

Thermodynamic stabilities of Cu⁺ and Li⁺ complexes of dimethoxyalkanes (MeO(CH₂)_nOMe, n = 2–9) in the gas phase: conformational requirements for binding interactions between metal ions and ligands[†]

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ABSTRACT: The relative free energy changes for the reaction $ML^+ = M^+ + L$ ($M = Cu^+$ and Li^+) were determined in the gas phase for a series of dimethoxyalkanes ($MeO(CH_2)_nOMe$, $n = 2-9$) by measuring the equilibrium constants of ligand-transfer reactions using a FT-ICR mass spectrometry. Stable 1:1 Cu^+ -complexes (CuL^+) were observed when the chain is longer than $n = 4$ while the 1:2 complexes (CuL_2^+) were formed for smaller compounds as stable ions. The dissociation free energy for CuL^+ significantly increases with increasing chain length, by 10 kcal mol^{-1} from $n = 4$ to 9. This increase is attributed to the release of constrain involved in the cyclic conformation of the Cu^+ -complexes. This is consistent with the geometrical and energetic features of the complexes obtained by the DFT calculations at B3LYP/6-311G level of theory. On the contrary, the corresponding dissociation free energy for LiL^+ increases only 3 kcal mol^{-1} from $n = 2$ to 9, although the structures of the 1:1 Li^+ -complexes are also considered to be cyclic. From these results it is concluded that the $Cu[MeO(CH_2)_nOMe]^+$ requires linear alignment for O—Cu—O, indicating the importance of sd_σ hybridization of Cu^+ in the first two ligands binding energy, while the stability of the Li^+ complex is less sensitive to binding geometries except for the system forming a small ring such as $n = 1$ and 2. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: Cu^+ complexes; Li^+ complexes; dimethoxyalkanes; ligand-transfer equilibria; FT-ICR

INTRODUCTION

Quantitative characterization of noncovalent interactions between metal ions and neutral molecules are attracting continuous attention from a wide field of chemical and biological disciplines.^{1–3} Experimental techniques developed for study of the thermochemistry of the metal ion–organic ligand complexes in the gas phase have provided a growing data that is particularly useful for exploring the details of such noncovalent interactions, because the measurements on the thermodynamic stability of the isolated ion–molecule complexes allow separation of intrinsic properties of the interaction from effects due to solvation and solvent induced phenomena.^{4–13} These

studies shed light on the interesting nature of the interactions in the complexes containing more than one ligand bound to a metal ion. For example, experimental data on transition metal ions bound to neutral molecules such as H_2O and dimethylether in the gas phase indicate that the first two ligands binding energies are comparable and much larger than the nearly equal third and fourth ligand binding energies, while the binding energies with alkali metal ions progressively decrease as each ligand is added.^{14–18} Thus, relative ligand binding energies for transition metal ions differ substantially from those for the alkali metal ions. This unique feature of the transition metal ions has been considered to be due to sd_σ hybridization of Cu^+ .^{3,19} The sd_σ hybridization reduces the charge density along the σ axis and both ligands benefit from reduced repulsion while sharing the energetic cost of hybridization, resulting in the larger second ligand binding energy than the first. Taking account of sd_σ hybridization in the second ligand for the transition metal complexes, if a ligand with two basic functional groups is flexible, two basic sites can

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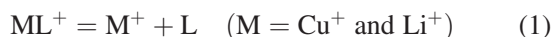
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simultaneously interact with the metal ion, resulting in cyclic complexes linked by metal ions. In such a case the binding energy should significantly depend on the geometrical feature of a ligand, that is, the size of the formed ring. Indeed, it was found that triglyme, tetraglyme, 15-crown-5, and 18-crown-6 with multi-binding sites form exclusively 1:1 complexes with Co⁺, Cu⁺, and Ni⁺ (ML⁺, L = ligand) while monoglyme gives only 1:2 complexes (ML₂⁺), and diglyme gives a mixture of both complexes.²⁰ Similar additional stabilization through intramolecular interactions was frequently observed for acidity, basicity, and lithium cation affinity flexible and difunctional compounds in the gas phase.^{4b,21–25}

It is important to study quantitatively the geometrical requirements in the first two ligand-binding energies for understanding of geometrical features of the metal ion–ligand complexes. Ligand exchange reactions used for making an estimate of the relative metal binding energies with organic ligands will be extended to multi-liganded metal ions.^{6,26–28} In the present work we describe determinations of the relative free energy changes for the reaction (Eqn (1)) in the gas phase for a series of dimethoxyalkanes (MeO(CH₂)_nOMe, *n* = 2–9) by measuring the equilibrium constants of ligand-transfer reactions using a FT-ICR mass spectrometry.



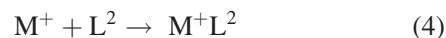
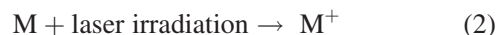
In addition, theoretical calculations were conducted at B3LYP/6-311G level of theory to obtain the geometrical properties and cyclization energies of these complexes in the gas phase.

EXPERIMENTAL

ICR measurements

Equilibrium-constant measurements were performed on an Extrel FTMS 2001 spectrometer equipped with a dual-cell system. An IonSpec Data Station was also used for several measurements. Details of the experimental techniques used for measuring the equilibrium constants for the ligand transfer reaction were similar to those used for the previously described proton-transfer measurements.²⁹ Only significant changes and/or additional procedures are given here. All measurements were performed at 50–70°C at a constant magnetic field strength of 3.0 T. The pressures of the neutral reactants were measured by means of a Bayard–Alpert type ionization gauge with appropriate correction factors being applied to correct the gauge readings for the different ionization cross sections of various compounds.³⁰ The overall pressures of the reagents were maintained at 2–4 × 10^{−7} Torr by controlled flow rates through leak valves (Anelva) from a parallel inlet manifold into the ICR cell in the vacuum chamber.

