

## NOVEL POLYNUCLEAR ALKALI AND ALKALINE-EARTH METAL COMPLEXES WITH 'METAL COMPLEXES AS LIGANDS'

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A number of divalent transition and non-transition metal complexes with O-N donor ligands and having oxygen-bridges with dimeric (metal-Schiff bases, metal-oxinates, metal-glycinates), trimeric/tetrameric (metal-acetylacetonates, metal-salicylaldehydes) and polymeric (metal-oxalates, metal-glyoximates) structures, depolymerise under suitable conditions, and break up into monomers. These monomers *in situ*, behave as a single or double faced bidentate oxygen donor Lewis Bases, and combine with partially covalent bonded alkali and alkaline-earth cations, to form oxygen-bridged polynuclear complexes.

**Key Words :** Unusual Ligand, 'Metal Complexes as Ligands'

### INTRODUCTION

IN most of the Inorganic chemistry text books, under the chapter ligands, the conventional ligands (ammonia, oxalic acid, EDTA and so on) are grouped together. In some texts, the unconventional  $\pi$ -acid ligands are also mentioned. But till now, in no inorganic text books has the third type of ligand, the 'metal complexes', found its place, though quite a lot of work has been reported with 'Metal Complexes as Ligands'.<sup>1-18</sup>

The present work deals with oxygen-bridged polynuclear alkali and alkaline-earth metal complexes, with 'Metal Complexes as Ligands'. It has been observed that even after the ligands combine with cations forming stable metal compounds, the coordinating ability of the ligands, is not fully saturated, and in turn, the metal-complexes so formed still have donor properties (rather enhanced donor properties), acting as a Lewis Base; and under suitable circumstances, react with Lewis Acids, forming stable polynuclear mixed-ligand complexes.

An attempt has been made to put forward the reaction mechanism, wherein the 'Metal Complexes' so formed, show co-ordinative unsaturation, and still show donor properties.

### DISCUSSION

Covalence two of oxygen is well known; and in a number of cases (co-ordinated water, bridged hydroxo group, co-ordinated keto group, alkoxides and so on), a covalence of three for oxygen is mentioned. But when the covalence of oxygen is

more than three, or rather four, it is expected that these oxygen atoms will be behaving in a different fashion and form novel compounds.

All the divalent transition and non-transition metal-complexes with O-N donor ligands that have been used as 'Metal Complex Ligands' in the formation of oxygen-bridged polynuclear complexes, have been found to have a dimeric, trimeric, tetrameric or polymeric structure (Table I). The central metal ions (Ni/Co) in these complexes have an octahedral (a few square planar) stereochemistry. These 'metal complexes' in absolute ethanol media in presence of partially covalent-bonded alkali and alkaline-earth metal cations, suffer degradation. The alkali metal salts suffer slight hydrolysis and the soln is slightly alkaline (*pH* 8–10). It is well known that alkali promotes degradation; and quite likely depolymerise these metal complexes into monomers. These monomers *in situ*, behave as a single or double-faced bidentate oxygen donor Lewis Bases, and combine with partially covalent bonded alkali and alkaline-earth cations, to form oxygen-bridged polynuclear complexes.

TABLE I

| Metal Complexes as Ligands  | Structure           | Stereochemistry of the central metal ion in complexes [Ni/Co] | Stereochemistry of the central metal ion (monomer) in adducts [Ni/Co] | References |
|-----------------------------|---------------------|---|---|------------|
| Schiff Bases                | Dimer               | Sq pl   | Td  | 11, 13     |
| Quinolinates                | Dimer               | Sq pl   | Td  | 19         |
| Acetylacetonates            | Trimer/<br>Tetramer | Oh  | Td  | 12, 17     |
| Salicylaldehydes            | Trimer/<br>Tetramer | Oh  | Td  | 15         |
| Oxalates. 2H <sub>2</sub> O | Polymer             | Oh  | Td  | 14         |
| Oxalates. en                | Polymer             | Oh  | Td  | 18         |
| Glyoximates                 | Polymer             | Sq pl   | Td  | 16         |
| Glycinates                  | Polymer             | Oh  | Td  | 20         |
| Alaninates                  | Polymer             | Oh  | Td  | 21         |
| Salicylaldoximates          | Polymer             | Sq pl   | Td  | 22         |

As a representative example, let one look into the degradation of the trimer  $[\text{Ni}(\text{acac})_2]_3$  into a monomer and finally its formation of polynuclear alkali metal complexes (Fig. 1). Looking into the trimeric structure of  $[\text{Ni}(\text{acac})_2]_3$ , one finds that out of twelve ligating oxygen atoms, six of them are terminal ones (with a covalence of two); and the other six are bridged ones (with covalence of three), attached to two nickel ions. Under suitable condition (when *pH* is 8–10), if the trimer breaks into a monomer, and the bond between the bridged oxygen atoms and the second nickel ion is snapped, these oxygen atoms, in the monomer, now have the third/fourth covalence free. These *in situ*, behave as a double-faced bidentate oxygen donor Lewis Base. The partially covalent bonded alkali metal

