STRUCTURAL STATISTICS FOR THE NICKEL (II) AND COPPER (II) COMPLEXES WITH TETRAAZACYCLOTETRADECANE LIGANDS

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Abstract:
210 metal(II) compounds, including 120 Ni(II) and 90 Cu(II) macrocyclic complexes, have been analyzed and discussed about bond lengths, chelate angles, conformation, configuration and many other factors. The hydrogen bonds exist between the ligands and water/anions and play an important role to stabilize the crystal structures. There exhibit two distinct peaks on the histogram of the average Ni-N distances, whereas the Cu(II) complexes occur in only one peak in the Cu-N distance distribution. The average Ni-N distances, corresponding to the two peaks of four and six coordination, are 1.949(7) and 2.091(7) Å, respectively. The favorable structures of Ni(II) macrocyclic compounds have six and four coordinations and planar configuration. Those of the Cu(II) structures have six and five coordinations and planar configuration.

1. Introduction

The macromolecules, such as natural heme proteins, chlorophyll and vitamin B_{12}, reveal distinctive coordination chemistry and biological importance of complexes with macrocyclic ligands (Busch, 1978). Stereochemical studies (Liang et al., 1979) of the complexes with synthetic macrocyclic ligands have received a new impetus since the discovery of the natural macromolecules. The coordination chemistry of macrocyclic ligands with pendant functional groups has attracted growing interest bacause of their potential biomedical application (Bernhardt & Lawrance, 1990; Bunzli & Choppin, 1986). The X-ray structures of metal (II) tetraaza ligands have been studied by the first author since 1981 (Lu et al., 1981). Hence many properties of the 14-membered macrocyclic structures of tetraaza ligand complexes have been studied herein.

The tetraazacyclotetradecane complexes with alternative five- and six-membered chelate rings were reviewed by Curtis (1979). Afterwards, the structure of 14-membered macrocyclic quadridentate ligands were analyzed by the first author (Lu et al., 1991). As macrocyclic complexes of chemical, biological and medical importance, the structures of the complexes of these tetraazacyclotetradecane ligands were accumulated in the Cambridge Structural Database (since 1986). 210 metal (II) complexes were found, consisting of 120 Ni(II) and 90 Cu(II) compounds.

The complexes under study consist of a macrocyclic ligands with metal (II), namely Ni(II) and Cu(II), and tetraazacyclotetradecane ligands (Fig 1). Here, we also studied about the hydrogen bond scheme between ligands and water/perchlorate ions/other anion groups.

The common features of the macrocyclic compounds are deduced from the relations among the metal ion-nitrogen distances, the chelate angles, the axial lengths, the coordination numbers, the conformations of the central five atoms, the symmetry elements at the metal atoms and configuration of the ligands relative to the macrocyclic plane. The above common features are summarized in this work.

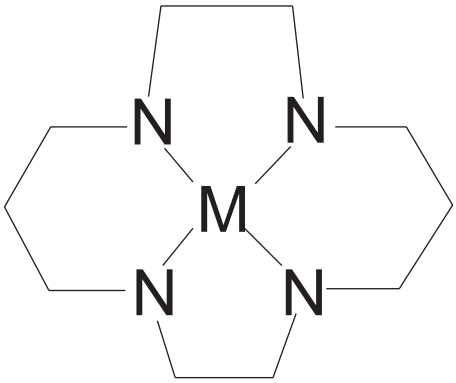


Fig. 1

2. Discussion

2.1 Structures of the macrocyclic compounds

We investigated for the common features of macrocyclic structures, say, bond distance, chelate angle and axial length, particularly about the interaction between the metal ion and the surrounding anions or/and water molecules. The structures from Cambridge Crystallographic Data Center (CCDC) since 1986 have been searched for the statistical analysis. Total number of the Cu(II) and Ni(II) complex structures of the tetraazacyclotetradecane ligands is 210. The structure index (ID), the mean bond distance between the metal (II) ion and its four basic bonding nitrogen atoms (M-N), the minimum chelate angle (NA), the maximum chelate angle (MA), the short (SAL) and long (LAL) axial distances, the coordination number (CN), the conformation (CS) of the two six-membered rings, the configuration of the axial ligands relative to the equatorial plane (TR), the symmetry element occurred in the metal atom (SE) and the conformation (CF) of the central five atoms (MN_4) are given in Table 1 and Table 2 for the Ni(II) and Cu(II) macrocyclic compounds, respectively. There are many factors found in the crystal structure determination. These factors depend upon the molecular structure of the ligand and the environmental molecules surrounding the ligand, such as water molecules and other anion groups. Between the Ni(II) and Cu(II) macrocyclic compounds, there are lot of differences

occurred. The metal (II) ion-nitrogen distance, the chelate angle, the coordination number of the metal (II), the configuration of the coordinated ligand relative to the macrocyclic plane, metal (II) ion symmetry and the conformation of the central five atoms are separately discussed for Ni(II) and Cu(II) compounds.

(i) Nickel (II) - nitrogen distances

For the average bond length (Ni-N) between the Ni(II) atom and the nitrogen atoms of the ligand, the first two columns of Table 1 show the reference indices (ID) and the average (Ni-N) bond length in ascending order. Two peaks occur in the histogram (Fig 2) of the distribution of Ni-N distances. From these two peaks, it will clear that one peak is in six coordination and another is in four coordination. As shown in Table 1 the distribution of the coordination number (CN) is clearly related to the distribution of the Ni-N distances. The larger Ni-N lengths are correlated with the coordination number six, whereas the smaller lengths are related to the coordination number four. The mean Ni-N distance for the four and six coordinations are 1.949(7) and 2.091(7) Å, respectively.

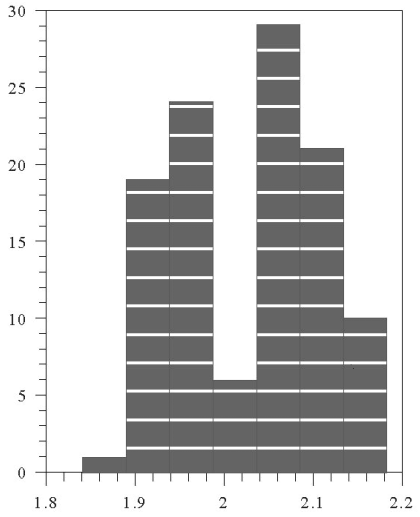


Fig. 2

The bond distance (M-N) between metal atom and nitrogen atoms depends upon its surroundings. The sizes of the substituents attached to the nitrogen atoms bonded to the metal, the number of methyl and/or ethyl substitutents connected to the carbon atoms on the macrocyclic ligands and the anions and/or the water molecules coordinated to the metal atom conclusively affect the M-N distances. If the metal atom is at the origin and several spheres with various radii are drawn, then the substituent that increase the M-N distance most is that which is located on the smallest sphere and is closest to the metal atom. The subsituent groups attached to the nitrogen atoms affect the M-N distance more than the substituent groups connected to the carbon atoms of the six-membered rings of the ligand.

Under the influences of the atoms or groups of atoms situated at different position, their steric effects on the MN_4 geometry (CF), the coordination number (CN), the symmetry element (SE), the cis or trans configuration (TR), the conformation of the six-membered rings (CS) and the metal axial lengths (SAL and LAL) sorted in Table 1 are also correlated with the M-N bond distance. In the upper part of Table 1 of Ni-N bond distance, four six coordination compounds occur. The smallest region of 37 Ni-N distances have in common structures of planar conformation, except one structure has folded conformation. In the central part of the data distribution for the sorted Ni-N distances, the factors to affect the Ni-N distances are mixed and compensate to each other. Hence, the most informative factors can only be drawn from the two ends of the data distribution.

