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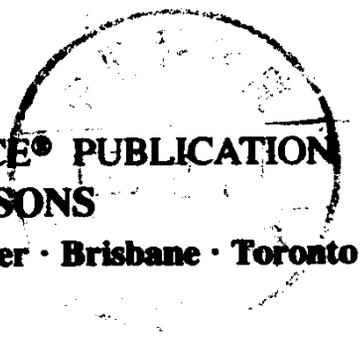

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The Specification of Bonding Cavities in Macrocyclic Ligands

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I. INTRODUCTION

Hole size is a fundamental parameter of macrocyclic ligands which may influence very greatly the properties of resulting metal complexes relative to those of the corresponding open-chain analogues. While there is now extensive documentation of hole-size variation affecting properties, by comparison, there has been much less attention directed toward closely defining the factors which influence hole size in macrocyclic systems. This situation is so even though a very considerable amount of X-ray structural data for macrocyclic ligands and their metal complexes have now been published and may be conveniently retrieved from the X-ray crystallographic data bases.

Classically, macrocyclic hole sizes have been estimated using molecular models (28, 92, 94). However limitations often arise because of uncertainties associated with selecting such parameters as the appropriate donor atom radii (ionic, covalent or intermediate), the appropriate size for the metal atom, and the exact hybridization for the different ligand structural elements; difficulties may also occur in mimicking the subtle (and often cumulative) effects of distortions from ideal stereochemistries throughout the structure. Further, uncertainties may arise when additional features, such as the presence of metal-ligand π-bonding or the existence of extensive electron delocalization, are present in the system being modeled. In an alternate procedure, hole sizes in a restricted number of N_4-donor macrocycles have been estimated using calculations based on molecular mechanics (74, 101). Although this procedure shows much promise, it is relatively complicated and is also not without its difficulties for treating particular systems (1, 64).

The redox behavior of cyclic systems (including the stabilization of unusual oxidation states for coordinated metals) (12, 48, 63, 97, 99, 108), ligand control of kinetic (41, 43, 96) and thermodynamic stabilities (3, 5, 85, 94) of cyclic complexes and the unusual spectral and magnetic properties often exhibited by cyclic complexes (17, 139) may all be profoundly affected by the macrocyclic hole size present in the respective complexes. There is, therefore, a need for a simple procedure for specifying the hole sizes in both two-dimensional and three-dimensional (cage) macrocycles. In this article, we present such a procedure which appears to be widely applicable.

The new procedure should assist in the design of tailor-made ligands by establishing how the bonding cavities available to metal ions vary with changes in ligand structure. In order to establish semiquantitative guidelines concerning such variation of bonding cavities, it is first necessary to have available X-ray structures of series of compounds which show systematic alteration of their structural parameters. In general, X-ray structure determinations have tended to be undertaken to assist characterization of new compounds rather than to observe

trends within a series of closely related complexes. For this reason, in this review we illustrate the discussion using structural data for macrocyclic complexes of nickel together with some related free ligand structures; the complexes of nickel provide by far the most comprehensive series of structural variations at present available. Nevertheless the procedures described should also prove useful for treating the macrocyclic complexes of other metal ions.

II. CALCULATION OF BONDING CAVITIES

A. Ligand "Hole Size" and "Bonding Cavity" Radii

As mentioned previously, it has often been the practice to estimate the ligand hole size from a molecular model of the ligand (28, 92, 94, 129). Commonly, the mean distance between diametrically opposed donor atoms has been used to define the diameter of the donor-atom hole; a similar procedure based on X-ray structural data rather than molecular models has also been used. However, this general procedure for estimating hole size is of limited applicability because, for example, for macrocyclic ligands with an odd number of donor atoms it is not possible to define diametrically opposed donors. Also, for nonplanar arrangements of donor atoms, the procedure may give an erroneous estimate of the hole defined by the donor-atom nuclei. An example of such an effect is illustrated in Fig. 1.

In order to specify the bonding cavities available to a metal ion in macrocyclic ligands, two steps are necessary. The first requires a geometric procedure to obtain the radius of the hole (R_H) defined by the nuclear positions of the donor atoms. It is then necessary to correct the "hole size" to allow for the covalent radii of the donor set to yield the bonding cavity which would be available to the metal ion. Hence the bonding cavity is defined here as the void which is occupied (or is available to be occupied in the case of a free ligand) by a metal ion. In this context, the metal ion is considered to be a solid sphere of fixed radius.

