

Metal Complexes as ligand : Binuclear Ni(II) and Cu(II) metal chelates of p-Methylisonitrosoacetophenone with Alkaline earth metal salts

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Abstract: A number of new binuclear complexes have been synthesised by interaction of stable Ni(II) and Cu(II) metal chelates of p-Methylisonitrosoacetophenone with Alkaline earth metal salts having general formula $[M_a(p\text{-MeINAP})_2M_bL_2 \text{ or } M_bX_2]$ where $M_a = \text{Ni(II) or Cu(II)}$, p-MeINAP = deprotonated p-Methylisonitrosoacetophenone, $M_b = \text{Ca}^{++} \text{ or } \text{Mg}^{++}$, L = deprotonated ortho amino benzoic acid and 8-hydroxyquinoline X = ClO_4^- or Cl^- . The IR Spectral studies suggest that the Ni(II) and Cu(II) metal chelates act as ligand and coordination towards alkaline earth metal salts takes place through oxygen atom of oximino group. The diffuse reflectance electronic spectra and magnetic moment values of the metal chelates and binuclear complexes with alkaline earth metal salts indicate the change in geometry during complex formation.

Keyword: p-Methylisonitrosoacetophenone, Ortho amino benzoic acid, perchlorate, chloride and 8-hydroxyquinoline.

Introduction

In recent years the formation of oxygen bridged binuclear complexes containing two different ligands¹⁻¹⁸ has become of interest to coordination chemists. The work deals with oxygen-bridged alkaline earth metal complexes with "metal complexes as ligands". It has been observed that even after the ligands combined with cation forming stable metal compound, the coordinating ability of the ligand, is not fully saturated and in turn, the metal complexes so formed still have donor properties acting as a lewis base and under suitable condition, react with lewis acid, forming stable polynuclear mixed metal mixed ligand complexes.

In view of the above, it was decided to extend the investigation by a systematic examination of the complexes of Ni(p-MeINAP)_2 and Cu(p-MeINAP)_2 with alkaline earth metal salts, which may be useful in understanding the transport and absorption mechanism of alkaline earth metal ions from soil to plant.

Experimental

Our usual method of synthesis was to take Ni(p-MeINAP)_2 or Cu(p-MeINAP)_2 in an absolute ethanol and to add alkaline earth metal salts to it in 1:1 stoichiometry ratio, usually slight excess of alkaline earth metal salts were taken. The reaction mixture was refluxed with constant stirring on hot plate for about 3 to 4 hours at 60°C . The whole substance went in to solution and subsequently the adducts were precipitated in hot condition during the process of refluxing. They were filtered, washed several times with absolute ethanol and then dried in oven at 80°C .

Result and discussion

The adducts are stable under dry condition, but decompose on exposure to moisture, as such they were kept in a desiccator over anhydrous CaCl_2 . The colour, decomposition temperature and analytical values of these complexes are given in table 1.

Table 01

Compound	Colour	Transition($t^{\circ}c$) or decomposition($d^{\circ}c$)temp.	(%) Found				(%) Calculated				Magnetic moment Values of μ_{eff} in B.M.
			C	H	N	M	C	H	N	M	
Ni(p-MeINAP) ₂	Light green	285d	55.07	03.98	07.39	15.75	55.17	04.05	07.57	15.88	02.76
Ni(p-MeINAP) ₂ Mg(8HQ) ₂	Yellow	>320	62.0	3.92	8.00	8.36	62.15	4.02	8.05	8.44	3.74
Ni(p-MeINAP) ₂ Mg(Clo ₄) ₂	Light Brown	>300 250 t	35.65	2.23	4.60	9.68	35.76	2.31	4.63	10.16	3.68
Ni(p-MeINAP) ₂ CaCl ₂	Yellowish brown	295 d	43.66	3.14	5.59	11.81	43.75	3.24	5.67	11.89	3.31
Cu(p-MeINAP) ₂	Green	130 m and d	54.33	03.89	07.39	16.82	54.47	04.00	07.47	16.95	01.19
Cu(p-MeINAP) ₂ Mg(Clo ₄) ₂	Green	185 d	35.28	2.50	4.55	10.30	35.36	2.61	4.58	10.39	1.85
Cu(p-MeINAP) ₂ Ca(OABA)	Light Brown	260 d	54.80	3.92	7.94	9.00	54.89	4.00	8.00	9.07	2.20

INFRARED SPECTRA

Detailed discussion of Infrared spectra, magnetic properties and electronic spectra of binuclear alkaline earth metal adducts have been done to establish their structure and bonding

Infrared spectral measurements were made in Nujol mull/KBr disc in the region between 4000-200 cm^{-1} . pertinent IR data for the metal chelates as well as the adducts have been recorded in table 2.

