

Template Synthesis of Complexes of Co^{2+} , Ni^{2+} , Zn^{2+} , and Cd^{2+} with Hexadentate Ligands: Structures of Highly Distorted Six-co-ordinate Zn^{2+} Complexes with a New Schiff Base and an Aminopodand

Mikhail L. Tulchinsky,^a Lyudmila I. Demina,^a Sergei V. Lindeman,^b Aslan Yu. Tsivadze,^a and Yuri T. Struchkov^b

^a Kurnakov Institute of General and Inorganic Chemistry, USSR Academy of Sciences, 31 Leninsky Ave., Moscow 117907, USSR

^b Nesmeyanov Institute of Organoelement Compounds, USSR Academy of Sciences, 28 Vavilov St., Moscow 177334, USSR

Template condensation of 3-oxa-1,5-diaminopentane (L^1) and acetone in the presence of $\text{M}(\text{ClO}_4)_2$ ($\text{M} = \text{Co}, \text{Ni}, \text{Zn}, \text{Cd}$) results in (2) which forms (3) after reduction; Zn^{2+} complexes were characterized by a crystal structure analysis.

Condensation of transition metal-amine complexes with aliphatic carbonyl compounds were reported to give rise to a variety of azamacrocyclic complexes.¹ However this reaction has not been extended to the synthesis of metal complexes with open-chain ligands, as a mixture of compounds is usually produced.² Here we report the first example of introducing a diaminoether, 3-oxa-1,5-diaminopentane (L^1), into this condensation. The ligand L^1 has been known to form non-cyclic Schiff bases in some template reactions.^{3,4} Template condensation of L^1 with acetone in the co-ordination sphere of Co^{II} , Ni^{II} , Zn^{II} , and Cd^{II} yielded acyclic complexes.

In a typical procedure, the 1:2 mixture of anhydrous $\text{M}(\text{ClO}_4)_2$ and L^1 in acetone was heated in a sealed tube for 3 h at 100 °C. On concentration, (2) was crystallized (80–90%). The same reaction occurs with an acetone solution of (1), the latter obtained from $\text{M}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and L^1 in ethanol.⁵ The heating of L^1 or $\text{L}^1 \cdot \text{HClO}_4$ with acetone in the absence of a metal ion does not result in a Schiff base like L^2 , indicating the template effect of M^{II} . Complex (2) can be reduced to form (3): e.g., the refluxing of (2c) with NaBH_4 in methanol for 2 h, followed by solvent evaporation to 1/10th of the initial volume, yields (3). The extra heating of (2) in acetone up to 10 h (100 °C) does not afford new products. All isolated complexes were characterized by microanalysis, IR, and ^{13}C NMR.[†] The molecular structures of compounds (2c) and (3) were confirmed by X-ray crystal structure analysis (Figure 1).[‡]

