complexed in the presence of slight excess of Lu(III)-MP-IX. The amplitude of fluorescence in apomyoglobin is due to tryptophan and tyrosine. The intensity of fluorescence of tryptophan and tyrosine depends upon the degree of quenching mediated by interaction with the metal porphyrin. The Lu(III)-MP-IX effectively quenches the fluorescence of tryptophan and tyrosine residues in the protein complex because of its central position and the overlap of its absorption spectrum with emission spectra of tryptophan and tyrosine. The protein fluorescence of Lu(III)-Mb is comparable with sperm whale metmyoglobin. Therefore they must have the same mean separation of the tryptophan and tyrosine fluorophores from metal porphyrin and thus have the same structures.8

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PREPARATION AND CHARACTERIZATION OF COPPER(II) NITRATE COMPLEXES WITH NICOTINIC ACID AND RELATED LIGANDS

Nicotinic acid (NA), nicotinamide (NIA) and iso-nicotinamide (INA)—pyridine derivatives with a carboxyl or amido group in the ring—are important constituents of coenzymes which participate in various oxidation-reductions of physiological importance. Metal complexes of biologically important ligands are often more effective than the free ligands. This study describes the coordination compounds formed by the interaction of NA, NICA and INA with copper(II) nitrate which are likely to exhibit significant biological effects. Molar conductance, magnetic susceptibility, electronic and i.r. spectral studies down to 200 cm⁻¹ have been carried out to elucidate
the mode of metal-nitrate bonding and the tentative stereo-chemistries of the compounds.

NA, NICA and INA were obtained from B.D.H. and used as such. The complexes were prepared by mixing together solutions of copper(II) nitrate and an excess of the corresponding ligand in ethanol. The mixtures were stirred on a water-bath and cooled. The complexes which crystallized out were suction-filtered, washed with ethanol, then ether and finally dried in an air oven at \( \sim 70^\circ \text{C} \). Conductivity measurements were made on freshly-prepared \( \sim 10^{-3} \text{M} \) solutions of the complexes at \( 25^\circ \text{C} \) with a Philips conductivity bridge Model PR 9500. Electronic spectra were recorded as nujol mulls in the range \( 3300-6000 \text{ cm}^{-1} \) on a Cary 14 spectrophotometer. The mulls were smeared on filter-paper and run against a reference consisting of a similar piece of filter-paper soaked in nujol. i.r. spectra of the uncoordinated ligands and of the complexes were recorded as nujol mulls on a Perkin-Elmer 621 spectrophotometer. Magnetic susceptibilities were measured at room temperature by the Faraday's method with a Cahn R.G. Electrobalance Model 7550. HgCo(NCS)\(_4\) was used as the magnetic susceptibility standard. Pascals' constants were used for diamagnetic corrections. Magnetic moments were calculated using the equation

\[
\mu_{\text{eff}} = 2.84 \sqrt{\frac{\chi_{\text{m}} \text{corr}}{\tau}}
\]

Analytical data and characteristic i.r. bands and their assignments in uncoordinated ligands and the complexes are listed in Table I along with the electronic bands. The complexes are soluble in most of the common organic solvents. The assignments of the i.r. characteristic bands for the nitrate groups are reported in Table II. The conductivity measurement values are typical of the 1:2 electrolytes.