Metal ions, Cu⁺ and Li⁺, were generated by a laser irradiation of an Nd:YAG (Continuum, Minilite II) at 532 nm (10 mJ) to the pure metal pieces mounted at the end-face of the solid probe rod (Eqn (2)).



$$K_5 = \frac{I(M^+L^2)P(L^1)}{I(M^+L^1)P(L^2)} \quad (6)$$

$$\delta\Delta G^0(M^+) = -RT \ln K_5 \quad (7)$$

When there are two compounds (L¹ and L²) in the ICR cell, the corresponding metal adduct ions, M⁺L¹ and M⁺L², were formed (Eqn (3) and Eqn (4)). After an appropriate reaction period of 5–20 sec, depending upon the reactant and pressures, the ligand-transfer equilibrium (Eqn (5)) was attained as shown in Fig. 1 and the equilibrium constants were calculated by Eqn (6), where *I*(M⁺L¹) and *I*(M⁺L²) are the equilibrium abundances (mass spectrometric integrated intensities) of M⁺L¹ and M⁺L² complexes and *P*(L¹) and *P*(L²) are partial pressures of the neutral compounds L¹ and L². For cooling excited metal ions helium or argon gas was added by using a pulsed valve but significant differences were not observed in the ligand-transfer equilibrium. Therefore, most of measurements were carried out without buffer gas. Each experiment was performed at several ratios of partial pressures and at different overall pressures. The arithmetic mean values of equilibrium constants (*K*₅) were used to calculate δΔ*G*⁰ (Eqn (7)) at

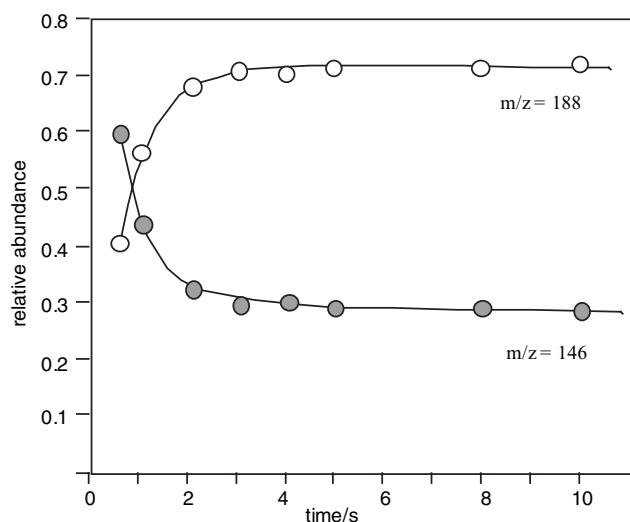


Figure 1. Time-profile of a ligand-transfer reaction for a binary mixture of MeO(CH₂)₆OMe and MeO(CH₂)₉OMe with Li⁺. Partial pressures; 1.1 × 10^{−7} and 1.0 × 10^{−7} Torr for MeO(CH₂)₆OMe and MeO(CH₂)₉OMe, respectively. Relative intensity gives *K* = 1.67 and Δ*G*⁰ = −0.4 kcal mol^{−1} at 343 K

343 K with an average uncertainty of ± 0.3 kcal mol⁻¹ in most of these cases. The occurrence of the ligand-transfer reaction was examined by an ion-eject experiment using the SWIFT technique.³¹

Chemicals

Most of the compounds used in this study were prepared by methylation of the corresponding diols according to a general procedure.³² Dimethoxyethane was purchased from Tokyo Kasei Ltd.

General procedure of preparation of dimethoxyalkanes (MeO(CH₂)_nOMe, n = 2–9). In a 200 mL three-necked round-bottomed flask were placed 0.02 mol of alkanediol, 1.44 g (0.06 mol) of sodium hydride washed by dry benzene, and 50 mL of THF. The resulting mixtures were stirred at reflux overnight. To the reaction mixture 17.0 g (0.12 mol) of methyl iodide was added at room temperature and the reaction mixture was stirred at reflux for 8 h and then solvent was removed roughly. To the reaction solution 25 mL of water was added. The product was extracted by ether and was dried over anhydrous magnesium sulfate. The crude product was purified by preparative VPC and was characterized by ¹H-NMR (500 MHz, CDCl₃) as follows. *1,3-dimethoxypropane*: $\delta = 1.843$ (q, $J = 6.3$ Hz, 2H), 3.454 (t, 4H, $J = 6.4$ Hz), 3.336 (s, 6H). *1,4-dimethoxybutane*: $\delta = 1.621$ – 1.646 (m, 4H), 3.331 (s, 6H), 3.393 (t, $J = 6.25$ Hz, 4H). *1,5-dimethoxybutane*: $\delta = 1.375$ – 1.419 (m, 2H), 1.566– 1.624 (m, 4H), 3.327 (s, 6H), 3.374 (t, $J = 6.5$ Hz, 4H). *1,6-dimethoxyhexane*: $\delta = 1.350$ – 1.380 (m, 4H), 1.564– 1.591 (m, 4H), 3.328 (s, 6H), 3.368 (t, $J = 6.5$ Hz, 4H). *1,7-dimethoxyheptane*: $\delta = 1.330$ – 1.361 (m, 6H), 1.540– 1.582 (m, 4H), 3.327 (s, 6H), 3.361 (t, $J = 6.75$ Hz, 4H). *1,8-dimethoxyoctane*: $\delta = 1.315$ – 1.589 (m, 12H), 3.327 (s, 6H), 3.360 (t, $J = 6.5$ Hz, 4H). *1,9-dimethoxynonane*: $\delta = 1.300$ – 1.574 (m, 14H), 3.328 (s, 6H), 3.360 (t, $J = 6.75$ Hz, 4H).

