ChemComm

www.rsc.org/chemcomm

Volume 46 | Number 7 | 21 February 2010 | Pages 993–1172



ISSN 1359-7345

RSCPublishing

COMMUNICATION Tatsuya Nabeshima *et al.* Highly efficient regulation of cation recognition and promotion of selfassembly by metalation of a macrocyclic bis(N₂O₂) ligand with nickel(II)

FEATURE ARTICLE Michael D. Fryzuk *et al.* The hydride route to the preparation of dinitrogen complexes



1359-7345(2010)46:7;1-D

Highly efficient regulation of cation recognition and promotion of self-assembly by metalation of a macrocyclic bis(N_2O_2) ligand with nickel(II)[†]

Shigehisa Akine, Fumihiko Utsuno and Tatsuya Nabeshima*

Received (in Cambridge, UK) 31st July 2009, Accepted 12th November 2009 First published as an Advance Article on the web 1st December 2009 DOI: 10.1039/b915722k

Metalation of a bis(N_2O_2) macrocyclic ligand 1 with nickel(II) acetate afforded a dinuclear metallohost 2, resulting in a significant enhancement of recognition ability of alkali metal ions and the promotion of self-aggregation.

Macrocyclic host molecules having several chelating moieties have been used to prepare cooperative recognition systems that can regulate guest recognition by metalation with transition metals.^{1,2} In particular, salen (H₂salen = N,N'-bis(salicylidene)ethylenediamine) and its analogues are useful as a constituent for such a host molecule.² We can introduce various kinds of metal ions in the salen-type tetradentate coordination site. Metalation of the salen moiety makes the phenol oxygen more negative. Due to these negative charges, the phenoxo groups tend to coordinate to another cation (Scheme 1(a)). In addition, the four coordination bonds from the salen ligand fix the phenoxo groups suitably for chelate coordination. Indeed, salen-containing crown ethers are useful for cooperative metal coordination.² We have investigated the complexation behavior of macrocyclic tris(salen)-type ligands,³ which are effective for the formation of a homonuclear cluster with a bowl-shaped structure.⁴ However, it is difficult to selectively introduce transition metal ions into the salen-type coordination sites, because the transition metal ions intended for the salentype coordination sites also occupy the guest-binding site consisting of six phenoxo groups. If such macrocyclic metallo-salen compounds have a vacant cavity or the transition metal ions do not compete with the guest in the binding, the central binding site will exhibit a strong affinity toward guest cations due to the negative charges.^{2,4,5} In addition, metallohosts having square-planar metals are expected to form stacked aggregated structures because of the increased molecular planarity. We have now designed a new bis(salen)-type macrocycle 1 which has a diaryl ether oxygen between the neighboring salen units. The metalation of the macrocycle 1 with nickel(II) efficiently afforded the dinuclear metallohost 2, which showed a dramatic enhancement of the recognition ability toward alkali metal ions (Scheme 1(b)) and promoted the formation of the stacked aggregate structure. To the best of our knowledge, this is the

Graduate School of Pure and Applied Sciences,

University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan.

E-mail: nabesima@chem.tsukuba.ac.jp; Fax: +81-29-853-4507; Tel: +81-29-853-4507 first example of a stacked one-dimensional array of a metallosalen macrocycle bearing both transition metal and alkali metal ions,⁶ which would show unique physical and chemical properties.

The synthesis of the macrocycle 1 is shown in Scheme 2. The diol 3 was obtained by dilithiation of diphenyl ether⁷ followed by the reaction with trimethyl borate and subsequent treatment with hydrogen peroxide under basic conditions.

After the *ortho*-bromination of the diol **3** with NBS/ diisopropylamine,⁸ the dibromide was lithiated and then allowed to react with DMF to afford the dialdehyde **4**. The reaction of the dialdehyde **4** with *o*-phenylenediamine in a 1:1 molar ratio in acetonitrile afforded the macrocycle **1** in 64% yield as orange crystals. In the ¹H NMR spectrum, the CH and OH protons of the salicylaldimine moiety appeared as singlets at 8.97 and 13.52 ppm, respectively, being consistent with a highly symmetric cyclic structure. The ESI mass



Scheme 1 (a) Metalation of salen-type ligand promotes the binding to hard metal cations. (b) Design of bis(salen)-type macrocycle 1 and the conversion to dinuclear metallohost 2.



