¹H NMR and single crystal X-ray crystallography and the results are presented.
Experimental:

Reaction of \([(\mu-O)_{2}(MoO_{2})_{2}(H_{4}nsb)_{2}] \cdot 2C_{2}H_{5}OH\) (I) with benzoyl hydrazine, \(C_{6}H_{5}CONHNH_{2}\).

The complex \((\mu-O)_{2}[(MoO_{2})_{2}(H_{4}nsb)_{2}] \cdot 2C_{2}H_{5}OH\) (I) (1.00 g, 1.62 mmol) was suspended in ethanol (100 mL). To this suspension was added a solution of benzoyl hydrazine (0.66 g, 4.85 mmol) in ethanol (25 mL). The resulting mixture was refluxed for 3 hours. The solution rapidly turned dark red. It was filtered while hot and the filtrate on concentration and standing for one week yielded reddish-brown crystals of the complex (II). M.p. 158 °C. Yield: 70%. Anal. calcd for \(C_{66}H_{51}N_{12}Mo_{2}O_{13}\) : Mo, 13.59; C, 56.14; H, 3.64; N, 11.90. Found: Mo, 13.95; C, 56.76; H, 3.62; N, 12.03. It is soluble in EtOH, MeOH, DMF and DMSO and insoluble in \(Et_{2}O\), benzene, CHCl₃, CH₂Cl₂ and other common organic solvents.

IR (KBr) cm⁻¹, 3469m, 3390w (v O-H); 1600s (v (>C=O—N=C<)); 1553 m (v NCO); 1484w, 1434w (v (N=N)). ¹H NMR (DMSO-d₆) δ 9.95s (1H, -CH=N), 7.18 - 8.80m (multiplet, \(C_{6}H_{5}\) + \(C_{11}H_{8}O\)); δ 6.53s (1H, O-H(CH₃CH₂OH)); δ 3.43q (2H, -CH₂(CH₃CH₂OH)); δ 1.05 t (3H, -CH₃(CH₃CH₂OH).

![Scheme 1: Reaction showing the formation of complex I and II](image-url)
Characterization of complex II

The complex II, benzoyldiazenido(1-)-benzoylhydrazido(2-)(2-hydroxy-1-naphthaldehydebenzoylhydrazone)molybdenum(VI) was obtained in 70% yield by the reaction of benzoyl hydrazine with dioxomolybdenum(VI) complex \((\mu-O)_2\)\((\text{MoO}_2)\)\(_2\)(\(\text{H}_2\text{sh}_2\))\(_2\).\(\text{C}_2\text{H}_5\text{OH}\) (I) and was characterized by IR, \(^1\text{H}\) NMR and single crystal X-ray crystallography. It is soluble in EtOH, MeOH, DMF and DMSO and insoluble in Et\(_2\)O, benzene, CHCl\(_3\), CH\(_2\)Cl\(_2\) and other common organic solvents.

The acyldiazenido and acylhydrazido ligands may be either monodentate when they are bonded to the metal centre through the terminal nitrogen atom or bidentate when they are bonded through the nitrogen and the oxygen atom. In addition, the mode of binding to the metal centre depends on the hydrazide from which it originates as diazenido(1-) or diazenido(3-), hydrazido(1-), or hydrazido(2-). These binding modes [1] are shown in Fig.1. In the present work, one of the benzoyl hydrazine moiety acts as a monodentate ligand and is bonded to the metal centre as diazenido(1-)unit while the other benzoyl hydrazine fragment acts as a bidentate ligand and is bonded to the metal centre as hydrazido(2-)unit. The complex III can be assigned formal charges of Mo\(^{6+}\)(NNHCOC\(_6\)H\(_5\))\(^2-\)(NNCO\(_6\)H\(_5\))\(^2-\)(C\(_6\)H\(_5\)CONNCHOC\(_{11}\)H\(_7\))\(^2-\).

\[
\begin{align*}
\text{Mo} & \quad \text{N=N} \quad \text{R} \\
\text{Diazenido(1-)} & \quad \text{Diazenido(3-)} \\
\text{Mo} & \quad \text{N} \quad \text{N} \quad \text{H} \\
\text{Hydrazido(2-)} & \quad \text{Hydrazido(1-)}
\end{align*}
\]