All the materials were degassed prior to use by several freeze-pump-thaw cycles on the sample-inlet system of the ICR. Their purities were checked on mass spectra of the FT-ICR mass spectrometer in an electron-impact ionization mode.

DFT calculations

Conformational searches were carried out using Spartan '04 program (Wavefunction, Inc.) and several conformers having the low energy were further optimized at RHF/6–31G* level of theory to search the lowest energy conformer (global minimum). Finally, the geometries were fully optimized at the B3LYP/6–311G level of theory with normal convergence using the Gaussian 98 program.³³ Vibrational normal mode analyses were performed at the same level to ensure that each optimized structure was a true minimum

on the potential energy surface. Relative thermochemical values were obtained from isodesmic reactions of each ligand transfer reaction with the reference compound.

RESULTS AND DISCUSSION

Figure 2 shows that the reaction of the generated metal ions with the MeO(CH₂)₇OMe produces exclusively the corresponding 1:1 complexes M[MeO(CH₂)₇OMe]⁺. This indicates that there is no side reaction such as fragmentation mediated by transition metal ions under the present conditions.^{34,35} In the case of the reaction between Cu⁺ and MeO(CH₂)_nOMe with $n = 2$ and 3, the 1:1 complexes formed in a short reaction time rapidly decreased with time and their dimer ions, Cu₂⁺, appeared as major ions after several seconds as shown in Fig. 3. The 1:2 Cu⁺-complexes were generally observed as stable adduct ions for ligands having a single binding site.^{6c,9} The present result suggests that the stable 1:1 Cu⁺-complexes observed for larger compounds with $n \geq 4$ have cyclic structures in which Cu⁺ binds with two oxygen atoms in MeO(CH₂)_nOMe. In the case of Li⁺, the 1:1 complexes were observed for MeO(CH₂)_nOMe ($n = 2$ – 9) as stable ions under relatively low pressure of neutrals at 2 – 4×10^{-7} Torr. The structures of the 1:1 Li⁺-complexes are also assumed to be cyclic. This is supported by the fact that the lithium cation affinity of MeO(CH₂)₂OMe is significantly 15.4 kcal mol⁻¹ (1 kcal mol⁻¹ = 4.184 kJ mol⁻¹) higher than Me₂O with a single binding site.²⁸ This additional stabilization in the complex of Li⁺ with MeO(CH₂)₂OMe suggests bidentate cyclic structure because the polar effect of the X = MeOCH₂ on the lithium cation affinity of the XCH₂OMe system should be comparable to the methyl group or less than the latter.³⁶ Similar additional stabilization compared with parent alcohols and monoethers having a single binding site was observed for compounds with difunctional groups such as methoxy-, halogen-, and phenyl-substituted alcohols.²⁸ These results have been attributed to the intramolecular interaction in their cyclic conformations. The present system, MeO(CH₂)_nOMe, is also the case.

The free energy changes, $\delta\Delta G^0$, obtained for ligand-transfer equilibria are given in Fig. 4 and the ladders of free energy changes for the respective systems provide a scale of the relative dissociation free energies, $\Delta G^0(M^+)$, for M[MeO(CH₂)_nOMe]⁺. For the Li⁺ complex the relative free energies were converted into the absolute scale by adding each of the relative experimental values to the known value of MeO(CH₂)₂OMe as an anchor.²⁸ Since such a reference absolute dissociation free energy for Cu⁺-complex is not available for the present range, the $\Delta G^0(M^+)$ values are given in Fig. 4 as the relative values to that for $n = 9$. The absolute dissociation free energy for Cu(Et₂O)₂⁺ was evaluated to be

