CHAPTER V

SALICYLIDENEAMINOCARBOXYLATE COMPLEXES
OF COPPER(II) AND NICKEL(II): NITROSYL ADDUCTS
OF SALICYLIDENEGLYCINATO COMPLEXES OF IRON(III),
NICKEL(III) AND COPPER(III).

Abstract:

The nitrosyl adducts of salicylideneglycinato complexes of empirical formulae MSg.NOnHgO, have been prepared, where M = Fe(III), Ni(III) and Cu(III), by reacting NO gas with the parent salicylideneglycinato complexes in benzene suspension. The compounds have been characterized by analyses, molar conductance, room temperature magnetic moment and electronic spectral data. The u-oxo-salicylideneglycinatoiron(III) has also been prepared and characterized.

Introduction:

The salicylideneaminocarboxylate complexes of copper(II) and nickel(II) have been shown in earlier chapters to accept various donors to form complexes of different geometry. This chapter describes the addition of π donor ligand, NO, to salicylideneglycinato complexes of copper(II).

Nitric oxide, although a significant π donor like CO, can also behave as NO, NO⁺ and NO⁻.
A. Chemicals & Solvents - All chemicals used were of pure/Analar grade. Solvents were used after necessary purification.

i. Methanol - Analar grade methanol was treated with quick lime and distilled through a fractionating column. The fraction collecting at 65°C was used in this work.

ii. Benzene - Benzene used in this work was purified by successively shaking with concentrated sulphuric acid (to remove thiophene), sodium bicarbonate solution and water. It was then dried over fused calcium chloride and was distilled over sodium.

B. Synthesis -

i. Nitric Oxide - Nitric oxide was obtained by adding concentrated solution of ferrous sulphate to a mixture of concentrated sulphuric acid and powdered potassium nitrate. The gas was subsequently passed through concentrated sulphuric acid to get dry nitric oxide.

ii. \([\text{FeOS})_2\text{O} \cdot \text{H}_2\text{O}\] - aquo-μ-oxo-salicylidene-glycinato complex of iron(III) was prepared by the same method as the salicylidenediamino-carboxylato complexes of nickel(II) and copper(II), but using ferrous ammonium sulphate hexahydrate.
iii. Dehydration of the Fe(III), Ni(II) and Cu(II) complexes was carried out by heating the aquo complexes under vacuum at 140°C for 24 hours. The compounds dehydrated excepting \([\text{FeS}_{5}gO_{3}H_{5}]n\) which decomposed.

iv. No Adducts - The NO adducts of Fe(III), Ni(III) and Cu(III) complexes were prepared by suspending the respective complex of Fe(III), Ni(II) or Cu(II) with salicylidene glycine in dry benzene medium and passing dry NO gas into it in a properly sealed round-bottomed flask. The Ni(III) and Cu(III) adducts isolated were highly hygroscopic and turned into a gummy mass on removal from benzene. They were, therefore, preserved in dry benzene. Fe(III) compound was quite stable. It could be filtered, washed with ether and vacuum dried.

C. Physical measurements -

Fe(III) compound could easily be analysed for the magnetic moment, molar conductance, infra-red, as well as, electronic spectra. The Ni(III) and Cu(III) complexes had to be handled in a dry box. These compounds were filtered and kept immediately in tightly corked capsules. They were then weighed for the electronic spectra, molar conductance and
chemical analyses of metal and nitrogen.

For magnetic measurements, the latter two compounds were quickly filtered as above, powdered, rammed into a Gouy tube and tightly corked. The rest of the measurements were done as described in chapter III.

Results and Discussion:

Nitric oxide (NO) is very similar to carbon monoxide (CO) in forming a wide range of complexes with transition elements. NO has an additional electron in the antibonding $\pi^{*}$ of NO which is readily lost to give nitrosonium, $\text{NO}^{+}$, ion increasing the stability of the molecule. Overlap of the $\pi$ orbitals and back donation of electrons of metal $\pi$ orbitals into the vacant $\pi^{*}$ of $\text{NO}^{+}$ results in a stronger bond formation. NO$^{-}$ is also formed and it bonds with metal ions donating a pair of electrons.

