

d^{10} Metal Complexes of a Tripodal Amine Ligand

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Research on tripodal complexes has grown in recent decades and has been subject of numerous reports.¹⁻¹¹ The reasons for this interest include their relevance to model functions of metalloenzymes¹⁻³ and their potential applications in catalysis.¹³⁻¹⁷ The ligand system used most in this category has been tren, the tripodal tetraamine $N(CH_2CH_2NH_2)_3$, and its derivatives.⁴ The bz_3tren is a versatile tetradentate ligand, known to form stable complexes not only with transition metals⁵⁻¹¹ including Cu^{2+} , Zn^{2+} and Co^{2+} but also anion species.¹² However, only few results on the d^{10} metal complexes with bz_3tren have been reported by us¹⁰ and others.^{6,7} As a part of on going efforts, we therefore focus our attention to extend other d^{10} system that includes heavy metal ions.

Results and Discussion

The ligand bz_3tren was synthesized according to the procedure published by Ibrahim *et al.*⁵ Its metal complexes **1**, **2** and **3** were prepared and characterized by X-ray structure analysis. Reaction of $Hg(NO_3)_2$ with bz_3tren in methanol followed by addition of NH_4PF_6 afforded colorless X-ray quality crystalline product **1**. The IR spectrum of **1** shows strong bands at 1385 and 831 cm^{-1} due to NO_3^- and PF_6^- ions, respectively, in addition to the ligand peaks. The crystal structure of **1** is shown in Figure 1, with selected geometric parameters. The crystallographic analysis reveals that **1** is an 1 : 1 (metal to ligand) complex of formula $[Hg(bz_3tren)(NO_3)]PF_6$. The Hg atom in **1** is six-coordinated by one bridgehead N atom (N_{br}), three secondary amino N atoms and two O atoms of one bidentate nitrate ion. In fact, the narrow bite angle [$O1-Hg-O2$: 49.4(2) $^\circ$] of the bidentate nitrate ion for Hg atom allows the pseudo-trigonal bipyramidal geometry, in which the three secondary amino N atoms define the equatorial plane. The Hg atom is deflected out of this plane by 0.549 Å towards nitrate ion. Three benzyl end-groups spread out to accommodate the anion coordination. The potential threefold symmetry of **1** seems to be broken due to the anion species and/or crystal packing. The Hg- N_{br} bond (2.467(6) Å) is significantly longer than the other Hg-N bonds (2.329-2.352 Å). The bidentate nitrate group is bonded asymmetrically to the mercury with bond lengths (Hg-O1 2.588(8), Hg-O2 2.512(7) Å) that fall within the range observed for other bidentate nitrate complexes of

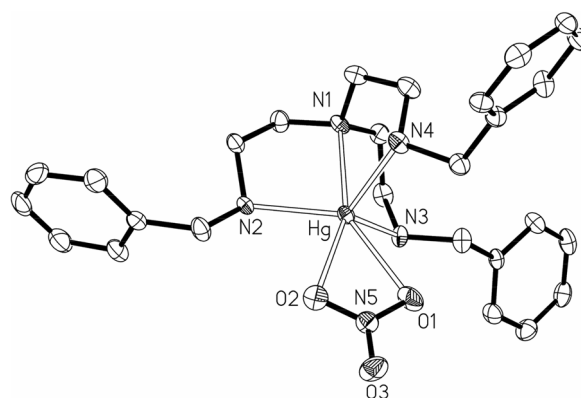


Figure 1. Crystal structure of **1**, $[Hg(bz_3tren)(NO_3)]PF_6$. Non-coordinating anion is omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Hg-N(1) 2.467(6), Hg-N(2) 2.329(7), Hg-N(3) 2.346(6), Hg-N(4) 2.352(7), Hg-O(1) 2.588(8), Hg-O(2) 2.512(7), N(1)-Hg-N(2) 76.3(2), N(1)-Hg-N(3) 76.2(2), N(1)-Hg-N(4) 76.8(2), N(2)-Hg-N(3) 112.3(2), N(3)-Hg-N(4) 109.6(2), N(2)-Hg-N(4) 122.0(3), O(1)-Hg-O(2) 49.4(2).