Fig. 1. Types of ligation and binding modes of diazenido hydrazido ligands

IR spectrum of the complex II exhibit strong bands in the region 3390–3469 cm\(^{-1}\) centered at 3430 cm\(^{-1}\) which is attributed to arise from \(\nu(\text{OH})\) vibrations of lattice water and ethanol.
molecules. The C—H stretchings [1] for ethyl group and ligand molecules appear in the region 2859–2932 cm\(^{-1}\). The absence of a strong band in the region 167 –1620 cm\(^{-1}\) clearly indicates that the ligand 2-hydroxy-1-naphthaldehydebenzoylhydrazone exists in the enol form in the complex. The appearance of a strong band at 1600 cm\(^{-1}\), characteristic of \(>\text{C}=\text{N}-\text{N}=\text{C}<\) group in hydrazones produced as a result of condensation of \(\text{NH}_2\) group of benzoyl hydrazone and \(>\text{C}=\text{O}\) group of 2-hydroxy-1-naphthaldehyde and its consequent enolization [2] in the complex. This is also corroborated from the presence of a strong new band at 1553 cm\(^{-1}\) which is characteristic of newly formed NCO\(^{-}\) group. A new weak band at ~ 1700 cm\(^{-1}\) is present in the complex. This band is observed neither in the IR spectrum of free benzoyl hydrazone nor in that of 2-hydroxy-1-naphthaldehydebenzoylhydrazone. Hence this band is assigned to \(>\text{C}=\text{O}\) group of coordinated diazenido(1-) unit in the complex. The absence of a strong band in the region 900 – 1000 cm\(^{-1}\) and any band in the region 1550 – 1650 cm\(^{-1}\) characteristic of \(-\text{NH}_2\) group confirms the condensation of molybdenyl unit with the hydrazide \(-\text{NH}_2\) group. This viewpoint is corroborated from the appearance of two medium to strong bands at 1484 cm\(^{-1}\) and 1434 cm\(^{-1}\) in the IR spectra of the complex and these bands were assigned to \(\nu(\text{N}=\text{N})\) vibrations. The strong band observed at 1248 cm\(^{-1}\) is assigned to bending vibration of naphtholic \(\text{C}=\text{O}\) group coordinated to the molybdenum centre. The weak intensity bands observed at 1062 and 1029 cm\(^{-1}\) are attributed to arise due to \(\nu(\text{N}-\text{N})\) vibration of benzoylhydrazido(2-) unit coordinated to the metal centre and the hydrazone ligand respectively.

In the \(^1\text{H}\) NMR spectra of the complex (II), the singlet observed at \(\delta\) 9.95 ppm is assigned to azomethine proton (-CH=N-) of the 2-hydroxy-1-naphthaldehydebenzoylhydrazone(HNBH). Signals due to aromatic protons of benzoyl hydrazone and 2-hydroxy-1-naphthaldehyde appear in the region \(\delta\) 7.18 – 8.80 ppm. Further, the signals observed at \(\delta\) 1.05, 83.43 and 6.53 are assigned to –CH\(_3\), -CH\(_2\) and –OH protons of ethanol molecule which are present in the lattice structure of the complex. The signal due to NH proton is not visible even in \(^1\text{H}\) NMR spectrum because of its very broad nature due to its coupling with quadrupolar nitrogen nucleus.
X-ray Crystal Structure of

\[(\text{Mo}(\text{C}_6\text{H}_5\text{CON}=(\text{O})---\text{NH}--\text{N}=(\text{C}_10\text{H}_5\text{OCH}=\text{N}--\text{N}=\text{CO}\text{C}_6\text{H}_5))\] (II)

