

Synthesis and Structural Characterization of Five-Coordinate Cobalt(II) Complexes Based on *tris*(2-Benzimidazolymethyl)amine Ligand

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The synthesis and characterization of three new complexes $2[Co(ntb)(H_2mpda)] \cdot (CH_3COCH_3) \cdot 4H_2O(1), [Co(ntb)(H_2mpda)] \cdot 3H_2O(2)$ and $2[Co(ntb)Cl] \cdot [Co(edta)] \cdot 6H_2O(3)$ (ntb = *N*,*N*,*N*-*tris*(2-benzimidazolymethyl)amine, H₄mpda = 1,3-phenylenedinitrilotetraacetic acid and H₄edta = ethylenediamine tetraacetic acid) are reported. The molecular structures of these complexes are confirmed by single-crystal X-ray structure analysis. The reaction of $Co(NO_3)_2$ with ntb and H₄mpda in acetone/H₂O/ethanol or DMF/H₂O/methanol gives 1 and 2, respectively, while the reaction of $Co(l_2)$ with ntb and H₄edta in H₂O/methanol gives 3. Mononuclear [Co(ntb)(L)] motif is found in all the compounds, in which Co(II) is in a five-coordinate environment with a tetradentate N₄ coordination ntb ligand and a monodentate second ligand. The diversity of solvent in 1 and 2 results in slight difference in the coordinate and crystal packing structure. 3 is an ionic compound, containing [Co(ntb)Cl]⁺ cations and [Co(edta)]²⁻ anions. The solvent plays significant role in the stabilization of all the threedimensional supramolecular networks through hydrogen bonds.

Keywords: Co(II) complex, N,N,N-tris(2-benzimidazolymethyl)amine, Five-coordination, Crystal structure.

INTRODUCTION

Upon coordination of primary ligand to a metal center, there are many factors could influence the coordination structures of metal ion, such as the properties of second ligand and uncoordinated solvent^{1,2}. Moreover, compared with coordination polymer, discrete mononuclear complex is more susceptible to the external noncovalent interactions, such as hydrogen bonding, hydrophobic, steric repulsion, aromatic ring stacking and electrostatic interactions³⁻⁵. Of course, it is more difficult to predict and control the crystalline assembly.

tris(2-Benzimidazolymethyl)amine (ntb) is a potential ligand for synthesis of a number of complexes with potential applications, in which the coordinated units have different geometries⁶⁻⁸. But, there are few cases about uncoordinated supramolecular extending mode around basic unit. In order to investigate the construction of metal-based supramolecular assemblies, the ntb and second ligand with prominent features of the multiple interaction groups have been employed in this research to generate three Co(II) complexes: $2[Co(ntb)(H_2mpda)] \cdot (CH_3COCH_3) \cdot 4H_2O$ (1), $[Co(ntb)(H_2mpda)] \cdot (2)$ and $2[Co(ntb)Cl] \cdot [Co(edta)] \cdot 6H_2O$ (3)(ntb = *N*,*N*,*N*-*tris*(2-benzimidazolymethyl)amine, H₄mpda = 1,3-phenylenedinitrilotetraacetic acid and H₄edta = ethylenediamine tetraacetic acid). The variation of coordination structures of

metal center and three-dimensional networks are mainly achieved by altering solvent and ion.

EXPERIMENTAL

Reagents and solvents used were purchased from commercial sources and used without further purification. *N*,*N*,*N*-*tris*(2benzimidazolymethyl)amine (ntb) ligand was prepared following the literature⁹. 1,3-Phenylenedinitrilotetraacetic acid (H₄mpda) was synthesized by a previously reported method¹⁰. IR spectra were recorded on a Perkin Elmer Specture one spectrometer in range 4000-400 cm⁻¹ as KBr pellets. Elemental analyses were determined on an Elementar Vario EL elemental analyzer. TGA (thermal gravimetric analysis) was performed under nitrogen with a heating rate of 10 °C/min using a Mettler Toledo TAG/SDTA 851e system.