We have suggested elsewhere (38, 59) that the radius of the donor-atom hole

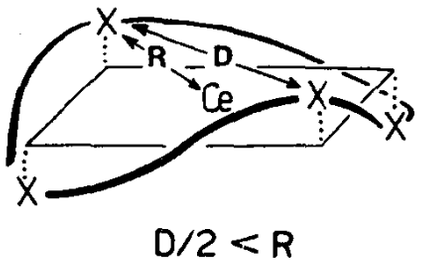


Figure 1. An example of the limitation of using the distance between the diametrically opposed donors to estimate the radius (R) of the "hole" defined by a nonplanar donor set. In this case the quadridentate donor set shows a tetrahedral distortion from planarity. Ce = centroid.

(R_H) can be estimated by defining the centroid of the donor atoms and then taking R_H as the mean distance of the donor atoms from their centroid. This method overcomes the limitations discussed previously and gives a truer estimate of the ligand hole available to a coordinated metal ion, provided that this ion is contained in the macrocyclic cavity. For the quadridentate macrocycles considered in this review, emphasis has been given to ligands which present a planar donor set to the central metal ion and which yield complexes which have either square-planar or octahedral geometries. Complexes containing the macrocycle in a nonplanar configuration are not considered. Similarly, nickel complexes of quadridentate macrocycles which are not pseudocentrosymmetric, such as square pyramidal or *cis* octahedral species or complexes which have the metal ion more than 0.10 Å from the least-squares plane defined by the four donor atoms, are also excluded from the tables of R_H values. Owing to a lack of published data only two examples of nickel complexes of "planar" quinquedentate macrocycles are discussed (Section III.A); no suitable data for similar complexes of sexadentate macrocycles were located.

Because the donor atoms are of finite size, it is necessary to correct the hole size R_H for the effective covalent radii of the donor set in a macrocyclic complex (Fig. 2) before the bonding cavity (of radius, R_A) available to a metal ion can be estimated. We have determined the covalent radii of donor atoms by initially obtaining mean bond lengths from nickel to the appropriate donor atoms by searching the Cambridge data base for relevent structures using CSSR programs. The Pauling covalent radius for nickel was then subtracted from the mean length of each type of nickel-donor bond. This procedure was carried out independently for both high-spin and low-spin nickel(II) complexes using Pauling's covalent radii of 1.39 and 1.20 Å, respectively (114). It is emphasized that the covalent radii for the donor atoms obtained by this procedure are derived solely from nickel complexes with the same spin-state and overall coordination geometry as

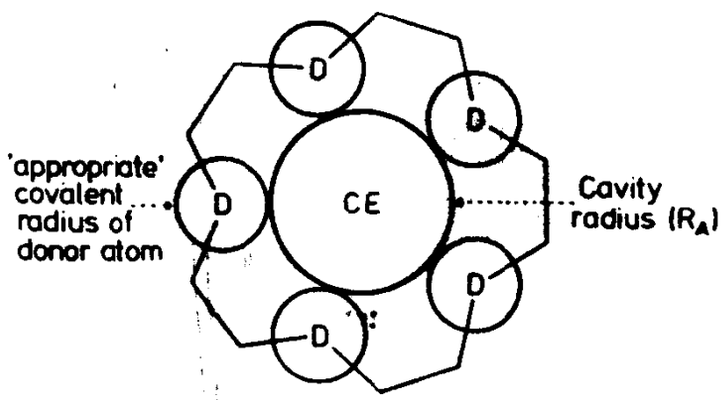


Figure 2. The bonding cavity radius (R_A) available to a metal ion in a symmetrical macrocyclic ligand (containing a single donor-atom type).

the complex being studied. As such, their use for hole-size estimation appears more appropriate than any of the established covalent radii. Although the values listed are generally similar to, for example, the corresponding Pauling covalent radii (114) for nitrogen, oxygen, phosphorus and sulfur, some differences do occur which may be of significance to particular systems. The use of the new radii in the calculations will tend to compensate for any additional factors affecting a given nickel-donor interaction such as the presence of a π-component in the bond. Further, although this procedure depends on the use of Pauling radii for the metal ions which may not be completely appropriate for the particular system under study, the assessment of the goodness of fit (vide infra) of the metal for the bonding cavity (defined as just described) will still be valid provided the Pauling radius of the metal is again used for comparison with R_A. The calculated covalent radii for a range of donor-atom types are given in Table I.

