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Bond Length Contraction in Zinc-Triad Complexes Ligated by Hydrotris(pyrazolyl)borate: [M(Cl){HB(3,5-^{i}Pr$_2$pz)$_3$}] (M = Zn^{II}, Cd^{II}, and Hg^{II})

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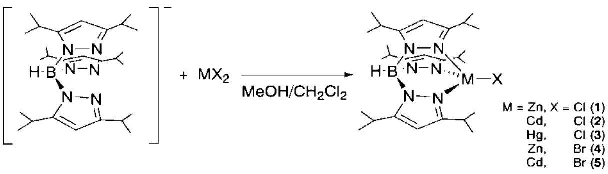
Bond length contraction in zinc-triad chloro complexes, which were characterized by X-ray crystallography and metal–halogen stretching frequency, is reported.

There is a growing interest in bond length contraction in transition-metal complexes in recent years because of current debates concerning the relevance of relativistic effects in inorganic and organometallic chemistry.[1–4] In particular, gold is considered the "relativistic element" par excellence, and therefore, its atomic and molecular parameters are the subject of scrutiny in both theoretical calculations and experimental studies.[1–5] For these experimental researches, accurate X-ray diffraction studies are needed (1) under strictly comparable experimental conditions, (2) on isomorphous single crystals, and (3) with the same composition (coordination number and geometry) and stoichiometry (ligand and counter ion). A direct comparison of the structure of a gold(I) complex with that of a corresponding silver(I) or copper(I) complex is normally impossible because the univalent Group 11 metal ions have different dominant structures. By selecting the appropriate ligand systems, the covalent radii of gold(I) have been found to be smaller than those of silver(I) in [M(PMes$_3$)$_2$]BF$_4$ (PMes$_3$ = trimesitylphosphine, M = Au^I and Ag^I),[6] [M(AsPh$_3$)$_4$]BF$_4$ (M = Au^I and Ag^I),[7] and (NEt$_4$)[M(SAd)$_2$] (HSAd = 1-adamantanethiol, M = Au^I, Ag^I, and Cu^I).[8] These results agree very well with calculated data obtained in theoretical treatments involving relativistic effects.

On the other hand, these relativistic effects involving other group metals have not been studied accurately under the above experimental conditions.[1–4] Mercury is also a relativistic element.[1–4] Therefore, it is worth while to study Group 12 metal complexes. The divalent Group 12 metal ions have slightly different preferred coordination geometries: 4, 5, or 6 coordination for zinc(II) and cadmium(II); 2, 4, 5, or 6 coordination for mercury(II).[2] In this paper, we report the first observation of M–Cl bond length contraction in zinc-triad chloro compounds ligated by hydrotris(pyrazolyl)borate. This ligand was used because it acts as a "tetrahedral enforcer."[9]

All complexes are readily prepared from the equivalent reaction between metal halide and hydrotris(3,5-diisopropyl-1-pyrazolyl)borate anion in methanol/dichloromethane (65–89% yield). From slow evaporation of concentrated methanol/dichloromethane mixed solution at room temperature, single crystals suitable for X-ray crystal determinations were obtained as large, transparent isomorphous crystals (monoclinic space group $P2_1/m$, see Table 1).



(1)

The structure of **3** with its atomic numbering scheme is shown in Fig. 1. The mercury atom has a distorted C_{3v} tetrahedral geometry as evidenced by the three acute Npz–Hg–Npz (Npz: the pyrazole nitrogens) bond angles (average, 84.2(6)°) and three accordingly obtuse Cl–Hg–Npz bond angles (average, 129.2(20)°), which are typical for hydrotris(pyrazolyl)borate metal complexes.[9] The Hg–Cl distance of 2.301(3) Å is similar to the reported distances of four-coordinate mercury(II) chloro complexes.[10] All of the structural parameters for **1**–**5** are also listed in Table 1. The average Npz–M–Npz angles in [M(Cl){HB(3,5-^{i}Pr$_2$pz)$_3$}] decrease from zinc(II) to mercury(II), while the average Cl–M–Npz angles increase. The same tendency in [M(Br){HB(3,5-^{i}Pr$_2$pz)$_3$}] from zinc(II) to cadmium(II) is also observed. Remarkably, the averaged parameters of **1** are very close to those of **4**. This is the same for **2** and **5**. It means that they are not dependent on the size of halogenide ion.[11]

Interestingly, this Hg–Cl distance in **3** (2.301(3) Å) is much shorter than the Cd–Cl one in **2** (2.332(2) Å) by 0.031(3) Å, namely between the zinc(II) derivative (2.172(2) Å) and Cd^{II} one. To our knowledge, this is the first direct observation of "relativistic effects" in zinc-triad complexes with the supporting ligand (heteroleptic ligand system) under the above experimental conditions (Table 1). The different value of 0.031(3) Å is smaller than our previous reported value of 0.051(4) Å for (NEt$_4$)[M(SAd)$_2$] (M = Ag^I and Au^I).[8] It means that mercury does not exhibit strong relativistic effects. This is consistent with theoretical considerations.[1–4] These differences should be reflected in the physicochemical properties including the ν(M–Cl) energy in far-IR and FT-Raman spectroscopy.