(ii) The chelate angle

Many factors are involved in the chelate angles. The chelate angle depends upon the interaction of the surrounding groups with the metal ion and with the macrocyclic ligands. In general, the chelate angle has lower value at the five-membered ring side, whereas at the six membered ring side the chelate angle is larger. If the ring size increases, the chelate angles also increase. The structure of the folded conformation (CF = F) commonly maintain smaller chelate angles in both five-membered and six-membered rings of the ligand compare with the average chelate angles of NA and MA. There is no positive evidence that the smallest NA corresponds to the largest MA. In the folded conformations of the central five atoms, the smallest NA structures also appear in the smallest MA structures. The surrounding groups affect the chelate angle to some extent as they influence the M-N distances. In the histogram of the NA (Fig 3) and MA values exhibit only a single peak. The mean NA and MA values are 85.5(1)^o and 94.9(3)^o, respectively for the Ni(II) macrocyclic compounds.

(iii) Miscellaneous factor for the Ni(II) compounds

Table 3 shows the statistical results of the Ni(II) macrocyclic compounds. From Table 3, one can conclude that the structures which contain six coordinations about the Ni(II) atom, the planar conformation for the central five atoms, the trans configuration of the axial ligands relative to the equatorial plane, the chair conformation of the six-membered ring are the most favorable.

(iv) Copper (II) macrocyclic complexes

There are 90 Cu(II) macrocyclic compounds for the investigation of the above mentioned factors. The sorted data for the Cu-N distances (M-N), minimum (NA) and maximum (MA) chelate angles, small (SAL) and large (LAL) axial lengths are summarized in Table 2. The statistical percentages of CN, CS, TR, SE and CF for these 90 Cu(II) compounds are given in Table 3. The Cu(II) structures have more possible six and five coordination and least possible four coordinations, whereas the Ni(II) complexes have

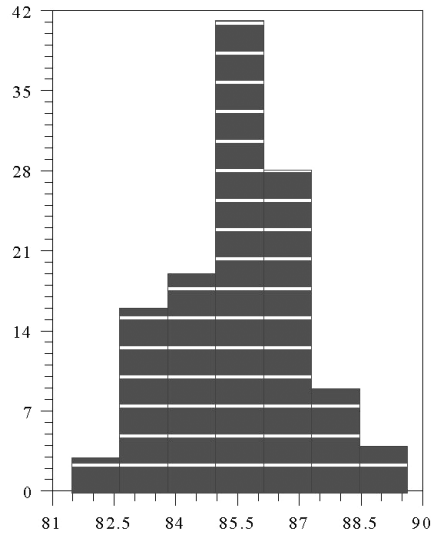
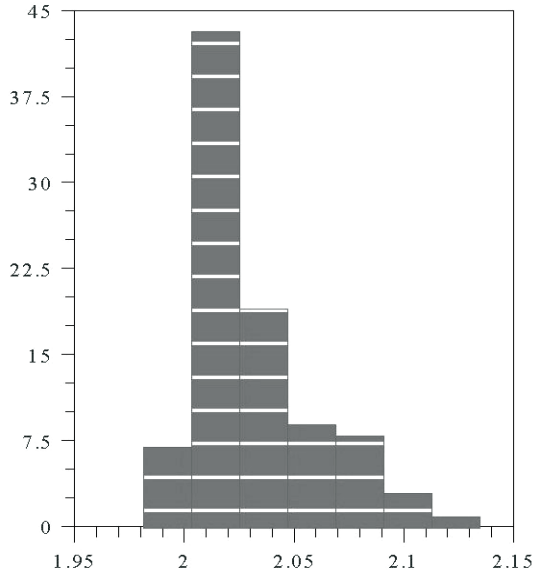


Fig. 3

more abundant with six and four but least in five coordination. In the Cu(II) complexes, there exists nearly the same possibility of trans and cis configurations. Only one peak occurs in the histogram of Cu-N distance (Fig 4), minimum and maximum chelate angles. The average Cu-N distance, the minimum chelate angle and the maximum chelate angle are 2.032(3)A, 85.8(1)^o and 94.2(1)^o, respectively.



3. General Features of the Metal (II) compounds:

The structures of the Ni(II) and Cu(II) macrocyclic compounds, have been scrutinized and studied about their bond length, chelate angles, conformation, coordination and configuration, resulting in many structural features. The coordination bond lengths and the chelate angles correlate with the structural features about the metal (II) ion.

Intra- or inter- molecular hydrogen bonding exists among the ligands and water molecules or anions, and plays an important role in the structure, such as the stability of the crystal structure. Generally, the temperature factor of the atoms, which is close to the metal atom is lower than faraway atoms. The faraway atoms vibrate more strongly along the direction perpendicular to the bond than parallel to the bond. In most case, the structures of Ni(II) macrocyclic compounds have coordination number six and planar conformation for the central five atoms.

In general, the axial bond lengths of the Ni(II) macrocyclic compounds are nearly the same as the equatorial bond length, whereas the axial length of Cu(II) macrocyclic compounds are longer than the equatorial bond lengths;

$(Ni\text{-}L)_{ax} \simeq \langle Ni\text{-}N\rangle_{eq}$, $(Cu\text{-}L)_{ax}$ longer than $\langle Cu\text{-}N\rangle_{eq}$.

The above point is due to Jahn-Teller distortion (Deeth & Hitchman, 1986).

The mean Ni-N distances for the six-coordinate and four-coordinate complexes are 2.091(7) and 1.949(7) Å, respectively. The average Ni-N distance for the four-coordinate complexes is significantly shorter than that for the six-coordinate complexes. They are correspondent to the low-spin square planar complexes and the high-spin octahedral complexes, respectively. The average Cu-N distance is 2.032(3) Å. The substituents attached to the nitrogen atoms affect the distance between the metal ion and nitrogen atom more than the substituents connected to the carbon atoms on the tetradendate ligands.

A nonsymmetrical configuration of the anion groups has the most influence on the chelate angles. A nonsymmetrical attachment of the substituents commonly widens the chelate angle in the neighborhood of the substituent. The chelate angle is smaller for the five-membered ring than that for the six-membered. In general case, the chelate angle is increased, when the ring size is increased. The average minimum and maximum chelate angles are; 85.5(1)^o and 94.9(3)^o for Ni(II) macrocyclic compounds, 85.8(1)^o and 94.2(1)^o for Cu(II) macrocyclic compounds. These values agree with the values reported in literature (Lu et al., 1991).

Out of 90 Cu(II), only 17 macrocyclic complexes have four coordination. From this study, the Cu(II) compounds have higher coordination (either five or six). In five coordination Cu(II) complexes, the Cu(II) ion is slightly above the mean plane of the four nitrogen atoms and towards the axial coordinated atom. 38% Ni(II) complexes have trans conformation, whereas 22% structures are in the cis conformation, and planarity configuration is 88%, whereas 12% have folded configuration. The Cu(II) complexes have almost equally cis and trans configurations, and highly populated planar conformation than folded conformations at the central five atoms. In both metal(II) complexes, the most probable conformations of the two six-membered rings exhibit stable chair form.

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References

Adam, K. R., Antolovich, M., Brigden, L. G., Leong, A. J., Lindoy, L. F., Baillie, P. J., Uppal, D. K., McPartlin, M., Shah, B., Proserpio, D., Fabbrizzi, L. and Tasker, P. A. (1991) *J.Chem.Soc.,Dalton Trans*., 2493.

Alcock, N. W., Benniston, A. C., Grant, S. J., Omar, H. A. A. and Moore, P. (1991) *J.Chem.Soc.,Chem.Comm*., 1573.

Antsyshkina, A. S., Porai-Koshits, M. A., Makhaev, V. D., Borisov, A. P., Kedrova, N. S. and Maltseva, N. N. (1992) *Koord.Khim*., **18**, 474.

Barefield, E. K., Bianchi, A., .Billo, E. J., Connolly, P. J., Paoletti, P., Summers, J. S. and Van Derveer D. G.. (1986b) *Inorg.Chem*., **25**, 4197.

