



A Tetranuclear Zinc(II) Complex of a [4+4] Macrocyclic Schiff Base Ligand

YUEFEI SUN, QINGDAO ZENG, SHAOHUA GOU*, WEI HUANG, CHUNYING DUAN and JINGCAI YAO**

State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China

(Received: 10 April 2001; in final form: 4 September 2001)

Key words: tetranuclear zinc(II) complex, sodium template, Schiff base cyclocondensation

Abstract

The cyclocondensation reaction between sodium 2,6-diformyl-4-methylphenolate (sdmp) and 1,5-diamino-3-(1-hydroxyethyl)azapentane (dhap) followed by *in situ* transmetallation with $Zn(ClO_4)_2 \cdot 6H_2O$ produced a tetranuclear zinc(II) complex of the current biggest-sized [4+4] Schiff base macrocyclic ligand. The structure of the complex has been determined by X-ray techniques, indicating that the hydroxyethyl group of the amine, dhap, has been eliminated in the process. For comparison, the reaction of sdmp with diethylenetriamine has also been carried out. The resulting product has been characterized by its infrared and positive ion FAB mass spectra, which turned out to be a mixture of the corresponding [3+3] and [4+4] macrocyclic Schiff bases together with the common [2+2] mode.

Introduction

Although binucleating macrocyclic ligands derived from the [2+2] condensation of dicarbonyl precursors and diamino derivatives have been thoroughly investigated for their coordination chemistry [1], metal complexes of [3+3] and [4+4] macrocyclic Schiff base ligands for polynuclear systems are still rare. There may be two reasons for this. One is the difficulty of synthetic techniques for preparing these 'big macrocycles', and the other is the instability of related macrocycles. So far only a few [3+3] Schiff base macrocyclic complexes have been prepared with metal templates [2]. As for [4+4] macrocyclic Schiff bases, there has been an early report [3] that a [4+4] macrocycle with four Mn(II) ions has been formed when $Mn(ClO_4)_2$ is used in a transmetallation reaction of the relevant barium [2+2] macrocycle. The most recent report is by Brooker and co-workers [4] that a dinuclear lead [4+4] macrocyclic complex has been obtained by template condensation of 3,6-diformylpyridazine with 1,3-diaminopropane. Moreover, a novel octaamino tetraphenol macrocyclic ligand has been prepared via an *in situ* reduction of [4+4] condensation products of 2,6-diformyl-4-methylphenol with 1,2-diaminoethane in the presence of magnesium nitrate [5], and the Schiff base analogue with tetranuclear Cu(II) and Ni(II) complexes of the fully reduced ligand has been obtained [6].

In continuation of our project on the preparation of Schiff base macrocyclic ligands and their metal complexes *via* the reaction of sodium 2,6-diformyl-4-substitutedphenolates with polyamines, a number of macrocycles of [2+2] and

[2+3] modes have been obtained by this method [7]. Recently we have successfully isolated and analyzed [3+3] macrocycles from the reaction products of sodium 2,6-diformyl-4-methylphenolate (sdmp) with three alkyl diamines H_2RNH_2 [$R=(CH_2)_n$, $n = 4, 5, 6$] by a capillary electrophoresis technique coupled to a mass spectrometer *via* an electrospray ionization interface, demonstrating the independent formation of both tetraamine and hexamine macrocycles [8]. In our recent attempt to prepare a series of novel pendant-arm macrocyclic complexes, the cyclocondensation of sodium 2,6-diformyl-4-substitutedphenolate with 1,5-diamino-3-(1-hydroxyethyl)azapentane (dhap) has been designed and undertaken, in which a [4+4] macrocycle has been obtained unexpectedly. For comparison, the condensation reaction between sdmp and diethylenetriamine has also been carried out and the product has been spectrally characterized. We herein report the preparation and crystal structure of a tetranuclear zinc(II) complex of the 'biggest-sized' Schiff base macrocyclic ligand together with the infrared and mass spectral analysis on the product derived from the sdmp and diethylenetriamine.