mercury.¹⁸⁻²¹

Reaction of $Cd(NO_3)_2$ in methanol with bz_3tren in dichloromethane afforded colorless precipitate. Vapor diffusion of diethyl ether into DMF solution of the precipitate afforded colorless X-ray quality crystalline product **2**. The IR spectrum of **2** shows strong band at 1385 cm^{-1} due to NO_3^- ion. The crystal structure of **2** is shown in Figure 2, with selected geometric parameters. The crystallographic analysis reveals that **2** is a complex of formula $[Cd(bz_3tren)(NO_3)]NO_3$. In fact, the structure of **2** exhibits no significant difference with that of **1** except the weak interaction of nitrate ion instead of non-coordinating PF_6^- ion. Accordingly, the principal distortion of the coordination sphere in **2** arises from such weak coordination of the nitrate ion ($Cd \cdots O3$ 2.746 Å). The largest deviations from the N_3 plane around the Cd atom involve the angles $N4-Cd-N2$ 108.52(14) $^\circ$ and $N2-Cd-N3$ 119.60(14) $^\circ$. Also the Cd atom is deflected out of trigonal plane by 0.584 Å towards the nitrate ions. These distortions may reflect the coordination from bidentate nitrate ion as well as the presence of an additional long-range interaction of the second nitrate ion.

The preparation of crystalline complex of bz_3tren with $AgNO_3$ was not available. Instead of the nitrate form,

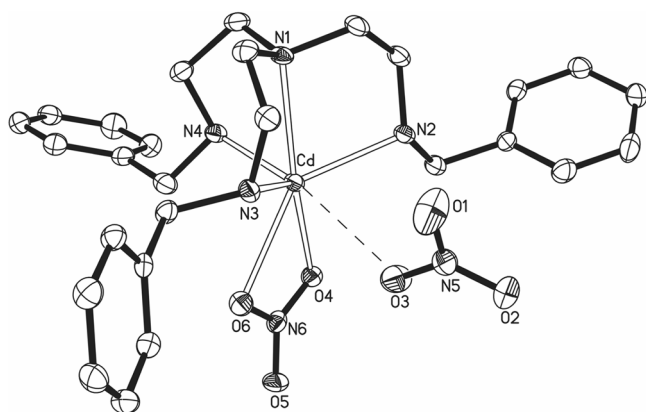


Figure 2. Crystal structure of **2**, $[\text{Cd}(\text{bz}_3\text{tren})(\text{NO}_3)]\text{NO}_3$. Selected bond lengths (Å) and angles ($^\circ$): Cd-N(1) 2.460(3), Cd-N(2) 2.314(4), Cd-N(3) 2.315(4), Cd-N(4) 2.339(4), Cd-O(4) 2.439(3), Cd-O(6) 2.483(3), N(1)-Cd-N(2) 75.88(12), N(1)-Cd-N(3) 75.74(13), N(1)-Cd-N(4) 74.61(13), N(4)-Cd-N(2) 108.52(14), N(4)-Cd-N(3) 113.47(13), N(2)-Cd-N(3) 119.60(14).

reaction of AgCF_3SO_3 and bz_3tren in methanol afforded colorless X-ray quality crystalline product **3**. The crystal structure of **3** is shown in Figure 3, with selected geometric parameters. The crystallographic analysis reveals that **3** is a complex of formula $[\text{Ag}(\text{bz}_3\text{tren})]\text{CF}_3\text{SO}_3$ without anion coordination. Thus, this representation shows a C_3 -symmetrical Ag complex. Unlike **1** and **2**, the three benzyl end-groups in **3** form picket fences around the Ag atom. The Ag complexes of bz_3tren and its NS_3 derivative with similar pseudo-cage structure have been reported by us¹⁰ and Kaden *et al.*¹¹ In these case, however, the threefold symmetry of the complex cation, $[\text{Ag}(\text{bz}_3\text{tren})]^+$ is broken by anion species and aromatic end-group.^{10,11} The structure of **3** is also similar to that of copper(I) complex, $[\text{Cu}(\text{bz}_3\text{tren})]\text{ClO}_4$ which show a trigonal pyramidal geometry.⁶ The Ag atom in **3** is four-coordinated by one bridgehead N atom (N_{br}) and three secondary amino N atoms. However, it is surprising to see