Barefield, E. K., Freeman, G. M. and Van Derveer, D. G. (1986a) *Inorg.Chem.*, **25**, 552.

Battaglia, L. P., Bianchi, A., Corradi, A. B., Garcia-Espana, E., Micheloni, M. and Julve, M. (1988) *Inorg.Chem*., **27**, 4174.

Belsky, V. K., Streltsova, N. R., Kuzmina, E. N. and Nazarenko, A. Y. (1993) *Polyhedron*, **12**, 831.

Bencini, A., Caneschi, A., Dei, A., Gatteschi, D., Zanchini, C. and Kahn, O. (1986) *Inorg.Chem.*, **25**, 1374.

Benelli, B., Dei, A., Gatteschi, D. and Pardi, L. (1988) *Inorg.Chem*., **27**, 2831.

Bernhardt, P. V. (1996) *J.Chem.Soc.,Dalton Trans*., 4319.

Bernhardt, P. V., Byriel, K. A., Kennard, C. H. L. and Sharpe, P. C. (1996c) *J.Chem.Soc., Dalton Trans*., 145.

Bernhardt, P. V. and Comba, P. (1993) *J.Chem.Soc., Chem.Comm*., 113.

Bernhardt, P. V., Harrowfield, J. M., Hockless, D. C. R. and Sargeson, A. M. (1994) *Inorg.Chem*., **33**, 5659.

Bernhardt, P. V., Hetherington, J. C. and Jones, L. A. (1996a) *J.Chem.Soc.,Dalton Trans*., 4325.

Bernhardt, P. V. and Jones, L. A. (1997a) *J.Chem.Soc, Chem.Comm*., 655.

Bernhardt, P. V., Jones, L. A. and Sharpe, P. C. (1997b) *J.Chem.Soc.,Dalton Trans*., 1169.

Bernhardt, P. V. and Lawrance, G. A. (1990) *Acc. Chem. Res.,* **104**, 297.

Bernhardt, P. V. and Sharpe, P. C. (1996b) *J.Chem.Soc.,Chem.Comm*., 1267.

Bernhardt, P. V. and Sharpe, P. C. (1998) *Inorg.Chem*., **37**, 1629.

Beveridge, K. A., McAuley, A. and Xu, C. (1991) *Inorg.Chem*., **30**, 2074.

Bharadwaj, P. K., Potenza, J. A. and Schugar, H. J. (1988) *Inorg.Chem*., **27**, 3172.

Bu, X, H., An, D. L., Chen, Y. T., Shionoya, M. and Kimura, E. (1997) *J.Inclusion Phenom*., **27**, 245.

Bu, X. H., Cao, X. C., Zhang, Z. H., Zhu, Z. A., Chen, Y. T., Shionoya, M. and Kimura, E. (1996a) *Polyhedron*, **15**, 1203.

Bu, X, H., Zhang, Z. H., An, D. L., Chen, Y. T., Shionoya, M. and Kimura, E. (1996b) *Inorg.Chim.Acta*, **249**, 125.

Bulach, V., Mandon, D., Fischer, J., Weiss, R., Bill, E., Butzlaff, C. and Trautwein, A. X. (1994) *New J.Chem.(Nouv.J.Chim.)*, **18**, 709.

Bunzli, J. -C. G. and Choppin, G. R. (1986) *Lanthanide Probes in Life, Chemical and Earth Sciences, Theory and Practice*. Elsevier, Amsterdam.

Busch, D. H. (1978) *Acc. Chem. Res.,* **11**, 392.

Calligaris, M., Carugo, O., Crippa, G., De Santis, G., Di Casa, M., Fabbrizzi, L., Poggi, A. and Seghi, B. (1990) *Inorg.Chem*., **29**, 2964.

Chapman, J., Ferguson, G., Gallagher, J. F., Jennings, M. C. and Parker, D. (1992) *J.Chem.Soc.,Dalton Trans*., 345. **C49**, 1284.

Choi, K. -Y., Kim, J. C., Jensen, W. P., Suh, I, -H., Choi, S. -S. (1996) *Acta Cryst*., **C52**, 2166.

Choi, K. -Y., Kim, D. -W., Kim, K, -H., Oh, M. -R. and Suh, I. -H. (1998) *Acta Cryst.*, **C54**, 627.

Choi, K. -Y., Oh, M. -R. and Suh, I. -H. (1997) *Chem.Lett*., 147.

Clark, I. J., Creaser, I. I., Engelhardt, L. M., Harrowfield, J. M., Krausz, E. R., Moran, G. M., Sargeson, A. M. and White, A. H. (1993) *Aust.J.Chem*., **46**, 111.

Colacio, E., Dominguez-Vera, J. M., Escuer, A., Kivekas, R. and Romerosa, A. (1994) *Inorg.Chem*., **33**, 3914.

Colacio, E., Dominguez-Vera, J. M., Escuer, A., Kivekas, R., Klinga, M., Moreno, J. -M. and Romerosa, A. (1997) *J.Chem.Soc.,Dalton Trans*., 1685.

Colacio, E., Dominquez-Vera, J. M., Escuer, A., Kivekas, R., Klinga, M. and Romerosa, A. (1996) *Acta Chem.Scand.*, **50**, 178.

Colacio, E., Dominguez-Vera, J. M., Romerosa, A., Kivekas, R., Klinga, M. and Escuer, A. (1995) *Inorg.Chim.Acta*, 23**4**, 61.

Collins, T. J., Nichols, T. R. and Uffelman, E. S. (1991) *J.Am.Chem.Soc*., **113**, 4708.

Comba, P., Curtis, N. F., Lawrance, G. A., Sargeson, A. M., Skelton, B. W. and White, A. H. (1986) *Inorg.Chem*., **25**, 4260.

Curtis, N. F. (1979) *Coordination Chemistry of Macrocyclic Compounds*; Melson, E. A. Ed., pp219-345, Plenum, New York, NY, USA.

Curtis, N. F., Gainsford, G. J., Hambley, T. W., Lawrance, G. A., Morgan, K. R. and Siriwardena, A. (1987) *J.Chem.Soc.,Chem.Comm*., 295.

Curtis, N. F., Gainsford, G. J., Siriwardena, A. and Weatherburn, D. C. (1993) *Aust.J.Chem*., **46**, 755.

Deeth, R. J. and Hitchman, M. A. (1986) *Inorg. Chem.*, **25**, 1225.

Drew, M. G. B. and Mok, K. F. (1987) *Acta Cryst*., **C43**, 666.

Dumas, S., Lastra, E. and Hegedus, L. S. (1995) *J.Am.Chem.Soc.*, **117**, 3368.

Edwards, R., Newman, P. D., Stephens, F. S., Vagg, R. S. and Williams, P. A. (1993) *Inorg.Chim.Acta*, **204**, 125.

Emsley, J., Arif, M., Bates, P. A. and Hursthouse, M. B. (1988) *J.Chem.Soc., Chem.Comm*., 1387.

Engelhardt, L. M., Harrowfield, J. M., Sargeson, A. M. and White, A. H. (1993) *Aust.J.Chem*., **46**, 127.

Escuer, A., Vicente, R., El Fallah, M. S., Ribas, J., Solans, X. and Font-Bardia, M. (1993b) *J.Chem.Soc.,Dalton Trans*., 2975.

Escuer, A., Vicente, R., El Fallah, M. S., Solans, X. and Font-Bardia, M. (1996a) *Inorg.Chim.Acta*, **247**, 85.

Escuer, A., Vicente, R., El Fallah, M. S., Solans, X. and Font-Bardia, M. (1996b) *J.Chem.Soc.,Dalton Trans*., 1013.

Escuer, A., Vicente, R., Ribas, J., Costa, R. and Solans, X. (1992) *Inorg.Chem.*, **31**, 2627.