For ligands containing donor atoms of a single type, the covalent radius of this donor was subtracted from R_H, the radius of the hole defined by the nuclear positions of the donors, to obtain the radius (R_A) of the bonding cavity available to a metal ion. For ligands with mixed donor sets, the mean of the covalent radii

TABLE I
Covalent Radii of Donor Atoms in Nickel(II) Complexes

Donor atom	Covalent radii[a,b] (Å) in complexes of: low-spin Ni(II)	high-spin Ni(II)[b]
N(secondary amine)	0.72 (54)	0.72 (89)[c]
N(imine)	0.67 (60)[d]	0.66 (25)[c]
N(pyridine)	0.69 (7)	0.70 (89)
O(ether)	—[e]	0.76 (12)[c]
P(alkyl/arylphosphine)	1.02 (29)[f]	—[e]
S(thioether)	0.97 (14)	1.05 (19)

[a]Values have been calculated using the Pauling covalent radii for low-spin and high-spin Ni(II) of 1.20 and 1.39 Å, respectively (see text).

[b]Values in parentheses are the number of nickel-donor bonds used from the Cambridge Crystallographic Data Base to estimate each radius.

[c]See ref. 59.

[d]The values were estimated independently for structures containing neutral imine donors and those in which the imine is contained in a conjugated ligand with an anionic donor set. Values are 0.68(2) and 0.67(3) Å respectively. The value quoted is the average for both types of nitrogen.

[e]Insufficient structure determinations are available to allow reliable estimates to be made for these types of bond.

[f]No attempt has been made to consider *trans*-influences on Ni—P bond lengths. The majority of the structures contain donor sets with two *cis*-phosphine groups (as does the only phosphorus-containing macrocycle in Table III).

of the donors was used in the above procedure. In both cases the procedure amounts to the subtraction in a planar ligand system of an annulus from the macrocyclic hole defined by the donor-atom positions, or subtraction of a shell for a three-dimensional cage system.

An alternative procedure to that just described involves subtraction of the radii of the donor atoms from the corresponding observed metal-donor bond lengths and then using the mean value of these "corrected" lengths to define the radius of the bonding cavity (38). For a number of systems it has been observed that this latter procedure gives near identical results to the procedure based on the centroid of the donor atom positions. However, the centroid approach has the advantage that it enables hole sizes in metal-free macrocycles to be estimated and this is especially useful for direct comparisons of metal-free and metal-containing systems.

It should be noted that in certain cases the centroid as calculated from the nuclear positions of the donor atoms will not coincide with the position of the metal atom. This situation can arise in ligands with mixed donors which have different covalent radii and for ligands with unsymmetrical structures which present an arrangement of the donors that does not define a regular coordination polyhedron. However, as a result of the averaging procedure (vide supra) used to obtain the radius of the "spherical" bonding cavity (R_A), an apparent displacement of this type does not invalidate the R_A value calculated.

B. The Goodness of Fit Parameter

As mentioned previously, it is of considerable relevance to much macrocyclic-ligand chemistry to examine in a semiquantitative manner how the fit of a particular metal ion for the ligand cavity changes with structural variation of the macrocycle. In view of this, we propose the use of a new parameter, the "goodness of fit," to specify the match or mismatch of a metal ion for a macrocyclic ligand cavity. The goodness of fit is defined here as the ratio of the bonding cavity radius (R_A) to the Pauling covalent radius (R_P) for the metal ion involved, 1.20 Å for square-planar nickel and 1.39 Å for octahedral nickel. Thus a value of unity for R_A/R_p represents a perfect match of the metal ion for the bonding cavity.

