

# Mixed ligand hetero-bimetallic complexes of Nickel(II) dimethylglyoxime and aluminium(III) metal chelates of some organic acids

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## ABSTRACT

The formation of oxygen bridged complexes containing two different ligands have been of interest to coordination chemists. In order to extend the studies of oxygen bridged complexes, we have selected bivalent nickel dimethylglyoximate, and have synthesised mixed ligand bimetallic complexes of aluminium metal with them, of the general formula,  $[\text{Ni}(\text{DMG})_2(\text{AlL}_2)_2]$ , where L = deprotonated o-nitrophenol(ONP), 2,4-dinitrophenol(DNP), 2,4,6-trinitrophenol(TNP), 8-hydroxy-quinoline(8HQ) or 1-nitroso-2-naphthol(1N2N) and DMG = dimethylglyoxime.

**Keyword:-**DMG,ONP,DNP,TNP,8HQ,Ni(II) metal & Al(III) metal chelate,Infrared spectra.

## INTRODUCTION

The synthesis of oxygen bridge complexes of copper(II) bis(salicyaldoximate) and nickel(II) bis(salicyaldoximate), using metal complex as ligands, phenolic and oximino oxygen atoms. On the basis of their infrared, electronic spectra and magnetic properties of adducts, we have suggested the coordination of aluminium metal through phenolic and oximino oxygen atoms.

In order to extend the studies of oxygen bridged complexes, we have selected nickel(II) dimethylglyoximate as our ligand. In this chapter an attempt has been made to synthesise and characterise mixed ligand bimetallic complexes of aluminium(III) metal cheletes of organic acids, e.g., o-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol, 1-nitroso-2-naphthol and 8-hydroxyquinoline with Ni(II) dimethylglyoxime [denoted by  $\text{Ni}(\text{DMG})_2$ ].

Dimethylglyoxime is the most widely applied and accepted gravimetric reagent for both Ni(II) and Pd(II). It is also used in detection and separation of traces of nickel in cobalt salts.It provides potential bonding sites for metal ions (e.g.  $\text{Ni}^{2+}$ ).

The X-ray structure determination<sup>83</sup> of  $\text{Ni}(\text{DMG})_2$  has revealed two features of interest. Planar molecules of the compound are so arranged with planar parallel that nickel atoms of adjacent molecules are only 3.24 apart (alternative molecules living rotated through  $90^\circ$  to allow room for the methyl group, and indicate weak metal-metal bonding. This conclusion appears to be supported by the peculiar dichroism exhibited by the complex. Further more, the oxygen-oxygen distance (2.44) is the shortest known separation of hydrogen bonded oxygen atoms. Also it has been reported that the hydrogen bonds in the complexes

investigated are not of the symmetrical type, in the sense that the proton does not occupy a central position between two oxygen atoms. The observed symmetry of the nickel and the palladium dimethyl glyoxime complex may be of a statistical character, which would simply the peaks of the spectra due to the vibration C=N & N-O.

Reaction of aluminium isopropoxide with palladium(II) is chelate of dimethyl glyoxime and some ortho-hydroximes shows<sup>86</sup> that the O-H...O bridges in the Pd(II) bis chelates of this ligands are completely replaced by the O-Al(O-Pr<sup>i</sup>)<sub>2</sub>-O-bridges-bridges and pure Al(OPr<sup>i</sup>)<sub>2</sub> bridges complexes are isolated. This observation are in good agreement with the fact that the alkoxides have a powerful tendency to react with the labile protons<sup>87</sup>.

## EXPERIMENTAL

Analar quality of DMG, ONP, DNP, TNP, 8HQ, 1N2N were used for the preparation of Ni(II) and Al(III) chelates and adducts.

### Oxygen bridged adducts of Al(III) metal chelates with Ni(DMG)<sub>2</sub> :

#### 1. Adducts with aluminium metal chelates of o-nitrophenol :

Ni(DMG)<sub>2</sub> was taken in absolute ethanol in a conical flask and aluminium metal chelate of organic acid (viz. ONP, DNP, TNP, 8HQ, 1N2N) was added to it in the ratio of 1 : 2 (mole). It was refluxed at 80°C with constant stirring on hot plate for one hour. Whole mass went into solution and pink colour adduct was precipitated in hot condition. It was cooled, filtered, washed with absolute ethanol and dried in an electric oven at 80°C. Yield : 0.719 gm (80%)

## RESULTS AND DISCUSSION

**Physical properties :** Some physical properties of the metal chelate [Ni(DMG)<sub>2</sub>] and its aluminium (III) metal adducts are listed in Table - 1.