Escuer, A., Vicente, R., Ribas, J., El Fallah, M. S. and Solans, X. (1993a) *Inorg.Chem*., **32**, 1033.

Fabbrizzi, L., Licchelli, M., Lanfredi, A. M. M., Vassalli, O. and Ugozzoli, F. (1996b) *Inorg.Chem*., **35**, 1582.

Fabbrizzi, L., Licchelli, M., Poggi, A., Vassalli, O., Ungaretti, L. and Sardone, N. (1996a) *Inorg.Chim.Acta*, **246**, 379.

Ferguson, G., Lough, A. J. and Bembi, R. (1990) *Acta Cryst*., **C46**, 213.

Ferlay, S., Mallah, T., Vaissermann, J., Bartolome, F., Veillet, P. and Verdaguer, M. (1996) *J.Chem.Soc.,Chem.Comm*., 2481.

Fortier, D. G. and McAuley, A. (1989) *Inorg.Chem*., **28**, 655.

Hambley, T. W. (1986) *J.Chem.Soc.,Dalton Trans*., 565.

Hancock, R. D., Ngwenya, M. P., Wade, P. W., Boeyens, J. C. A. and Dobson, S. M. (1989) *Inorg.Chim.Acta*, **164**, 73.

Harrowfield, J. M., Sargeson, A. M., Skelton, B. W. and White, A. H. (1994) *Aust.J.Chem*., **47**, 181.

Hay, R. W., Clifford, T., Klein, J. and Lightfoot, P. (1996) *Polyhedron*, **15**, 2315.

Hay, R. W., Pujari, M. P., Moodie, W. T., Craig, S., Richens, D. T., Perotti, A. and Ungaretti, L. (1987) *J.Chem.Soc.,Dalton Trans*., 2605.

Helps, I. M., Parker, D., Chapman, J. and Ferguson, G. (1988) *J.Chem.Soc.,Chem.Comm*., 1094.

Iitaka, Y., Koike, T., and Kimura, E. (1986) *Inorg.Chem*., **25**, 402.

John, E., Bharadwaj, P. K., Krogh-Jespersen, K., Potenza, J. A. and Schugar, H. J. (1986a) *J.Am.Chem.Soc*., **108**, 5015.

John, E., Bharadwaj, P. K., Potenza, J. A. and Schugar, H. J. (1986b) *Inorg.Chem*., **25**, 3065.

Kajiwara, T., Yamaguchi, T., Kido, H., Kawabata, S., Kuroda, R. and Ito, T. (1993) *Inorg.Chem*., **32**, 4990.

Kajiwara, T., Yamaguchi, T., Oshio, H. and Ito, T. (1994) *Bull.Chem.Soc.Jpn.*, **67**, 2130.

Kang, S. -G., Kim, M. -S., Choi, J. -S., Whang, D. and Kim, K. (1995) *J.Chem.Soc., Dalton Trans*., 363.

Kato, M. and Ito, T. (1986) *Bull.Chem.Soc.Jpn*., **59**, 285.

Kido, H., Takada, M., Suwabe, M., Yamaguchi, T. and Ito, T. (1995) *Inorg.Chim.Acta*, **228**, 133.

Kimura, E., Haruta, M., Koike, T., Shionoya, M., Takenouchi, K. and Iitaka, Y. (1993) *Inorg.Chem*., **32**, 2779.

Kimura, E., Koike, T., Nada, H. and Iitaka, Y. (1986) *J.Chem.Soc.,Chem.Comm*., 1322.

Kimura, E., Koike, T., Nada, H. and Iitaka, Y. (1988) *Inorg.Chem*., **27**, 1036.

Kimura, E., Kotake, Y., Koike, T., Shionoya, M. and Shiro, M. (1990a) *Inorg.Chem*., **29**, 4991.

Kimura, E., Koike, T., Uenishi, K., Hediger, M., Kuramoto, M., Joko, S., Arai, Y., Kodama, M. and Iitaka, Y. (1987b) *Inorg.Chem*., **26**, 2975.

Kimura, E., Shionoya, M., Mita, T. and Iitaka, Y. (1987a) *J.Chem.Soc.,Chem.Comm*., 1712.

Kimura, E., Wada, S., Shionoya, M., Takahashi, T. and Iitaka, Y. (1990b) *J.Chem.Soc., Chem.Comm*., 397.

Kobiro, K., Nakayama, A., Hiro, T., Suwa, M., Kakiuchi, K., Tobe, Y. and Odaira, Y. (1990) *Chem.Lett.*, 1979.

Kobiro, K., Nakayama, A., Hiro, T., Suwa, M. and Tobe, Y. (1992) *Inorg.Chem*., **31**, 676.

Konig, B., Pelka, M., Moller, O., Dix, I. and Jones, P. G. (1997) *Chem.Ber*., **130**, 521.

Konig, B., Pelka, M., Zieg, H., Jones, P. G. and Dix, I. (1996) *J.Chem.Soc.,Chem.Comm*., 471.

Krajewski, J. W., Gluzinski, P., Korybut-Daszkiewicz, B., Kemme, A. and Mishnyov, A. (1991) *Bull.Pol.Acad.Sci.,Chem.*, **39**, 279.

Lampeka, Y. D., Prikhodko, A. I., Nazarenko, A. Y. and Rusanov, E. B. (1996) *J.Chem.Soc.,Dalton Trans*., 2017.

Lancashire, R. J., Newman, P. D., Stephens, F. S., Vagg, R. S. and Williams, P. A. (1995) *J.Coord.Chem*., **34**, 345.

Lawrance, G. A., Skelton, B. W., White, A. H. and Comba, P. (1986) *Aust.J.Chem*., **39**, 1101.

Lee, T. -Y., Hsieh, M. -Y., Lee, T. -J., Chen, J. -W. and Chung, C. -S. (1986) *Acta Cryst.*, **C42**, 1001.

Liang, B. F., Margerrum, D. W. and Chung, C. -S. (1979) *Inorg. Chem.*, **18**, 2001.

Lin, Y. -J. (1988) *J.Struct.Chem*., **7**, 107.

Lin, Y. -J., Chen, L. -Q., Ni, S. -S. and Xu, J. -D. (1995) *J.Struct.Chem*., **14**, 44.

Lin, Y. -J., Ni, S. -S. and Xu, J. -D. (1986) *J.Struct.Chem*., **5**, 5.

Lin, Y. -J., Ye, X. -M., Hao, B. and Song, L. -J. (1996) *J.Struct.Chem*., **15**, 362.

Lu, T. -H., Chung, C. -S. and Ashida, T. (1991) *J. Chin. Chem. Soc. (ROC).*, **38**, 147.

Lu, T. -H., Lee, T. -J., Liang, B. -F. and Chung, C. -S. (1981). *J. Inorg. Nucl. Chem.*, **43**, 2333.

Lu, T. -H., Liang, W. -C., Wu, D. -T. and Chung, C. -S. (1986a) *Acta Cryst.*, **C42**, 801.

Lu, T. -H., Tahirov, T. H., Liu, Y. -L., Chung, C. -S., Huang, C. -C. and Hong, Y. -S. (1996) *Acta Cryst.*, **C52**, 1093.

Lu, T. -H., Wu, D. -T. and Chung, C. -S. (1986b) *J.Chem.Soc.,Dalton Trans*., 1999.

Makhaev, V. D., Antsyshkina, A. S. and Shulga, Y. M. (1996) *Zh.Neorg.Khim*., **41**, 1022.

McAuley, A., Fortier, D. G., Macartney, D. H., Whitcombe, T. W. and Xu, C. (1994) *J.Chem.Soc.,Dalton Trans*., 2071.

McAuley, A., Palmer, T. and Whitcombe, T. W. (1993) *Can.J.Chem*., **71**, 1792.

McAuley, A. and Subramanian, S. (1991) *Inorg.Chem*., **30**, 371.