Experimental

Physical measurements

Microanalyses for C H N were performed with a Perkin Elmer Elemental Analyser model 240C. Zinc element analysis was measured on a Jarrell-Ash 110+2000 ICP quantimeter. Infrared spectra ($4000-400\text{ cm}^{-1}$), as KBr pellets, were recorded on a Nicolet 170X FT-IR spectrophotometer. Positive FAB mass spectra were measured utilizing a VG-2AB-HS mass spectrometer with NOBA as the mat-

* Author for correspondence.

** Permanent address: Luoyang Teacher's College, Luoyang 471022, China.

rix solvent. Electrospray ionization mass spectra (ESI-MS) were obtained on a Finnigan MAT SSQ710 spectrometer in a scan range 200–1200 amu.

Materials

The sodium salt of 2,6-diformyl-4-methylphenolate (sdmp) was prepared as reported previously [7]. All other solvents and chemicals were of analytical grade and used as received.

Preparations

Dhap-3HCl·2H₂O

To an alcoholic solution (400 mL) of salicylaldehyde (23.20 g, 0.19 mol) and diethylenetriamine (9.78 g, 95 mmol), 2-chloroethanol (7.62 g, 95 mmol) and dry Na₂CO₃ (10.07 g, 95 mmol) were added. The mixture was stirred under reflux for 30 h, then filtered at room temperature. The filtrate was distilled to remove ethanol, and extracted with THF. After removal of the solvent from the extraction, the residue was treated with 5M HCl in ethanol (500 mL). The resulting suspension was kept refluxing for 5 h and filtered. The products were collected and recrystallized in H₂O–C₂H₅OH. Yield: 82%. Anal. Calcd. for C₆H₂₄Cl₃N₃O₃: C, 24.62; H, 8.21; N, 14.36%. Found: C, 24.48; H, 8.26; N, 14.51%.

Polynuclear zinc(II) complex of the [4+4] macrocyclic Schiff base ligand

To an aqueous solution (5 mL) of dhap·3HCl·2H₂O (0.293 g, 1 mmol) NaOH (0.12 g, 3 mmol) was added, sodium chloride precipitated immediately by adding ethanol (50 mL) into the above solution. After removing the solids, the filtrate was blended with sdmp (0.19 g, 1 mmol). The subsequent condensation reaction was carried out by stirring the mixture at 0 °C for 5 h, then Zn(ClO₄)₂·6H₂O (0.74 g, 2 mmol) was added. The suspended solution was kept refluxing for a further 2 h, and gradually became clear red. After concentration, the polycrystalline products deposited, which were obtained and dried. Yield 72%. Anal. Calcd. for C₅₂H₆₆Cl₈N₁₂O₄Zn₅: C, 40.69; H, 4.30; N, 10.96; Zn, 21.36%. Found: C, 40.25; H, 4.54; N, 11.12; Zn, 21.64. Main IR absorptions (cm⁻¹): 3294 (m, ν_{NH}), 1651 and 1641 (s, ν_{C=N}). Principal ESI-MS peaks: m/z 512 {[Zn₄H₅L⁴Cl₄]ZnCl₄}³⁺/3, 430 [Zn₄H₂L⁴Cl₃]³⁺/3, 412 [Zn₄HL⁴Cl₂]³⁺/3 and 405 [Zn₄L⁴Cl] ³⁺/3.

Macrocyclic sodium compounds

The condensation reaction between sdmp and diethylenetriamine was carried out by the following procedure. To a suspension of sdmp (0.19 g, 1 mmol) in absolute ethanol (20 mL) equimolar amine in ethanolic solution (10 mL) was added. The suspension stirring at room temperature gradually became dissolved, and was filtered after 3 h to remove insoluble impurities. Then the filtrate was concentrated, and diethyl ether was added until a great deal of solid deposited. The product was collected and dried. It should be pointed out

that the substance obtained in the reaction should be kept in a vacuum desiccator over P₂O₅, otherwise it increases weight in air. No crystalline water has been considered for the calculation of yields, because the product has been immediately weighed in stoppered tubes once it was collected. Yield: 63%. Anal. Calcd for C₅₂H₆₄N₁₂O₄Na₄·10H₂O: C, 52.35; H, 7.05; N, 14.09%. Found: C, 52.13; H, 7.04; N, 14.50%. IR (cm⁻¹): 3420 (br, ν_{OH}), 1636 (s, ν_{C=N}). Principal FAB-MS peaks: m/z 507(13) [Na₂HL²]⁺, 485(100) [NaH₂L²]⁺, 694(9) [H₄L³]⁺, 1013(9) [Na₄HL⁴]⁺, 991(7) [Na₃H₂L⁴]⁺, 969(19) [Na₂H₃L⁴]⁺. [2+2], [3+3] and [4+4] macrocyclic Schiff bases are abbreviated as H₂L², H₃L³ and H₄L⁴, respectively.