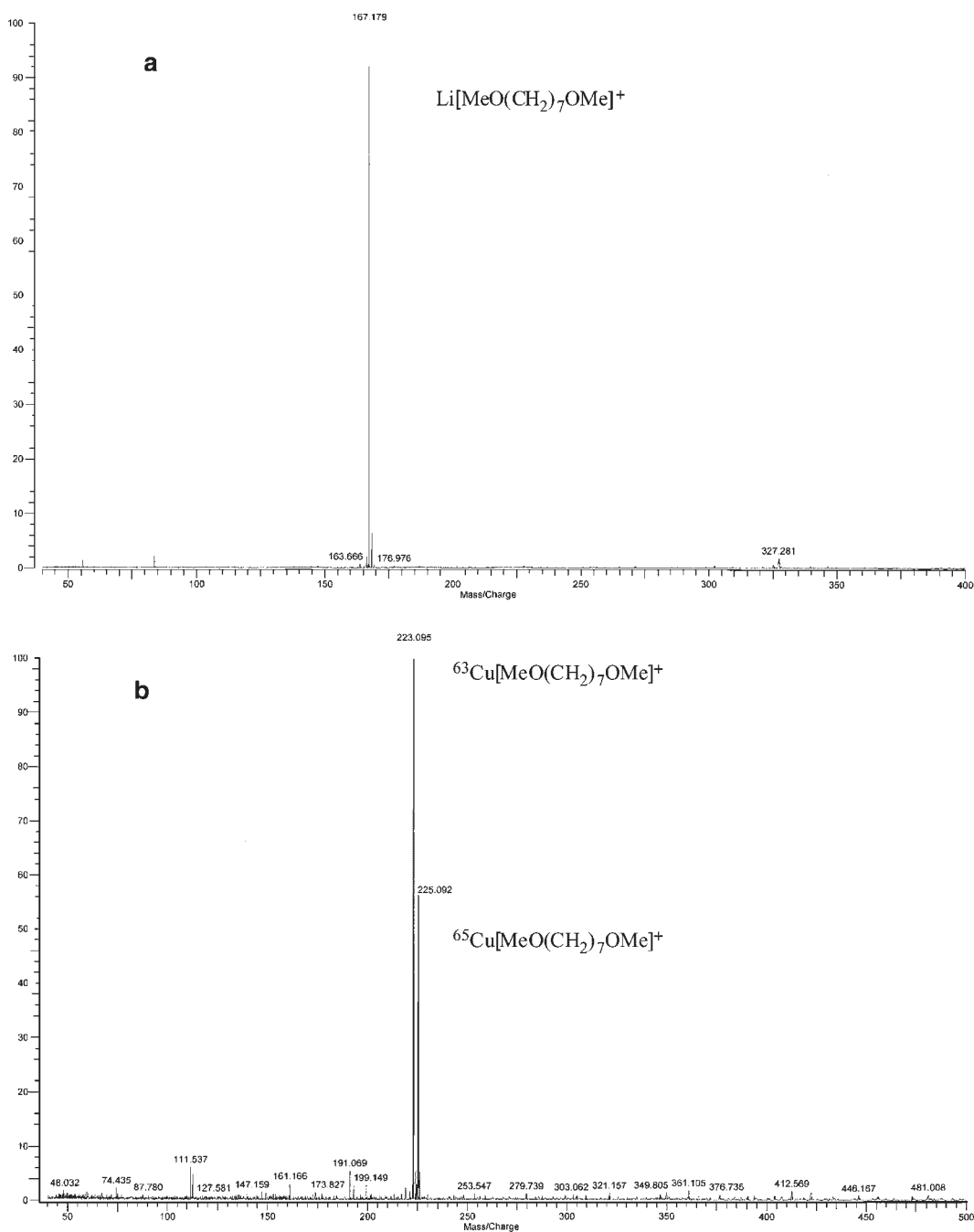


Figure 2. Mass spectra of a reaction of MeO(CH₂)₇OMe with Li⁺ (a) and Cu⁺ (b). Pressure; 2.5×10^{-7} Torr, a reaction time; 10 sec

77.5 kcal mol⁻¹ by Deng and Kebarle.⁹ Considering the similarity of the structure of the Cu⁺ complex, the cyclic Cu⁺-complex with a larger MeO(CH₂)_nOMe may be assumed to have a similar dissociation free energy, indicating that Cu⁺ binds strongly with a ligand compared with Li⁺. The relative free energy values will be enough for the present discussion because our aim of this work is to clarify the effect of a chain length on the dissociation free energy for M[MeO(CH₂)_nOMe]⁺.

Figure 5 shows a plot of the relative dissociation free energies of CuL⁺ and LiL⁺ against the chain length in

MeO(CH₂)_nOMe. The $\Delta G^0(\text{Cu}^+)$ value significantly increases with the chain length from $n=4$ to 6 and reaches the plateau at $n=7$. In contrast to this result, the $\Delta G^0(\text{Li}^+)$ value gradually increases only 3 kcal mol⁻¹ regardless of a large change in chain length from $n=2$ to 9. These results indicate clearly that the thermodynamic stability of the 1:1 Cu⁺-complexes is severely dependent on the chain length, that is, the ring size, and that the stability of the Li⁺-complexes is less sensitive to their geometrical conformations.

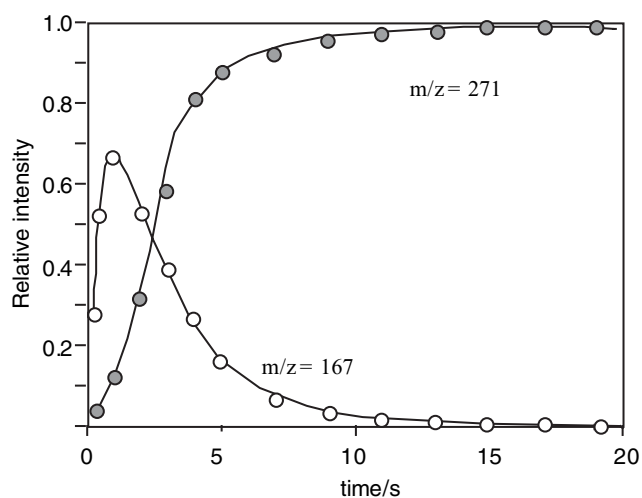
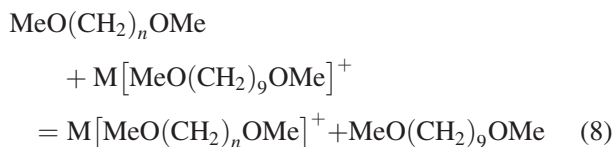