McAuley, A., Subramanian, S. and Whitcombe, T. W. (1987) *J.Chem.Soc., Chem.Comm*., 539.

McAuley, A., Subramanian, S. and Zaworotko, M. J. (1992) *J.Chem.Soc.,Chem.Comm*., 1321.

Mitsumi, M., Okawa, H., Sakiyama, H., Ohba, M., Matsumoto, N., Kurisaki, T. and Wakita, H. (1993) *J.Chem.Soc.,Dalton Trans*., 2991.

Miyamura, K., Kohzuki, M., Narushima, R., Saburi, M., Gohshi, Y., Tsuboyama, S., Tsuboyama, K. and Sakurai, T. (1987) *J.Chem.Soc.,Dalton Trans*., 3093.

Mochizuki, K., Kondo, T., Manaka, S., Kajiwara, T. and Ito, T. (1996a) *J.Coord.Chem*., **37**, 205.

Mochizuki, K. and Kondo, T. (1995) *Inorg.Chem*., **34**, 6241.

Mochizuki, K., Manaka, S., Takeda, I. and Kondo, T. (1996b) *Inorg.Chem*., **35**, 5132.

Moi, M. K., Yanuck, M., Deshpande, S. V., Hope, H., DeNardo, S. J. and Meares, C. F. (1987) *Inorg.Chem*., **26**, 3458.

Moran, J. K., Olmstead, M. M. and Meares, C. F. (1995) *Acta Cryst.*, **C51**, 621.

Munoz, M. C., Cano, J., Ruiz, R., Lloret, F. and Faus, J. (1995) *Acta Cryst*., **C51**, 873.

Nazarenko, A. Y., Belsky, V. K. and Streltsova, N. R. (1996) *Zh.Neorg.Khim*., **41**, 1119.

Oberholzer, M. R., Neuberger, M., Zehnder, M. and Kaden, T. A. (1995) *Helv.Chim.Acta*, **78**, 505.

Oshio, H. (1993) *Inorg.Chem*., **32**, 4123.

Oshio, H., Okamoto, H., Kikuchi, T. and Ito, T. (1997) *Inorg.Chem*., **36**, 3201.

Panneerselvam, K., Lu, T. -H., Chi, T. -Y., Chung, C. -S., Chen, Y. -J. and Kwan, K. -S. (1998) *Acta Cryst*., **C54**, 25.

Pattrick, G., Ngwenya, M. P., Dobson, S. M. and Hancock, R. D. (1991) *J.Chem.Soc., Dalton Trans*., 1295.

Pickardt, J. and Hoffmeister, I. (1995) *Z.Naturforsch.,Teil*., **B50**, 828.

Planinic, P., Matkovic-Calogovic, D. and Meider, H. (1997) *J.Chem.Soc.,Dalton Trans*., 3445.

Prasad, L., Nyburg, S. C. and McAuley, A. (1987) *Acta Cryst*., **C43**, 1038.

Ram, M. S., Riordan, C. G., Ostrander, R. and Rheingold, A. L. (1995) *Inorg.Chem*., **34**, 5884.

Ram, M. S., Riordan, C. G., Yap, G. P. A., Liable-Sands, L., Rheingold, A. L., Marchaj, A. and Norton, J. R. (1997) *J.Am.Chem.Soc*., **119**, 1648.

Rawle, S. C., Moore, P. and Alcock, N. W. (1992) *J.Chem.Soc.,Chem.Comm*., 684.

Riesen, A., Zehnder, M. and Kaden, T. A. (1988) *Acta Cryst*., **C44**, 1740.

Rossignoli, M., Bernhardt, P. V., Lawrance, G.. A. and Maeder, M. (1997) *Aust.J.Chem*., **50**, 529.

Ruiz, R., Julve, M., Cano, J., Soto, J., Martinez-Manez, R., Munoz, C. and Paya, J. (1993) *Transition Met.Chem*., **18**, 523.

Schmid, C. L. Kempf, C., Taubert, A., Neuberger, M., Zehnder, M., Kaden, T. A., Bujno, K. and Bilewicz, R. (1996) *Helv.Chim.Acta*, **79**, 1011.

Schmid, C. L., Neuburger, M., Zehnder, M., Kaden, T. A., Bujno, K. and Bilewicz, R. (1997) *Helv.Chim.Acta*, **80**, 241.

Scott, M. J. and Holm, R. H. (1994) *J.Am.Chem.Soc*., **116**, 11357.

Shionoya, M., Kimura, E. and Iitaka, Y. (1990) *J.Am.Chem.Soc*., **112**, 9237.

Siegfried, L., Neuburger, M., Zehnder, M. and Kaden, T. A. (1994) *J.Chem.Soc., Chem.Comm*., 951.

Stranger, R., McMahon, K. L., Gahan, L. R., Bruce, J. I. And Hambley, T. W. (1997) *Inorg.Chem*., **36**, 3466.

Studer, M., Riesen, A. and Kaden, T. A. (1989) *Helv.Chim.Acta*, **72**, 1253.

Studer, M., Riesen, A. and Kaden, T. A. (1990) *Acta Cryst*., **C46**, 741.

Szalda, D. J., Fujita, E., Sanzenbacher, R., Paulus, H. and Elias, H. (1994) *Inorg.Chem*., **33**, 5855.Tahirov, T. H., Lu, T. -H., Liao, F. -L., Wang, S. -L., Chen, B. -H., Chi, T. -Y. and Chung, C. -S. (1996) *Acta Cryst*., **C52**, 2687.

Tahirov, T. H., Lu, T. -H., Liu, G. -S., Chi, T. -Y. and Chung, C. -S. (1995) *Acta Cryst*., **C51**, 2018.

Tendero, M. J. L., Benito, A., Cano, J., Lloris, J. M., Martinez-Manez, R., Soto, J., Edwards, A. J., Raithby, P. R. and Rennie, M. A. (1995) *J.Chem.Soc.,Chem.Comm.*, 1643.

Toriumi, K., Wada, Y., Mitani, T., Bandow, S., Yamashita, M. and Fujii, Y. (1989) *J.Am.Chem.Soc*., **111**, 2341.

Tschudin, D., Riesen, A. and Kaden, T. A. (1989) *Helv.Chim.Acta*, **72**, 131.

Vicente, R., Escuer, A., El Fallah, M. S., Solans, X. and Font-Bardia, M. (1997) *Inorg.Chim.Acta*, **261**, 227.

Vicente, R., , A., Ribas, J., Dei, A, Solans, X. and Calvet, T. (1990) *Polyhedron*, **9**, 1729.

Wang, A., Lee, T. -J., Chen, B. -H., Yuan, Y. -Z. and Chung, C. -S. (1996a) *Acta Cryst*., **C52**, 3033.

Wang, A., Lee, T. -J., Chi, T. -Y., Liao, F. -L., Liu, G. -S. and Chung, C. -S. (1996c) *Acta Cryst*., **C52**, 806.

Wang, Z., Willett, R. D., Molnar, S. and Brewer, K. J. (1996b) *Acta Cryst.*, **C52**, 581.

Weisman, G. R., Wong, E. H., Hill, D. C., Rogers, M. E., Reed, D. P. and Calabrese, J. C. (1996) *J.Chem.Soc., Chem.Comm*., 947.

Xin, L., Curtis, N. F. and Weatherburn, D. C. (1992) *Transition Met.Chem*., **17**, 147.

Xu, J. -D., Ni, S. -S. and Lin, Y. -J. (1986) *Inorg.Chim.Acta*, **111**, 61.

Xu, J. -D., Ni, S. -S. and Lin, Y. -J. (1988) *Inorg.Chem*., **27**, 4651.

Yamashita, M. and Miyamae, H. (1989) *Inorg.Chim.Acta*, **156**, 71.