The three types of NO can be detected from the infra-red absorptions. $\tilde{\nu}$ (NO) at 1876 cm$^{-1}$, 2200-2300 cm$^{-1}$ and 1100-1200 cm$^{-1}$ respectively are for neutral, cationic and anionic forms of NO. Neutral NO does not seem to form complexes. However, NO$^{+}$ can suffer an equivalent donation and back donation resulting a band similar in order to the neutral NO having $\tilde{\nu}$ (NO) in the region 1600-1900 cm$^{-1}$. These compounds usually have exceptional stability due to $d\pi$-$p\pi$ bonding.
The NO\textsuperscript{-} adducts of pentamine and pentacyano compounds of Co(III), Cr(III), Mn(IV) etc.\textsuperscript{3} have been well-established and the $\nu$(NO) has been detected within 1100-1200 cm\textsuperscript{-1} by isotopic substitution. The bonding here is through oxygen atom as in the nitrate complexes.

Complexes having mixed NO species are also known in Fe(NO)\textsubscript{4}, Fe(NO)\textsubscript{3}Cl, (Ph\textsubscript{3}P)\textsubscript{2}Ni(NO)\textsubscript{2} etc.\textsuperscript{3} with both anionic and cationic NO in them.

The Ni(III) and Cu(III) compounds are hygroscopic and become gummy after removal from benzene suspension. But the Fe(III) compound is quite stable and isolated as crystalline solids.

A number of binuclear, oxo-bridged iron(III) complexes are known.\textsuperscript{4} An iron(II) complex with Schiff-bases usually gets oxidised during preparation in the atmospheric air to a compound of type, Fe(III)-O-Fe(III). Such compounds are usually planar having some definite amount of spin-exchange coupling.

During the present preparation from Fe(NH\textsubscript{4})\textsubscript{2}(SO\textsubscript{4})\textsubscript{2}\textsubscript{6}H\textsubscript{2}O and salicylidene glycine the mixture quickly darkened and produced fine crystals, which on analysis corresponded to the empirical formula, (Fe\textsubscript{2}S\textsubscript{2}O\textsubscript{2}.H\textsubscript{2}O).

Infra-red spectrum of the compound has been obtained as sharp distinct bands confirming its purity and showing different modes of vibrations. The compound when heated at 140\textdegree C under vacuum loses the water molecule without substantial change in colour and form.

The broad i.r. band at 3520 cm\textsuperscript{-1} indicates the
presence of lattice water. A sharp and broad band at 1310 cm\(^{-1}\) indicates a monodentate phenolic group to be present. The very sharp band at 1621 cm\(^{-1}\) shows the presence of azomethine group. The carboxylate band vibrations seen at 1542 and 1450 cm\(^{-1}\) may be assigned to \(\nu_{as}\) and \(\nu_{s}\) vibrations. The difference, \(\Delta\nu\), is 92 cm\(^{-1}\) suggesting bidentate nature of carboxylate group. Several workers suggest\(^4\) a band within 800-1000 cm\(^{-1}\) is responsible for oxo-bridged iron(III) complexes. The present compounds have a set of new bands, over and above those due to the free or complexed ligands, at 990, 975 and 825 cm\(^{-1}\), suggesting Fe(III)-O-Fe(III) linkage (Structure-V.1).

Electronic spectrum taken in nujol mull show bands at 16,700 and 20,000 cm\(^{-1}\). They may be assigned to \(\varepsilon_{A1g} \rightarrow 4T_{1g}\) and \(\varepsilon_{E2g}\) transitions in an octahedral symmetry of Fe(III).\(^4\) The \(10D_{1}, 4D_{1}, \text{ and } 3(\varepsilon_{A1g} \rightarrow 4E_{g})\) have been calculated to be 10,340; 795 and 30,200 cm\(^{-1}\) respectively.

Magnetic moment has been found to be 5.28 B.M. Such a low moment is unusual against a normal value of 5.9 B.M. for d\(^5\) electronic configuration with \(\varepsilon_{A1g}\) ground state. It is usually free from orbital and TIP contribution. A low magnetic moment observed can be explained due to superexchange through oxo-bridge resulting a large quenching of the moment. Such low moments are also observed in oxo-bridged Fe(III) complexes with \(-\)amino-phenol and \(-\)aminothiophenol.\(^4\)

\[ \text{Fe}_{2}\text{O}_{3} \text{NO} \text{H}_{2} \]  This compound was formed when the dehydrated Fe(III) complex just described, was suspended in benzene and NO gas was passed through it. A chocolate coloured micro-
Structure V.1

Structure V.2

Structure V.3

M = Ni, Cu
crystalline compound was isolated in pure state which is soluble in methanol, benzene and chloroform.