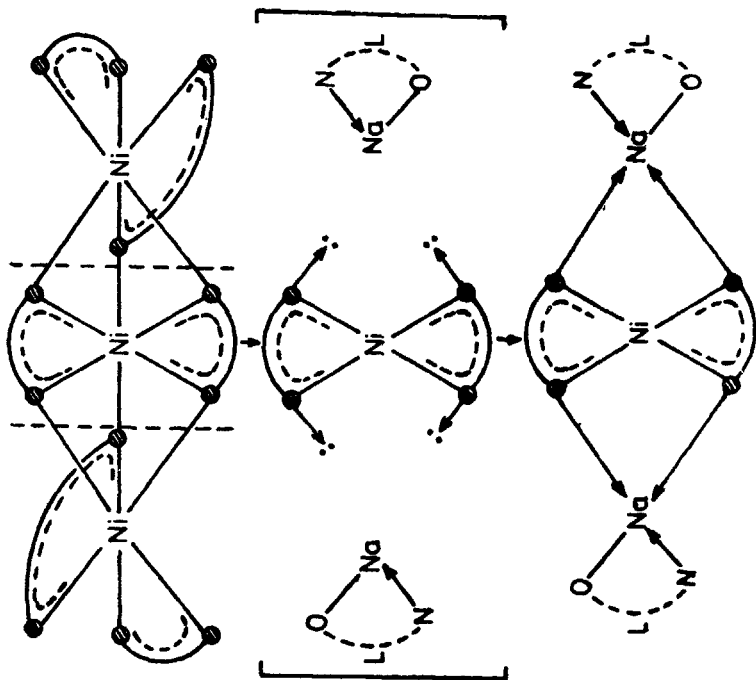


FIG 1

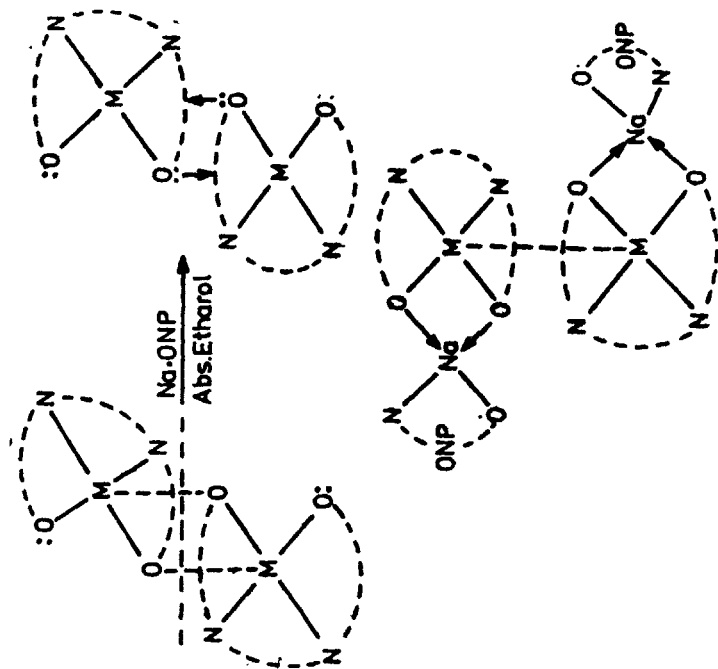


FIG 2

Note: For  $\xrightarrow{\text{Na-ONP}}$ , read  $\xrightarrow{\text{Na-ONP}}$   
 For  $\xrightarrow{\text{Abs. Ethanol}}$ , read  $\xrightarrow{\text{Abs. Ethanol}}$

salts, which are Lewis Acids, and are floating around, are now grabbed by the monomer  $[\text{Ni}(\text{acac})_2]$ , and form oxygen-bridged polynuclear complexes. A break in the polymerised system leads the six-co-ordinated octahedral central metal ion to co-ordination number four, and assume a tetrahedral structure. And the magnetic and spectral data support the above views.

All the 'metal complexes' mentioned in Table I, under suitable conditions, break up into monomers, and these monomers in turn have ligating oxygen atoms, where the covalence of oxygens have been found to be more than three. As such, possessing the unusual property, these very easily grab the Lewis Acids, forming polynuclear oxygen-bridged compounds.

The alkali-metal adducts (especially of sodium *ortho-nitro* phenolate, Na.ONP) with copper(II)-oxinates and Cu.ES, show unusually low magnetic properties. Though in all other adducts, they exhibit normal magnetic values of one unpaired electron, in the above two compounds copper(II) show diamagnetism.

