

Design and properties of phenoxo-bridged binuclear, trinuclear and tetranuclear macrocyclic complexes

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Abstract. Multinuclear complexes derived from binucleating and tetranucleating macrocyclic ligands of the types tetraaminodiphenol and octaaminotetraphenol are reported. The effect of electronic interactions between metal centres held in close proximity by the macrocyclic ligands on chemical reactivities, redox and magnetic properties of the complexes is discussed. Systematic changes in the structure and stereochemistry of the metal complexes brought about by variation of the auxiliary axial ligands are examined. A magneto-structural relation for the binuclear nickel(II) complexes implicating linear dependence of spin-exchange integral (J) on Ni–O(phenoxide)–Ni bridge angle or Ni...Ni separation is discussed.

Keywords. Macrocyclic complexes; electrochemistry; phenoxo-bridged metal complexes.

1. Introduction

In the past two decades there have been extensive studies on the phenoxide-bridged metal complexes of the binucleating Schiff base macrocyclic ligands derived from the condensation reaction between 2,6-diformyl-4-methylphenol or its analogues and N,N'-diaminoalkanes (Pilkington and Robson 1970; Lindoy 1989; Nag 1990). The focus of attention has been to modulate potentials for stepwise one-electron reductions in binuclear complexes, to determine intramolecular electron transfer rates in mixed-valence Cu^{II}Cu^I species, and to estimate intramolecular magnetic exchange interactions in homo- and hetero-binuclear systems. A few recent studies dealing with the formation of polynuclear phenoxo-bridged macrocyclic complexes have disclosed the occurrence of some novel structural motifs (Bell *et al* 1989; Hoskins *et al* 1990; McKee and Tandon 1991; Edwards *et al* 1992; Tandon *et al* 1992).

In all these cases binuclear and polynuclear complexes have been synthesized by resorting to metal-induced template condensation reaction of the appropriate amine and aldehyde derivatives. On the other hand, by using preformed macrocyclic ligands greater control on stereochemistry of the complexes and a wider variety of products could be expected, especially for metal ions that are not amenable to induce template condensation. Designed syntheses of electron-communicable multinuclear complexes require the use of tailor-made macrocyclic ligands. Unfortunately, metal-free aza-phenol Schiff base macrocyclic ligands are mostly prone to ready hydrolytic