NO gas does not possibly reduce the Fe(III) as it gives similar electronic spectrum as the starting material. The bridging oxygen is possibly replaced by NO. Literature suggests that nitric oxide usually behaves like NO⁻ type of ligand with higher valent metal ions. NO⁻ stabilizes a higher valency state, whereas, NO⁺ stabilizes a lower valency state.

Electronic spectrum has similar band disposition at 16,130 and 21,050 cm⁻¹ as in (Fe3Sg)2O·H2O indicating an octahedral geometry. The IODq, B and \( \gamma_3 \) were calculated to be 10,250, 780 and 30,450 cm⁻¹ respectively.

Infra-red spectrum gives an additional sharp band at 1155 cm⁻¹ in addition to those present in the parent compound confirming the presence of NO⁻ group.\(^3\) Excepting for a weak band at 850 cm⁻¹ for the modified \( \gamma (C=N) \) vibration of the salicylidene glycine ligand, the band pattern of \( \mu \)-oxo compound within 900-1000 cm⁻¹ is absent in the NO adduct. This, therefore, confirms the absence of the bridging Fe-O·Fe system.

Coordination of the Sg group to Fe(III) in this compound is indicated through the vibrations of \( \tilde{\nu} (C=N) \), \( \tilde{\nu} (C-O) \) and \( \tilde{\nu} (COO⁻) \). The \( \tilde{\nu} (C=N) \) band, associated with \( \tilde{\nu} (C=C) \), appears at 1632 cm⁻¹. The \( \tilde{\nu} (C-O) \) (phenolic) band at 1315 cm⁻¹ indicates a monodentate phenolic group. The asymmetric and symmetric carboxylate vibrations at 1580 and 1462 cm⁻¹ \((\Delta \tilde{\nu} = 113 \text{ cm}^{-1})\) indicate a possible bidentate character of carboxylate group.

One can, therefore, conclude an octahedral structure for this compound to explain the behaviours observed. Magnetic
moment of 3.95 B.M. indicates a strong field contributed by the NO group to cause spin-pairing in the t_{2g} set of Fe(III) orbitals. The quenching of the free ion value in the parent compound is due to oxo-bridge. A NO-bridged complex is not expected to have a greater quenching. Such a large quenching can, therefore, be only explained by spin-pairing (Structure-V.2).

[Co(NO)₃] This compound was obtained in pure state as a chocolate red powder by passing NO gas through a suspension of dehydrated salicylidene glycinate nickel(II) compound in benzene. It is fairly soluble in methyl alcohol and water to give green solution but insoluble in benzene, ether and chloroform. The compound does not liberate iodine from acidified solution of potassium iodides.

Good infra-red spectrum could not be obtained due to ready conversion of the compound to gummy state on exposure. The poor spectrum gave large humps due to moisture and only very weak ligand bands could be obtained. However, weak bands within 1435 - 1630 cm⁻¹ probably due to the schiff base moiety could be observed. Similarly another band at 1148 cm⁻¹ was also observed which may be due to Ñ(NO⁻) in co-ordination with the metal³ (Structure V.2).

The compound is non-electrolyte in methanol. The magnetic moment, though not reliable as it turns easily into gum, is found to be 2.10 B.M.

The electronic spectrum in methanol has a sharp broad band (¢ = 220) at 16,130 cm⁻¹ with main absorptions at 20,000 and 13,245 cm⁻¹. This indicates a highly distorted octahedral form of nickel(II)¹,² which might have been formed due
to solvolysis with methanol.

The above observations, though not very clear, indicate a probable formula of \([(\text{NiS}_2)^{\text{NO}^-}]\) for the complex.

It must, however, be emphasised that this formulation is highly speculative. The inability to liberate iodine from iodide ion may be due to decomposition of the compound in aqueous solution.

\[\text{[CuS}_2\text{NO]}\] This compound was also obtained in a similar manner as the corresponding \text{Ni(III)} complex as a dark-green amorphous powder. Its solubility is also similar. It is hygroscopic and decomposes at 96°C.

It has a magnetic moment of 2.65 B.M. and low molar conductance indicating its non-electrolytic nature.

