

Complexation of Zn(II) ion with macrocyclic ligands containing nitrogen-oxygen donors

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Abstract - Protonation and stability constants have been determined for the interaction of macrocyclic ligands containing nitrogen and oxygen donor atoms with protons and Zn(II) cations. Information of the nature of the ligand-Zn(II) complex in solution was obtained using ^1H NMR spectroscopy.

Macrocyclic ligands containing nitrogen and oxygen donor atoms, such as 1,12-diaza-3,4:9,10-dibenzo-5,8-dioxacyclopentadecane (NTOE), 1,13-diaza-3,4:10,11-dibenzo-5,9-dioxacyclohexadecane (NTOT), 1,15-diaza-3,4:12,13-dibenzo-5,8,11-trioxacycloheptadecane (NEOD), 1,15-diaza-3,4:12,13-dibenzo-5,8,11-trioxacyclooctadecane (NTOD), 1,12,15-triaza-3,4:9,10-dibenzo-5,8-dioxacycloheptadecane (NDOE), and 1,15,18-triaza-3,4:12,13-dibenzo-5,8,11-trioxacycloeicosane (NDOD), have been synthesized by the methods reported elsewhere (ref. 1). These ligands were characterized by elementary analysis (Perkin Elmer 240 B CHN analyzer), ^1H and ^{13}C nmr spectroscopy (Bruker AM 200 MHz), infrared spectroscopy (Hitachi 270-30), and by their melting points.

The structures of the ligands are shown in Fig. 1. The ligands are N_2O_2 types with 15 and 16 ring members in the first row, N_2O_3 types with 17 and 18 ring members in the second row, and N_3O_2 and N_3O_3 types with 17 and 20 ring members in the third row, respectively.

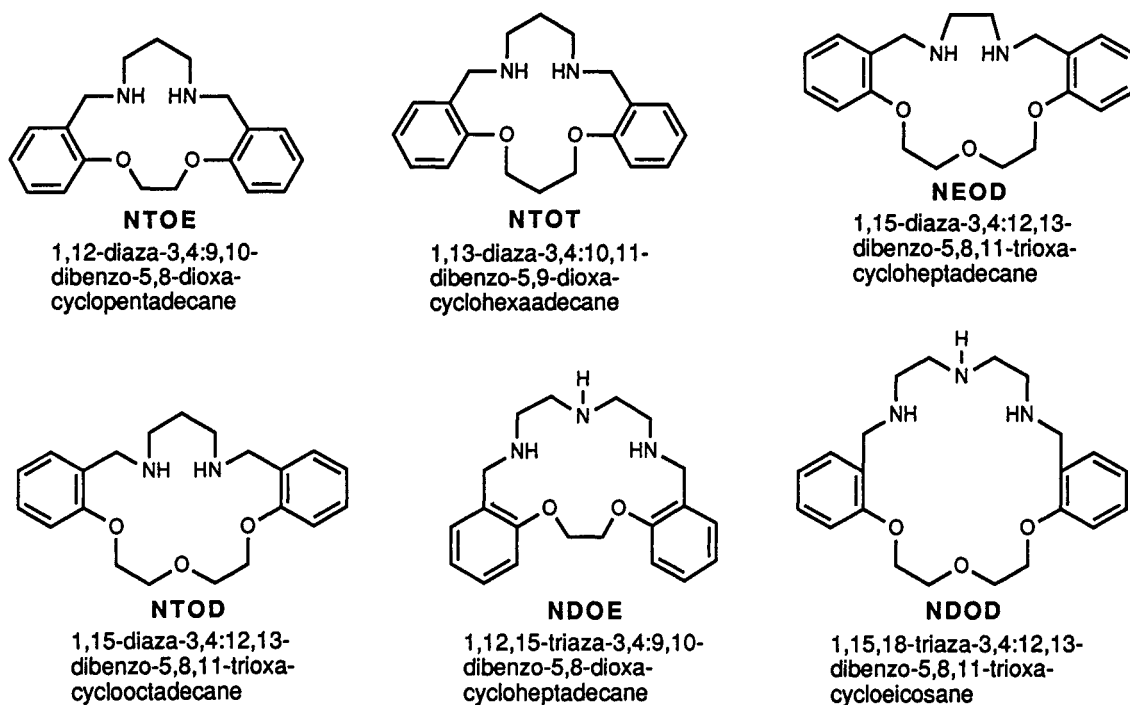


Fig. 1. Structural formulas of macrocyclic ligands

LIGAND PROTONATION CONSTANTS

To obtain some information of the dominant factor influencing the basicity of the ligand, the protonation constants of the ligands were determined by potentiometry at 25°C.