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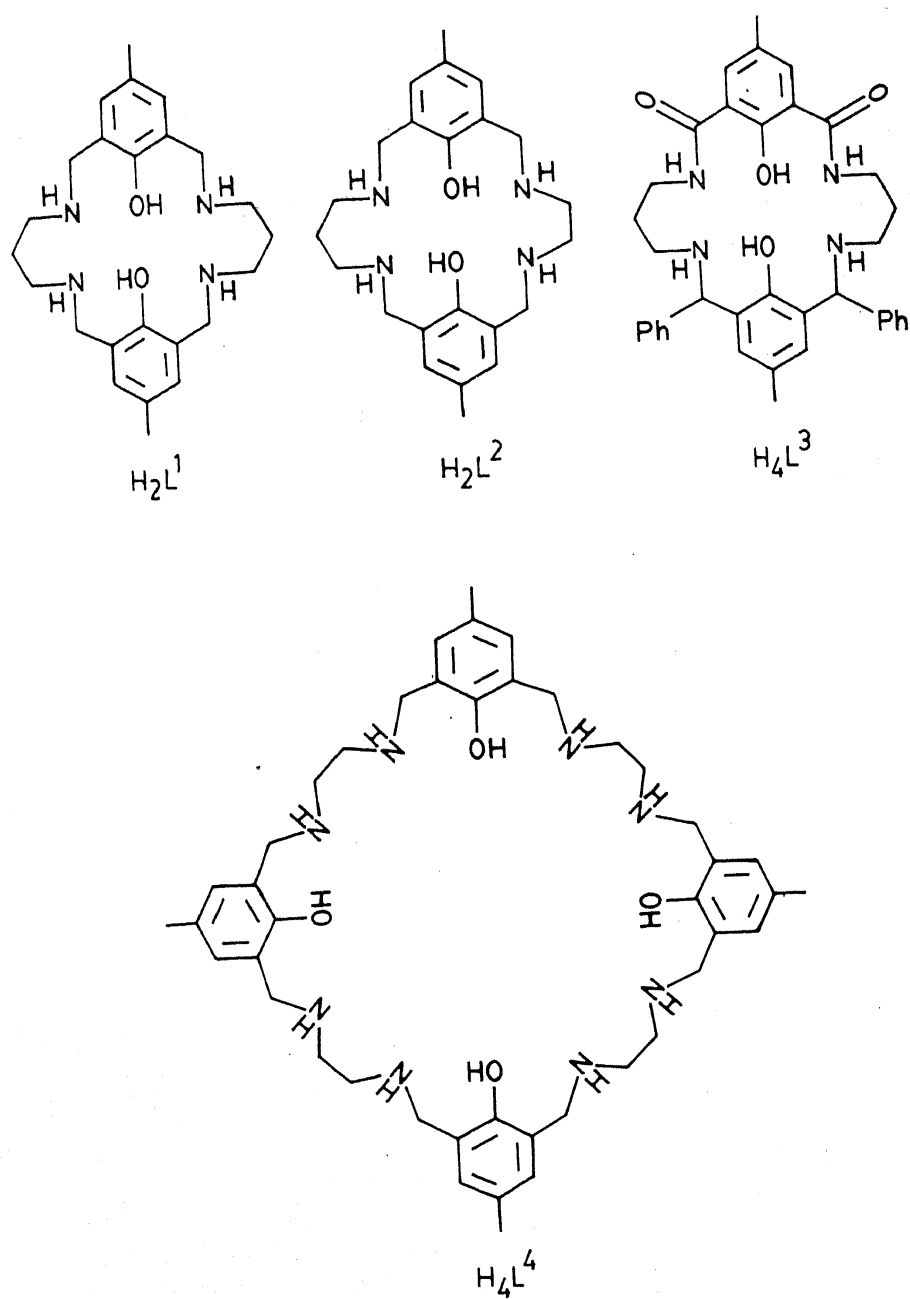


Figure 1. Structures of the complexes studied.

cleavage and therefore are not available in a free state. To alleviate this problem we have synthesized a few polyamino-polyphenolic macrocyclic ligands (figure 1). The macrocyclic ligands H_2L^1 (Mandal and Nag 1986), H_2L^2 (Nanda *et al* 1993b), H_4L^3 (Adhikary *et al* 1992) and H_4L^4 (Nanda *et al* 1993d) differ from the previously mentioned Schiff base macrocycles both in flexibility and in the coordinating ability of the nitrogen donors. In contrast to systems having C=N linkages, ligands with sp^3 hybridized nitrogen donors can be expected to respond more favourably towards stabilization of complexes in higher oxidation states. In this paper an overview is given on certain aspects of the chemistry of metal complexes derived from ligands H_2L^1 – H_4L^4 .

2. Stereochemistry and structure

The binucleating macrocyclic ligands H_2L^1 with copper(II) perchlorate produces square-planar, square-pyramidal and axially elongated octahedral dicopper(II) complexes. In $[Cu_2L^1(ClO_4)_2]$, long range perturbations involving bridging perchlorates (Cu–O, 2.821(3) Å) distort the copper coordination spheres severely to produce axially elongated octahedra (Mandal *et al* 1987a). The two copper atoms are separated by 2.993(2) Å with Cu–O(phenoxide)–Cu bridge angle of 102.8(2)°. In the square pyramidal $[Cu_2L^1(CH_3OH)_2](ClO_4)_2$ complex *trans*-axial methanol molecules are weakly bound (Cu–O, 2.413(3) Å) and the two copper centres are displaced from the mean plane in opposite direction by 0.11 Å. Compared to the previous compound both Cu...Cu separation (3.088 Å) and CuOCu bridge angle (103.9°) are greater.

The stereochemistry of the dinickel(II) complexes derived from H_2L^1 changes from octahedral to varying degree of tetragonal distortion with the variation of axial donors. When the axial donors are the nitrogens of heterocyclic bases the coordination number of the metal ion changes from six to five.