It is evident from the reported¹⁹ trinuclear alkaline earth metal adducts with Ni(DMG)₂ and Pd(DMG)₂ that C=N and N-O frequencies of the metal chelates got appreciable shift on the adduct formations.

The C=N frequency of Ni(DMG)₂ at 1576 cm^{-1} shifts to 1580-1590 cm^{-1} in the alkaline earth metal adducts, and the corresponding C=N frequency of Pd(DMG)₂ at 1552 cm^{-1} again shows the upward trend in its adducts, and are observed at 1560-1572 cm^{-1} .

The N-O band of Ni(DMG)₂ at 1241 cm^{-1} shows a downward trend in the alkaline earth metal adducts (between 1214-1230 cm^{-1}). Similar trend has also been observed for Pd(DMG)₂; the ligand N-O vibration at 1259 cm^{-1} shows up at 1206-1212 cm^{-1} in the corresponding alkaline earth metal adducts. The other ligand N-O band at 1103 cm^{-1} for Ni²⁺ and 1091 cm^{-1} for Pd²⁺, are also slightly changed on their corresponding alkaline earth metal adducts.

Same type of observation²⁰ is also found in the trinuclear alkaline earth metal adducts of Ni(II) bis-salicylaloximates and Cu(II) bis-salicylaloximate chelates. The C=N frequency of the Ni(SAO)₂ observed at 1558 cm^{-1} in the trinuclear alkaline earth metal adducts and the corresponding C=N of Cu(SAO)₂ at 1548 cm^{-1} again shows the upward trend in its adducts and are observed at 1560-1580 cm^{-1} . The characteristic absorption of C-O stretching vibration observed at 1020 cm^{-1}

Table 2
IR absorption bands in cm^{-1}

Adducts	V ClO ₄ ⁻	V C=O	V C=N	V N-O	V M-N	V M-O
Ni(p-MeINAP) ₂		1588s	1552s	1170s	486br	395br
Ni(p-MeINAP) ₂ Mg(ClO ₄) ₂	1080m, 1102m 1162sh, 1000s 930s	1595vs	1570s	1185m	484m	400s, 350m, 250m, 300sh
Ni(P-MeINAP) ₂ Mg(8HQ) ₂		1600m	1580s	1180s		
Cu(p-MeINAP) ₂		1588vs	1545s	1174vs	502m	385s
Cu(P-MeINAP) ₂ Ca(OABA) ₂		1610br	1550s, 1530s	1170m,		
Cu(p-MeINAP) ₂ Mg(ClO ₄) ₂	1177s, 1115m, 1110m, 930m	1585vs	1550vs	1190m	510m, 500 br	390br, 350s, 330br

and 1030cm^{-1} in Ni(SAO)₂ and Cu(SAO)₂ respectively, show upward shift in the range of 1035 to 1040cm^{-1} in the alkaline earth metal adducts. The N-O stretching vibration observed at 1220 and 1202cm^{-1} in Ni (SAO)₂ show upward shift to 1230 - 1245cm^{-1} and the corresponding N-O of Cu (SAO)₂ at 1193cm^{-1} also shifts to 1210 - 1220cm^{-1} in the trinuclear alkaline earth metal adducts of the chelates. Table-2 shows the infrared absorption observed in Ni (p-MeINAP)₂ and Cu(p-MeINAP)₂ metal chelates and its binuclear derivatives.

The band near 1588 , 1552 , and 1170cm^{-1} in Ni(p-MeINAP)₂ and 1588 , 1545 , and 1174cm^{-1} in Cu(p-MeINAP)₂ have been assigned to the $\nu\text{C}=\text{o}$, $\nu\text{C}=\text{N}$ and $\nu\text{N}-\text{o}$ stretching frequency. In the alkaline earth adducts of metal chelates of Ni(p-MeINAP)₂, the C=N frequency shifts to 1570 - 1580cm^{-1} and the corresponding C=N frequency of Cu(p-MeINAP)₂ shows the same trend in its adducts and are observed at 1530 - 1550cm^{-1} .