Crystallography

Single crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of the sample in CH₃CN–MeOH–CH₂Cl₂. Crystal data for [Zn₄H₂L⁴Cl₄CH₂Cl₂]ZnCl₄, empirical formula C₅₃H₆₇Cl₁₀N₁₂O₄Zn₅, dimensions 0.30 × 0.20 × 0.20 mm, tetragonal, space group I $\bar{4}$, *a* = 11.708(5) Å, *c* = 24.340(7) Å, *U* = 3336(2) Å³, *Z* = 2, *d*_{calc} = 1.610 g cm⁻³, μ = 2.224 mm⁻¹, *F*(000) = 1642, *T* = 293(2) K. Data were measured on a Siemens P4 four-circle diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293(2)K using the ω-2θ scan method. A total of 3658 reflections were collected, of which 2912 were independent and 2906 (*R*_{int} = 0.1315) observed and 189 parameters led to convergence, with a final value of *R*₁ = 0.0786 and *wR*₂ = 0.1436 with *I* > 2σ(*I*).

The intensity data were corrected for Lorentz and polarization effects during data reduction using XSCANS [9]. The structure was solved by direct methods and refined on *F*² by full-matrix least-squares methods using SHELXTL version 5.0 [9]. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in calculated positions (C–H, 0.96; N–H, 0.90 and O–H, 0.85 Å) assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic *U* of the atoms to which they are attached (1.5 times for the O–H and methyl groups) and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure-factor calculations. All computations were carried out on a PC-586 computer using the SHELXTL-PC Program Package [10]. Analytical expressions of neutral-atom scattering factors employed and anomalous dispersion corrections were incorporated [11].

Results and discussion

Macrocyclic tetranuclear Zn(II) complex - [Zn₄H₂L⁴Cl₄CH₂Cl₂]ZnCl₄

The preparation of the zinc(II) complex involves the template reaction of sdmp with dhap followed by *in situ* transmetallation of the resulting multinuclear sodium ion macrocyclic compound, usually unstable and difficult to