that the Ag atom is not in the center of tetrahedral environment but deflected out of trigonal plane by 0.595 Å towards the benzyl end-groups. Thus, the Ag atom coordination cannot be described simply in terms of a regular polyhedron. Furthermore, the Ag- N_{br} bond (2.522(5) Å) is significantly longer than expected. It is conceivable that the exceptional large dislocation of the Ag atom as well as the elongation of Ag- N_{br} distance in **3** are due to the weak π -coordination (dashed lines in Figure 3a; $\text{Ag1}\cdots\text{C}_\alpha$ 3.499, $\text{Ag1}\cdots\text{C}_\beta$ 3.467 Å). In addition, three aromatic rings are essentially planar and lie roughly perpendicular to each other, displaying dihedral angle of 66.15° . This permits also weak edge-to-face π - π interactions between aromatic end-groups, with a distance from one C atom to the centroid of the adjacent ring of 3.913 Å.

To provide insight into the complexes in solution state, ^1H NMR spectra of bz_3tren and its mercury(II), cadmium(II) and silver(I) complexes (all as nitrates) were obtained in CD_3CN . The signals of three methylene ($\text{H}_{1,3}$) and aromatic (~ 7.2 ppm) protons for the free bz_3tren were well resolved and identified (Fig. 4a). In cases of mercury(II) and cadmium(II) complexes (Fig. 4b and 4c), every protons of the ligand shifted downfield, suggesting the complex formations in similar mode. The order of magnitude of the chemical shift variation is $\text{H}_3 > \text{H}_1, \text{H}_2$, indicating that the mercury(II) or cadmium(II) is strongly coordinated by secondary amine N atoms, and the N_{br} atom interacts with these metal ions weakly, similar to the cases in solid state. On the whole, the larger downfield shifts were observed by mercury(II) than those of cadmium(II) due to the higher binding strength of mercury(II) towards bz_3tren .

In case of silver(I) complex (Fig. 4d), however, shows different pattern. For example, the metal ion induced chemical shifts are almost negligible and the aromatic signal is divided into two parts with 3 : 2 ratio. These are caused by both the π -coordination of silver(I) and π - π interaction. The aromatic protons in *o*-position interact with silver(I)