Nicotinic acid, nicotinamide and isonicotinamide possess two potential donor sites: (i) pyridine ring nitrogen and (ii) carboxyl oxygen in the case of NICA and INA or carboxyl oxygen in NA. As monodentate ligands bonding may take place through either the pyridine ring nitrogen or the carboxyl/carboxyl oxygen. Owing to the fixed orientation in space the two sites in INA cannot coordinate simultaneously to the same metal ion. However, one cannot rule out the possibility of the two coordination sites bonding to different metal ions (bidentate bridging ligand) resulting in polymeric structures. Significant absorption bands due to amide group in NICA and INA are \( \nu \text{NH, } \nu \text{CO and } \nu \text{CN} \) (Table I). In complexes of amides\(^8\) and other carboxyl donors\(^9\) a significant negative carboxyl frequency shift takes place on coordination through the carboxyl oxygen. In the present study these frequencies remain either unperturbed or undergo slight positive shifts which clearly indicate the non-participation of amido group in coordination. The carboxyl group vibrations of NA remain unperturbed in the i.r. spectrum of 1:2 copper(II) nitrate-NA complex thus excluding the possibility of metal-to-oxygen coordination. On the other hand, i.r. spectra of these complexes display appreciable perturbations in the fundamental frequencies of the pyridine part of the molecule. Absorption bands at \( \sim 1590 \) and \( \sim 1550 \text{ cm}^{-1} \) due to C \( \cdots \) C and C \( \cdots \) N stretching modes, respectively, in uncoordinated NA, NICA and INA and the pyridine ring vibrations of these ligands at \( \sim 930, 605 \) and \( 405 \text{ cm}^{-1} \) undergo significant positive shifts. These frequency shifts (Table I) indicate conclusively that coordination of the ligands occur via their pyridine ring nitrogen only.

Comparison of the i.r. spectra of the copper(II) nitrate complexes with those of the corresponding uncoordinated ligand spectra and the halide complexes facilitated the assignment of bands to coordinated nitrate groups. In addition to the six fundamental modes due to nitrate groups the nitrate combination modes in the range 1800-1700 \text{ cm}^{-1} \) have been observed for all the copper(II) complexes reported here. The band positions are given in Table II. The assignments were made following those of earlier workers\(^9\). Data of representative mono- and bi-dentate nitrate ligands are given.

I.r. spectroscopy has frequently been used in efforts to establish whether the coordinated nitrate group in metal-nitrate complexes is mono- or bi-dentate. It is, however, generally accepted that the splitting of the bands at \( \sim 1360 \text{ cm}^{-1} \) in the nitrate spectrum is not a good criterion for such purposes as the coordinated mono- (ONO\(_2\)) and bi-dentate (O\(_2\)NO) groups have the same local site symmetry (C\(_{3v}\)). Curtis et al.\(^8\) suggested that the region 2300-2500 \text{ cm}^{-1} \) can be utilized for the identification of the nitrate combination mode. They showed that a separation of 200-300 \text{ cm}^{-1} \) between the combination modes in this region would indicate bidentate nitrate groups. Lever et al.\(^8\), suggested that the energy region 1800-1700 \text{ cm}^{-1} \) provides a better choice for the identification of the nitrate combination mode. The combination bands appearing in this region are stronger than the bands in the region 2300-2500 \text{ cm}^{-1} \). They suggested that an ionic nitrate shows only a single band in this region while mono- and bi-dentate nitrate ligands show two bands with a separation of \( \sim 20 \text{ cm}^{-1} \) for the mono- and \( \sim 40 \text{ cm}^{-1} \) for the bi-dentate nitrate ligands.

Values of the magnetic moments of these complexes, 1.7-2.2 B.M., suggest negligible magnetic interactions in these complexes (Table I). In tetrahedral copper(II) complexes with triplet ground state one should theoretically expect magnetic moments above 2.0 B.M. but rarely one does because distortion almost
**Table I**

**Analytical, magnetic moments, electronic bands and partial i.r. spectral data (cm⁻¹)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \mu_{eff} ) (B.M.)</th>
<th>Electronic band</th>
<th>Metal Found</th>
<th>Nitrate (Calc.) %</th>
<th>( \nu_{NH} )</th>
<th>( \nu_{CO}^* )</th>
<th>( \nu_{C=\equiv C} )</th>
<th>( \nu_{C=\equiv N} )</th>
<th>Ring vibrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1685 s</td>
<td>1585 m</td>
<td></td>
<td></td>
<td>989 m</td>
</tr>
<tr>
<td>NICA</td>
<td></td>
<td></td>
<td>3330 s</td>
<td>1680 m</td>
<td>1580 m</td>
<td>1570 m</td>
<td>1120 m</td>
<td></td>
<td>996 m</td>
</tr>
<tr>
<td>JNA</td>
<td></td>
<td></td>
<td>3372 m</td>
<td>1660 m</td>
<td>1592 m</td>
<td>1548 s</td>
<td>1115 m</td>
<td></td>
<td>991 m</td>
</tr>
<tr>
<td>Cu(NA)₂(NO₃)₂</td>
<td>1.79</td>
<td>1330 s</td>
<td>15.1</td>
<td>29.5</td>
<td>1700 m</td>
<td>1625 m</td>
<td>1600 m</td>
<td></td>
<td>1027 m</td>
</tr>
<tr>
<td>Cu(NICA)₄(NO₃)₂</td>
<td>2.20</td>
<td>14285</td>
<td>9.7</td>
<td>10.7</td>
<td>3316 m</td>
<td>1700 m</td>
<td>1600 m</td>
<td>1140 w</td>
<td>1026 m</td>
</tr>
<tr>
<td>Cu(INA)₃(NO₃)₂</td>
<td>1.70</td>
<td>14705</td>
<td>15.3</td>
<td>29.5</td>
<td>3300 m</td>
<td>1705 m</td>
<td>1600 m</td>
<td>1130 m</td>
<td>1619 m</td>
</tr>
</tbody>
</table>