It is reported in the literature, that in a number of copper(II) compounds, in which the magnetic moments are substantially below the spin-only value, is composed of those in which the copper(II) ions are held close together in pairs. The spins of the two copper(II) ions are so strongly coupled that the dimer is sometimes diamagnetic. The X-ray analysis<sup>23</sup> has shown that N,N'-disalicylideneethylenediamine Copper(II) is dimeric with two copper-oxygen bonds of length 2.41 Å, binding the two units of the dimer in a similar manner to that found in dimethylglyoximates. The two Cu-O bonds join the two units of the dimer, and although Cu-O-Cu bridges are present, the magnetic measurements show that these do not give rise to any significant exchange interaction between copper atoms.

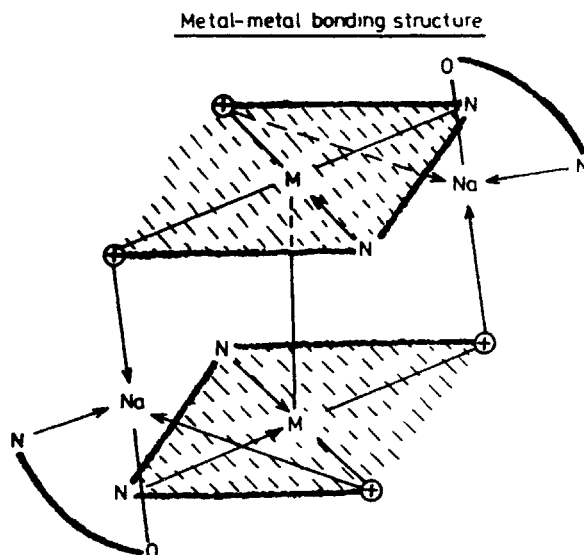


FIG 3

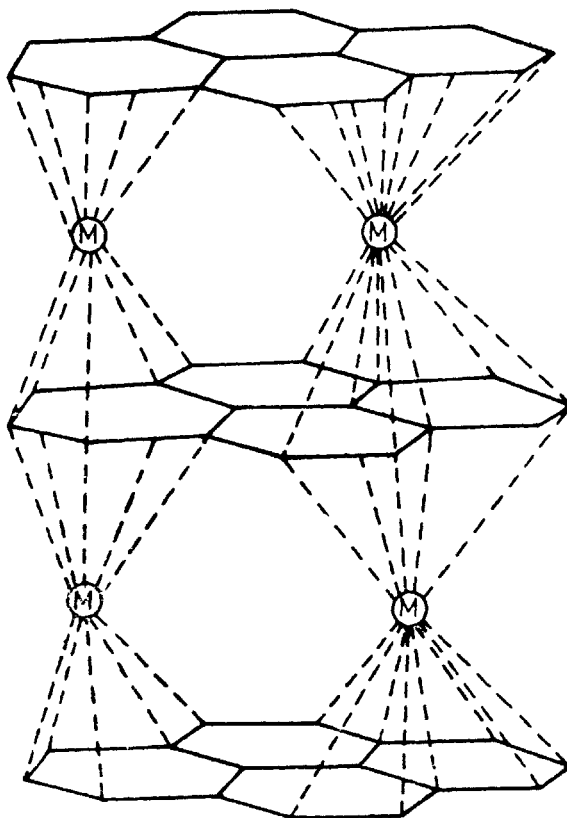
Graphite-metal complex

FIG 4

The adducts of alkaline metal salts of ONP with CuES are diamagnetic in character, and suggest that they are dimers. CuES is dimeric with weak Cu-O bonds linking pairs of monomers in a staggered form (Fig. 2). One CuES molecule is stacked over the other in a staggered form. When Na.ONP approaches CuES stacked together, the long Cu-O-Cu bond is snapped, and may be due to the presence of Na.ONP, a further reorientation takes place in the stacking. The phenolic oxygens being now bound to alkali metals, are no longer available for bonding to the second copper atom. The position of phenolic oxygen of one CuES, which was just beneath a copper atom of a second CuES, may now be replaced by copper atom of that second CuES. The Cu-Cu distance being short, there is now overlapping of the copper orbitals, resulting decrease in the paramagnetism of the polynuclear complex.

These Cu-Cu bonded compounds are thermally quite stable and only decompose at a temperature above 250 °C. However, it is most unlikely that a simple Cu-Cu bond will hold the two units so strongly together. So, besides the Cu-Cu bond

there must be other strong binding force between the two units. And very likely, there exists a structure similar to that of dimeric diaquo-copper(II) acetate; the third and fourth co-ordination positions of sodium of Na.ONP being occupied by two oxygens of two units of CuES (Fig. 3).

Vol'pin<sup>24</sup> also reported the synthesis of metal complexes using graphite as the Lewis Base. By thermal degradation a similar break in the polymerised structure of graphite is expected. Snapping of the bond between the layers of graphite, give it a  $\pi$ -acid character; and the metallic iron or FeCl<sub>3</sub> find their place between the layers of graphite chain (Fig. 4). By insertion of metals (Fe) and metallic salts (FeCl<sub>3</sub>), the distance between the layers of graphite increase from 3.38 Å to 5.6–9.8 Å.

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