Diffraction quality crystals of the complex(II) were obtained by slow evaporation of an ethanolic solution of the complex. Single crystals of complex II were mounted on a glass fiber and placed on a Oxford Diffraction Xcaliber-S diffractometer (CrysAlis CCD) [3]. (Mo Kα, λ = 0.710 73 Å, graphite monochromator). Cell refinement and data reduction were done using CrysAlis RED [3]. Intensity data were collected using the Ω scan technique. The intensity data were corrected for Lorentz and polarization factors, and an empirical absorption correction based on multi scan using spherical harmonics implemented in SCALE 3 ABSPACK algorithm [3] was applied to the raw data. The structure was solved by using SHELXS97 (Sheldrick, 1997) program and structure refinement was done by using SHELXL97 (Sheldrick, 1997) [4]. Molecular graphics were generated using ORTEP-3 (Farrugia, 1997). Atomic scattering factors were taken from reference 5. The positions and anisotropic thermal parameters of all non-H atoms were refined against $F_0^2$ using full-matrix least-squares techniques. The crystal data and data collection and refinement parameters are summarized in Table 1.

![ORTEP diagram of [Mo(C6H5CON) (C6H5CONHN)(C10H5OCHNOCOC6H5)](II) with atom labeling scheme at 50% probability label](image-url)
Fig. 3. Unit cell structure of C$_{66}$H$_{50}$Mo$_2$N$_{12}$O$_{13}$ showing two molecules of [Mo(C$_6$H$_5$CONN)(C$_6$H$_5$CONHN)(C$_{10}$H$_5$OCHNNCOC$_6$H$_5$)], one ethanol and four water molecules.
### Table 1. Crystallographic and Refinement Data for

\[\text{[Mo(C}_{6}\text{H}_{5}\text{CONN})(\text{C}_{6}\text{H}_{5}\text{CONHN})(\text{C}_{10}\text{H}_{5}\text{OCHNCO}_{6}\text{H}_{5})]\]

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<th>Property</th>
<th>Value</th>
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<td>c, Å</td>
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<td>(\theta_{\text{Max}})</td>
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<td>(hkl) range</td>
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<td>Reflections collected</td>
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<td>Reflections unique</td>
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<tr>
<td>Parameters</td>
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<tr>
<td>(R) [I&gt;2σ(I)]</td>
<td>(R_1 = 0.0733; wR_2 = 0.1515)</td>
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<tr>
<td>(R) (all data)</td>
<td>(R_1 = 0.1809; wR_2 = 0.1814)</td>
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<tr>
<td>GOF on (F^2)</td>
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<td>Largest difference peak and hole (e Å(^{-3}))</td>
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\(w = 1/[σ^2(F_0^2) + (0.0785P)^2 + (0.00P)]\) where \(P = [F_0^2 + 2F_c^2]/3\)
**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for [Mo(C₆H₅CONN)(C₆H₅CONN)(C₁₀H₅OCHNNCOC₆H₅)]

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<th>Bond Lengths</th>
<th>Angles</th>
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<tr>
<td>Mo(1)-N(5)</td>
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<td>Mo(1)-N(1)</td>
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<td>2.151(6)</td>
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<td>Mo(1)-O(1)</td>
<td>2.160(5)</td>
</tr>
<tr>
<td>Mo(1)-O(2)</td>
<td>2.018(5)</td>
</tr>
<tr>
<td>Mo(1)-O(3)</td>
<td>1.959(7)</td>
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<td>N(1)-N(2)</td>
<td>1.388(8)</td>
</tr>
<tr>
<td>N(3)-N(4)</td>
<td>1.406(8)</td>
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<td>N(5)-Mo(1)-O(3)</td>
<td>98.0(3)</td>
</tr>
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<td>N(5)-Mo(1)-N(1)</td>
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<td>N(1)-Mo(1)-N(4)</td>
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</tr>
<tr>
<td>N(1)-Mo(1)-O(1)</td>
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</tr>
<tr>
<td>N(4)-Mo(1)-O(3)</td>
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<td>N(4)-Mo(1)-N(5)</td>
<td>101.0(3)</td>
</tr>
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<td>N(6)-N(5)-Mo(1)</td>
<td>175.4(6)</td>
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Table 3. Comparison of structural features of hydrazido and diazenido ligands