Figure 3. Time-profile of a reaction of Cu^+ and $\text{MeO}(\text{CH}_2)_3\text{OMe}$, pressure of the neutral = 2.5×10^{-7} Torr. Open circles; $\text{Cu}[\text{MeO}(\text{CH}_2)_3\text{OMe}]^+$ and closed circles; $\text{Cu}[\text{MeO}(\text{CH}_2)_3\text{OMe}]_2^+$

In order to obtain geometrical information on these metal ions complexes we optimized the structures of the complexes at B3LYP/6-311G level of theory. The calculated geometries and energetics of the metal ion-bound complexes are summarized in Tables 1 and 2. The calculated relative dissociation free energies for the metal ion complexes were obtained from a following isodesmic reaction (Eqn (8)),



Both cyclic and open conformations were calculated for the metal ion complexes. The cyclization free energies

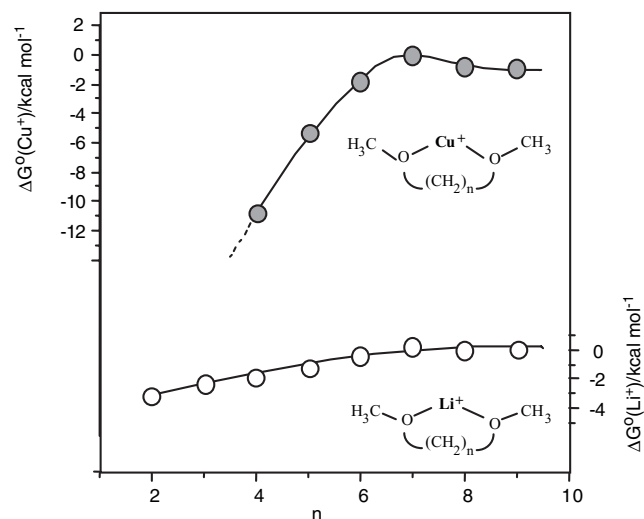


Figure 5. Plot of relative dissociation free energies for $\text{M}[\text{MeO}(\text{CH}_2)_n\text{OMe}]^+$ vs. the chain length (n)

(ΔG_{cyc}^0) that are defined by differences between the cyclic and the open conformations indicate that the cyclic conformations of Cu^+ - and Li^+ -complexes are more stable than their open structures. The most stable structures of neutral molecules were found to be linear. The calculated $\Delta G^0(\text{Cu}^+)$ values are in good agreement with the observed values, $\Delta G^0(\text{Cu}^+)_{\text{calcd}} = 0.3 + 1.11\Delta G^0(\text{Cu}^+)_{\text{obs}}$ ($R = 0.989$). Although the agreement for $\Delta G^0(\text{Li}^+)$ value is not satisfactory, the calculated $\Delta G^0(\text{Li}^+)$ value varies with the chain length in a similar manner to that for the experimental results as shown in Fig. 6.

The cyclization free energies for the Cu^+ -complexes also increase with increasing chain length in a similar manner to the change in the dissociation free energy. Indeed, the cyclization free energies are correlated with

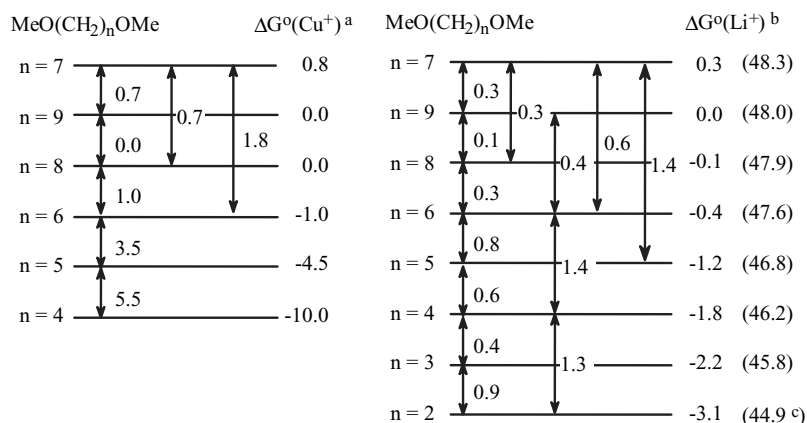


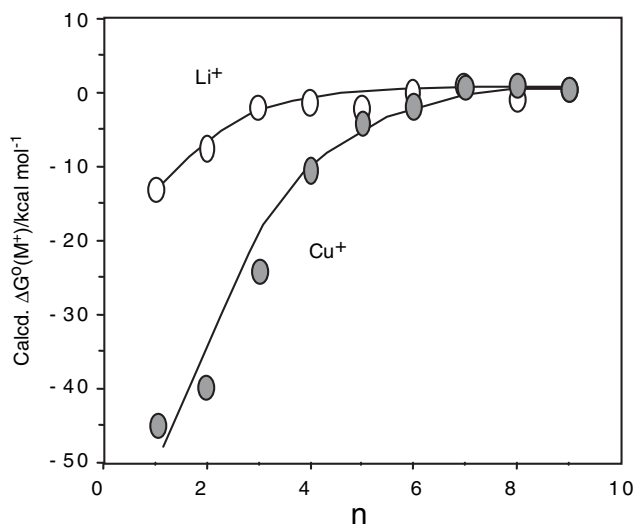
Figure 4. Ladder of ligand-transfer equilibria of metal-cation complexes. The numbers with the arrows are the experimental free energy changes ($\delta\Delta G^0$) for respective ligand-transfer equilibria. All values are given in kcal mol^{-1} . (a) Dissociation free energy $\Delta G^0(\text{Cu}^+)$ relative to $\text{Cu}[\text{MeO}(\text{CH}_2)_9\text{OMe}]^+$. (b) Dissociation free energy $\Delta G^0(\text{Li}^+)$ relative to $\text{Li}[\text{MeO}(\text{CH}_2)_9\text{OMe}]^+$. Values in parentheses are absolute dissociation free energies for LiL^+ anchored by $n = 2$. (c) Ref. 28