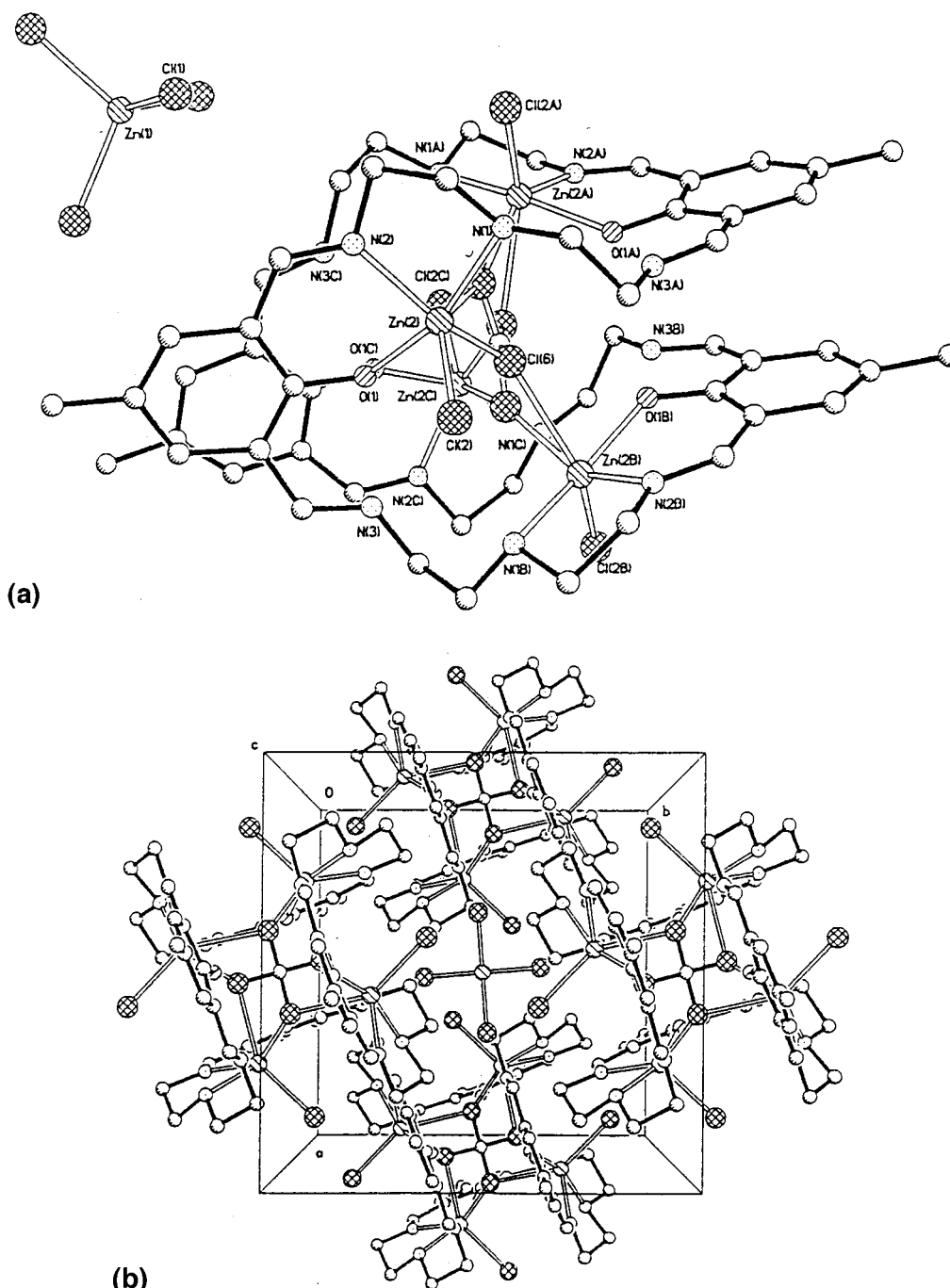


Figure 1. (a) Molecular structure of the zinc complex cation. (b) An overview of a unit cell.

isolate, with $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in ethanol. The infrared spectrum of the complex proved the formation of Schiff bases with two strong imine $\text{C}=\text{N}$ absorptions present at 1641 and 1651 cm^{-1} , respectively, indicative of the different situation of imine bonds. In addition, the band ascribed to ν_{NH} was conspicuously observed at 3294 cm^{-1} , suggesting the loss of the hydroxyethyl group from the amine dhap after the formation of an unexpected macrocyclic compound. The ESI-MS technique has been employed to study the mass spectrum of the polynuclear zinc(II) complex. No molecular ion peak was observed for this compound, but peaks corresponding to the triple-charged

complex cations were found as base peaks or in certain intensities. The reason is that ESI-MS depends upon pre-existing ions in solution and the triple-charged species of the complex cations are formed through the ionization of the metal complex in solution. A group of triple-charged peaks of $\{[\text{Zn}_4\text{H}_5\text{L}^4\text{Cl}_4]\text{ZnCl}_4\}^{3+}/3$, $[\text{Zn}_4\text{H}_2\text{L}^4\text{Cl}_3]^{3+}/3$, $[\text{Zn}_4\text{HL}^4\text{Cl}_2]^{3+}/3$ and $[\text{Zn}_4\text{L}^4\text{Cl}]^{3+}/3$ were characteristically observed, respectively, exhibiting the existence of a $[4+4]$ macrocycle (L^4).

The molecular structure of the complex cation together with a unit cell diagram is shown in Figure 1. Selected bond lengths and angles are given in Table 1.