The N-O stretching frequency shows significant higher shift to 1180 - 1185cm^{-1} and 1170 - 1190cm^{-1} respectively in the binuclear adducts of Ni(p-MeINAP)₂ and Cu(p-MeINAP)₂, suggesting the involvement of oxygen atom of N-O group in coordination with alkaline metal ion. Slight change in $\nu\text{C}=\text{o}$ absorption band has also been observed in the complexes probably due to change in stereochemistry viz trans from to cis form.

Further, in the low frequency region, the band observed at 486 and 395cm^{-1} in Ni(p-MeINAP)₂ and 502 and 385 in Cu(p-MeINAP)₂ are assigned to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$. The appearance of the additional bands around 375 - 250cm^{-1} are probably due to the bridging oxygen metal band and cis-isomeric form of the metal chelates of Ni(p-MeINAP)₂ and Cu(p-MeINAP)₂ in their adducts. These evidences clearly show that adduct formation is taking place through oxygen atom of N-O group.

The medium intensity peaks in the region at 1080 - 1185cm^{-1} show that band at region 1100cm^{-1} has split into two peaks. An extra peak at region 930 - 935cm^{-1} has also been spotted. These evidences clearly indicate the presence of coordinated perchlorate in the adducts of alkaline earth metal perchlorate.

Magnetic property

Magnetic measurements were taken on Cahn-Faraday electronic balance at 33°C . The results of the magnetic measurements are given in table-1.

The octahedral complexes of Ni(II) are always paramagnetic but the possibility of diamagnetic complexes cannot be ruled out. In most of the complexes, the room temperature magnetic moment values of the octahedral Ni(II) complexes are observed between 2.90 to 3.4 B.M. depending on the magnitude of the orbital contribution²¹. The planar complexes of Nickel(II) are almost diamagnetic, but theoretically paramagnetic planar complexes are possible²². Tetrahedral Ni(II) complexes are paramagnetic and their room temperature magnetic moment values are usually higher than the spin only values expected for two unpaired electrons²³ (3.4 to 4.2 B.M.), however, in some cases lower magnetic moment values have also been reported²⁴⁻²⁵. The high magnetic moment values of the complexes are due to orbital contribution and are the functions of temperature. It is noted that the high magnetic moment values also depend upon the detailed symmetry of the ligand field present, as well as, on the delocalization of the electron in the ligand molecule²⁶. Five coordinated complexes are either diamagnetic square pyramidal or paramagnetic trigonalbipyramidal with sp^3d hybridization and their magnetic moment values are similar to four coordinated tetrahedral Nickel(II) complexes²⁷⁻²⁸. Besides regular tetrahedral, planar and octahedral complexes, a large number of Ni(II) complexes have been reported²⁹⁻³³ in which the diamagnetic nature of the compound turned into paramagnetic, suggesting the octahedral or tetrahedral structure of the compounds or there is existence of equilibrium with two different structural species in the same crystal of sometimes as the mixture of two different geometrical isomers varying proportions. Thus,

a large number of Ni(II), complexes display anomalous magnetic moment values. **Haldar et al.**³⁴ reported the μ_{eff} value 2.76 at 293°k for the complex, Ni(INAP)₂, which are very close to the spin only value for two unpaired electrons in octahedral Ni(II) complexes.

They also showed that the magnetic moment of the Ni(INAP)₂ complex vary from 2.76 B.M. at 293°k to 1.98 B.M. at 80°k, indicating antiferromagnetic interaction. The temperature independent paramagnetism ($N\alpha$) was also calculated and on the basis of above observations, the dimeric nature of the Ni(II) complex was proposed. A similar behaviour was also observed by **Lintvedt et al.**³⁵

In the present investigation, the binuclear alkaline earth metal adducts of Ni(p-MeINAP)₂ possess room temperature magnetic moment values between 3.31 and 3.74 B.M., which are higher than the reported values for most of the octahedral Ni(II) complexes, but occur in the range of μ_{eff} values reported for tetrahedral complexes.