The X-ray structure analysis of $[Ni_2L^1(CH_3OH)(ClO_4)_2] \cdot 2NH(C_2H_5)_3ClO_4$ (Das and Nag 1991), $[Ni_2L^1(H_2O)_4]_2 \cdot 4NH_2CONH_2$ (Nanda *et al* 1993b), $[Ni_2L^1(NCS)_2(H_2O)_2] \cdot 2(CH_3)_2NCHO$ (Nanda *et al* 1993a), $[Ni_2L^1(imidazole)_2](ClO_4)_2$ (Nanda *et al* 1993a) and $[Ni_2L^1(pyridine)_2](ClO_4)_2$ (Nanda *et al* 1992) have established the presence of the centre of symmetry in all these crystals. Among the six-coordinate complexes, tetragonal distortion is maximum for $[Ni_2L^1(CH_3OH)_2(ClO_4)_2] \cdot 2NH(C_2H_5)_3ClO_4$; the Ni–O(ClO_4) distance (2.411 Å) is very long compared to the Ni–O(CH_3OH) distance (2.105 Å). From a consideration of the relevant structural parameters of these compounds it has turned out that even though the equatorial Ni–O and Ni–N distances belonging to the macrocyclic plane do not vary significantly, substantial increase in Ni...Ni separation from 3.106 to 3.205 Å or Ni–O(phenoxide)–Ni bridge angle from 99.2 to 105.7° occur on passing from octahedral $[Ni_2L^1(H_2O)_4](ClO_4)_2 \cdot 4NH_2CONH_2$ to square-pyramidal $[Ni_2L^1(py)_2(ClO_4)_2]$.

The nature of noncovalent interactions in the inclusion complexes $[Ni_2L^1(H_2O)_4](ClO_4)_2 \cdot 4NH_2CONH_2$ and $[Ni_2L^1(CH_3OH)_2(ClO_4)_2] \cdot 2NH(C_2H_5)_3ClO_4$ are quite different. In the first complex, the urea molecules are held in the crystal lattice by an extensive array of hydrogen bonding involving the perchlorate ions, secondary amines and coordinated water molecules. By contrast, the triethylammonium ions in the second complex are interposed between the layers of one-dimensionally stacked $[Ni_2L^1(CH_3OH)_2(ClO_4)_2]$ units and triethylammonium perchlorate salt is held in space by electrostatic and van der Waals forces.

$[Ni_2L^1(CH_3OH)_2(ClO_4)_2] \cdot 2NH(C_2H_5)_3ClO_4$ in methanol solution exists as $[Ni_2L(CH_3OH)_4]^{2+}$, from which the coordinated solvent molecules can be replaced easily. The reaction equilibrium $[Ni_2L(CH_3OH)_4]^{2+} + 2B \rightleftharpoons [Ni_2L(B)_2]^{2+}$ involving the stereochemical change from octahedral to square pyramidal has been studied (Nanda *et al* 1992) for a number of heterocyclic bases, B. When these bases offer no steric hindrance, the equilibrium constants show a linear dependence on the protonation constants of the bases.

$[Ni_2L^1(CH_3OH)_2(ClO_4)_2] \cdot 2NH(C_2H_5)_3ClO_4$, on reaction with glycine, alanine and glycylglycine, produces the μ -carboxylato complexes of composition $[Ni_2L^1$

$(^-O_2C-NH_3^+)(H_2O)_2](ClO_4)_2 \cdot nH_2O$. It may be noted that the occurrence of the above type of carboxylate bridging by amino acids in zwitterionic form is rare and unprecedented in nickel(II) chemistry. The structure of the glycinate complex has been determined (Das *et al* 1992). Carboxylate bridging occurs also with other aliphatic carboxylic acids and complexes of the type $[Ni_2L(-O_2CR)(H_2O)_2](ClO_4) \cdot 2RCO_2H$ have been characterized (Nanda *et al* 1993c). Acetamide gets readily deprotonated on reaction with $[Ni_2L(CH_3OH)_4]^{2+}$ and the carboxamide bridge complex $[Ni_2L(\mu-NHCOCH_3)(H_2O)_2](ClO_4) \cdot H_2O$ has been isolated (Nanda *et al* 1993d).