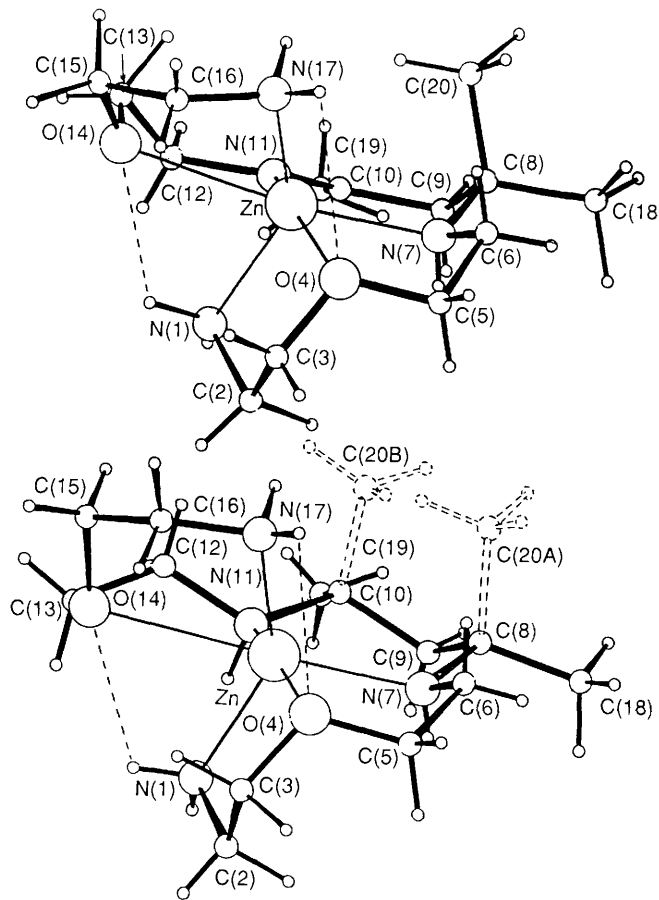
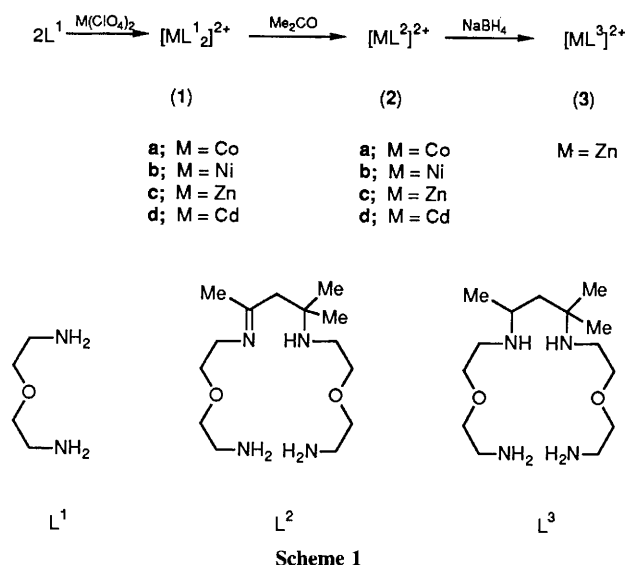


Figure 1. Perspective view of the cations (2c) (top), and (3) (bottom). Selected interatomic distances (Å) and angles (°) for (2c): Zn–N(1) 2.053(5), Zn–O(4) 2.674(4), Zn–N(7) 2.083(5), Zn–N(11) 2.068(5), Zn–O(14) 2.503(4), Zn–N(17) 2.044(5), C(10)–N(11) 1.274(8); N(1)–Zn–O(4) 71.5(2), N(1)–Zn–N(7) 110.8(2), N(1)–Zn–N(11) 104.0(2), N(1)–Zn–O(14) 78.2(2), N(1)–Zn–N(17) 118.7(2), O(4)–Zn–N(7) 73.6(2), O(4)–Zn–N(11) 164.8(2), O(4)–Zn–O(14) 116.7(1), O(4)–Zn–N(17) 76.3(2), N(7)–Zn–N(11) 95.3(2), N(7)–Zn–O(14) 168.7(2), N(7)–Zn–N(17) 107.8(2), N(11)–Zn–O(14) 75.4(2), N(11)–Zn–N(17) 117.7(2), O(14)–Zn–N(17) 71.9(2). For (3): Zn–N(1) 2.079(4), Zn–O(4) 2.473(3), Zn–N(7) 2.083(4), Zn–N(11) 2.100(4), Zn–O(14) 2.639(3), Zn–N(17) 2.042(4), C(10)–N(11) 1.510(6); N(1)–Zn–O(4) 74.3(1), N(1)–Zn–N(7) 109.0(2), N(1)–Zn–N(11) 100.7(2), N(1)–Zn–O(14) 73.9(1), N(1)–Zn–N(17) 127.7(2), O(4)–Zn–N(7) 76.3(1), O(4)–Zn–N(11) 171.8(1), O(4)–Zn–O(14) 108.1(1), O(4)–Zn–N(17) 79.1(1), N(7)–Zn–N(11) 99.6(2), N(7)–Zn–O(14) 175.5(1), N(7)–Zn–N(17) 107.2(2), N(11)–Zn–O(14) 76.3(1), N(11)–Zn–N(17) 109.1(2), O(14)–Zn–N(17) 72.8(1). Co-ordination bonds are designated by thin solid lines and the intramolecular H-bonds by thin dashed lines. The disordered Me group in (3) is drawn in dashed lines.