<table>
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<tr>
<th>Complex</th>
<th>Bond lengths, Å</th>
<th>Bond angles, (°)</th>
<th>Reference</th>
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<tr>
<td></td>
<td>Mo-N</td>
<td>N-N</td>
<td>Mo-N-N</td>
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<tr>
<td><strong>Diazenido(1-)</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>[Mo(N$_2$C$_6$H$_4$OCH$_3$-p)$_2$(S$_2$N$_2$C$_6$H$_4$)]</td>
<td>1.81(1)</td>
<td>1.28(2)</td>
<td>170.4(17)</td>
</tr>
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<tr>
<td>[Mo(C$_6$H$_5$)$_2$Cl($\mu$-C$_6$H$_5$)(C$_6$H$_5$NHNH$_2$)]</td>
<td>1.79(1)</td>
<td>1.23(1)</td>
<td>166.0(1)</td>
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<tr>
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<td>1.84(2)</td>
<td>1.24(2)</td>
<td>170.0(1)</td>
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<tr>
<td>[Mo(C$_6$H$_5$)$_2$Cl($\mu$-C$_6$H$_5$)(C$_6$H$_5$CONHO)]</td>
<td>1.817(8)</td>
<td>1.24(1)</td>
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<td>1.841(8)</td>
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<td>175.7(7)</td>
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<tr>
<td>[Mo$_2$(NNPh)$_2$Cl(OMe)$_2$(PhNHNNH$_2$)$_2$]</td>
<td>1.816(6)</td>
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<td>1.829(6)</td>
<td>1.243(9)</td>
<td>170.9(5)</td>
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<tr>
<td>[Mo(N$_2$C(O)Ph)NHNC(O)(PhC(S)N(Me)O)$_2$]</td>
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<td>(Mo(C$_6$H$_5$CON=N)(C$_6$H$<em>5$OCH=N-N=)(CO$</em>{10}$H$_5$OCH=N-N=))</td>
<td>1.957(7)</td>
<td>1.388(8)</td>
<td>120.4(5)</td>
</tr>
<tr>
<td><strong>Hydrazido(2-)</strong></td>
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<tr>
<td><a href="$%5Cmu$-CNMe$_2$">Mo(NNPh)$_2$</a>$_2$</td>
<td>1.74(1)</td>
<td>1.31(1)</td>
<td>169.9(8)</td>
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<tr>
<td>[Mo(NHNMePh)(NNMePh)(acac)Cl$_2$]</td>
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<td>1.301(3)</td>
<td>173.8(2)</td>
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<tr>
<td>([Mo(C$_6$H$_5$CON=N)(C$_6$H$<em>5$OCH=N-N=)(CO$</em>{10}$H$_5$OCH=N-N=))]</td>
<td>1.731(7)</td>
<td>1.285(8)</td>
<td>175.4(6)</td>
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<tr>
<td>[MoO(NNMePh)(acac)$_2$]</td>
<td>1.789(3)</td>
<td>1.281(4)</td>
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<td><strong>Hydrazido(1-)</strong></td>
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<td></td>
<td></td>
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<tr>
<td>[Mo(NHNMePh)(NNMePh)(acac)Cl$_2$]</td>
<td>1.948(2)</td>
<td>1.339(3)</td>
<td>142.9(2)</td>
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</table>
Discussion of Structure

The ORTEP diagram of complex(II) is shown in Fig.2. Selected bond lengths (Å) and bond angles(°) are set out in Table. 2. The unit cell structure of the complex(II) is shown in Fig.3. The unit cell structure of the complex consists of two molecules of [Mo(C₆H₅CONN)(C₆H₅CONHN)(C₁₀H₅OCHNCONCOC₆H₅)] alongwith one ethanol and four water molecules. The solvent molecules are present in the form of solvent of crystallization. It is interesting to note that the benzoyldiazenido(1-) unit is bonded to the molybdenum(VI) centre through nitrogen and carbonyl oxygen atom via deprotonation whereas the benzoxyldiazenido(2-) unit is coordinated to the metal centre only through nitrogen atom. The carbonyl oxygen of benzoxyldiazenido(2-) unit remains uncoordinated. The ligand 2-hydroxy-1-naphthaldehydebenzoylhydrazone is bonded to the Mo(VI) centre through one diazene nitrogen (N(4)) atom, the carbonyl oxygen atom (O(2)) of the benzyol hydrazine unit and the deprotonated hydroxyl oxygen (O(3)) of the 2-hydroxy-1-naphthaldehyde unit. The complex exhibits a distorted octahedral geometry with N(1) and N(4) occupying the axial positions (bond angle, N(1)-Mo(1)-N(4) = 164.9(2)°) and equatorial positions are occupied by one nitrogen (N(5)) and three oxygen atoms (O(1), O(3), and O(2)) respectively.