The macrocyclic ligand H_2L^2 , which contains one $-NH(CH_2)_3NH-$ and one $-NH(CH_2)_2NH-$ moiety, forms the mixed spin-state complex $[Ni_2L^2(H_2O)_2]I_2$ in which one metal centre is square-planar and the other octahedral. On reaction with pyridine, this complex produces the square-planar-square pyramidal complex $[Ni_2L^2(py)]I_2$. The low-spin Ni^{2+} of both these complexes is accommodated by the smaller N_2O_2 cavity provided by the phenolic oxygens and $-NH(CH_2)_2NH-$ nitrogens (Nanda *et al* 1993b). The Ni-O and Ni-N distances related to the square planar nickel(II) are about 0.15 Å shorter than those of the octahedral nickel(II). Again it may be pointed out that mixed spin-state nickel(II) complexes with the same inplane donors are rare and have no precedence in macrocyclic systems.

Several oxovanadium(IV) complexes $[VO(L^1)] \cdot H_2O$, $[VO(H_2L^1)(SO_4)] \cdot 3H_2O$, $[(VO)_2(L^1)(\mu-SO_4)] \cdot CH_3OH \cdot 3H_2O$ and $[Zn(L^1)VO(SO_4)] \cdot 4H_2O$ have been synthesized from H_2L^1 (Das *et al* 1993b). In $[VO(L^1)] \cdot H_2O$, stacking of the molecules occurs due to $\dots V=O \dots V=O \dots$ interactions. The two secondary amino groups in $[VO(H_2L)(SO_4)] \cdot 3H_2O$ are protonated and the unidentate sulphate is bound to the octahedral vanadium. $[(VO)_2L(\mu-SO_4)] \cdot CH_3OH \cdot 3H_2O$ is one of few structurally characterized dioxovanadium(IV) complexes in which vanadyl groups are in *syn* configuration rather than more prevalent *anti* configuration.

Two structural modifications of the heterobinuclear Ni(II)-V(IV) complexes of composition $[Ni(L^2)VO](ClO_4)_2$ have been obtained from the asymmetric macrocyclic ligand H_2L^2 . In one case Ni^{2+} occupies the smaller N_2O_2 cavity in low-spin state, while in the other case high-spin Ni^{2+} is accommodated in the larger N_2O_2 cavity. A third variety of heterotrinary Ni(II)-V(V) complex has also been structurally characterized. This complex has the composition $[Ni(V^VO)(L^2)(H_2O)] [V^VO_2]L^2 (ClO_4)_2 \cdot \text{solvent}$. In this case the *cis*-dioxo groups of $[(VO)_2L^2]$ unit interact with monooxovanadium(V) and nickel(II) atoms of $[Ni(VO)(L^2)(H_2O)]$ to help them in achieving six-coordination.

Although binuclear isovalent complexes $[M^II L^1 X_2(CH_3OH)_2] \cdot H_2O$ ($M(II)=Co$ or Mn ; $X=Cl$ or Br), $[Fe^II L^1(imidazole)_2(CH_3OH)_2](ClO_4)_2 \cdot 2CH_3OH$ and mixed-valent complexes $[M^II M^III X_2(CH_3OH)_2]Br$ ($M=Co$ or Mn ; $X=Cl$ or Br) have been characterized (Das *et al* 1993a), similar binuclear complexes with trivalent cations could not be isolated. Apparently, the juxtaposition of two M(III) centres at such close proximity leads to strong electrostatic repulsion. Recently, of course, we have structurally characterized a novel aqua-bridged diiron(III) complex of composition $[Fe_2^{III} L^1(\mu-H_2O)_2](ClO_4)_2$. This compound has a centrosymmetric structure with the macrocyclic ligand providing N_2O_2 donor atoms to the iron(III) centre and in doing so the ligand has undergone a remarkable twist incapacitating two other nitrogen atoms to get involved in coordination. It is well known that iron(III) undergoes hydrolysis at very low pH and that is why all known dimeric or oligomeric iron(III)