[†] Spectroscopic properties and elemental analyses were found to be in accord with the proposed formulations. Selected spectroscopic data for (2c): IR (Nujol) ν_{NH_2} 3190, 3280, 3320; ν_{NH} 3240; $\nu_{\text{C=N}}$ 1660 cm^{-1} ; $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, CD_3CN) δ 21.2, 23.8, 26.9 (3Me), 50.5 (CCH_2C), 55.3 (Me_2C), 184.4 (C=N). For (3): IR (Nujol) ν_{NH_2} 3180, 3275, 3320; ν_{NH} 3230 cm^{-1} ; $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, CD_3CN) δ 21.4, 23.8, 27.3 (3Me), 50.5 (CCH_2C), 55.4 (Me_2C).

[‡] Crystal data for (2c): $\text{C}_{14}\text{H}_{32}\text{Cl}_2\text{N}_4\text{O}_{10}\text{Zn}$, $M = 552.72$, orthorhombic, space group $Pbca$, $a = 10.082(7)$, $b = 15.40(1)$, $c = 29.05(3)$ Å, $U = 4511(3)$ Å³, $Z = 8$, $D_c = 1.628$ g cm^{-3} , $R = 0.044$ and $R_w = 0.048$ for 2054 unique reflections with $I \geq 3\sigma(I)$. For (3): $\text{C}_{14}\text{H}_{34}\text{Cl}_2\text{N}_4\text{O}_{10}\text{Zn}$, $M = 554.73$, monoclinic, space group $P2_1/c$, $a = 10.001(3)$, $b = 15.793(3)$, $c = 14.550(3)$ Å, $\beta = 99.52(2)^\circ$, $U = 2267(2)$ Å³, $Z = 4$, $D_c = 1.626$ g cm^{-3} , $R = 0.049$ and $R_w = 0.046$ for 3426 unique reflections with $I \geq 3\sigma(I)$. The analyses of (2c) and (3) were carried out with a Syntex P2₁ diffractometer at 153 K (Mo- K_α radiation, $\theta/2\theta$ scan, $\theta_{\text{max}} = 26.5$ and 30° , respectively). The structures were solved by direct methods and refined by block-diagonal least-squares procedure in anisotropic (isotropic for H atoms located in the difference Fourier maps) approximation. All calculations were performed with an Eclipse S/200 computer using INEXTL programmes.¹⁰ Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



The Zn^{2+} ion co-ordination in complexes (2c) and (3) is effected mainly by the N atoms of the L^2 and L^3 ligands: the Zn–N distances are equal to 2.04–2.10 Å, whereas the normal Zn–N bond lengths are in the range of 2.0–2.2 Å.^{6,7} The co-ordination of the Zn^{2+} ion by the O atoms is substantially weakened, the Zn–O distances being equal to 2.47–2.67 Å while their normal values are in the range of 2.05–2.10 Å.^{8,9} This weakening is evidently due to competition on the part of the intramolecular interactions of the N(1)–H···O(14) and N(17)–H···O(4) type [bond distances N···O 2.87–2.96, H···O 2.36–2.72 Å; bond angles N–H···O 97–118, Zn–O···H(N) 53–82°]. As a result, the Zn^{2+} co-ordination in both complexes is distorted from the octahedral towards the trapezoido-bipyramidal [with the O(4), N(7), N(11), and O(14) atoms in the vertices of the equatorial trapezium and the N(1) and N(17) atoms in the apical positions] or bicapped-tetrahedral {the deviation of angles N–Zn–N from the ideal values does not exceed 18° and the displacement of the O atoms from the lines drawn through the mid-points of the [N(1), N(7), N(17)] and [N(1), N(11), N(17)] faces is not larger than 5°}. In general the co-ordination polyhedra in (2c) and (3) are very much alike, although in the latter structure the Zn^{2+} co-ordination is somewhat closer to the octahedral.