The colour of Ni(DMG)<sub>2</sub> is red. The colour of the adducts prepared from the Ni(DMG)<sub>2</sub> are usually brown or pink. Therefore, it is clear that from the colour the adducts [M<sub>a</sub>(DMG)<sub>2</sub>(M<sub>b</sub>L<sub>2</sub>)<sub>2</sub>] are different from the complex ligand.

The decomposition temperature of these adducts are also different from those of their respective ingredients. The higher decomposition temperatures of these adducts compared to that of Ni(DMG)<sub>2</sub>, show the strong bonding through oxygen atoms of the complex ligands to the alkaline earth metal.

The adducts are slightly soluble in ethanol and benzene. These are stable under dried condition, but decompose on exposures to moisture, as such, were kept in a desiccator over solid anhydrous calcium chloride.

TABLE – 1

Physical properties of Ni(DMG)<sub>2</sub> & its adducts with aluminium(III) metal salts of some organic acids

Compound	Colour	Decomp./ Trans. Temp.(°C)	Conductivity*
Ni(DMG) <sub>2</sub> (Nickel dimethylglyoxime)-	Red	170t	---
Ni(DMG) <sub>2</sub> .[Al(ONP) <sub>2</sub> ] <sub>2</sub>	Pink	> 280	8.1
Ni(DMG) <sub>2</sub> .[Al(DNP) <sub>2</sub> ] <sub>2</sub>	Brick red	245t	9.8
Ni(DMG) <sub>2</sub> .[Al(TNP) <sub>2</sub> ] <sub>2</sub>	Pink	240t	7.8
Ni(DMG) <sub>2</sub> .[Al(8HQ) <sub>2</sub> ] <sub>2</sub>	Brown red	280d	8.5
Ni(DMG) <sub>2</sub> .[Al(1N2N) <sub>2</sub> ] <sub>2</sub>	Brown	295d	6.5

\*Molar conductivity (ohm<sup>-1</sup>cm<sup>2</sup>mole<sup>-1</sup>) solution in DMF at 30°C

**Infrared spectra :** Infrared spectra measurements were made in Nujol Mull for complex ligands[Ni(DMG)<sub>2</sub>] & adducts between 4000–400 cm<sup>-1</sup>. Selected absorption bands in different region of Ni(II)-dimethylglyoximate are given in Table - 2.

The most important feature is that while there are important differences between the infrared spectrum of Ni(DMG)<sub>2</sub> and binuclear complexes formed when it acts as a ligand, the spectra of the various complexes are essentially the same. This tells us that the basic structure of the complexes are the same. Obviously the effect of coordination will be most for bands associated with the oxime oxygen, and progressively less for linkages further from the coordination sites.

It was proved by these experiments that the C = N frequencies of the complexes were always in the range of 1500–1600 cm<sup>-1</sup>. The bands in the range 1600–1800 cm<sup>-1</sup> were OH deformation bands. It has been possible to assign reliably the peaks of the spectra due to the vibration C=N and N–O.

TABLE – 2

IR absorption bands of Ni(DMG)<sub>2</sub> & aluminium (III) metal complexes (in cm<sup>-1</sup>)

Compound	Selected IR absorption bands (in cm <sup>-1</sup> )	
	C=N	N-O
Ni(DMG) <sub>2</sub> (Nickel dimethylglyoxime)	1576	1238 1100
Ni(DMG) <sub>2</sub> .[Al(ONP) <sub>2</sub> ] <sub>2</sub>	1639, 1568	1217 1094
Ni(DMG) <sub>2</sub> .[Al(DNP) <sub>2</sub> ] <sub>2</sub>	1627, 1537	1216 1095
Ni(DMG) <sub>2</sub> .[Al(TNP) <sub>2</sub> ] <sub>2</sub>	1635, 1521	1216 1096
Ni(DMG) <sub>2</sub> .[Al(8HQ) <sub>2</sub> ] <sub>2</sub>	1604, 1580	1217 1114
Ni(DMG) <sub>2</sub> .[Al(1N2N) <sub>2</sub> ] <sub>2</sub>	1651, 1635	1219 1088

Measurement of infrared and ultraviolet spectroscopy have proved that the two N–O groups in dimethylglyoxime are not equivalent in the complexes, as in the DMG. This phenomenon has also been supported by the investigation of Ni(II) dimethylglyoxime by X-ray diffraction, when it has been noted that two different distances of metal-nitrogen bond exist in these complexes.

After comparing the infrared spectrum of dimethylglyoxime with those of the complexes, the character and shape of the broad OH band proved that with the exception of cobalt (III) complexes, all the complexes had stable hydrogen bridges<sup>90</sup>.