Table 1. Selected bond distances (Å) and angles (deg) for the zinc complex

Zn(2)–O(1)	2.017(6)	Zn(2)–Cl(6)	2.091(11)
Zn(2)–N(1)	2.160(7)	Zn(2)–N(2)	2.067(8)
Zn(2)–Cl(2)	2.282(3)	Zn(2)–Cl(6)#4	2.552(11)
O(1)–C(10)	1.303(11)	N(1)–C(1)	1.426(11)
N(1)–C(2)	1.470(11)	N(2)–C(3)	1.438(12)
N(2)–C(4)	1.330(12)	N(3)–C(11)	1.280(12)
N(3)–C(12)	1.446(11)	Zn(1)–Cl(1)	2.267(3)
C(14)–Cl(6)	1.250(10)		
O(1)–Zn(2)–N(2)	84.1(3)	O(1)–Zn(2)–N(1)	160.6(3)
N(2)–Zn(2)–Cl(6)	141.5(4)	O(1)–Zn(2)–Cl(6)	82.1(4)
N(2)–Zn(2)–N(1)	80.3(3)	N(1)–Zn(2)–Cl(6)	103.2(4)
O(1)–Zn(2)–Cl(2)	95.9(2)	N(2)–Zn(2)–Cl(2)	118.4(2)
N(1)–Zn(2)–Cl(2)	101.6(2)	Cl(6)–Zn(2)–Cl(2)	98.7(3)
O(1)–Zn(2)–Cl(6)#4	80.4(3)	N(2)–Zn(2)–Cl(6)#4	98.7(3)
Cl(6)–Zn(2)–Cl(6)#4	43.6(4)	N(1)–Zn(2)–Cl(6)#4	90.6(3)
Cl(2)–Zn(2)–Cl(6)#4	142.3(2)	Cl(6)–C(14)–Cl(6)#4	90.58(11)
Cl(1)–Zn(1)–Cl(1)#1	109.37(7)		

#1: $y, -x, -z$; #4: $y - 1/2, -x + 1/2, -z + 1/2$.

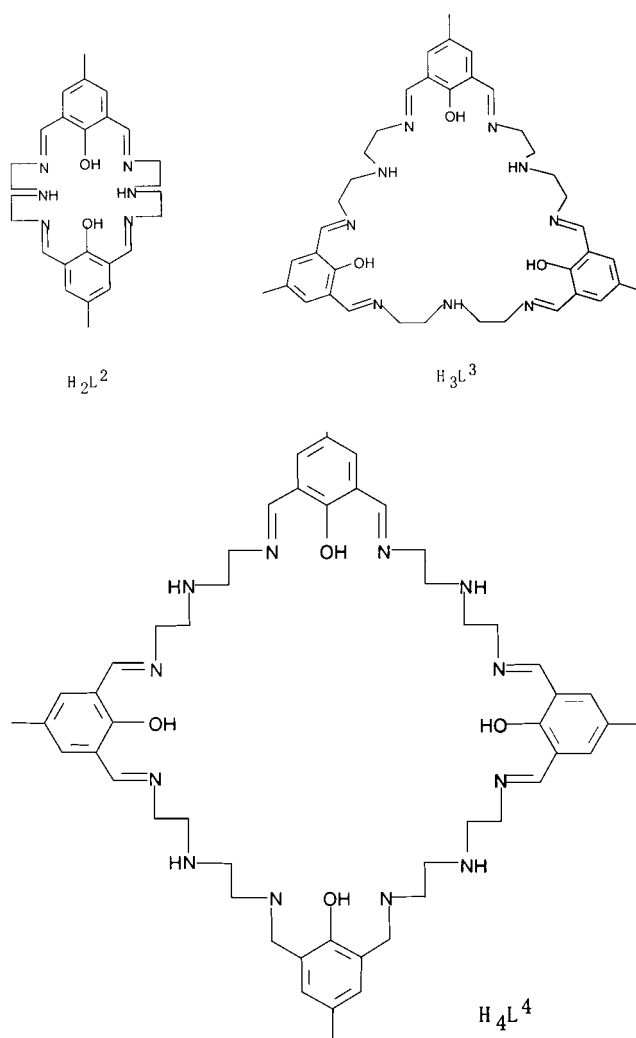
The structure consists of a discrete tetranuclear cation $[\text{Zn}_4\text{H}_2\text{L}^4\text{Cl}_4\text{CH}_2\text{Cl}_2]^{2+}$ balanced by a ZnCl_4 counter ion, formulated as $[\text{Zn}_4\text{H}_2\text{LCl}_4(\text{CH}_2\text{Cl}_2)]\text{ZnCl}_4$. The complex cation has a $\bar{4}$ axis possessing $I\bar{4}$ crystallographic symmetry. The macrocycle, which appears as the condensation product of 2,6-diformyl-4-methylphenol with diethylenetriamine, is composed of forty eight members, actually the biggest Schiff base macrocycle at present. The huge ring is symmetrically half-folded, two phenyl ring planes on the opposite position are parallel to one another and perpendicular to the other two. It is noticed that the macrocycle acts as a divalent anion instead of a tetravalent one as expected. Each Zn atom on the ring is coordinated by a secondary amine N atom, an imine N atom, the adjacent phenolic O atom and one Cl anion as well as one chlorine atom from the dichloromethane molecule, respectively. Thus the coordination geometry around the Zn atom is distorted square pyramidal. It is obvious that chloride anions resulting from the neutralization of the amine hydrochloride have led to the formation of ZnCl_4 groups. As confirmed by its infrared spectrum, the coordination behavior of the two imine moieties on one edge is different, coordinated and uncoordinated. This has also been reflected by the values of their C=N bond lengths [N(2)–C(4):1.330(12)Å and N(3)–C(11):1.280(12)Å]. It is of much interest to note that one dichloromethane molecule, disordered, has been ‘trapped’ in the center, with the Cl atom being very close to Zn atoms with the Zn–Cl distance of 2.091(11) and 2.552(11) Å. It appears that molecular recognition functions as the preference of the polynuclear zinc(II) complex cation to fixing one solvent molecule through the supramolecular interaction between the host and the guest molecules.