Scheme 2 Synthesis of macrocycle 1. *Reagents and conditions:* (i) (1) *n*-BuLi, TMEDA, hexane; (2) B(OMe)₃, (3) H₂O₂, KOH, yield 71%; (ii) (1) NBS, *i*-Pr₂NH, (2) NaH, *n*-BuLi, (3) DMF, yield 28%; (iii) o-C₆H₄(NH₂)₂, CH₃CN, yield 64%.

[†] Electronic supplementary information (ESI) available: Synthesis of macrocyclic ligand 1 and metallohost 2. See DOI: 10.1039/b915722k

(a)

spectrum showed a strong peak at m/z 661.2, which agrees with the 2:2 macrocyclic structure.

The reaction of the macrocycle **1** with nickel(II) acetate in DMSO–acetonitrile afforded the dinuclear metallohost **2** in 93% yield as dark brown crystals. The ESI mass spectrum exhibited peaks at m/z 387.0 and 773.0, corresponding to the dinuclear species $[2 + 2H]^{2+}$ and $[2 + H]^{+}$. The ¹H NMR spectrum showed well-resolved sharp signals, indicative of the formation of diamagnetic species having square-planar nickel(II) ions.

The molecular structures of the macrocycle 1 and metallohost 2 were determined by X-ray crystallography.[‡] The macrocycle 1 adopted a non-planar C_2 symmetric structure in which two of the benzene rings lie almost perpendicular to the macrocycle plane (Fig. 1(a)). On the contrary, the metallohost 2 adopted a nearly planar structure (Fig. 1(b)). All of the oxygen donor atoms lie on a plane and the lone pairs are directed inside the cavity. The distances between the opposite oxygen atoms and those of the neighboring oxygen atoms are in the range of 5.167-5.238 and 2.529-2.636 Å, respectively, which are similar to the corresponding distances found in the crystal structure of $[(18-crown-6)Na]^+$.⁹ Consequently, the six oxygen atoms seem to be arranged in a fashion suitable for the recognition of guest ions such as Na⁺.

The recognition abilities of the macrocycle 1 and metallohost 2 toward alkali metal cations were investigated by ¹H NMR spectroscopy. Although the macrocycle 1 has a cyclic cavity with six oxygen donors, it showed a very poor affinity toward alkali metal cations. The addition of Na⁺ into a DMSO solution of the macrocycle 1 resulted in almost no change in the chemical shifts, indicating a very weak interaction with Na⁺. The association constant was estimated to be approximately 13 M^{-1} . On the other hand, the chemical shifts of the metallohost 2 significantly changed upon the addition of Na^+ (Fig. 2(a) and (b)) The plots of the chemical shift vs. the equivalents of Na⁺ clearly showed a strong binding in a 1:1 stoichiometry. The Na⁺ binding also caused a hypsochromic shift in an absorption band at 501 nm to 493 nm in the visible absorption spectra. The association constant for the binding is determined to be $\log K_a = 5.8 (K_a \text{ in } M^{-1})$ by a non-linear least squares analysis. The binding affinity was enhanced

(b)

Fig. 1 X-Ray crystal structure of (a) macrocycle **1** and (b) metallohost **2** with thermal ellipsoids plotted at the 50% probability level.

View Article Online



Fig. 2 ¹H NMR spectra (400 MHz, DMSO- d_6) of metallohost **2** (1.0 mM) in the presence of 1 equiv. of alkali metal ions (a) none; (b) Na⁺; (c) K⁺; (d) Rb⁺; (e) Cs⁺. Asterisks denote the signals of the counter-anion (tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) of the alkali metal cations.

approximately 50 000-fold. The ESI mass spectrum of the solution of **2** containing 1 equiv. of Na⁺ exhibited a strong peak at m/z 795.0 confirming the formation of the 1:1 host-guest complex (Fig. 3(a)). Consequently, the Na⁺ recognition ability of the macrocycle is drastically enhanced upon the conversion into the nickel(II) dinuclear metallohost **2**, *i.e.*, the recognition was completely regulated in an almost on/off fashion.