* \( \nu_{OCO} \) for nicotinic acid.
TABLE II
Coordinated nitrato bands (cm⁻¹)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v_1)</th>
<th>(v_2)</th>
<th>(v_3)</th>
<th>(v_4)</th>
<th>(v_5)</th>
<th>(v_6)</th>
<th>Combination mode</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(NA)₂(NO₃)₂</td>
<td>(a) 1316 s</td>
<td>1008 w</td>
<td>710 w</td>
<td>1434 s</td>
<td>736 w</td>
<td>814 m</td>
<td>1754 w</td>
<td>This work</td>
</tr>
<tr>
<td>Cu(NICA)₄(NO₃)₂</td>
<td>(a) 1332 s</td>
<td>1012 m</td>
<td>716 w</td>
<td>1465 s</td>
<td>740 w</td>
<td>818 m</td>
<td>1780 w</td>
<td>This work</td>
</tr>
<tr>
<td>Cu(INA)₄(NO₃)₂</td>
<td>(a) 1466 s</td>
<td>1056 w</td>
<td>750 w</td>
<td>1300 s</td>
<td>711 w</td>
<td>818 m</td>
<td>1786 w</td>
<td>This work</td>
</tr>
<tr>
<td>Cu(β₄)₄(NO₃)₂</td>
<td>(a) 1306</td>
<td>1026</td>
<td>730</td>
<td>1498</td>
<td>718</td>
<td>820</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Cu(βy)₂(NO₃)₂</td>
<td>(b) 1474</td>
<td>1024</td>
<td>1282</td>
<td>814</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Monodentate nitrato ligands (-ONO₃); (b) Bidentate nitrato ligands (-O₂NO).

Invariably removes the degeneracy of the ground state. On the other hand, copper(II) complexes with no triplet ground state moments above 1.7 B.M. are achieved by mixing of excited orbitally degenerate term with the ground state term. The process of mixing is directly proportional to the spin-orbit coupling constants [very large for copper(II)] and inversely proportional to the energy separation between the ground state and excited state terms. For different stereochemistries variations are observed in the energy separation between the ground state and excited states. Further, it is necessary to see whether the difference between the two ligands is real but in the present study it seems as though NNA causes a larger decrease in spin-orbit coupling than caused by NA and NICA.

The d⁹ configuration of copper(II) with D₄h term is split in a regular octahedral field into a lower doublet E_g level and an upper triplet T₂g level and only one spin-allowed transition should result. However, the crystal field theory predicts larger distortion for cubic symmetry for the octahedral complexes of copper(II). Hence the d⁹ ground state being Jahn-Teller unstable shows further splitting of the E̐ and T̐₂g levels so that even in a complex with six identical donors a regular octahedral configuration is not achieved.

Electronic spectrum of the 1:2 copper nitrate-NA complex shows a broad single band at 13330 cm⁻¹ consistent with the pseudotetrahedral structure for the complex. The d-d bands of highly distorted, virtually planar complexes occur in the range 14000–18000 cm⁻¹. Distortion of the planar structure towards a tetrahedral structure lowers the band frequencies. Bands at 7000–10000 cm⁻¹ and 12000–13000 cm⁻¹ have been assigned from the frequencies and relatively low intensity to crystal field transition of the copper(II) in a pseudotetrahedral environment. Hence the observed band for the NA complex strongly supports a pseudotetrahedral structure.