Synthesis of complex 1: To a solution of ntb (0.1 mmol) in 10 mL of methanol was added Co(NO₃)₂·6H₂O (0.1 mmol) in H₂O (2 mL) and H₄mpda (0.1 mmol). This mixture was heated for 2 h. To the reaction solution was added 1 mL acetone. This mixture was stirred at room temperature for 1 h, then filtrated and allowed to stand at room temperature. After a few days, pink crystals suitable for X-ray crystallography were obtained. IR (KBr, v_{max} , cm⁻¹): 3440, 3013, 2929, 1708, 1610, 1576, 1454, 1399, 1316. Yield: 41 %. The sample lost solvent molecules quickly while being exposed to air. After solvent

molecules were removed under vacuum, the elemental analysis based on $Co(ntb)(H_2mpda)$ was performed. Anal. calcd. $C_{38}H_{35}N_9O_8Co: C, 56.72; H, 4.38; N, 15.67.$ Found: C, 56.22; H, 4.97; N, 15.17.

Synthesis of complex 2: The mixture of ntb (0.1 mmol) in 10 mL of methanol, H₄mpda (0.1 mmol) in 5 mL DMF and Co(NO₃)₂·6H₂O (0.1 mmol) in H₂O (5 mL) was refluxed for 2 h. The slow evaporation at room temperature of the resulting mixture affords **2** as pink crystals. IR (KBr, v_{max} , cm⁻¹): 3442, 3029, 2925, 1714, 1654, 1607, 1578, 1453, 1383, 1314. Yield: 32 %. The sample lost solvent molecules quickly while being exposed to air. After solvent molecules were removed under *vacuum*, the elemental analysis based on Co(ntb)(H₂mpda) was performed. Anal. calcd. C₃₈H₃₅N₉O₈Co: C, 56.72; H, 4.38; N, 15.67. Found: C, 56.89; H, 4.98; N, 15.33.

Synthesis of complex 3: Solutions of ntb (0.1 mmol) in 10 mL methanol, H₄edta (0.1 mmol) in 10 mL methanol and $CoCl_2 \cdot 6H_2O$ (0.1 mmol) in 5 mL water were combined and refluxed for 1 h. After cooling to room temperature, purple crystals appeared by slow evaporation the mixture. Yield: 68 %. IR (KBr, v_{max}, cm⁻¹): 3491, 3062, 2938, 1644, 1959, 1473, 1455, 1398, 1280, 1044, 974, 750. The sample lost solvent molecules quickly while being exposed to air. After solvent molecules were removed under vacuum, the elemental analysis based on 2[Co(ntb)Cl]·[Co(edta)] was performed. Anal. calcd. $C_{58}H_{54}N_{16}O_8Cl_2Co_3$: C, 51.57; H, 4.03; N, 16.59. Found: C, 51.04; H, 4.64; N, 16.97.

X-ray crystallography: Diffraction data for **1**, **2** and **3** were measured on a Bruker SMART CCD diffractometer at 190(2) K using graphite monochromated, MoK_{α} radiation ($\lambda = 0.71073$ Å). The collected data were reduced with the SAINT program¹¹ and empirical absorption correction was done with the SADABS¹² program. Both structures were solved by the direct method and refined by the full-matrix least-squares method on F² with anisotropic thermal parameters for all non-hydrogen atoms¹³. The summary of the crystal data, experimental details and refinement results for **1**, **2** and **3** are listed in Table-1.

RESULTS AND DISCUSSION

The single-crystal analysis of 1 and 2 revealed that 1 and 2 have almost identical structures as shown in Fig. 1. In both mononuclear complexes, the ligand ntb coordinates with the Co(II) ion through four N atoms by a typical tripodal coordination mode. Three benzimidazole N atoms form the equatorial planes of the trigonal-bipyramid polyhedra. The central Co atom in 1 was displaced 0.489 Å away from the equatorial plane, while the value is 0.521 Å in 2. The ntb ligand wraps around the central Co(II) ion showing clockwise (Δ enantiomer) propeller coordination fashion in both cases (Fig. 2). The tertiary nitrogen atom of ntb and an oxygen atom of carboxylate group from the H₂mpda²⁻ ligand occupy the two apical positions. The H₂mpda²⁻ ligand is not in the space between the benzimidazole groups of ntb, but in the underside of one benzimidazole ring. The dihedral angle between N(2) containing benzimidazole ring and phenyl ring of H₂mpda²⁻ is 86.18° in 1, that value is 89.33° in 2. Carboxylic acid and carboxylate groups of H2mpda2- ligand form intramolecular