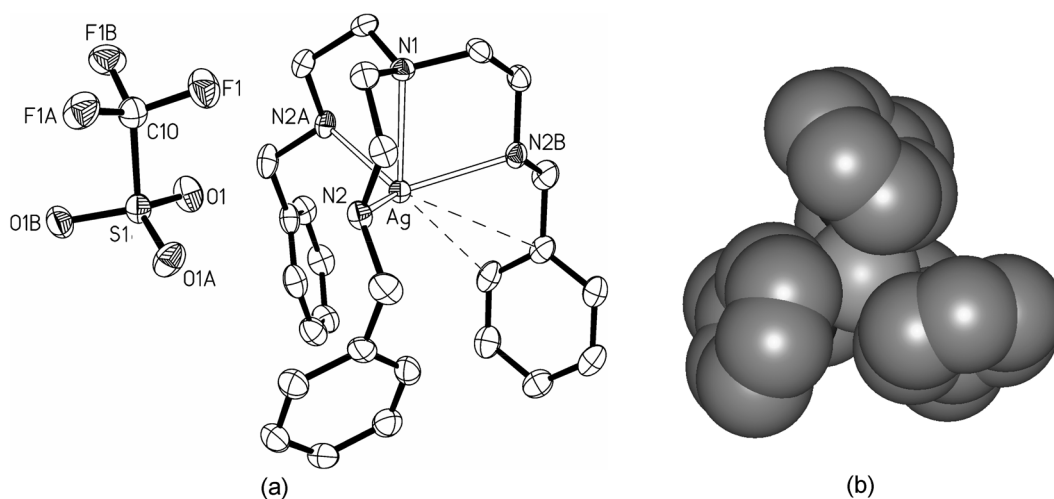
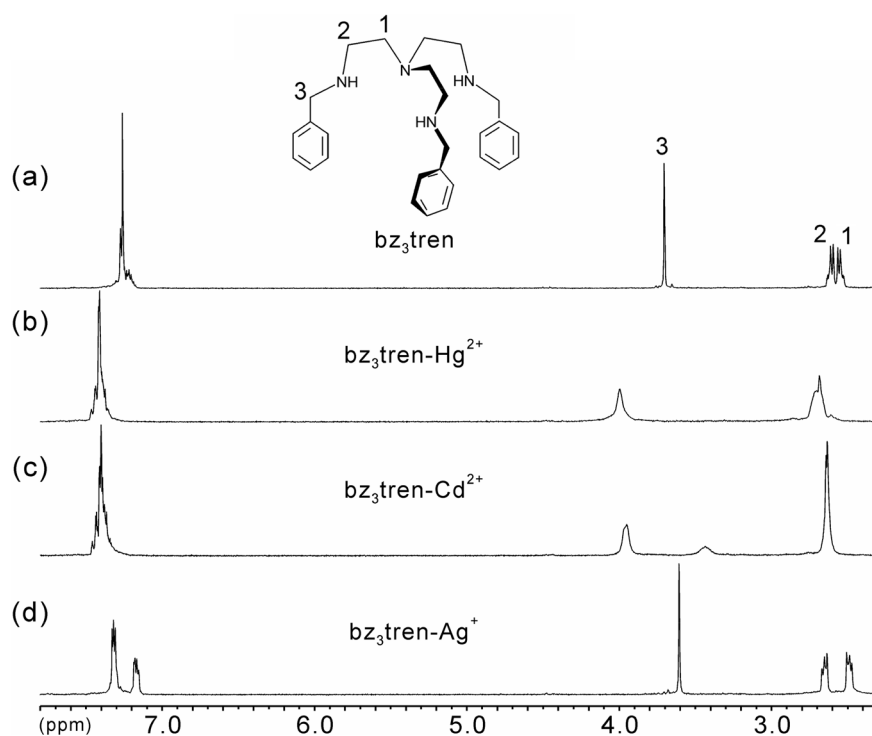


Figure 3. (a) General view of **3**, $[\text{Ag}(\text{bz}_3\text{tren})]\text{CF}_3\text{SO}_3$ and (b) bottom view of complex cation of **3** (space-filling diagram, N donors are not shown). Selected bond lengths (Å) and angles ($^\circ$): Ag-N(1) 2.522(5), Ag-N(2) 2.346(3), N(1)-Ag-N(2) 75.30(8), N(2)-Ag-N(2A) 113.79(7), N(2)-Ag-N(1) 75.30(8). Symmetry code: (A) $-y - 1, x - y, z$.

Table 1. Crystallographic data for [Hg(bz₃tren)(NO₃)]PF₆ (**1**), [Cd(bz₃tren)(NO₃)]NO₃ (**2**) and [Ag(bz₃tren)]CF₃SO₃ (**3**)