The infra-red spectrum was of poor quality as in the case of corresponding \text{Ni(III)} compound. Weak broad bands due to schiff base moiety were obtained in the region 1635-1450 cm\(^{-1}\). Similarly broad bands were also obtained in the region 1145-1130 cm\(^{-1}\) which may be ascribed to \(\nu(\text{NO}^-)\) ligated to the metal.

In the same manner as in the case of the corresponding \text{Ni(III)} complex, one may speculate a probable formula of \[\text{[Cu(S}_2\text{)^{\text{NO}^-}]}\].

*****
****
**
*
Table V.1

Analysis, melting point, magnetic moment and molar conductance data of salicylideneaminocarboxylato complexes of Fe(III) and the nitrosyl adducts of Fe(III), Ni(III) and Cu(III) compounds.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Colour and form</th>
<th>Melting point (°C)</th>
<th>Analyses a</th>
<th>$\mu_{\text{eff}}$ (in mhos cm$^2$/mole)</th>
<th>$\lambda_{M}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[(\text{FeSg})_2\text{H}_2]^n$</td>
<td>Reddish brown, Amorphous</td>
<td>$&gt;250^\circ$</td>
<td>22.4</td>
<td>5.5</td>
<td>5.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>22.34 (5.60)</td>
<td>3.6 (3.50)</td>
<td></td>
</tr>
<tr>
<td>$[(\text{FeSgNO})_2\text{H}_2]^n$</td>
<td>Chocolate red, micro-crystalline</td>
<td>$&gt;250^\circ$</td>
<td>19.5</td>
<td>10.0</td>
<td>3.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>19.83 (9.97)</td>
<td>6.5 (6.41)</td>
<td>34.9</td>
</tr>
<tr>
<td>$[(\text{NiSgNO})]$</td>
<td>-do-</td>
<td>147 $^\circ$ d</td>
<td>22.1</td>
<td>10.4</td>
<td>2.10 $^*$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>22.10 (10.54)</td>
<td></td>
<td>7.9</td>
</tr>
<tr>
<td>$[(\text{CuSgNO})]$</td>
<td>Dark green, Amorphous</td>
<td>96 $^\circ$ d</td>
<td>28.6</td>
<td>10.2</td>
<td>2.65 $^*$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>23.48 (10.35)</td>
<td></td>
<td>10.9</td>
</tr>
</tbody>
</table>

a. The figure in parenthesis are calculated values.

* Data not very reliable.
Table-V.2

Infra-red spectra of salicylideneglycinate and other related compounds of Fe(III) (in cm⁻¹).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>ν(C=O)</th>
<th>ν(C=N)+</th>
<th>ν_as(COO⁻)</th>
<th>ν_s(COO⁻)</th>
<th>Δν(COO⁻)</th>
<th>ν(C–O)</th>
<th>ν(N–O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[FeSG₂O₆.H₂O]ₙ</td>
<td>3520</td>
<td>1621</td>
<td>1542</td>
<td>1450</td>
<td>92</td>
<td>1310</td>
<td></td>
</tr>
<tr>
<td>[FeSG.NO]₂·H₂O</td>
<td>3450</td>
<td>1532</td>
<td>1580</td>
<td>1462</td>
<td>113</td>
<td>1315</td>
<td>1155</td>
</tr>
</tbody>
</table>
### Table V.3

Electronic spectra of salicylideneglycinato and other related compounds of Fe(III), Ni(III) and Cu(III) (in cm⁻¹).*

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Electronic Bands (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(FeSG)₂O₄H₂O]ₙ</td>
<td>16,700 (ν₁) 20,000 (ν₂) 30,200 (ν₃, calculated)</td>
</tr>
<tr>
<td>[(FeSG₂O)₂(H₂O)₂]</td>
<td>16,130 (ν₁) 21,060 (ν₂) 30,450 (ν₃, calculated)</td>
</tr>
<tr>
<td>[NiSG₂O₄]</td>
<td>13,245 16,130 20,000</td>
</tr>
<tr>
<td>[CuSG₂O₄]</td>
<td>17,545</td>
</tr>
</tbody>
</table>

* Spectrum of the first compound taken in nujol mull and the spectra of the rest taken in methanol.
References


3. Ref. 1, Page 255, 627.


Fig. V.1 - Electronic spectra of (I) $[\text{FeS}_5\cdot\text{NO}]_2\cdot\text{H}_2\text{O}$, (II) $[\text{NiS}_5\cdot\text{NO}]$ and (III) $[\text{CuS}_5\cdot\text{NO}]_2$ in methanol.