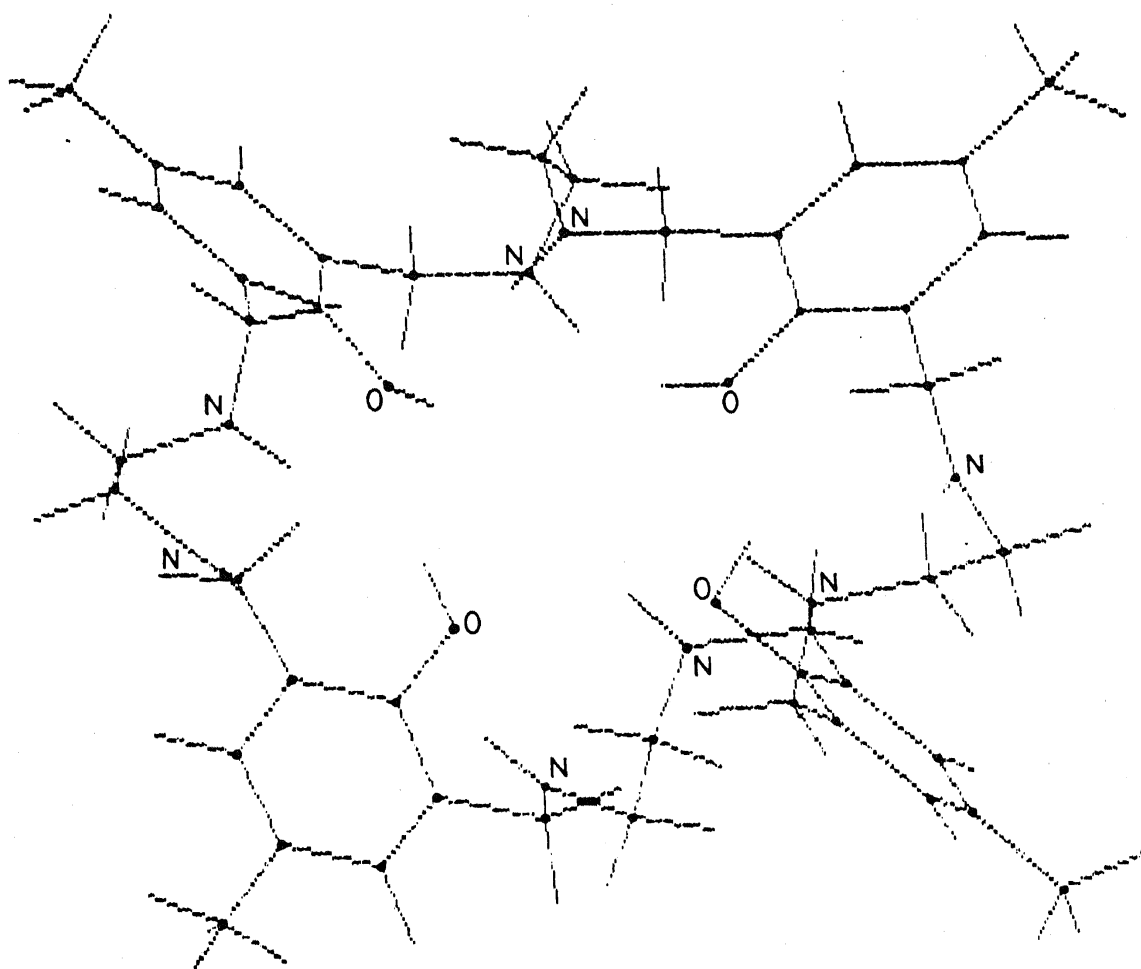


Figure 2. Stereoview of H_4L^3 .

complexes are either hydroxo- or oxo-bridged. The first observation of diaqua-bridging in iron(III) complexes is rather extraordinary. This finding might turn out to be useful in deciphering the active sites of some iron-containing biomolecules because hitherto the possibility of iron(III) getting involved in aqua bridging was never considered.

A 36-membered octaaminotetraphenol macrocyclic ligand H_4L^4 in which the four phenyl rings are connected by 28 single bonds has been synthesized (Nanda *et al* 1993d). Because this ligand can be subjected to considerable deformation and twist, its minimum energy configuration has been found out by force field molecular mechanics calculations. Figure 2 shows the stereoview of H_4L^4 . Molecular models indicate that self-assembly of metal ions and H_4L^4 , assisted by other coordinating anions or molecules e.g. OH^- , OR^- , Cl^- , N_3^- , NCS^- , H_2O , imidazole or pyrazole, can produce various structural motifs. Stereochemistry of the metal ions should play a domineering role to regulate the course of self-assembly.