The M–Cl stretching frequency should be observed in the region below 500 cm^{-1}.[12] Although the spectral patterns of **1**–**3** are very similar to each other in the entire region, the strong band at 357 cm^{-1} in **1** is shifted to that at 320 cm^{-1} in **2** and 322 cm^{-1} in **3**. These ν(M–Cl) frequencies are also observed in FT-Raman spectra (353 cm^{-1} (**1**), 320 cm^{-1} (**2**), and 322 cm^{-1} (**3**)) (Fig. S1). This order (ν(M–Cl): **1** > **3** > **2**) is in inverse proportion to the M–Cl distances from X-ray structural characterization (d(M–Cl): **1** < **3** < **2**). To confirm these assignments, we also prepared and measured the bromo derivatives (**4** and **5**), of which the structures were determined by X-ray crystallography. These ν(M–Br) frequencies are also

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Table 1. Crystal Data for [M(Cl){HB(3,5-^{i}Pr$_2$pz)$_3$}] (M = Zn (**1**), Cd (**2**), and Hg (**3**)) and [M(Br){HB(3,5-^{i}Pr$_2$pz)$_3$}] (M = Zn (**4**) and Cd (**5**)), and Their M–X Stretching Frequencies

	1	**2**	**3**	**4**	**5**
Space group	$P2_1/m$	$P2_1/m$	$P2_1/m$	$P2_1/m$	$P2_1/m$
a/Å	9.894(1)	9.863(1)	9.846(4)	9.887(3)	9.852(4)
b/Å	16.539(1)	16.583(2)	16.577(3)	16.553(3)	16.530(3)
c/Å	9.993(1)	10.146(2)	10.157(3)	10.078(3)	10.312(3)
β/°	102.674(8)	101.94(1)	102.11(3)	103.01(2)	102.42(2)
V/Å^3	1595.3(3)	1623.4(3)	1621.0(9)	1607.0(8)	1640.0(8)
Temperature/K	296(1)	296(1)	296(1)	296(1)	296(1)
X–M–Npz[a)]	123.2(4)	127.7(13)	129.2(20)	123.2(3)	127.7(9)
Npz–M–Npz[a)]	92.8(1)	86.5(5)	84.2(6)	92.9(3)	86.5(2)
d(M–X)/Å	2.172(2)	2.332(2)	2.301(3)	2.3055(9)	2.4508(9)
ν(M–X)/cm^{-1}					
far-IR	357	320	322	283	245
FT-Raman	353	320	322	281	246
d(M–Npz)/Å[a)]	2.019(5)	2.221(5)	2.274(9)	2.017(5)	2.215(6)
ν(M–Npz)/cm^{-1}					
far-IR	191	159	nd[b)]	192	160

a) Averaged value. b) Not detected.

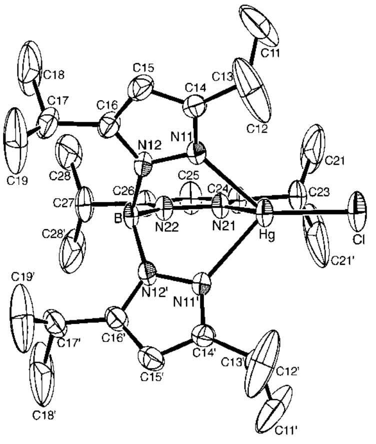

Fig. 1. Molecular structure of [Hg(Cl){HB(3,5-^{i}Pr$_2$pz)$_3$}] (**3**). Selected bond lengths (Å) and angles (°): Hg–Cl 2.301(3), Hg–N11 2.281(7), Hg–N21 2.260(9); Cl–Hg–N11 128.1(2), Cl–Hg–N21 131.5(3), N11–Hg–N11′ 84.9(3), N11–Hg–N21 83.9(2). Primed atoms are related by the symmetry operation x, $1/2 - y$, z.

shifted to 283 cm^{-1} in **4** and 245 cm^{-1} in **5**, from 357 cm^{-1} in **1** and 320 cm^{-1} in **2** (Fig. S2). The results are summarized in Table 1. Comparing the reported values of tetrahedral homoleptic halogeno complexes [MX$_4$]$^{2-}$,[12] our data are on the higher energy side ((NEt$_4$)$_2$[ZnCl$_4$],[13] 276 cm^{-1}, (NEt$_4$)$_2$[ZnBr$_4$],[13] 171 cm^{-1}, (NBu$_4$)$_2$[CdCl$_4$],[14] 255 cm^{-1}, (NBu$_4$)$_2$[CdBr$_4$],[14] 161 cm^{-1}, (NH$_4$)$_2$[HgCl$_4$],[15] 267 cm^{-1}). This difference comes from the different ligand donor sets, i.e., N$_3$X type versus X$_4$ type. Moreover, M–N bond distances and M–N stretching frequencies should show the same phenomenon. However, different trends (d(M–Npz): **1** < **2** < **3**) were observed as shown in Table 1. In addition, we did not obtain clear Hg–N stretching frequency in its far-IR spectrum (ν(M–Npz): **1** > **2**). Further researches are in progress to obtain more insight into the coordination chemistries and physicochemical properties of Group 12 metal(II) complexes.