As seen from the X-ray structural results, the hydroxyethyl group from the amine dhap has been lost. A similar elimination in the reaction of sodium 2,6-diformyl-4-methylphenolate with *N,N*-bis(2-aminoethyl)-2-hydroxybenzylamine, followed by *in situ* transmetalation of

$\text{Fe}(\text{ClO}_4)_3$ or $\text{Mn}(\text{ClO}_4)_2$ has been observed by us, in which a mononuclear Fe(III) or Mn(III) complex of an asymmetric [2+2] Schiff base macrocycle has been formed and confirmed by X-ray crystallographic data [11]. It is assumed here that the hydroxyethyl group elimination from the amine precursor during the reaction may partly result from the presence of Zn^{2+} ions under the basic condition, because experiments have shown that the R–OAr bond could be broken in the presence of certain divalent metal ions such as Cu^{2+} under similar circumstances [13]. But further experiments should be undertaken to elucidate the mechanism.

Synthesis and characterization of the corresponding macrocyclic sodium compound

The synthetic scheme for the reaction is the same as before [7], three possible macrocyclic ligands are shown below.



The product derived from the reaction between sdmp and diethylenetriamine has been characterized by element analyses, infrared and mass spectra, respectively. Like other macrocyclic sodium compounds [6], the product is easily hygroscopic, it gained in weight during the microanalytical measurement. The analytical data would only be in agreement with the theoretical values when crystalline water was

added. A strong $\nu_{C=N}$ band was observed at 1636 cm^{-1} in the infrared spectrum, indicative of the formation of Schiff bases. Besides, a ν_{O-H} band was also observed owing to the presence of crystalline water. Since this substance is hardly soluble in either organic solvents or water, the related $^1\text{H-NMR}$ data of the product have not been obtained.