Electronic spectra of the NICA and INA complexes are characterized by the presence of strong bands at 1125 and 14780 cm⁻¹, respectively, with shoulders at 11500 cm⁻¹ characteristic of the distorted octahedral coordination. In this symmetry three bands are expected. The broad high energy main band may be assigned to the superimposed transition \(B_1 \rightarrow B_1\) and \(B_1 \rightarrow E\) and the other band or shoulder to the \(B_1 \rightarrow A_1\) transition. One could expect the main band at higher energies in the NICA than INA complex provided the effect of distortion from octahedral symmetry and steric hindrance in both the complexes is comparable. From the position of the bands (14780 cm⁻¹ vs. 14285 cm⁻¹ in NICA) the INA complex seems to be more distorted than NICA complex. Furthermore, the i.r. bands due to coordinated nitrate groups (Table II) indicate clearly the presence of terminally bonded monodentate nitrate ligands in the NA and NICA complexes and bidentate chelating nitrate ligands in the case of INA complex. Based upon the considerations of magnetic moments, electronic and i.r. spectral data the geometries proposed are: monomeric pseudotetrahedral for the 1:2 copper(II) nitrate-NA complex and six-coordinated.
distorted octahedral structures for the 1:4 copper(II) nitrate-NICA and 1:2 copper(II) nitrate-LNA complexes in the solid state.

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Sr$^{87}$/Sr$^{86}$ RATIO IN VEMPALLE DOLOMITIC LIMESTONES FROM PULIVENDLA

The study of Sr$^{87}$/Sr$^{86}$ in carbonates makes a definite conclusion regarding the nature and conditions of their formation. The higher values of Sr$^{87}$/Sr$^{86}$ (0.7059-0.7104) in the Vempalle dolomitic limestones than the average value (0.7035) for carbonates confirm that they are sedimentary in nature and not carbonatites as suggested by Narasimharao et al.

The Vempalle formation comes under Papagnh Group of Cuddapah Supergroup (Proterozoic period) and forms an important stratigraphic unit because of asbestos, baryte and steatite mineralization.

In recent years much attention has been made to revise the Cuddapah Supergroup. Narasimharao et al. attributed volcanoclastic origin to every formation in the Cuddapah Supergroup and considered the Vempalles as carbonatites. An attempt has been made here to confirm that the Vempalle dolomitic limestones (near Pulivendla 14°25'.78°14') are not carbonatites, based on strontium isotope study.

Sr$^{87}$/Sr$^{86}$ values for eight dolomitic limestones are determined (Table I) following the procedure adopted by Viser and Compston. The samples of about 30 mg weight are dissolved in 0.1 N HCl, the strontium centrifuged, traces of 84 Sr and 85 Rb added, then Rb and Sr extracted in cation exchange columns for mass spectroscopy. From Table I it is clear

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Sr$^{87}$/Sr$^{86}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.7059±3</td>
</tr>
<tr>
<td>101</td>
<td>0.7108±2</td>
</tr>
<tr>
<td>102</td>
<td>0.7071±4</td>
</tr>
<tr>
<td>103</td>
<td>0.7068±3</td>
</tr>
<tr>
<td>104</td>
<td>0.7079±4</td>
</tr>
<tr>
<td>105</td>
<td>0.7104±3</td>
</tr>
<tr>
<td>1250</td>
<td>0.7066±7</td>
</tr>
<tr>
<td>1255</td>
<td>0.7108±1</td>
</tr>
</tbody>
</table>

that the Sr$^{87}$/Sr$^{86}$ values for dolomitic limestones are higher than the average value (0.7035) for carbonatites and are comparable to values given for normal marine dolomites and limestones (0.706-0.709). The sedimentary origin of the dolomitic limestones is further evidenced by the nature, occurrence of stromatolites and oolites, chemical study and identification of the sedimentary features and structures of the overlying (Pulivendla quartzite) and underlying (Galcheru quartzite) stratigraphic units. The variations