Similarly, the macrocycle 1 has no recognition ability toward K^+ , Rb^+ and Cs^+ , while the metallohost 2 strongly interacts with these ions. The addition of 1 equiv. of these ions caused complete disappearance of the signals of the free metallohost 2, indicating that the binding toward K^+ , Rb^+ and Cs^+ is very strong as observed for Na⁺. When K⁺ was



Fig. 3 ESI mass spectra of metallohost 2 in the presence of 1 equiv. of (a) Na^+ and (b) Rb^+ .



Scheme 3 Plausible structure of complexes between metallohost 2 with alkali metal cations.

added, broad signals separately appeared from the free metallohost **2** (Fig. 2(c)). The addition of 1 equiv. of Rb^+ or Cs^+ resulted in the appearance of several sets of signals (Fig. 2(d) and (e)). These results indicate that the self-assembly and complexation/decomplexation process with these ions is slow and that several kinds of complexes were formed upon the complexation.

To clarify the complexation behavior, the ESI mass spectra of **2** in the presence of K⁺, Rb⁺ and Cs⁺ were investigated. It is noteworthy that several kinds of aggregated species, such as $[\mathbf{2}_2 \cdot \mathbf{M}]^+$, $[\mathbf{2}_3 \cdot \mathbf{M}_2]^{2+}$ or $[\mathbf{2}_4 \cdot \mathbf{M}_3]^{3+}$ (M = K, Rb, Cs), were observed in addition to the 1 : 1 complex $[\mathbf{2} \cdot \mathbf{M}]^+$ (Fig. 3(b) for M = Rb). The diffusion coefficients determined by DOSY experiments were 2.2×10^{-10} and 1.6×10^{-10} m² s⁻¹ for the 1 : 1 mixture of **2** with Na⁺ and Cs⁺, respectively. The smaller diffusion coefficient of the Cs⁺ complex coincides with the observation of aggregated species in the mass spectrum.

It is known that 18-crown-6 ethers can form a 2:1 or 3:2 complex with Rb^+ and Cs^+ .¹⁰ In addition, salen-nickel(II) complexes are known to form an infinite sandwich assembly or triple-decker sandwich complexes with alkali metal cations through μ -phenoxo bridges.¹¹ Since the cyclic array of oxygen atoms in a metallohost **2** is similar to the 18-crown-6 and contain salen-metal moieties, the observed oligomeric species would adopt a sandwich or club sandwich structure, in which two or more flat metallohosts are held together by the metal ions (Scheme 3). This is evidenced from the upfield shifted signals of the aromatic protons of the Rb^+ and Cs^+ complexes that appeared at around 5.8 ppm, which is attributed to the stacking structure.

Therefore, the conversion from the macrocycle 1 into the metallohost 2 not only enhances the ion recognition ability toward alkali metal cations, but also induces the metal-assisted assembly with stacking structures. This conversion makes the molecular structure more rigid and planar, favorable for the formation of the stacking aggregates. In addition, the resultant metallohost has the phenoxo groups with negative charges, which contribute to the aggregate formation induced by the alkali metal ions due to the -M-O-M-O bridging. This may suggest that the stabilization by the stacking structures and phenoxo bridging is greater than the destabilization due to the electrostatic repulsion between the guest cations.

In conclusion, the conversion of the macrocyclic imine 1 into the nickel(π) dinuclear metallohost 2 greatly enhances the

alkali metal ion recognition in the central O_6 site. The macrocycle worked as an on/off regulation system of ion recognition. The metalation also induces the aggregated molecular array structure when the metallohost **2** binds to larger guest cations. The stacking of the planar metal complexes has a significant influence on the physical and chemical properties of the metal complexes due to the interplane interactions between the metal centers. We are now investigating the changes in the properties induced by the inclusion of alkali metal cations.