A few tetranickel(II) complexes of H_4L^4 have been synthesized in which the metal ions are octahedrally disposed. One such compound, whose structure has been determined, is $[Ni_4L^4(\mu_3-OH)(\mu-H_2O)_2(ClO_4)(ClO_4)_2 \cdot 2CH_3COCH_3 \cdot H_2O]$ (Nanda *et al* 1993d). Each of the four metal centres are in distorted octahedral environment, but the coordination sphere of one nickel atom differs somewhat from that of the

other three nickel atoms. While a tricoordinated hydroxide ion anchors these three nickels, a perchlorate oxygen provides the sixth coordination site to the remaining nickel.

Instead of six-coordination if a metal ion prefers to adopt square-planar geometry it will be impossible to assemble four such metal centres in the cavity of H_4L^4 . The formation of a binuclear complex accompanied by twisting of the ligand helically, however, seems possible. Since there will be considerable strain in such configuration, a dynamic molecular motion will lead to coiling and uncoiling of the binuclear complex in solution. One way to stabilize this configuration would be to introduce a third metal ion, whose steric requirement will be nonspecific, but which would be capable of binding the uncoordinated nitrogen atoms. Zinc(II) is one such metal having the capacity to fulfil these requirements. The ternary complex $[Cu_2ZnL^4]-(ClO_4)_2 \cdot H_2O$ has been recently isolated and its X-ray structure determination has revealed that the macrocycle is indeed helically twisted.

3. Electrochemistry

The dicopper(II) and dinickel(II) complexes of H_2L^1 , $[Cu_2L^1(ClO_4)_2]$ and $[Ni_2L^1(CH_3OH)(ClO_4)_2] \cdot 2NH(C_2H_5)_3ClO_4$, exhibit unique redox behaviour for magnetically coupled binuclear systems. Both the complexes undergo sequential four one-electron transfers to generate bimetallic species whose oxidation states vary between +1 and +3 (Das and Nag 1991; Mandal *et al* 1987a). Stepwise reversible oxidation of the dinickel(II) complex in acetonitrile to produce $Ni^{II}Ni^{III}$ and $Ni^{III}Ni^{III}$ species ($E_{1/2} = 0.94, 1.08$ V vs SCE) occurs more easily relative to the similar two reversible oxidation steps involved in the dicopper(II) complex ($E_{1/2} = 1.19, 1.41$ V). Conversely, stepwise reduction of the dicopper(II) complex in dimethyl sulphoxide to produce $Cu^{II}Cu^I$ and Cu^ICu^I species takes place at less negative potentials ($E_{1/2} = -0.76, -0.90$ V) relative to the corresponding two one-electron reduction steps ($E_{1/2} = -1.32, -1.65$ V) for the dinickel(II) complex. Easier access to the higher oxidation state for nickel is more conspicuous in the electron-rich carboxylate-bridged complexes, $[Ni_2L^1-(\mu-O_2CR)(H_2O)_2](ClO_4)$. For example, the redox potentials for the stepwise oxidation of the propionate complexes are 0.79 and 0.98 V (Nanda *et al* 1993d).

Compared to a high-spin octahedral nickel(II), it is far more difficult to oxidize a low-spin square-planar nickel(II). Thus, in the mixed spin-state complex, $[Ni_2L^2(H_2O)_2]^{2+}$, while the octahedral nickel(II) gets oxidized at 1.16 V, the square-planar nickel(II) remains unaffected towards oxidation up to 1.7 V. On the other hand, for $[Cu_2L^2]^{2+}$ the oxidation process occurs in two steps at 1.24 and 1.44 V.

In contrast to the dinickel(II) or dicopper(II) complexes of H_2L^1 , the oxidation of the dicobalt(II) or dimanganese(II) complexes cannot be extended beyond the formation of $M^{II}M^{III}$ species. Although one-electron oxidation of $[M^{II}L^1(CH_3OH)_2Cl_2]$ ($M = Co$ or Mn) complexes takes place at rather less positive potentials (0.36 V for cobalt and 0.30 V for manganese), decomposition of the complex species takes place when potentials are greater than 1 V (Das *et al* 1993a).