The majority of the copper(II) complexes display magnetic moment values in the range of 1.75 to 2.20 B.M., while the magnetic moment values of some Cu(II) complexes are substantially below the spin only values (1.73 B.M.) and remarkably temperature dependent.

The complexes, which have magnetic moment values lower than the spin only value, are termed as magnetically subnormal complexes. In such complexes, the pairs or copper(II) atoms are held together by bridging halogens, hydroxo and carboxylate groups or ligand molecules³⁶⁻³⁷. In the extreme cases, copper(II) ions are so closely coupled that the dimers become diamagnetic³⁷⁻³⁸. In such dimers the unpaired electron of each copper(II) atom interacts with the other and the interaction is so effective that almost pure σ bond results between the two copper atoms, rendering negligible magnetic moment contribution to those copper(II) complexes. Polymeric copper(II) complexes also display subnormal magnetic moment values for the same reason. Copper(II) complexes whose magnetic moment values lie between 1.75 and 2.2 B.M. are termed as magnetically dilute complexes and their magnetic moment values are independent of temperature. A qualitative picture of the geometries, emerging from the range of magnetic moment values of the planar Cu(II) complexes is not always valid. The magnetic moment values of the planar complexes occur in the vicinity of spin only value (1.73 B.M.), while the room temperature magnetic moment values of tetrahedral and octahedral copper(II) complexes occur between 1.88 and 2.2 B.M.

In the present investigation the magnetic moment of Cu(p-MeINAP)₂ has been found to be 1.19 B.M. at room temperature. Which is markedly lower than the spin only value of 1.73 B.M.

Similar subnormal value was also observed by **Natrajan et al.**³⁹ and suggested that this lower magnetic moment value is due to antiferromagnetic interaction and this may arise through molecular associations involving oxobridges. The binuclear alkaline earth metal salt adducts of Cu(p-MeINAP)₂ display magnetic moment values between 1.85 to 2.20 B.M. Thus it is clear that the binuclear adducts are magnetically dilute and their magnetic moment values fall in the range of tetrahedral Cu(II) complexes.

ELECTRONIC SPECTRA

All diffuse reflectance electronic spectra were recorded on SHIMADZU UV-VIS-160A spectrophotometer in Nujol mull/Paraffin solvent. The bands observed in electronic spectra of Ni(p-MeINAP)₂ and Cu(p-MeINAP)₂ and their adducts are given in Table – 3.

Table - 3
Major diffuse reflectance bands (nm) for Ni(p-MeINAP)₂/Cu(p-MeINAP)₂
Complex and its alkaline earth metal adducts.

Compound	Diffuse Reflectance (nm)
Ni(p-MeINAP) ₂	974w, 620w, 365s, 343m, 302sh, 236m
Ni(p-MeINAP) ₂ Mg(ClO ₄) ₂	650w, 400br, 342s, 301m, 260br
Ni(p-MeINAP) ₂ CaCl ₂	640sh, 434br, 340m, 239m
Cu(p-MeINAP) ₂	636br, 410s, 341m, 300m, 246s
Cu(p-MeINAP) ₂ Mg(ClO ₄) ₂	1030m, 728sh, 369br, 341s, 301m, 260br

br= broad, s= strong, m= medium, w= weak, sh= shoulder, h= hump

The electronic spectra of Ni(p-MeINAP)₂⁴⁰ complexes in Nujol display bands in region 236-365 nm due to charge transfer. The band at 620nm and 970nm are assigned to the first and second spin allowed transition ³A_{2g}->³T_{1g}(F) and ³A_{2g}->³T_{2g}(F) respectively, characteristic of Ni(II) in an octahedral environment. The ³A_{2g}(F)->³T_{1g}(P) transition could not be observed owing to a very strong charge transfer band tailing into the visible region⁴¹. The spectra of binuclear adducts are different in nature and the band usually observed in the region 640-650nm may be assigned ³T₁(F) ->³T₁(P) transition⁴². Lower energy bands due to the transition ³T₁(F) ->³A₂(F) and ³T₁(F) could not be recorded in few cases due to limitations of the instrument. Hence the nature of

absorption band of alkaline earth metal adducts suggests that octahedral structure of Ni(p-MeINAP)₂ has probably been converted into tetrahedral structure, this fact is also supported by magnetic moment studies.