In the complexes of Fe(II), Fe(III) and Co(III) as well as in the complexes of Ni(II), Pd(II) and Pt(II), both molecules of dimethylglyoxime are situated in the same plane. The Fe(II) and Fe(III) complexes of compositions Fe(DMG)<sub>2</sub>OH and Fe(DMG)<sub>2</sub>(OH)<sub>2</sub>, have a distorted octahedral structure (two OH<sup>-</sup> or OH<sup>-</sup> and H<sub>2</sub>O filling in the fifth and sixth coordination position). The cobalt(II) complex of composition M(II)(DMG)<sub>2</sub> has a square planar structure similar to the complexes of Ni(II), Pd(II) and Pt(II).

In the Co(II) complex of the composition Co(DMG)<sub>3</sub>, the three molecules of dimethylglyoxime are in an octahedral symmetry. In this complex there is no possibility of formation of a hydrogen bridge analogous to that in other complexes. The Fe(II) complex showed in lowest frequency for the C=N vibration, denoting that in the chelate ring of this complex, more conjugation took place.

For the dimethylglyoxime molecule, the broad peak at 3400–3100 cm<sup>-1</sup> suggest that there has been strong hydrogen bonding. Again the observed 1440cm<sup>-1</sup> peak is too low for C=N frequency. However, a polymeric hydrogen bonded conjugation ring system, could account for the low C=N frequency .

When dimethylglyoxime forms complexes with di- and tri-valent metal ions, the observed C=N frequencies are between 1550–90 cm<sup>-1</sup>. All reported values show a single C=N bond for these complexes; but there always exist one shoulder along with the strong absorption bands of C=N. As has been reported earlier, the structure of these complexes show attachment of the metal ion with two nitrogens of C=N group, forming a five membered ring.

It is reported that C=N shifts to higher frequency on coordination. But the frequencies of coordinated C=N group in these complexes are low. Again the observed values would agree well with a resonance hybrid forming a pseudo-aromatic ring, where C=N losses and C–C acquires a double bond character (Fig.6). The observed shoulder along with C=N, thus can be explained due to presence of C–C frequency.

First proposed that the reaction of BF<sub>3</sub> with bis-(dimethylglyoximate) nickel(II) resulted in the substitution of the two protons involved in O.....O bridging by BF<sub>3</sub> unit yielding the macrocyclic trinuclear compound.

The infrared spectra showed a C=N band at 1638 cm<sup>-1</sup>. This band frequency in comparison to Ni(DMG)<sub>2</sub> was raised by 72 cm<sup>-1</sup>. This signified that the oxime - nitrogen atoms became positive, due to

the electromagnetic  $\text{BF}_2$  groups. The bands at  $1190\text{ cm}^{-1}$  and  $1105\text{ cm}^{-1}$  in this complex were assigned to N–O frequency; the corresponding N–O frequencies in  $\text{Ni}(\text{DMG})_2$  were at  $1238\text{ cm}^{-1}$  and  $1100\text{ cm}^{-1}$ . The C=N frequency of  $\text{Pd}(\text{DMG})_2$  has been reported<sup>92</sup> at  $1552\text{ cm}^{-1}$  and for the corresponding  $\text{Pd}(\text{DMG})_2 \cdot \text{B}_2(\text{n-C}_3\text{H}_7)_4$  it showed up at a higher frequency,  $1608\text{ cm}^{-1}$ .

The structure of binuclear aluminium metal adducts with  $\text{Ni}(\text{DMG})_2$  and correspondingly, C=N and N–O frequencies of the above two will be affected most when compared with the complex ligand, bis-dimethylglyoximate.

The C=N frequency of  $\text{Ni}(\text{DMG})_2$  at  $1576\text{ cm}^{-1}$  shows the upward trend in the aluminium metal adducts and an observed between  $1521\text{--}1651\text{ cm}^{-1}$ .

The N–O band of  $\text{Ni}(\text{DMG})_2$  at  $1238\text{ cm}^{-1}$  shows a downward trend in the aluminium metal adducts which are observed between  $1216\text{--}1219\text{ cm}^{-1}$ . The other N–O band at  $1100\text{ cm}^{-1}$  for  $\text{Ni}(\text{DMG})_2$  also shows a downward shift  $1088\text{--}1096$ , except  $\text{Ni}(\text{DMG})_2 \cdot [\text{Al}(\text{8HQ})_2]_2$  in their aluminium metal adducts.

#### **Electronic absorption spectra:**

Electronic absorption spectra of metal complex ligand,  $\text{Ni}(\text{DMG})_2$  and its Al(III) adducts were recorded on Systronic Double Beem UV-VIS spectrophotometer 2202 in methanol. The bands observed in electronic spectra of the compounds are listed in Table - 3.

The absorption band of medium intensity at  $475\text{ nm}$  for  $\text{Ni}(\text{DMG})_2$  suggests a square planar structure of  $\text{Ni}^{2+}$  ion. In  $\text{Ni}(\text{DMG})_2(\text{BF}_2)_2$ , again there has been only one broad absorption band at  $475\text{ nm}$ , suggesting that the stereo-chemistry of the central metal ion remains unchanged [i.e. square as that of  $\text{Ni}(\text{DMG})_2$ ].