The positive FAB mass spectrum of the product was measured in order to confirm the formation of macrocyclic Schiff bases and define the cyclocondensation mode. The principal FAB-MS peaks have been assigned. A [4+4] mode as well as [2+2] and [3+3] modes has been found as fragments of sodium-containing macrocycles and free macrocyclic Schiff bases. As pointed out previously, it is impossible for high grade condensation modes, e.g. [4+4] macrocyclic Schiff bases, to split into pieces of the corresponding low grade modes under the condition that FAB mass spectra are measured [7]. Hence we conclude that the product in the reaction is a blend of Na_2L^2 and Na_3L^3 and Na_4L^4 . The contrast reaction between sdmp and diethylenetriamine in the absence of any metal templates have been tested, but sticky polymer-like products have been obtained and characterized by FAB mass spectra in which no peaks attributed to cyclocondensation modes have been observed. This proves that sodium ions here play an important template role in the formation of these Schiff base macrocycles.

Acknowledgements

The authors express their gratitude to the National Natural Science Foundation of China for research grants (No. 29871016 and 29823001). S. G. is also indebted to the State Department of Education for a key research grant.

References

1. P. Guerriero, P.A. Vigato, D.E. Fenton, and P.C. Hellier: *Acta Chem. Scand.* **46**, 1025 (1992); M. Pietraszkiewicz: *J. Coord. Chem.* **27**, 151 (1992).
2. D.E. Fenton, S.J. Kitchen, C.M. Spencer, S. Tamburini, and P.A. Vigato: *J. Chem. Soc. Dalton Trans.* 685 (1988); B.F. Hoskins, R. Robson, and P.D. Smith: *J. Chem. Soc. Chem. Commun.* 488 (1990); S.S. Tandon, L.K. Thompson, and J.N. Bridson: *J. Chem. Soc. Chem. Commun.* 911 (1992).
3. S. Brooker, V. Mckee, W.B. Shepard, and L.K. Panell: *J. Chem. Soc. Dalton Trans.* 2555 (1987).
4. S. Brooker, R.J. Kelly, and G.M. Sheldrick: *J. Chem. Soc. Chem. Commun.* 487 (1994).
5. K.K. Nanda, K. Venkatsubramanian, D. Majumdar, and K. Nag: *Inorg. Chem.* **33**, 1581 (1994).
6. S. Mohanta, Kausik, K. Nanda, R. Werner, W. Haase, A.K. Mukherjee, S.K. Dutta, and K. Nag: *Inorg. Chem.* **36**, 4656 (1997).
7. S. Gou and D.E. Fenton: *Inorg. Chim. Acta* **223**, 169 (1994); K. Zhou, S. Gou, Z. Wang, and Z. Yuan: *Polyhedron* **14**, 3501 (1995); H. Adams, N.A. Bailey, P. Bertrand, C.O. Rodriguez de Barbarin, D.E. Fenton, and S. Gou: *J. Chem. Soc. Dalton Trans.* 275 (1995); Q. Zeng, J. Sun, S. Gou, K. Zhou, J. Fang, and H. Chen: *Trans. Met. Chem.* **23**, 371 (1998); Q. Zeng, S. Gou, L. He, Y. Gong, and X. You: *Inorg. Chim. Acta* **287**, 1 (1999); Q. Zeng, S. Gou, J. Fang, J. Zhu, and X. You: *J. Incl. Phenom. Macro. Chem.* **35**, 299 (1999).
8. S. Gou, K. Zhou, Q. Zeng, and J. Fang: *J. Coord. Chem.* **40**, 103 (1996).
9. Siemens, XSCANS (*Version 2.1*), Siemens Analytical X-ray instruments Inc., Madison, USA, 1994.
10. Siemens, SHELXTL (*Version 5.0*), Siemens Industrial Automation Inc., Analytical Instrumentation, USA, 1995.
11. A.J.C. Wilson: *International Table for X-ray Crystallography*, Volume C Kluwer Academic Publishers, Dordrecht (1992): Table 6.1.1.4 (pp. 500–502), 4.2.6.8 (pp. 219–222) and 4.2.4.2 (pp. 193–199) respectively.
12. Q. Zeng, M. Qian, S. Gou, H.-K. Fun, C. Duan, and X. You: *Inorg. Chem. Acta* **294**, 1 (1999); M. Qian, S. Gou, H. Ju, W. Huang, C. Duan, and X. You: *Transition Met. Chem.* **25**, 584 (2000).
13. Q. Zeng, M. Qian, and S. Gou, unpublished work.