Table 1. Sorted Ni-N distances for Ni(II) macrocyclic structures

ID	M-N	NA	MA	SAL	LAL	CN	CS	TR	SE	CF	REF
1	1.842	84.4	97.2			4	T		1	F	Collins et al., 1991
2	1.894	86.2	93.6			4	CB		m	P	Moran et al., 1995
3	1.894	83.3	98.5			4	T		1	P	Dumas et al., 1995
4	1.899	85.0	94.9			4	T		1	P	Dumas et al., 1995
5	1.907	83.1	96.2			4	C		1	P	Hancock et al., 1989
6	1.910	85.0	94.1			4	T		1	P	Dumas et al., 1995
7	1.913	85.4	94.8			4	CT		1	P	Chinn et al., 1993
8	1.913	85.6	94.4			4	C		i	P	Dumas et al., 1995
9	1.916	89.5	90.5			4	T		2	P	Barefield et al., 1986b
10	1.917	89.1	91.9			4	C		1	P	Kobiro et al., 1990
11	1.917	83.7	96.2			4	C		1	P	Hancock et al., 1989
12	1.917	88.2	91.8			4	T		i	P	Konig et al., 1996
13	1.917	84.3	96.9			4	C		1	P	Bu et al., 1996a
14	1.924	86.3	93.6			4	C		1	P	Mochizuki et al.,1996a
15	1.925	88.2	95.8			4	C		1	P	Kobiro, et al., 1992
16	1.926	87.6	93.6			4	C		1	P	Wang et al., 1996a
17	1.927	86.3	95.4			4	CT		1	P	Kimura et al., 1988
18	1.933	85.8	93.8			4	CB		1	P	Kido et al., 1995
19	1.938	86.5	96.6			4	C		1	P	Mochizuki et al,1996b
20	1.939	85.5	94.5			4	C		i	P	Adam et al., 1991
21	1.940	87.0	92.9			4	C		1	P	McAuley et al., 1987
22	1.940	85.7	94.3			4	C		i	P	Szalda et al., 1994
23	1.942	86.3	93.7			4	C		i	P	Drew et al., 1987
24	1.943	86.2	94.5			4	C		1	P	Kimura et al., 1993
25	1.943	86.5	94.9			4	C		1	P	Tahirov et al., 1995
26	1.948	86.0	94.0			4	C		i	P	Choi et al., 1996
27	1.950	87.2	93.2			4	C		1	P	Kimura et al., 1990b
28	1.952	85.5	94.6			4	C		1	P	Prasad et al., 1987
29	1.953	86.6	93.4			4	C		i	P	Munoz et al., 1995
30	1.954	86.9	93.1			4	C		i	P	Ferguson et al., 1990
31	1.954	87.5	92.5			4	C		i	P	Chapman, et al., 1992
32	1.958	85.1	98.2			4	C		1	P	Kobiro, et al., 1992
33	1.958	85.7	94.3			4	C		i	P	Szalda et al., 1994
34	1.960	87.8	94.7			4	CB		1	P	Bernhardt et al., 1994
35	1.961	85.1	95.6			4	C		1	P	Kobiro, et al., 1992
36	1.965	88.0	92.0			4	B		1	P	Bernhardt et al., 1994
37	1.966	87.2	92.8			4	C		i	P	Miyamura et al., 1987
38	1.971	86.3	94.2	.615	2.617	6	C	T	1	P	Toriumi et al., 1989
39	1.972	86.3	93.5			4	CT		1	P	Bernhardt et al., 1994
40	1.973	86.4	93.7	2.110	2.114	6	C	T	1	P	McAuley et al., 1993
41	1.982	87.8	92.2			4	C		i	P	Ruiz et al., 1993
42	1.983	86.4	94.9			4	C		1	P	Hambley, 1986
43	1.983	85.8	93.9	2.401	2.430	6	C	T	1	P	McAuley et al., 1991
44	1.987	86.3	95.2			4	C		1	F	Schmid et al., 1996
45	1.990	87.5	92.5			4	C		i	P	Barefield et al., 1986a
46	1.990	85.7	94.7			4	C		1	P	Oberholzer et al., 1995
47	1.995	86.7	94.5			4	C		1	P	Schmid et al., 1996
48	1.996	86.1	93.9	2.472	2.472	6	C	T	i	P	Yamashita et al., 1989
49	2.003	86.6	94.1			4	C		1	P	Schimd et al., 1997
50	2.012	85.7	96.0	2.881		5	C	C	1	P	Kajiwara et al., 1993
51	2.013	87.1	92.9			4	C		i	P	Lee et al., 1986
52	2.037	85.6	94.8	2.569	2.665	6	C	T	1	P	Kajiwara et al., 1994
53	2.052	84.5	97.7	2.130	2.547	6	CB	T	1	P	Curtis et al., 1993
54	2.057	84.2	96.7	2.142	2.166	6	CT	T	1	P	Kimura et al., 1988
55	2.059	83.8	100.5	2.153	2.172	6	C	T	1	P	McAuley et al., 1994
56	2.059	84.7	95.6	2.159	2.189	6	C	T	1	P	Kobiro, et al., 1992
57	2.062	85.0	95.3	2.123	2.237	6	T	T	1	P	Kimura et al., 1986
58	2.062	81.7	97.3	2.100	2.259	6	C	T	1	P	Vicente et al., 1997
59	2.062	85.0	94.1	2.165	2.172	6	C	T	1	P	Escuer et al., 1993a
60	2.063	85.1	94.9	2.137	2.137	6	C	T	i	P	Oshio, 1993