Table 1 Comparison of protonation constants of macrocyclic ligands at $\mu = 0.20 \text{ mol}\cdot\text{dm}^{-3}$

	$\log K_1$	$\log K_2$	$\log K_3$
NTOE(a)	9.27	7.19	
NTOT(a)	9.82	7.57	
NEOD(a)	8.73	6.17	
NTOD(b)	10.01	8.12	
NDOE(c)	9.45	8.23	2.18
NDOD(c)	9.08	8.02	3.64

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As shown in Table 1, the basicities are in the order NTOD > NTOT > NEOD > NTOE > NDOD > NEOD. In N_2O_2 and N_2O_3 systems, ligands with bigger cavities exhibit larger constants than those with smaller cavities, and it seems that a CH_2CH_2 -linkage between nitrogen atoms in the ligand may enhance the constants more than a CH_2CH_2 -linkage between oxygen atoms. N_3O_2 and N_3O_3 type ligands, however, have the nearly same protonation constants. It may be concluded that the dominant factor influencing the basicities of ligands seems to be the size of cavity.

COMPLEX STABILITY CONSTANTS

The stability constants of Zn(II)-complexes with the ligands, enthalpy changes, and entropy changes (Table 2) were determined in H_2O , MeOH, and DMSO by a polarographic method. From the data in Table 2, we obtained the following conclusions: (1) The stability constants are in the order NTOT < NTOE < NEOD < NTOD < NDOE < NDOD in the solvents studied. This order does not show any sharp correlations between the basicities of the ligands, but it correlates with the size of the ligand cavity. (2) All complexation reactions are exothermic, and desolvation processes of both metallic ions and ligands seem to play an important role for the magnitude of the stability. (3) The order of stabilities in solvents is MeOH > H_2O > DMSO. This indicates that the stability does not depend on dielectric constant, but on dipole moment of the solvent.

Table 2 Stability constants, enthalpy changes, and entropy changes for the formation of Zn(II)-complexes with some macrocycles at 25.0 °C and $\mu = 0.1$

Solvent	Ligand	$\log K$ (dm^3/mol)	$-\Delta H$ (kJ/mol)	ΔS (J/mol·K)
H_2O	NTOE	4.22	20.19	12.92
H_2O	NTOT	4.03	15.77	24.14
H_2O	NEOD	5.31	22.63	25.60
H_2O	NTOD	5.47	26.52	15.60
H_2O	NDOE	5.87	33.06	1.27
H_2O	NDOD	8.93	46.11	15.99

Table 2 (continued)

Solvent	Ligand	log <i>K</i> (dm ³ /mol)	-Δ <i>H</i> (kJ/mol)	Δ <i>S</i> (J/mol·K)
MeOH	NTOE	4.51	25.50	0.64
MeOH	NTOT	4.09	17.78	18.51
MeOH	NEOD	5.64	27.32	16.16
MeOH	NTOD	5.76	31.67	3.84
MeOH	NDOE	6.24	34.81	2.51
MeOH	NDOD	9.62	52.21	8.74
DMSO	NTOE	4.01	13.96	29.87
DMSO	NTOT	3.65	9.52	37.81
DMSO	NEOD	5.12	15.81	44.88
DMSO	NTOD	5.15	23.56	19.41
DMSO	NDOE	5.34	25.14	17.73
DMSO	NDOD	8.26	26.97	67.48

INFORMATION ON COMPLEX STRUCTURES IN SOLUTION

To obtain some structural information on the complexes in solution, proton nmr spectroscopy was used. Table 3 lists the proton chemical shift differences in DMSO-*d*₆ between the free ligands and the complexes.

Table 3 The differences in ¹H chemical shifts of the macrocyclic complexes in DMSO-*d*₆

Ligand	-NCH ₂	-NCH ₂ CH ₂	-ArCH ₂	-OCH ₂	-OCH ₂ CH ₂
NTOE(a)	0.31	0.33	0.23	0.02	
NTOT(a)	0.11	0.10	0.10	0.01	0.04
NEOD(a)	0.30		0.20	0.17	0.10
NTOD(b)	0.19	0.14		0.14	0.14
NDOE(c)	0.39		0.40	0.17	
NDOD(c)	0.14			0.18	

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The data in Table 3 suggests the following structures of complexes in solution. (1) N₂O₂ type ligands may be bound with Zn(II) ion through the nitrogen atoms only. Similar phenomena were reported for the solid complexes by Lindoy *et al* (ref. 2). (2) N₂O₃ type ligands may bind Zn(II) ion more tightly through the nitrogen atoms than through the oxygen atoms, and the oxygen atoms may participate in bonding somewhat loosely. (3) N₃O₂ and N₃O₃ ligands may bind Zn(II) ion through both nitrogen and oxygen atoms, and as a result, the Zn(II) ion might be located in the ligand cavity.

Acknowledgement This work was supported by Basic Science Research Institute Program (1991), Ministry of Education, Republic of Korea.

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