The group containing N(1), N(2) corresponds to benzoyldiazenido(1-) unit. It forms a five membered chelate ring with the molybdenum centre. The structural parameters for this diazenido(1-) chelate ring are quite different and distinctive. This is, most noticeably, reflected in the Mo(1)-N(1) bond distance (1.957(7)Å), N(1)-N(2) bond distance (1.388(8)Å) and C(1)-N(2) bond distance (1.326(9)Å). These values are very similar to those in another chelated diazenido-diazene complex, [Mo(NHNC(S)Ph)(N₂C(S)(PhC(S)N(Me)O)] [9]. The short bond lengths are indicative of considerable electron delocalization within the chelate ring. The Schiff base ligand 2-hydroxy-1-naphthaldehydebenzoylhydrazone is acting as a dibasic tridentate ligand and is coordinated to the Mo(VI) centre through the diazene nitrogen atom (N(4)), the carbonyl oxygen atom (O(2)) of the benzyol hydrazine moiety via enolization and deprotonated hydroxyl oxygen atom (O(3)) of the 2-hydroxy-1-naphthaldehyde moiety. It forms a five membered chelate ring comprising of Mo(1), N(4), N(3), C(9) and O(2) and a six membered chelate ring comprising of Mo(1), O(3), C(18), C(17), C(16) and N(4). The bond lengths, N(3)-N(4) (1.406(8)Å), N(3)-C(9) (1.319(9)Å), C(9)-O(2) (1.304(9)Å), Mo(1)-O(2) (2.018(5)Å), Mo(1)-N(4) (2.151(6)Å), Mo(1)-O(3) (1.959(5)Å), N(4)-C(16) (1.296(8)Å) are comparable to similar structures [13,14]. The group containing N(5), N(6) corresponds to benzoxyldiazenido(2-) unit. This benzoxyldiazenido(2-
unit exhibits a geometry consistent with molybdenum-nitrogen multiple bonding and extensive delocalization throughout the Mo(1)-N(5)-N(6) group. The Mo(1)-N(5) (1.731(8)Å), and N(5)-N(6) (1.285(8)Å) bond distances in the molybdenum benzoylhydrazido(2-) group are short and comparable to related structures [9]. They show significant double bonding and electron delocalization with essentially linear (Mo=N=COC6H5) entity (bond angle Mo(1)-N(5)-N(6) = 175.4(6)°) [6]. Further, the geometry of the benzoylhydrazido(2-) fragment suggests maximum π-interaction between the diazenido ligand π* orbitals and the molybdenum t2g orbitals [15]. This is supported by the short Mo(1)-N(5) distance (1.731(7)Å) and the wide angle (175.4(6)°) of the Mo(1)-N(5)-N(6) unit for the benzoylhydrazido(2-) ligand as described above.

Acknowledgement

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References


List of publications:

1. Synthesis and crystal structure of $[\text{Mn}_2(\text{H}_2\text{sal})_2(\text{Hsal})_2(\text{H}_2\text{O})_4]$. First example of the reductive synthesis of a binuclear manganese(I) salicylate complex.

2. Synthesis and spectroscopic Characterization and of Molybdenum (VI) Complexes Derived from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone.
   Ram A. Lal*, Mithun Chakrabarty and Sanjesh Choudhury (communicated).


   Ram A. Lal*, Mithun Chakrabarty and Sanjesh Choudhury and Aziz Ahmed (communicated).