ID	M-N	NA	MA	SAL	LAL	CN	CS	TR	SE	CF	REF
61	2.064	85.5	96.5	2.108	2.373	6	C	T	1	P	McAuley et al., 1994
62	2.065	86.4	93.6	2.128	2.128	6	C	T	i	P	Curtis et al., 1993
63	2.066	85.0	96.1	2.181	2.196	6	C	T	1	P	Mochizuki et al.,1996a
64	2.066	86.5	94.3	2.140	2.165	6	B	T	1	P	Curtis et al., 1993
65	2.067	85.3	94.7	2.084	2.092	6	C	T	1	P	Oshio et al., 1997
66	2.067	86.7	93.3	2.102	2.143	6	B	T	1	P	Curtis et al., 1993
67	2.067	84.6	95.4			4	C		i	P	Bernhardt et al., 1994
68	2.068	85.1	94.9	2.176	2.176	6	C	T	i	P	Mochizuki et al., 1995
69	2.069	85.1	96.1	2.385	2.563	6	C	T	1	P	Fortier et al., 1989
70	2.070	86.6	93.7	2.124	2.127	6	B	T	1	P	Curtis et al., 1987
71	2.070	86.6	93.7	2.124	2.127	6	B	T	1	P	Curtis et al., 1993
72	2.070	85.8	97.3	2.141	2.161	6	CT	T	1	P	Kimura et al., 1993
73	2.071	85.7	94.3	2.479	2.479	6	C	C	i	P	Shionoya et al., 1990
74	2.072	83.6	96.4	2.108	2.109	6	C	T	1	P	Choi et al., 1998
75	2.073	85.0	95.8	2.098	2.132	6	C	T	1	P	Kimura et al., 1987a
76	2.073	85.9	94.1	2.174	2.180	6	C	T	1	P	Vicente et al., 1997
77	2.078	84.9	96.6	2.015	2.401	6	C	T	1	P	Iitaka et al., 1986
78	2.078	85.0	94.5	2.065	2.223	6	C	T	1	P	Lin et al., 1986
79	2.079	87.0	100.8	2.051	2.104	6	CT	T	1	P	Lin et al., 1995
80	2.083	85.7	98.3	2.073	2.199	6	T	C	1	P	Xu et al., 1986
81	2.085	83.6	95.7	2.150	2.248	6	C	T	1	P	Krajewski et al., 1991
82	2.085	85.4	94.5	2.170	2.189	6	C	T	1	P	Escuer et al., 1993b
83	2.089	85.0	95.0	2.148	2.148	6	C	T	i	P	Kang et al., 1995
84	2.090	85.0	94.6	2.065	2.223	6	C	T	1	P	Xu et al., 1988
85	2.091	83.8	96.2	2.240	2.240	6	C	T	i	P	Ferlay et al., 1996
86	2.095	83.7	91.8	2.070	2.071	6	C	T	1	P	Battaglia et al., 1988
87	2.095	84.8	95.2	2.122	2.138	6	C	T	1	P	Colacio et al., 1996
88	2.100	83.4	92.9	2.130	2.140	6	C	C	1	F	Barefield et al., 1986b
89	2.101	85.6	94.6	2.068	2.092	6	C	T	1	P	Lin, 1988
90	2.101	85.6	94.6	2.068	2.092	6	C	T	1	P	Xu et al., 1988
91	2.102	83.4	91.2	2.083	2.232	6	C	C	1	F	Kimura et al., 1987a
92	2.107	86.2	93.8			4	C		i	P	Ram et al., 1995
93	2.109	85.2	88.9	2.665	2.665	6	C	C	m	F	Bencini et al., 1986
94	2.109	83.3	90.9	2.080	2.112	6	C	C	1	P	Kimura et al., 1990a
95	2.111	84.3	90.8	2.096	2.109	6	T	T	1	P	Clark et al., 1993
96	2.112	83.6	101.5	2.101	2.426	6	T	C	1	P	Stranger et al., 1997
97	2.119	84.5	90.6	2.058	2.084	6	C	C	1	P	Benelli et al., 1988
98	2.123	82.1	94.6	2.393		5	C	C	1	F	Schimd et al., 1997
99	2.124	84.1	93.7	1.937		5	C	C	1	F	Vicente et al., 1997
100	2.126	84.6	89.2	2.081	2.086	6	T	T	1	P	Engelhardt et al., 1993
101	2.127	89.6	102.9	2.128	2.133	6	C	C	1	P	Colacio et al., 1997
102	2.128	84.0	93.1	2.369		5	C	C	1	F	Ram et al., 1995
103	2.131	84.3	90.7	2.091	2.197	6	C	C	1	P	Colacio, et al.,1994
104	2.133	86.0	101.2	2.063	2.074	6	C	C	1	P	Escuer et al., 1992
105	2.134	85.0	93.7	1.991		5	C	C	1	F	Kato et al., 1986
106	2.136	84.4	94.6	1.984		5	C	C	m	F	Escuer et al., 1996a
107	2.139	89.3	102.2	2.142	2.142	6	C	C	m	P	Mitsumi et al., 1993
108	2.140	84.4	94.4	1.990	1.990	6	C	C	m	F	Escuer et al., 1996a
109	2.142	86.4	93.6	2.141	2.141	6	C	T	i	P	Barefield et al., 1986a
110	2.143	82.8	127.5	2.076	2.212	6	C	C	1	P	Escuer et al., 1996b
111	2.147	85.6	94.4	2.059	2.064	6	C	T	1	P	Hay et al., 1987
112	2.149	83.3	92.3	2.347		5	C	C	1	F	Ram et al., 1995
113	2.152	81.5	93.9	2.082	2.165	6	C	C	1	P	Calligaris et al., 1990
114	2.152	84.4	94.9	1.999		5	C	C	1	F	Tendero et al., 1995
115	2.154	84.2	91.6	2.041		5	C	C	1	F	Ram et al., 1997
116	2.160	83.5	99.2	2.470	2.485	6	C	C	1	P	Vicente et al., 1990
117	2.163	87.3	94.2	2.101	2.116	6	C	T	1	P	Kato et al., 1986
118	2.168	85.0	90.1	2.054	2.111	6	C	C	1	P	Colacio et al., 1995
119	2.181	84.4	92.4	2.306		5	C	C	1	F	Planinic et al., 1997
120	2.182	83.3	96.5	2.016	2.137	6	CT	T	1	P	Alcock et al., 1991

Note;

ID: The identification index of the molecular structure.

M-N: The average bond distance between the metal (II) (M) and its nearest neighboring nitrogen atom (N) in the main ligand.

NA: indicates the minimum value of the four chelate angles with metal (II) as its vertex.

MA: indicates the maximum value of the four chelate angles with metal (II) as its vertex.

SAL: represents the small axial length of the coordination bond between metal (II) and its ligands. Blank indicates the metal (II) atom is in 4 coordination.

LAL: represents the large axial length of the coordination bond between metal (II) and its ligands. Blank indicates the metal (II) atom is in either 4 or 5 coordination.

CN: represents the coordination number of the metal atom.

CS: represents the conformation of the two six-membered rings; C means chair form; T means twist form; B means boat form; CT means one is in chair and other is twist; CB means one is in chair and other is boat; TB means one is in twist and other is in boat.

TR: represents the cis (TR=C) or trans (TR=T) configuration for the fifth and or sixth coordinated ligands relative to the equatorial plane. TR = blank indicates that the basic coordination number is four.

SE: represents the symmetry element at the metal atom: i means inversion center; 2 means two fold axis perpendicular to the ligand plane and passing through the metal atom; m means mirror plane perpendicular to the ligand plane and passing through the metal atom; 2/m means two fold and also mirror plane perpendicular to the ligand plane and passing through the metal atom; 1 means no speacial symmetry.

CF: indicates the conformation of the MN_4 plane for the central five atoms (M represents metal atom); P means planar conformation; F means folded conformation. And REF: references.