	1	2	3
Chemical formula	C ₂₇ H ₃₆ F ₆ HgN ₅ O ₃ P	C ₂₇ H ₃₆ CdN ₆ O ₆	C ₂₈ H ₃₆ AgF ₃ N ₄ O ₃ S
Crystal system	Triclinic	Orthorhombic	Hexagonal
Space group	<i>P</i> -1	<i>Pbca</i>	<i>P</i> 6 ₃
<i>a</i> (Å)	10.0465(6)	14.3972(7)	9.4658(3)
<i>b</i> (Å)	11.2174(6)	16.0782(8)	
<i>c</i> (Å)	14.8979(8)	25.3155(12)	19.8942(12)
α (°)	94.3090(10)	90.00	90.00
β (°)	90.3290(10)	90.00	90.00
γ (°)	112.7950(10)	90.00	120.00
<i>V</i>	1542.31(15)	5860.1(5)	1543.73(12)
<i>Z</i>	2	8	2
<i>F</i> (000)	812	2688	692
<i>D</i> _c (g/cm ³)	1.775	1.480	1.449
<i>M</i> (mm ⁻¹)	5.115	0.795	0.773
<i>R</i>	0.0514	0.0550	0.0334
<i>wR</i>	0.1279	0.1099	0.0850

**Figure 4.** ¹H NMR spectra for (a) bz₃tren, (b) Hg(bz₃tren)(NO₃)₂, (c) Cd(bz₃tren)(NO₃)₂ and (d) Ag(bz₃tren)NO₃ in CD₃CN. The complex solutions (b, c and d) were prepared by dissolving equimolar amount of corresponding nitrate salts in 2.0 mM solutions of bz₃tren in CD₃CN.

generate the smaller peak in higher field (~7.15 ppm), whereas the larger peak in lower field (~7.3 ppm) is generated from those in *m*- and *p*-positions. In addition, the slightly upfield shifts of the ligand protons (H_{1,3}) in Ag(bz₃tren)NO₃ compared to those of the free ligand support the existence of the π - π stacking interaction. Notably, all the NMR data in Figure 4 agree with the binding mode in the solid state, suggesting that these structures are also retained in solution.

Experimental Section

General methods. All commercial reagents including solvents were of analytical reagent grade. NMR spectra were recorded on a Bruker Avance-300 spectrometer (300 MHz) at the Central Laboratory of Gyeongsang National University. Infrared spectra were measured with a Mattson Genesis Series FT-IR spectrophotometer. Melting points are uncorrected.

Complex synthesis. Reaction of $\text{Hg}(\text{NO}_3)_2$ with bz_3tren in methanol followed by addition of NH_4PF_6 afforded colorless X-ray quality crystalline product **1**: Mp 170-172° (decomp.). IR (KBr, cm^{-1}) 3130, 1402, 1385, 831, 559. Reaction of $\text{Cd}(\text{NO}_3)_2$ in methanol with bz_3tren in dichloromethane afforded colorless precipitate. Vapor diffusion of diethyl ether into DMF solution of the precipitate afforded colorless X-ray quality crystalline product **2**: IR (KBr, cm^{-1}) 3211, 2925, 1454, 1385, 1309, 1296, 1074, 1035, 991, 943, 752, 703. Reaction of AgCF_3SO_3 and bz_3tren in methanol afforded colorless X-ray quality crystalline product **3**: Mp 135-137°. IR (KBr, cm^{-1}) 3267, 2849, 1454, 1335, 1261, 1161, 1092, 1030, 999, 748, 700, 638.

X-ray crystallography. All data were collected on a Bruker SMART diffractometer equipped with a graphite monochromated $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation source and a CCD detector; 45 frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The two-dimensional diffraction images were collected, each of which was measured at $-100 \text{ }^\circ\text{C}$. The structure was solved by a direct method and refined by full matrix least square against F^2 for all data. All non-H atoms were refined with anisotropic displacement parameters. All hydrogen atoms were included in calculated position with isotropic thermal parameters 1.2 times those of attached atoms. Crystallographic data are summarized in Table 1.

Supplementary data. Supplementary crystallographic data associated to complexes **1**, **2** and **3** have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 289414, 289415 and 289416. Copies of the data can be obtained free of charge on application to CCDC, 12 Union road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk), or electronically via www.ccdc.cam.ac.uk/data_request/cif.

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