Experimental

General. Preparation and handling of all complexes were performed under an argon atmosphere by employing standard Schlenk line techniques. Dichloromethane was distilled from P$_2$O$_5$ prior to use.[16] Methanol was of commercially spectroscopic grade and used after bubbling argon gas. IR and far-IR spectra were recorded as KBr pellets in the 4600–400 cm^{-1} region and as CsI pellets in the 650–100 cm^{-1} region using a JASCO FT/IR-550 spectrophotometer. FT-Raman spectra were recorded in the 3600–150 cm^{-1} region using a Perkin-Elmer Spectrum GX spectrophotometer or JASCO RFT600 spectrophotometer. ^{1}H NMR (270 MHz) spectra were recorded on a JEOL EX-270 at ambient temperature in CDCl$_3$. Chemical shifts were reported as δ values downfield from an internal standard (CH$_3$)$_4$Si. Elemental analysis (C, H, and N) was performed by the Chemical Analysis Center of the University of Tsukuba. The synthesis of K{HB(3,5-^{i}Pr$_2$pz)$_3$} and Na{HB(3,5-^{i}Pr$_2$pz)$_3$} were carried out by the method previously reported.[17]

Preparations. The detailed procedures and data of **1**–**5** are given in the Supporting Information.

X-ray Crystallography. The diffraction data were measured on a Rigaku AFC 7S automated four-circle diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71069$ Å) radiation (50 kV, 26 mA). The structures were solved by direct-methods (SAPI 91[18] for **1**, **3**–**5** and heavy-atom Patterson methods[19] for **2**) and successive different Fourier syntheses,[20] then refined by full-matrix least-squares methods by teXsan.[21] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on the calculated positions and refined isotropically. Structural parameters are listed in Table 1 for direct comparison. Crystallographic data for **1**: C$_{27}$H$_{46}$N$_6$BClZn, fw = 566.34, colorless, monoclinic, space group $P2_1/m$ (#11), $Z = 2$, μ(Mo Kα) = 8.78 cm^{-1}, 3079 reflections measured, 2905 unique ($R_{\text{int}} = 0.024$), 2241 observed data ($I > 2\sigma(I)$), R (Rw) = 0.062 (0.083). **2**: C$_{27}$H$_{46}$N$_6$BCdCl, fw = 613.37, colorless, monoclinic, space group $P2_1/m$ (#11), $Z = 2$, μ(Mo Kα) = 7.80 cm^{-1}, 3130 reflections measured, 2953 unique ($R_{\text{int}} = 0.010$), 2608 observed data ($I > 2\sigma(I)$), R (Rw) = 0.047 (0.066). **3**: C$_{27}$H$_{46}$N$_6$BClHg, fw =

701.55, colorless, monoclinic, space group $P2_1/m$ (#11), $Z = 2$, $\mu(\text{Mo K}\alpha) = 48.7\,\text{cm}^{-1}$, 2809 reflections measured, 2645 unique ($R_{\text{int}} = 0.038$), 1984 observed data ($I > 2\sigma(I)$), R (Rw) = 0.044 (0.049). **4**: $C_{27}H_{46}N_6BBrZn$, fw = 610.79, colorless, monoclinic, space group $P2_1/m$ (#11), $Z = 2$, $\mu(\text{Mo K}\alpha) = 20.4\,\text{cm}^{-1}$, 4023 reflections measured, 3814 unique ($R_{\text{int}} = 0.019$), 2418 observed data ($I > 2\sigma(I)$), R (Rw) = 0.055 (0.067). **5**: $C_{27}H_{46}N_6BBrCd$, fw = 657.82, colorless, monoclinic, space group $P2_1/m$ (#11), $Z = 2$, $\mu(\text{Mo K}\alpha) = 19.1\,\text{cm}^{-1}$, 4114 reflections measured, 3898 unique ($R_{\text{int}} = 0.015$), 2601 observed data ($I > 2\sigma(I)$), R (Rw) = 0.054 (0.063). Crystallographic data and collection details are summarized in Table S1. The atomic numbering of **1**, **2**, **4**, and **5** are available in Figs. S3–S6. Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-250601 (**1**) to 250605 (**5**). Copies of the data can be obtained free of charge on application to the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk/conts/retrieving.html.

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Supporting Information

Detailed preparation methods and data of **1**–**5**, far-IR and Raman spectra of **1**–**3** (Fig. S1), far-IR spectral comparison of **1** with **4** and of **2** with **5** (Fig. S2), summary of crystallographic data of **1**–**5** (Table S1), and atomic numbering of **1**, **2**, **4**, and **5** (Figs. S3–S6). This material is available free of charge on the Web at http://www.csj.jp/journals/bcsj/.

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