Table 1. Calculated cyclization energies, selected geometries, and relative bond dissociation free energies for Copper (I)-complexes, Cu[MeO(CH₂)_nOMe]⁺

n	ΔG_{cyc}^0 ^a (kcal mol ⁻¹)	OCu distance ^b (Å)	OCuO bond ^b angle (deg)	$\Delta G_{\text{calcd}}^0$ ^{b,c} (kcal mol ⁻¹)
1	15.1	2.079	63.9	-44.4
2	17.7	2.003	88.6	-40.0
3	29.0	1.889	126.4	-24.3
4	42.7	1.864	150.5	-11.7
5	49.1	1.868	168.3	-4.0
6	50.4	1.877	178.0	-2.1
7	53.1	1.880	175.7	0.5
8	53.1	1.878	173.7	0.3
9	52.2	1.883	169.6	0.0

^aFree energy differences between the cyclic and the open conformations.^bThese values are for cyclic conformations.^cRelative dissociation free energies.**Table 2.** Calculated cyclization selected geometries, and relative bond dissociation free energies for Lithium Cation-complexes, Li[MeO(CH₂)_nOMe]⁺

n	ΔG_{cyc}^0 ^a (kcal mol ⁻¹)	OLi distance ^b (Å)	OLiO bond ^b angle (deg)	$\Delta G_{\text{calcd}}^0$ ^{b,c} (kcal mol ⁻¹)
1	20.9	1.872	72.3	-13.1
2	27.1	1.838	92.3	-7.5
3	28.4	1.815	110.3	-2.0
4	29.6	1.823	135.4	-1.6
5	28.0	1.833	148.3	-2.6
6	30.3	1.829	162.5	0.0
7	30.8	1.836	165.2	1.2
8	29.1	1.826	164.6	-1.0
9	29.3	1.834	138.6	0.0

^aFree energy differences between the cyclic and the open conformations.^bThese values are for cyclic conformations.^cRelative dissociation free energies.**Figure 6.** Plot of calculated relative dissociation free energies for M[MeO(CH₂)_nOMe]⁺ vs. the chain length (n)

the calculated and observed $\Delta G^0(\text{Cu}^+)$ values, giving a linear relationship with a slope of near unity as shown in Fig. 7.

$$\Delta G^0(\text{Cu}^+)_{\text{calcd}} = 1.06 \Delta G_{\text{cycl}}^0(\text{Cu}^+) - 56.0 \quad (9)$$

$$R = 0.997$$

$$\Delta G^0(\text{Cu}^+)_{\text{obs}} = 0.87 \Delta G_{\text{cycl}}^0(\text{Cu}^+) - 46.6 \quad (10)$$

$$R = 0.983$$

The cyclization free energies must be influenced by the steric constrain of the cyclic conformation. The maximum cyclization free energies for $n = 7-9$ suggest that these complexes have the least steric constrain. In addition, since the bond distance of O—Cu in the complex is almost constant except of $n = 1$ and 2, the steric constrain involved in the cyclic conformation would also be reflected in the bond angles. Indeed, the angle of OCuO increases with the chain length and reaches the plateau at $170^\circ-180^\circ$ for $n \geq 5$. There is a

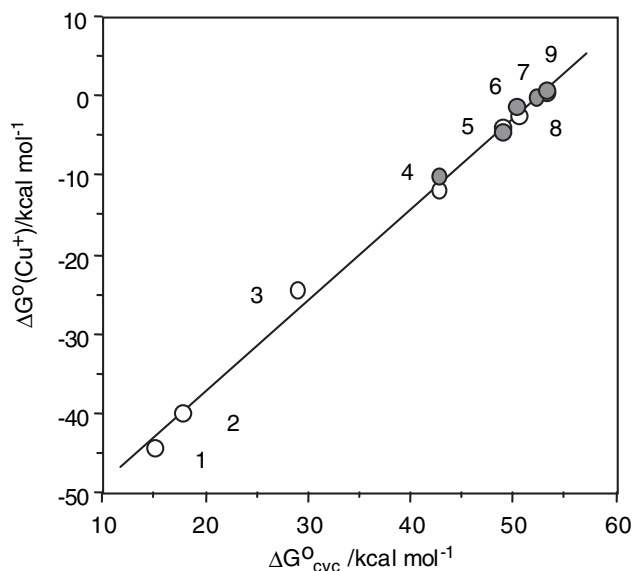


Figure 7. Plots of calculated (open circles) and observed (closed circles) $\Delta G^0(\text{Cu}^+)$ values against calculated cyclization free energies (ΔG^0_{cyc}). The numbers indicate n in $\text{Cu}[\text{MeO}(\text{CH}_2)_n\text{OMe}]^+$

good linear relationship between angles of OCuO and the calculated $\Delta G^0(\text{Cu}^+)$ as shown in Fig. 8.

$$\Delta G^0(\text{Cu}^+)_{\text{calcd}} = -74.7 + 0.42\angle\text{OCuO} \quad (11)$$

$$R = 0.990$$

In addition, a closer examination of the angles shows that the angles of OCuO for $n = 8$ and 9 are somewhat smaller than that for $n = 6$ and 7 , suggesting that these

cyclic structures have some constrain. This may be consistent with the result that the observed and calculated $\Delta G^0(\text{Cu}^+)$ values for $n = 8$ and 9 are somewhat smaller than that of $n = 7$. These results suggest that the release of the steric constrain of the cyclic conformation is mostly responsible for the increase in the dissociation free energy changes for the Cu^+ -complexes.