Absorption band of binuclear aluminium metal oxygen bridge adducts derived from  $\text{Ni}(\text{DMG})_2$  has been formed between  $490\text{ nm} - 525\text{ nm}$ . This suggests that even in them trinuclear oxygen bridged adducts, the central  $\text{Ni}^{2+}$  ion retain its square planar structure.

TABLE – 3

Electronic absorption spectra (in nm) for Ni(DMG)<sub>2</sub> and its adducts with aluminium metal salts of some organic acids

Compound	Absorption band ( in nm)
Ni(DMG) <sub>2</sub>	360
Ni(DMG) <sub>2</sub> .[Al(ONP) <sub>2</sub> ] <sub>2</sub>	495, 525
Ni(DMG) <sub>2</sub> .[Al(DNP) <sub>2</sub> ] <sub>2</sub>	495, 506, 515
Ni(DMG) <sub>2</sub> .[Al(TNP) <sub>2</sub> ] <sub>2</sub>	490, 510
Ni(DMG) <sub>2</sub> .[Al(8HQ) <sub>2</sub> ] <sub>2</sub>	498, 520
Ni(DMG) <sub>2</sub> .[Al(1N2N) <sub>2</sub> ] <sub>2</sub>	492, 512 525

### Magnetic property :

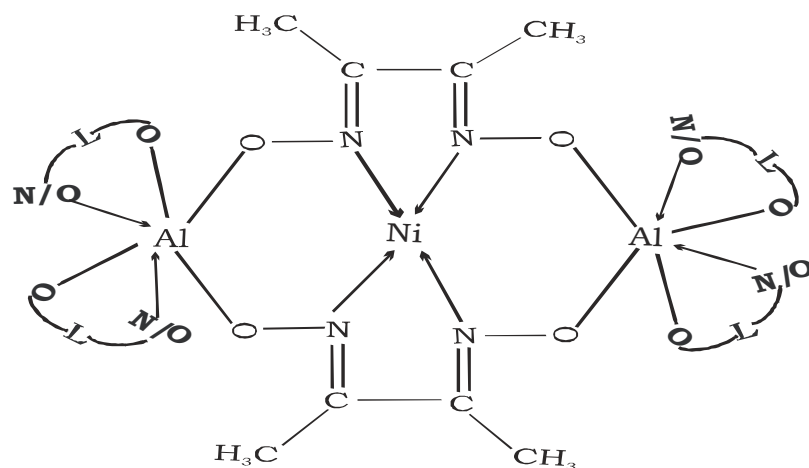
Magnetic measurement were taken on Cahn-Faraday electronic balance at 30° C. Bisdimethylglyoximato nickel(II) is diamagnetic, suggesting a square planar geometry with coordination number 4. The binuclear oxygen bridged complexes of aluminium metal cheletes with Ni(DMG)<sub>2</sub> are also diamagnetic in nature suggesting the same stereo-chemistry of Ni(DMG)<sub>2</sub> in adducts.

TABLE – 4

Compound	Values of $\mu_{\text{eff}}$ (in BM)
Ni(DMG) <sub>2</sub> (Nickeldimethylglyoxime)	Diamagnetic
Ni(DMG) <sub>2</sub> .[Al(ONP) <sub>2</sub> ] <sub>2</sub>	Diamagnetic
Ni(DMG) <sub>2</sub> .[Al(DNP) <sub>2</sub> ] <sub>2</sub>	Diamagnetic
Ni(DMG) <sub>2</sub> .[Al(TNP) <sub>2</sub> ] <sub>2</sub>	Diamagnetic
Ni(DMG) <sub>2</sub> .[Al(8HQ) <sub>2</sub> ] <sub>2</sub>	Diamagnetic
Ni(DMG) <sub>2</sub> .[Al(1N2N) <sub>2</sub> ] <sub>2</sub>	Diamagnetic

### STRUCTURE & BONDING

On the basis of elemental analysis, the molecular formula of binuclear aluminium metal oxygen bridged adducts has been suggested as [Ni(DMG)<sub>2</sub>(AlL<sub>2</sub>)<sub>2</sub>] where AlL<sub>2</sub> is Al(III) cheletes of deprotonated o-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol, 8-hydroxyquinoline and 1-nitroso-2-naphthol. An infrared studies of these adducts, suggests that Ni(DMG)<sub>2</sub> acts as a Lewis base to the Lewis acid (i.e. aluminium metal cheletes); coordination is through hard oxygen atoms. The probable structure of the oxygen bridged complex is shown in Fig. 1



(Fig. 1)

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