Table 2. Sorted Cu-N Distances for Cu(II) Macrocyclic Structures

ID	M-N	NA	MA	SAL	LAL	CN	CS	TR	SE	CF	REF
1	1.982	81.2	100.2	2.341		5	C	C	m	P	Pattrick et al., 1991
2	1.985	87.0	93.0			4	C		i	P	Konig et al., 1997
3	1.994	84.3	93.9	2.263		5	T	C	1	P	Bu et al., 1997
4	1.996	88.5	93.4	2.434		5	C	C	i	F	Lu et al., 1986a
5	2.002	85.4	94.5	2.338	2.859	6	C	T	1	P	Siegfried et al., 1994
6	2.002	85.2	95.5			4	T		1	P	Bu et al., 1996b
7	2.003	86.1	93.7	2.627		5	C	C	1	P	McAuley et al., 1992
8	2.004	86.2	93.5	2.368	2.428	6	C	T	1	P	Moi et al., 1987
9	2.004	86.7	97.3	2.333	2.668	6	T	T	1	P	Bernhardt et al., 1997b
10	2.004	86.1	93.9	2.887	2.887	6	C	T	i	P	Bernhardt et al., 1997b
11	2.004	84.6	97.0	2.629		5	C	C	1	F	Lancashire et al., 1995
12	2.005	86.4	93.6	2.439	2.439	6	C	T	i	P	Xin et al., 1992
13	2.005	85.4	94.6	2.544	2.544	6	C	T	i	P	Bernhardt et al., 1997b
14	2.006	85.6	94.4			4	C		i	P	Pickardt et al., 1995
15	2.007	79.9	98.3	2.204		5	TB	C	m	P	Pattrick et al., 1991
16	2.008	85.9	95.4	2.521	2.689	6	C	T	1	P	Lampeka et al., 1996
17	2.009	86.1	93.9			4	C		i	P	Lawrance et al., 1986
18	2.009	86.7	93.3			4	C		i	P	Bernhardt et al., 1996c
19	2.010	86.0	94.0			4	C		2/m	P	Bernhardt et al., 1993
20	2.013	85.5	94.5	2.484	2.484	6	C	T	2/m	P	Emsley et al., 1988
21	2.013	85.3	95.1	2.655	2.717	6	C	T	1	P	Bernhardt et al., 1997a
22	2.013	86.4	93.6	2.569	2.569	6	C	T	i	P	Bernhardt et al., 1997b
23	2.013	86.7	93.3	2.535	2.535	6	C	T	i	P	Fabbrizzi et al., 1996a
24	2.013	86.0	94.0	2.430		5	C	C	2/m	P	Lu et al., 1996
25	2.014	86.3	93.7			4	C		i	P	Bernhardt et al., 1998
26	2.014	86.0	94.0	2.506	2.506	6	C	T	i	P	Bernhardt, 1996
27	2.015	86.5	93.5	2.448	2.448	6	C	T	i	P	Scott & Holm, 1994
28	2.017	86.7	93.3	2.590	2.590	6	C	T	i	P	Rossignoli et al., 1997
29	2.018	86.6	93.4	2.514	2.514	6	C	T	i	P	Xin et al., 1992
30	2.018	86.8	93.3	2.451	2.451	6	C	T	2/m	P	Bernhardt, 1996
31	2.018	85.7	94.7	2.853	2.853	6	C	T	2/m	P	Studer et al., 1989
32	2.018	85.7	94.3	2.842	2.842	6	C	T	2/m	P	Bulach et al., 1994
33	2.019	85.6	98.8	2.351	2.515	6	C	T	1	P	Kato et al., 1986
34	2.020	85.4	94.6			4	C		i	P	Antsyshkina el al., 1992
35	2.020	86.7	93.3	2.658	2.658	6	C	T	i	P	Choi et al., 1997
36	2.020	85.2	94.8	2.953	2.953	6	C	T	i	P	Chen et al., 1996
37	2.020	85.7	94.3			4	C		i	P	Wang et al., 1996b
38	2.020	85.2	94.7	2.754	2.754	6	C	T	2	P	Pickardt et al., 1995
39	2.021	85.6	94.4	2.502	2.502	6	C	T	i	P	Oshio, 1993
40	2.021	86.0	94.0	2.570	2.570	6	C	T	i	P	Scott & Holm, 1994
41	2.022	85.2	94.8	2.652	2.652	6	C	T	i	P	Nazarenko et al., 1996
42	2.023	86.6	93.4			4	C		i	P	Antsyshkina el al., 1992
43	2.023	85.8	94.2	2.491	2.491	6	C	T	i	P	Oshio, 1993
44	2.023	86.2	93.8	2.535	2.535	6	C	T	i	P	Xin et al., 1992
45	2.023	85.1	94.9	3.193	3.193	6	C	T	i	P	Makhaev et al., 1996
46	2.023	86.4	94.0			4	C		1	P	Fabbrizzi et al., 1996b
47	2.024	85.7	94.3	2.524	2.524	6	C	T	i	P	Comba et al., 1986
48	2.024	85.5	94.3	2.148		5	C	C	1	P	Kimura et al., 1987b
49	2.024	86.1	93.9			4	C		i	P	Hay et al., 1996
50	2.025	86.5	93.7	2.557	2.640	6	C	T	1	P	Fabbrizzi et al., 1996a

Table 2 continuation

ID	M-N	NA	MA	SAL	LAL	CN	CS	TR	SE	CF	REF
51	2.026	87.7	94.2	2.879		5	C	C	1	F	Lu et al., 1986b
52	2.026	85.9	94.0			4	C		1	P	Rawle et al., 1992
53	2.026	85.1	96.0	2.232		5	C	C	1	P	Studer et al., 1990
54	2.026	84.9	95.9	2.256		5	C	C	1	P	Studer et al., 1990
55	2.026	86.0	94.0	2.539	2.539	6	C	T	i	P	Wang et al., 1996c
56	2.027	85.7	93.1	2.541		5	T	C	1	F	Bernhardt et al., 1998
57	2.028	84.5	95.5	2.648	2.648	6	C	T	i	P	Choi et al., 1996
58	2.029	85.2	94.8	2.409	2.409	6	C	T	i	P	Oshio, 1993
59	2.032	86.5	93.0	2.712		5	C	C	1	F	Lancashire et al., 1995
60	2.033	86.1	93.9	2.573	2.573	6	C	T	i	P	Nazarenko et al., 1996
61	2.033	85.3	93.4	2.519		5	T	C	1	F	Bernhardt et al., 1996b
62	2.033	86.6	93.4			4	C		i	P	Chapman et al., 1990
63	2.034	84.7	96.1	2.196		5	C	C	1	F	Bernhardt et al., 1996a
64	2.034	87.1	93.1	2.355		5	C	C	1	P	Tahirov et al., 1996
65	2.040	86.2	94.6	2.275		5	C	C	1	P	Beveridge et al., 1991
66	2.040	85.1	94.6	2.568		5	C	C	1	P	Bernhardt et al., 1996a
67	2.043	85.6	95.1	2.552		5	C	C	1	P	Fortier et al., 1989
68	2.044	87.4	93.7	2.223		5	T	C	1	P	Lin et al., 1996
69	2.046	86.6	95.0	2.515		5	C	C	1	P	Bernhardt et al., 1994
70	2.051	85.5	93.8	2.157		5	C	C	1	P	Panneerselvam et al.,1998
71	2.054	86.3	93.7	2.263	2.263	6	C	T	i	P	Helps et al., 1988
72	2.055	86.4	93.4			4	C		1	P	Edwards et al., 1993
73	2.055	85.0	93.1	2.305		5	C	C	1	F	Weisman et al., 1996
74	2.058	85.6	94.7	2.552		5	C	C	1	P	Tschudin et al., 1989
75	2.060	86.2	92.1	2.280		5	C	C	1	P	Bernhardt et al., 1994
76	2.063	84.5	91.8	2.327		5	C	C	1	F	John et al., 1986a
77	2.063	86.0	95.2			4	C		1	P	Oberholzer et al., 1995
78	2.065	87.8	92.2			4	C		i	P	Bharadwaj et al., 1988
79	2.074	85.9	94.8	2.223		5	C	C	1	F	Tschudin et al., 1989
80	2.079	85.2	93.9	2.160		5	C	C	1	F	Tschudin et al., 1989
81	2.081	86.4	93.6	2.309	2.309	6	C	T	i	P	Belsky et al., 1993
82	2.081	86.0	93.8	2.537		5	C	C	1	P	Tendero et al., 1995
83	2.082	87.0	93.0	2.248	2.248	6	C	T	i	P	Chen et al., 1993
84	2.083	87.1	92.9	2.368	2.368	6	C	T	i	P	Chapman et al., 1990
85	2.088	84.2	90.8	2.314		5	C	C	1	P	John et al., 1986b
86	2.090	85.0	94.8	2.610		5	C	C	1	F	Schmid et al., 1997
87	2.094	86.2	91.5	2.458		5	C	C	2	F	Harrowfield et al., 1994
88	2.100	86.7	93.3	2.228	2.302	6	C	T	1	P	Riesen et al., 1988
89	2.104	85.3	94.7	2.658		5	C	C	1	F	Schmid et al., 1997
90	2.134	84.7	94.2	2.296		5	C	C	1	F	Weisman et al., 1996

Table 3. The statistical percentages for the Ni(II) and Cu(II) macrocyclic structures

CN	P	CS	P	TR	P	SE	P	CF	P
6	52; 43	chair	78; 92	trans	38; 43	C_i	20; 42	planar	88; 83
5	8; 38	twist	9; 7	cis	22; 38	C_2	1; 2	folded	12; 17
4	40; 19	boat	4; 0	none	40; 19	C_m	4; 2		
		CT	6; 0			$C_{2/m}$	0; 7		
		CB	3; 0			P1	75; 47		
		TB	0; 1						

The percentages on the two sets of Ni(II) and 90 Cu(II) data are separated by the symbol ";"
CN = coordination number of the metal atom
CS = conformation of the two six-membered rings
TR = configuration of the fifth and the sixth coordinated ligands relative to the macrocyclic plane
SE = symmetry element at the central metal atom
CF = conformation geometry of the central five atoms
P = percentage