On the other hand, the calculated relative dissociation energies for the Li^+ -complexes, $\Delta G^0(\text{Li}^+)_{\text{calcd}}$, are almost constant at $-1 \pm 2 \text{ kcal mol}^{-1}$ except for $n = 1$ and 2 when the conformations of the complexes are cyclic, being qualitatively consistent with the trend in experimental values. In addition, the cyclization free energies for the Li^+ -complexes are also constant at $28 \pm 2 \text{ kcal mol}^{-1}$ except for $n = 1$. Although the bond distance of O—Li and the angle of OLiO change with the variation of the chain length in a similar manner to those for the Cu^+ -complex, there is no linear relationship between the angles and the calculated $\Delta G^0(\text{Li}^+)$ values. These geometrical and energetic features of the Li^+ -complexes suggest that the change in geometry is less important to determine the stability of the Li^+ -complex except for small compounds ($n = 1$ and 2) although there is a repulsive ligand–ligand interaction as the second ligand binds with Li^+ .

CONCLUSIONS

It has been shown that the stable 1:1 Cu^+ -complexes observed for dimethoxyalkanes ($\text{MeO}(\text{CH}_2)_n\text{OMe}$) with $n \geq 4$ have cyclic conformations. The Cu^+ dissociation free energy significantly increases with increasing chain length and reaches the plateau at $n = 7$. The large increase

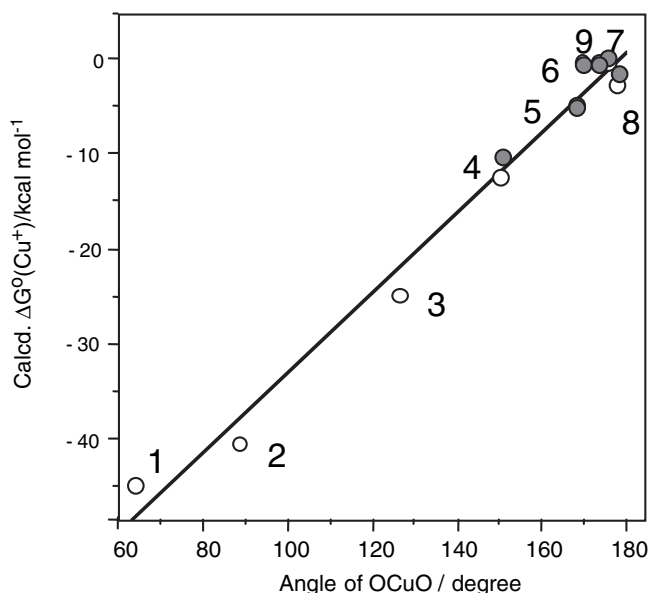


Figure 8. Plot of calculated (open circles) and observed (closed circles) $\Delta G^0(\text{Cu}^+)$ vs. angles of OCuO. The numbers indicate n in $\text{Li}[\text{MeO}(\text{CH}_2)_n\text{OMe}]^+$

is attributed to the release of constrain involved in the cyclic conformations. On the contrary, the corresponding dissociation energy for the Li⁺-complex increases only 3 kcal mol⁻¹ from $n=2$ to 9 although the stable conformations of LiL⁺ complexes are also cyclic. These results indicate that the Cu[MeO(CH₂)_nOMe]⁺ complexes require linear alignment for O—Cu—O, indicating the importance of sd_o hybridization of Cu⁺ in the first two ligands binding energy, while the stability of the Li⁺ complex is less sensitive to such specific binding geometries. This geometrical requirement in the Cu⁺-complex would be an important factor to determine the conformations of flexible molecules containing transition metal ions.