TABLE-1 CRYSTALLOGRAPHIC DATA FOR COMPLEXES 1-3						
Complex	1	2	3			
Formula	$\begin{array}{c} 2(C_{38}H_{35}CoN_9O_8)\cdot\\ C_3H_6O{\cdot}4(H_2O) \end{array}$	$\begin{array}{c} C_{38}H_{35}Co\\ N_9O_8{\cdot}3(H_2O) \end{array}$	$\begin{array}{c} 2(C_{24}H_{21}ClCoN_7) \cdot \\ C_{10}H_{12}CoN_2O_8 \cdot \\ 6(H_2O) \end{array}$			
Formula weight	1739.50	858.73	1458.96			
Crystal system	Triclinic	Triclinic	Monoclinic			
a, Å	12.495(2)	12.509(2)	16.158(1)			
b, Å	12.860(2)	12.728(2)	24.533(2)			
c, Å	14.715(3)	14.731(2)	16.652(1)			
α, deg	76.750(3)	77.307(2)	90.00			
β, deg	65.994(3)	66.054(2)	101.350(1)			
γ, deg	77.532(3)	77.312(2)	90.00			
V/Å ³	2082.3(6)	2068.6(3)	6471.7(7)			
Temperature/K	190(2)	190(2)	190(2)			
Space group	P1	P1	C2/c			
Ζ	1	2	4			
µ/mm ⁻¹	0.481	0.484	0.919			
R _{int}	0.0430	0.0238	0.0233			
R indices	$R_1 = 0.0814$	$R_1 = 0.0624$	$R_1 = 0.0607$			
$(I > 2\sigma(I))$	$wR_2 = 0.1874$	$wR_2 = 0.1919$	$wR_2 = 0.1776$			
Final R indices	$R_1 = 0.1552$	$R_1 = 0.0918$	$R_1 = 0.0711$			
(all data)	$wR_2 = 0.2292$	$wR_2 = 0.2170$	$wR_2 = 0.1869$			
Goodness of fit on F ²	1.032	1.072	1.052			

hydrogen bonds [In 1: $O(4)\cdots O(2)$ 2.43 Å, O(4)-H(4) $\cdots O(2)$ 156.12°; O7 \cdots O5 2.53 Å, O7-H7 \cdots O5 161.95°. In 2: $O(4)\cdots O(2)$ 2.44 Å, O(4)-H(4) $\cdots O(2)$ 158.07°; O7 \cdots O5 2.533 Å, O7-H7 \cdots O5 16.75°]. The subtle difference of the coordination environment between 1 and 2 is listed in Table-2. All water molecules of 1 and 2 are linking coordination units to form a three dimensional hydrogen bonded network. The acetone molecule is trapped in the supramolecular cavity by C-H $\cdots\pi$ interaction, that is, acetone molecule does not have a significant effect on the coordination sphere.