This work was supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Notes and references

‡ Crystallographic data: 1-2MeCN (C₄₄H₃₄N₆O₆ = 742.77): orthorhombic, *Pbcn*, *a* = 21.7674(9), *b* = 8.3961(4), *c* = 20.4083(9) Å, V = 3729.8(3) Å³, Z = 4, μ (Mo-K α) = 0.090 mm⁻¹, $D_c = 1.323$ g cm⁻³, *F*(000) = 1552, *T* = 120 K, $R_1 = 0.0488$ (3681 data with $I > 2\sigma(I)$), w $R_2 = 0.1425$ (all 4248 data; $R_{int} = 0.0290$), GOF = 1.064¹²

2.4DMSO (C₄₈H₄₈N₄Ni₂O₁₀S₄ = 1086.56): triclinic, $P\overline{1}$, a = 11.2439(8), b = 11.7378(8), c = 11.7488(9) Å, $\alpha = 63.3210(18)$, $\beta = 66.059(2)$, $\gamma = 60.3036(16)^\circ$, V = 1169.48(15) Å³, Z = 1, μ (Mo-K α) = 1.048 mm⁻¹, $D_c = 1.543$ g cm⁻³, F(000) = 564, T = 120 K, $R_1 = 0.0475$ (4514 data with $I > 2\sigma(I)$), w $R_2 = 0.1345$ (all 5298 data; $R_{\rm int} = 0.0312$), GOF = 1.080.¹²

- (a) T. Nabeshima, Coord. Chem. Rev., 1996, 148, 151–169;
 (b) T. Nabeshima, S. Akine and T. Saiki, Rev. Heteroat. Chem., 2000, 22, 219–239.
- For reviews, see: (a) F. C. J. M. van Veggel, W. Verboom and D. N. Reinhoudt, *Chem. Rev.*, 1994, 94, 279–299; (b) W. Verboom, D. M. Rudkevich and D. N. Reinhoudt, *Pure Appl. Chem.*, 1994, 66, 679–686; (c) M. M. G. Antonisse and D. N. Reinhoudt, *Chem. Commun.*, 1998, 443–448.
- 3 S. Akine, T. Taniguchi and T. Nabeshima, *Tetrahedron Lett.*, 2001, 42, 8861–8864.
- 4 (a) T. Nabeshima, H. Miyazaki, A. Iwasaki, S. Akine, T. Saiki, C. Ikeda and S. Sato, *Chem. Lett.*, 2006, **35**, 1070–1071; (b) A. J. Gallant, J. H. Chong and M. J. MacLachlan, *Inorg. Chem.*, 2006, **45**, 5248–5250; (c) T. Nabeshima, H. Miyazaki, A. Iwasaki, S. Akine, T. Saiki and C. Ikeda, *Tetrahedron*, 2007, **63**, 3328–3333; (d) S. Akine, S. Sunaga, T. Taniguchi, H. Miyazaki and T. Nabeshima, *Inorg. Chem.*, 2007, **46**, 2959–2961.
- 5 For related compounds, see: (a) H. Shimakoshi, H. Takemoto, I. Aritome and Y. Hisaeda, *Tetrahedron Lett.*, 2002, **43**, 4809–4812; (b) H. Shimakoshi, T. Takemoto, I. Aritome and Y. Hisaeda, *Inorg. Chem.*, 2005, **44**, 9134–9136.
- 6 Formation of a tubular assembly of metal-free tris(N₂O₂) macrocycle induced by alkali metal cations is reported, see: A. J. Gallant and M. J. MacLachlan, *Angew. Chem., Int. Ed.*, 2003, 42, 5307–5310.
- 7 For dilithiation of diphenyl ether, see: J. W. Raebiger, A. Miedaner, C. J. Curtis, S. M. Miller, O. P. Anderson and D. L. DuBois, J. Am. Chem. Soc., 2004, **126**, 5502–5514.
- 8 For ortho-bromination of phenols, see: S. Fujisaki, H. Eguchi, A. Omura, A. Okamoto and A. Nishida, Bull. Chem. Soc. Jpn., 1993, 66, 1576–1579.
- 9 For crystal structures of complexes between 18-crown-6 and Na⁺, see: J. W. Steed and P. C. Junk, *J. Chem. Soc., Dalton Trans.*, 1999, 2141–2146.
- 10 For Rb⁺ or Cs⁺ complexes of 18-crown-6, see: C. J. Pedersen, J. Am. Chem. Soc., 1970, 92, 386–391.
- 11 D. Cunningham, P. McArdle, M. Mitchell, N. Ní Chonchubhair, M. O'Gara, F. Franceschi and C. Floriani, *Inorg. Chem.*, 2000, **39**, 1639–1649.
- 12 G. M. Sheldrick, SHELXL 97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.