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REFERENCES

- Martell AE, Hancock RD. *Metal Complexes in Aqueous Solution*. Plenum: New York, 1996.
- Frausto da Silva JJR, Williams RJP. *The Biological Chemistry of the Elements*. Clarendon: Oxford, 1991.
- Frenking G, Fröhlich N. *Chem. Rev.* 2000; **100**: 7170–7774.
- (a) Dzidic I, Kebarle P. *J. Phys. Chem.* 1970; **74**: 1466–1474; (b) Yamdagni R, Kebarle P. *J. Am. Chem. Soc.* 1973; **95**: 3504–3510; (c) Davidson WR, Kebarle P. *J. Am. Chem. Soc.* 1976; **98**: 6125–6133; (d) Sunner J, Kebarle P. *J. Am. Chem. Soc.* 1984; **106**: 6135–6139; (e) Castleman AW, Keesee RG. *Chem. Rev.* 1986; **86**: 589–618.
- (a) McLuckey SA, Cameron D, Cook RG. *J. Am. Chem. Soc.* 1981; **103**: 1313–1317; (b) Wysocki VH, Burinsky DJ, Cooks RG. *J. Org. Chem.* 1985; **50**: 1287–1291.
- (a) Wietung RD, Staley RH, Beauchamp J. *J. Am. Chem. Soc.* 1975; **97**: 924–926; (b) Staley RH, Beauchamp J. *J. Am. Chem. Soc.* 1975; **97**: 5920–5921; (c) Jones RW, Staley RH. *J. Am. Chem. Soc.* 1982; **104**: 2296–2300.
- Taft RW, Anvia F, Gal J-F, Walsh S, Capon M, Holmes MC, Hosn K, Oloumi G, Vasanwala R, Yazdani S. *Pure Appl. Chem.* 1990; **62**: 17–23.
- Dunbar RC. *Adv. Gas-Phase Ion Chem.* 1996; **2**: 87–124.
- Deng H, Kebarle P. *J. Am. Chem. Soc.* 1998; **120**: 2925–2931.
- Nielsen SB, Masella M, Kebarle P. *J. Phys. Chem. A.* 1999; **103**: 9891–9898.
- (a) Armentrout PB. *Acc. Chem. Res.* 1995; **28**: 430–436; (b) Rodger MT, Armentrout PB. *Mass Spectrom. Rev.* 2000; **19**: 215–247; (c) Rodger MT, Armentrout PB. *Acc. Chem. Res.* 2004; **37**: 989–998.
- Combariza MY, Fahey AM, Milshcheyn A, Vachet RW. *Int. J. Mass Spectrom.* 2005; **244**: 109–124.
- Vitale G, Valina AB, Hsaung H, Amunugama RA, Rodgers MT. *J. Phys. Chem. A* 2001; **105**: 11351–11364.
- Koizumi H, Zhang X-G, Armentrout PB. *J. Phys. Chem. A* 2001; **105**: 2444–2453.
- (a) More MB, Glendening ED, Ray D, Feller D, Parmentrout B. *J. Phys. Chem.* 1996; **100**: 1605–1614; (b) More MB, Ray D, Armentrout PB. *J. Phys. Chem. A* 1997; **101**: 831–839; (c) Rodgers MT, Armentrout PB. *J. Phys. Chem. A* 1997; **101**: 1238–1249.
- Holland PM, Castleman AW, Jr. *J. Chem. Phys.* 1982; **76**: 4195–4205.
- Marinelli PJ, Squires RR. *J. Am. Chem. Soc.* 1989; **111**: 4101–4103.
- Magnera TF, David DE, Stulik D, Orth RG, Jonkman HT, Michl J. *J. Am. Chem. Soc.* 1989; **111**: 5036–5043.
- (a) Bauschlicher CW, Jr., Langhoff SR, Partridge H. *J. Chem. Phys.* 1991; **94**: 2068–2072; (b) Langhoff SR, Jr., Bauschlicher CW, Partridge H, Sodupe M. *J. Phys. Chem.* 1991; **95**: 10677–10681; (c) Bauschlicher CW, Jr., Partridge H, Langhoff SR, Jr. *J. Phys. Chem.* 1992; **96**: 3273–3278.
- Blair S, Goolsby B, Brodbelt J. *Int. J. Mass Spectrom.* 1999; **185/186/187**: 49–59.
- Chiavarino B, Crestoni ME, Fornarini S. *Int. J. Mass Spectrom.* 2004; **234**: 145–154.
- Crowder GA, Bartmess JE. *Am. Soc. Mass Spectrom.* 1993; **4**: 723–726.
- Hellman T, Beauchamp JL. *J. Am. Chem. Soc.* 1972; **94**: 3671–3672.
- Karty JM, Wu Y, Brauman JI. *J. Am. Chem. Soc.* 2001; **123**: 9800–9805.
- Kumar MK, Rao JS, Prabhakar S, Vairamani M, Sastry GN. *Chem. Commun.* 2005; 1420–1422.
- Kappes MM, Staley RH. *J. Am. Chem. Soc.* 1981; **104**: 1235–1238.
- Deng H, Kebarle P. *J. Phys. Chem. A.* 1998; **102**: 571–579.
- Burk P, Koppel IA, Koppel I, Kurg R, Gal J-F, Maria P-C, Herreros M, Notario R, Abboud J-LM, Anivia F, Taft RW. *J. Phys. Chem. A.* 2000; **104**: 2824–2833.
- Mishima M, Mustanir, Fujio M, Tsuno Y. *Bull. Chem. Soc. Jpn.* 1996; **69**: 2009–2018.
- (a) Bartmess JE, Georgiadis RM. *Vacuum.* 1983; **33**: 149–153; (b) Miller KJ. *J. Am. Chem. Soc.* 1990; **112**: 8533–8542.
- (a) Marshall AG, Wang T-CL, Ricca TL. *J. Am. Chem. Soc.* 1985; **107**: 7893–7897; (b) Guan S, Marshall AG. *Int. J. Mass Spectrom. Ion Process.* 1996; **157/158**: 5–37.
- Hogan JC, Gandour RD. *J. Org. Chem.* 1992; **57**: 55–61.
- Frisch MJ, Trucks GW, Schlegel HB, Scuseria MA, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck DK, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzales C, Challacombe M, Gill PMW, Johnson BG, Chen W, Wong MW, Andres JL, Head-Gordon M, Replogle ES, Pople JA. *Gaussian 98, Revision A.5*. Gaussian: Pittsburgh, PA, 1998.
- Beauchamp JL, Stevens AE, Corderman RR. *Pure Appl. Chem.* 1979; **51**: 967–978.
- Prusse T, Fieder A, Schwarz H. *J. Am. Chem. Soc.* 1991; **113**: 8335–8339.
- Hansch C, Leo A, Taft RW. *Chem. Rev.* 1991; **91**: 165–195.