The electronic spectra of the Cu(p-MeINAP)₂ complex in chloroform exhibit a broad envelope centred in the region 636 nm. This may arise from a combination of at least two transitions for tetragonal complexes of Cu(II)⁴³. Charge transfer bands also appear in the region 246-410nm.

Sacconi and Ciampolini⁴⁴ have examined the spectra of a number of Cu(II) complexes and found that the ligand field absorption bands in the region 600-1250nm, shift to higher wave length as the environment about the copper atoms, tends from octahedral/tetragonal/planar to tetrahedral.

Same conclusions have also been observed in the formation of oxygen bridged complexes. The diffuse reflectance spectra of some alkaline earth metal adducts of the Cu(p-MeINAP)₂ complexes in table 4 show the bands in the region at 728-1030nm. Hence, the change in the position and intensity of the absorption bands indicates the adduct formation as well as change in the geometry from tetragonal to tetrahedral.

CONCLUSIONS (STRUCTURE AND BONDING)

On the basis of elemental analysis, the molecular formula of binuclear alkali metal adducts has been suggested as [M_a(p-MeINAP)₂.M_bL₂] and [M_a(p-MeINAP)₂.M_bX₂] for alkaline earth metal adducts where M_a is Ni⁺⁺ or Cu⁺⁺ and M_b=Ca⁺⁺Mg⁺⁺, L is deprotonated 8-hydroxyquinoline and ortho amino benzoic acid, X=ClO₄⁻, Cl⁻.

The infrared spectral studies of these adducts, suggest that M_a(p-MeINAP)₂ acts as a Lewis base to the Lewis acid (alkaline earth metal salt); coordination is through hard oxygen atoms. The bonding between the bis-p-Methylisonitrosoacetophenonato complexes, M_a(p-MeINAP)₂ and the alkaline metals, most likely occur by dative bonding via the oximino oxygen atoms of the ligand which has been supported by the I.R. spectra. The magnetic properties and electronic spectral studies also support the change in stereochemistry in the adducts of alkaline metal salts. The structure and bonding of the newly prepared bridged complexes is shown in fig. 1 .

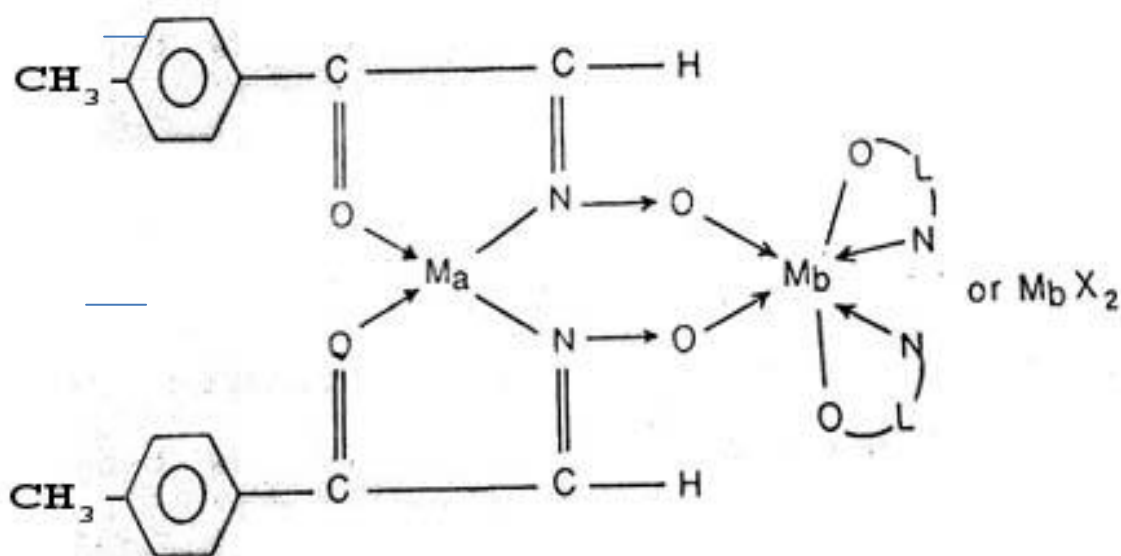


Fig 1

Where M_a= Cu⁺⁺, Ni⁺⁺ M_b=Li⁺, Na⁺, K⁺ L = deprotonated 8HQ or OABA X=ClO₄⁻, SCN⁻

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