The polydentate ligands L^2 and L^3 form the helix-shaped cradle for the Zn^{2+} ion, which therefore becomes a centre of chirality. Naturally in the course of the reaction the racemic mixture is formed [crystals (2c) and (3) are centrosymmetric], both in respect to Zn^{2+} and to the C(10) chiral centre in the cation (3). In the latter case both pairs of diastereoisomers are

found in the crystal: the mutually superimposed Λ, R - and Λ, S -diastereoisomers and the pair of their centrosymmetrically related counterparts. The superposition of diastereoisomers is manifested in the disorder of the C(20) methyl group over two positions bonded to the C(8) or C(10) atoms. Other atoms do not exhibit any signs of disorder which shows that in fact there is no interaction between the chiral centres at the Zn^{2+} and C(10) atoms. The configuration of other chiral centres {at the O(4), N(7), N(11) [in (3)], and O(14) atoms} is pre-defined by the chelate ring's optimum linkage conditions. Conformations of corresponding chelate cycles in (2c) and (3) in most cases are very much alike, the only exception being the cycles involving the N(11) atom: upon hydrogenation of the C(10)–N(11) double bond the six-membered chelate ring conformation is changed from the C_8 -sofa to the chair, whereas the neighbouring five-membered ring is inverted from $12\alpha, 13\beta$ - to the $12\beta, 13\alpha$ -half-chair.

Generally template formation of ether-containing ligands with metal–ether bonds is quite rare in the chemistry of both non-alkaline and non-alkaline-earth metals.¹¹ The remarkable feature of the condensation (Scheme 1) is the effect of Zn^{2+} and Cd^{2+} , whereas they are inactive in reactions with azaligands.¹ The intramolecular H-bond in (2) seems to be responsible for the inertness of the terminal NH_2 -groups of L^2 for further condensation. Thus, reduction of the co-ordinated Schiff base leads to the new open-chain saturated ligand, aminopodand.

Received, 3rd January 1990; Com. 0100055H

References

- N. F. Curtis, *Coord. Chem. Rev.*, 1968, **3**, 3; N. F. Curtis, in 'Comprehensive Coordination Chemistry,' vol. 2, eds. G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon Press, Oxford, 1987, p. 899.
- M. M. Blight and N. F. Curtis, *J. Chem. Soc.*, 1962, 1204.
- S. M. Nelson and C. V. Knox, *J. Chem. Soc., Dalton Trans.*, 1983, 2525.
- E. Konefal, S. J. Loeb, D. W. Stephan, and C. J. Willis, *Inorg. Chem.*, 1984, **23**, 538.
- L. Kh. Minacheva, M. L. Tulchinsky, S. V. Bocharov, V. G. Sakharova, A. Yu. Tsviadze, and M. A. Porai-Koshits, *Koord. Khim.*, 1989, **15**, 955.
- C. A. Bear, K. A. Duggan, and H. C. Freeman, *Acta Crystallogr., Sect. B*, 1975, **31**, 2713.
- N. V. Podbereskaya and S. V. Borisov, *Zh. Strukt. Khim.*, 1971, **12**, 1114.
- A. Boardman, R. W. H. Small, and I. J. Worrall, *Acta Crystallogr., Sect. C*, 1983, **39**, 1005.
- K. Folting, J. C. Huffman, R. L. Bansemer, and K. G. Caulton, *Inorg. Chem.*, 1984, **23**, 3289.
- R. G. Gerr, A. I. Yanovskii, and Yu. T. Struchkov, *Kristallografiya*, 1983, **28**, 1029.
- G. A. Lawrance, T. M. Manning, B. W. Skelton, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1988, 1344.