TABLE-2						
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (DEG)						
1						
Co(1)-N(1)	2.349(5)	N(1)-Co(1)-N(6)	76.7(2)			
Co(1)-N(6)	2.033(6)	Co(1)-N(4)	2.044(5)			
Co(1)-O(1)	2.037(5)	N(1)-Co(1)-N(4)	75.5(2)			
Co(1)-N(2)	2.043(6)	N(1)-Co(1)-O(1)	169.9(2)			
N(1)-Co(1)-N(2)	76.2(2)	Co(1)-N(6)	2.033(6)			
2						
Co(1)-N(1)	2.442(4)	N(1)-Co(1)-N(6)	75.54(15)			
Co(1)-O(1)	2.021(4)	Co(1)-N(4)	2.036(4)			
N(6)-Co(1)-O(1)	96.52(16)	N(1)-Co(1)-N(4)	74.70(15)			
Co(1)-N(2)	2.046(4)	N(1)-Co(1)-O(1)	167.15(16)			
N(1)-Co(1)-N(2)	75.47(16)	Co(1)-N(6)	2.038(4)			
3						
Co(1)-N(1)	2.360(3)	N(1)-Co(1)-N(6)	74.85(13)			
Co(1)-Cl(1)	2.345(2)	Co(1)-N(4)	2.039(4)			
N(6)-Co(1)- Cl(1)	101.11(10)	N(1)-Co(1)-N(4)	75.07(14)			
Co(1)-N(2)	2.054(4)	N(1)-Co(1)-	174.85(10)			
		Cl(1)				
N(1)-Co(1)-N(2)	76.85(13)	Co(1)-N(6)	2.057(3)			

Complex **3** consists of cationic and anionic coordination units with a molar ratio of 1:2. The coordination geometry of $[Co(ntb)Cl]^+$ unit is best described as being based on a trigonal bipyramidal arrangement in which the axial positions are



Fig. 2. View of coordination environment from different directions in 1(a) and 2 (b)



Fig. 1. Plots of complex 1(a) and 2(b). The uncoordinated solvent molecules and hydrogen atoms except these attaching nitrogen and oxygen atoms have been omitted for clarity

defined by the N(1) and Cl(1) atoms (Fig. 3a). Cobalt atom lies 0.511 Å out of the plane in the direction of the Cl(1) atom. The Co-Cl distance of 2.345(2) Å is comparable to reported distances in [Co(II)(ntb)Cl]Cl complex¹⁴. Three atoms in the axial direction are closer to the linear arrangement [N(1)-Co(1)-Cl(1) 174.85(10)°] than that in 1 [N(1)-Co(1)-O(1) 169.9(2)°] and 2 [N(1)-Co(1)-O(1) 167.15(16)°], which is mainly attribute to the steric repulsion of chlorine is smaller than H_2 mpda²⁻ ligand (Fig. 3b). In counter [Co(edta)]²⁻ unit, each Co(II) atom is surrounded by two nitrogen donors as well as four oxygen atoms from same edta⁴⁻ organic anion, which exhibits a distorted octahedral coordination sphere. The Co-O bond lengths range between 2.044(3) and 2.131(3) Å, while the Co-N bond length is 2.137(4) Å, which is in the normal range. Each anionic coordination unit is directly connected to two cationic coordination units by hydrogen bonds between carboxylic group and benzimidazole [N(3)····O(2) (symmetry code: 1/2-x,1/2-y,-z) 2.70 Å, N(3)-H(3)-O(2) 151.27°]. They are also indirectly connected through the bridging water molecules to form complicated three dimensional supramolecular networks.

Conclusion

In summary, three five-coordinate cobalt(II) complexes $2[Co(ntb)(H_2mpda)] \cdot (CH_3COCH_3) \cdot 4H_2O(1)$, [Co(ntb)(H₂mpda)] $\cdot 3H_2O(2)$ and $2[Co(ntb)Cl] \cdot [Co(edta)] \cdot 6H_2O(3)$ have been synthesized and characterized. They exhibit mixed-ligand

three-dimensional hydrogen bonding supramolecular networks. The coordination of negative divalent ligand H_2mpda^{2-} to the cobalt(II) ions leads to neutral complexes 1 and 2. In complex 3, cationic coordination unit is reached by auxiliary ligand Cl⁻, anionic Co(edta)²⁻ counterbalancing the charge in this case. Complex 1 and 2 show that the variation of uncoordinated solvent molecules don't lead to obvious different coordination modes. The structure of complex 3 indicates that the smaller second ligand is able to reduce the space steric hindrance effect.



Fig. 3. Crystal structure of the cationic coordination unit (a) and coordination environment (b) in complex **3**

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