The concept of a goodness of fit appears to allow considerable potential for correlating the properties of series of related macrocyclic-ligand complexes. For example, it has been demonstrated that the ligand-field parameters for the nickel complexes of (planar) tetra-aza macrocycles are strongly influenced by macrocyclic ring size—with the smaller rings resulting in increased field strength owing to forced constriction of the respective nickel–nitrogen bond lengths (17). Indeed, the smaller rings tend to yield square-planar complexes which are low-spin

whereas the larger ring complexes tend to be six coordinate (with axial monodentate ligands) and high-spin. Related spin-state changes and spin-state equilibria have been observed in solution and have been demonstrated to be strongly dependent on the size of the macrocyclic hole in the respective ligands (4, 46). The goodness of fit parameter appears to be potentially useful for defining more precisely the relationship between hole-size variation and spectroscopic behavior (and/or magnetic behavior) or macrocyclic systems of the above type. A number of examples of such correlations involving other properties of macrocyclic-ligand systems are mentioned in following sections of this review.

C. Tabulation of Radii for Octahedral and Square-Planar Nickel Complexes

The Cambridge Crystallographic Data Base was searched to retrieve relevant structures published up to 1982 of nickel complexes of quadridentate and quinquedentate macrocyclic ligand systems incorporating 12- to 20-membered inner great rings. Structures were retrieved using both the SRAD (83) and CSSR (44) search programs. Additional structures published subsequently have been obtained by scanning primary journals.

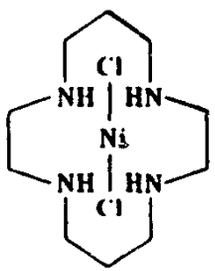
Tables II and III list values of R_H and R_A for high-spin (octahedral or pseudo-octahedral) and low-spin (square-planar) nickel complexes. These parameters for two planar quinquedentate ligands and their nickel(II) complexes are discussed in Section III. The tables contain entries in order of increasing ring size, with the most symmetrical donor-atom patterns listed first. The donor-atom patterns are specified by giving the chelate ring sizes defined by the donors around the macrocyclic great ring. Thus, for example, the 14-membered ring with a 5656 donor pattern contains alternating 5- and 6-membered chelate rings in its metal complexes. This and other donor-atom arrangements for 14-membered macrocycles are illustrated in Fig. 3. For all the complexes listed, the nickel ion lies within 0.1 Å of the donor-atom plane of the respective macrocycles. In the tables, ligands with the same ring size and donor pattern are tabulated in order of increasing unsaturation level, specified by half the number of sp^2-hybridized atoms in the inner great ring (see Fig. 4) and by donor-set type (in the order: N, O, P, S).

For comparison purposes, a table of hole sizes (R_H) in metal-free quadridentate macrocycles (Table IV) is also given. However it is emphasized that in some cases the conformation of the free ligand differs markedly from that observed in its metal complexes and hence a direct comparison of the relative hole size in the complexed and uncomplexed state will not always be valid.

TABLE II

Ligand Hole Sizes (R_H) and Bonding Cavity Radii (R_A) in High-Spin Octahedral Nickel(II) Complexes

Compound	Ring size	Donor pattern	Unsaturation level[a]	Donor set	Axial ligands	R_H (Å)	R_A (Å)	R_A/R_p	Reference
1	14	5656	0	N_4	$2Cl^-$	2.06	1.34	0.96	15
2	14	5656	0	N_4	$2F^-$	2.09[b]	1.37	0.99	138
3	14	5656	0	N_4	2Cl	2.08	1.36	0.98	78
4	14	5656	0	N_4	$2ClO_4^-$	2.07[b]	1.35	0.97	68
5	14	5656	2	N_4	$2NCS^-$	2.07	1.35	0.97	70
6	14	5656	2	O_2N_2	$2Cl^-$	2.05	1.31	0.94	70
7	14	5656	4	O_2N_2	$2I^-$	2.00	1.29	0.93	80
8	14	5566	1.5	N_4	$2(NO_2^-)$	2.04	1.32	0.95	37
9	14	5557	0	N_4	$2Cl^-$	2.06	1.34	0.96	134



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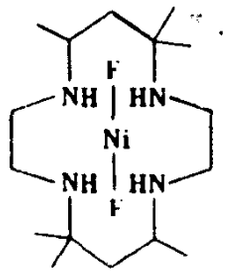