Unlike the systems discussed above, binuclear metal(II) complexes of the macrocyclic Schiff base analogues of H_2L^1 cannot be oxidized to produce their higher valent species, thereby underscoring the requirement of sp^3 hybridized nitrogen donors

for the removal of electron(s) from metal centres. The removal of electron from a metal centre can be further facilitated by incorporating deprotonated amido groups in the macrocyclic ring (H_4L^3). Thus, the first one-electron oxidation potential for the $[Cu_2L^3(H_2O)_2]$ complex is only 0.31 V, which is far less compared to 1.19 V observed for $[Cu_2L^1(ClO_4)_2]$ complex. However, further oxidation of the amido complex leads to its decomposition. By contrast, no oxidation process could be detected upto 1 V for the dicopper(II) complex derived from the Schiff base analogue of H_4L^3 .

4. Magnetochemistry

The electronic structure of the coupled polynuclear systems is receiving ever-increasing attention for designing magnetic materials and understanding the role of exchange interactions in metallobiomolecules. Major emphasis is placed on rationalizing the sign and the value of the exchange parameter, J , in the light of structural data. More generally, a correlation is sought between the values of J and a single structural parameter in a series of related complexes. An elegant correlation has been established in planar dihydroxo-bridged dicopper(II) complexes in which J varies linearly with Cu–O–Cu bridge angle (Crawford *et al* 1976). Although magnetic properties of dinickel(II) complexes have been studied extensively, perhaps next to dicopper(II) systems, no definite magneto-structural correlation has emerged as yet. This is because several structural parameters seem to affect exchange interactions in a complicated way. The phenoxo-bridged macrocyclic dinickel(II) complexes described here provide a unique opportunity to find a definite magneto-structural relation. As already noted in §2 for the five nickel(II) complexes of H_2L^1 , an increase of Ni–O–Ni bridge angle from 99.2 to 105.7° is accompanied by an increase in separation between the two nickel centres from 3.106 to 3.205 Å. Variable-temperature (5–300 K) magnetic susceptibility measurements of these compounds (Nanda *et al* 1993a) have established that all of them exhibit antiferromagnetic interaction and the value of $-J$ lies between 17 and 70 cm^{-1} . In fact, $-J$ values increase linearly with Ni–O–Ni angle or Ni...Ni distance. When extrapolated, a ferromagnetic crossover point is reached for a Ni–O–Ni bridge angle of 96.0°. It may be noted that for high-spin d^8 nickel(II) $d_{x^2-y^2}$ and d_{z^2} are the two magnetic orbitals. The dominant pathway involved in exchange interaction between two nickel(II) centres is $d_{x^2-y^2}$ orbitals of the metal ions and s and p orbitals of the phenoxy oxygens. Antiferromagnetic exchange coupling integral ($-J$) increases as the Ni–O–Ni bridge angle and hence Ni...Ni distance increases. The dependence of the value of $-J$ on Ni...Ni separation might appear contradictory at first sight. However, this anomaly can be dispelled by considering the contribution of d_{z^2} orbitals on exchange interaction. While d_{z^2} orbitals are not involved in the superexchange, they interact ferromagnetically through space; the magnitude of exchange coupling depends on the distance between the two metal centres. Thus, for dinickel(II) complexes, larger displacement of the metal centres simultaneously leads to augmentation of antiferromagnetic coupling and depletion of ferromagnetic coupling. The net effect is predominant antiferromagnetic interaction.

Magnetic properties of $[Ni_2L(\mu-O_2CR)(H_2O)_2](ClO_4)$ complexes have also been studied (Nanda *et al* 1993). These compounds exhibit weak exchange interaction, the value of J lies between +3 and $-3 cm^{-1}$.

In the dicopper(II) complexes of H_2L^1 , where superexchange occurs through $d_{x^2-y^2}$ orbitals, very strong antiferromagnetic interactions are observed, $-J = 420 - 400 \text{ cm}^{-1}$ (Mandal *et al* 1987b). On the other hand, in the dioxovanadium(IV) complex $[(VO)_2L^1(\mu-SO_4)] \cdot \text{solvent}$, where d_{xy} orbitals are involved in superexchange, $-J = 128 \text{ cm}^{-1}$ (Das *et al* 1993b).

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