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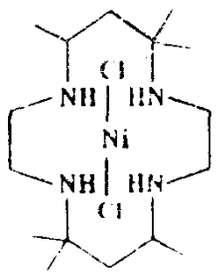

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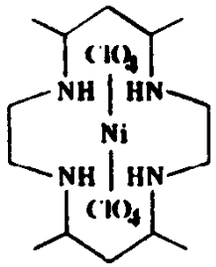
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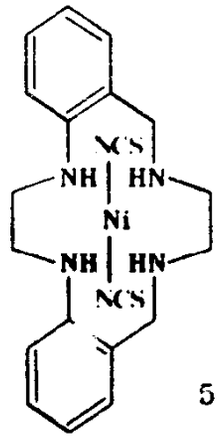
HN
Ni
NH
HN
ClO4

4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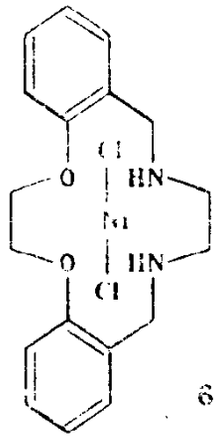
HN
Ni
NH
HN
NCS

5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Ni
O
HN
Cl

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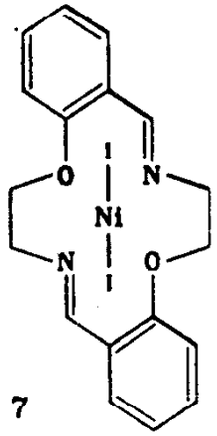
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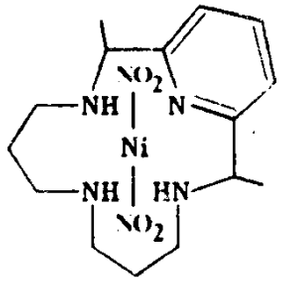
Ni
N
O

7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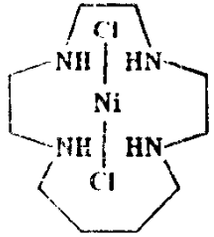
N
Ni
NH
HN
NO2

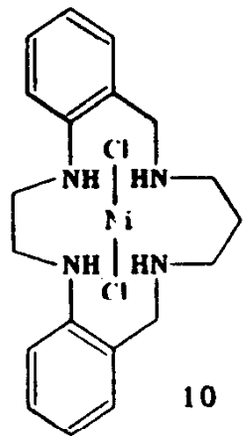
8


Cl
NH
HN
Ni
NH
HN
Cl

9

TABLE II (*Continued*)

Compound	Ring size	Donor pattern	Unsaturation level[a]	Donor set	Axial ligands	R_H (Å)	R_A (Å)	R_A/R_p	Reference
10	15	5666	2	N_4	$2Cl^-$	2.11	1.39	1.00	38
11	15	5666	2	O_2N_2	$2NCS^-$	2.09	1.35	0.97	11
12	15	5666	2	O_2N_2	$2Cl^-$	2.09	1.35	0.97	42
13	15	5666	2	S_2N_2	$2Cl^-$	2.27	1.39	1.00	38
14	16	6666	2	O_2N_2	$2Br^-$	2.14	1.40	1.01	2, 59
15	16	6666	4	O_2N_2	$2Br^-$	2.07	1.36	0.98	59
16	16	5559	0	N_4	$2Cl^-$	2.14	1.42	1.02	134



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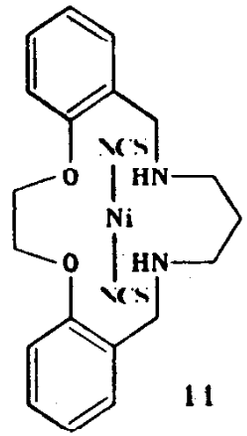

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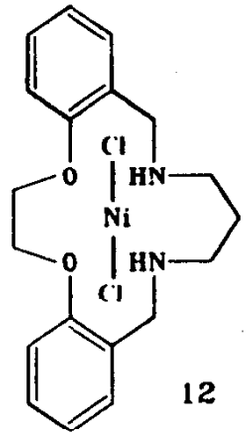

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