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Encapsulation of the Be^{II} Cation: Spectroscopic and Computational Study

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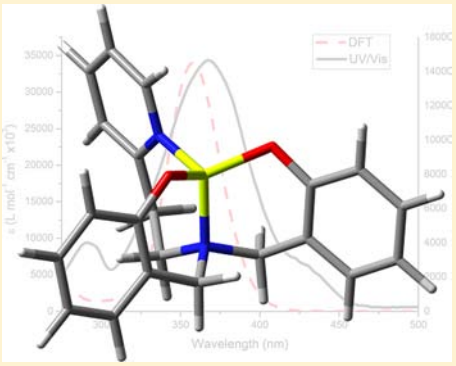
Supporting Information

ABSTRACT: The structures of a series of tetracoordinate beryllium(II) complexes with ligands derived from tertiary-substituted amines have been computationally modeled and their ^{9}Be magnetic shielding values determined using the gauge-including atomic orbital (GIAO) method at the 6-311++g(2d,p) level. A good correlation was observed between calculated ^{9}Be NMR chemical shifts when compared to experimental values in polar protic solvents, less so for the values recorded in polar aprotic solvents. A number of alternative complex structures were modeled, resulting in an improvement in experimental versus computational ^{9}Be NMR chemical shifts, suggesting that in some cases full encapsulation on the beryllium atom was not occurring. Several of the synthesized complexes gave rise to unexpected fluorescence, and inspection of the calculated molecular orbital diagrams associated with the electronic transitions suggested that the rigidity imparted by the locking of certain conformations upon Be^{II} coordination allowed delocalization across adjacent aligned aromatic rings bridged by Be^{II}.



INTRODUCTION

Beryllium is a particularly important metal for a number of applications that are vital to the aerospace, automotive, and electronics industries, particularly when alloyed with metals such as copper.[1,2] Beryllium has been described as one of the most toxic nonradioactive metals on the periodic table,[3] primarily due to the latent toxicity associated with beryllium sensitization,[4] which can lead to chronic beryllium disease (CBD), an incurable sometimes fatal lung disease.[5−8] The mode of delivery of the toxicity, for example, whether as a carcinogen, immune response, or sensitization, and the extent to which each play a role is currently under renewed debate.[9−15]

Our groups have been engaged in beryllium studies focused on the fundamental understanding of the nature of selective binding sites for Be^{II}. To this end we explored the development of applications to detect the presence of or sequester Be^{II} in the environment[16−18] and for tracking Be^{II} within biological systems.[19−21] In the course of our studies, we also developed theoretical modeling methods based on measurement of ^{9}Be NMR to predict Be^{II} speciation in solution with the aim of predicting the structure of beryllium complexes. This method is both convenient and avoids potential exposure to beryllium particulates.[22]

In the present work we are interested in investigating ligands which have the potential to fully encapsulate the Be^{II} cation. To do this we employed tetradentate ligands containing mixed N/O donors capable of providing the beryllium atom with tetrahedral coordination geometry upon chelation. There are relatively few examples of ligands which provide this mode of coordination. One rare example is the coordination of Be^{II} to nitrilotripropionate (NTP), a tertiary-substituted amine with three appended carboxylic acid donors which provided a tetrahedral binding environment.[23] We observed that bidentate ligands with mixed N/O donors such as pyridine−phenol[24] and 10-hydroxybenzoquinoline[18] show promise as selective coordinators of beryllium and have in the past extended these platforms using a binaphthyldiimine ligand, which has the ability to completely encapsulate Be^{II} via tetradentate tetrahedral coordination using both phenol and imine donors.[17]

In the present study we sought to use a series of related tetradentate ligands capable of tetrahedral coordination akin to the earlier NTP-type ligands. These new ligands contain a mix of neutral and charged N-pyridine and O-phenolate donor atoms which due to their decreased conformational flexibility may lead to enhanced selectivity of Be^{II}. Using our established ^{9}Be NMR characterization techniques we then evaluated these ligands for their ability to coordinate to Be^{II} and explored their photophysical properties.

EXPERIMENTAL SECTION

Unless otherwise stated, all reagents and solvents were purchased from commercial sources and used without further purification. NMR spectra were collected on Bruker Avance 300, 400, and 500 MHz spectrometers; the particular instrument is specified for each

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compound. All chemical shifts are reported relative to residual solvent (^{1}H, ^{13}C). ^{9}Be NMR spectra were recorded at a concentration of 28 mmol L^{-1} and a temperature of 298 K on a Bruker Avance 300 at 42.17 MHz and referenced to an internal standard of $Be(H_2O)_4^{2+}$ (as the sulfate salt). All NMR samples containing beryllium were contained within Teflon sleeves in addition to the standard NMR glass tube. Microanalyses were performed at the Campbell Microanalytical Laboratory at the University of Otago. Electrospray mass spectra were recorded on a Micromass ZMD spectrometer run in positive-ion mode. High-resolution mass spectra were recorded on a microTOF-Q mass spectrometer at the University of Auckland operating at a nominal voltage of 3500 V. IR spectra were recorded on a Bruker Alpha-P diamond anvil system. UV−vis spectra were recorded on a Shimadzu UV-3101PC spectrophotometer using UV Probe v1.1. Fluorescence measurements were made on a Perkin-Elmer LS50B luminescence spectrometer using FL Winlab v4.00.02. Reactions were followed by TLC on aluminum-backed silica gel 60 F_{254} sheets from E-Merck, visualized by UV light. Flash column chromatography was performed using Scharlau silica gel 60, 0.04−0.06 mm, 230−400 mesh. The length of silica was typically 20 cm, and the diameter was varied according to reaction scale. The silica gel slurry was compacted with the specified solvent system of hexanes/EtOAc or CH_2Cl_2/MeOH. The compound was then loaded onto the column and eluted with the specified solvent under positive pressure.

Synthesis. *General Procedure for Secondary Amines **1a**−**f**.* The appropriate starting primary amine (4.10 mmol) and 2-hydroxybenzaldehyde (4.10 mmol) in MeOH (10 mL) were stirred for 30 min at RT. $NaBH_4$ (6.48 mmol) and NaOH (0.82 mmol) in H_2O (2 mL) were added to the reaction mixture, and the resulting solution was stirred for 1 h. The reaction was diluted with CH_2Cl_2 (200 mL) and washed with water (200 mL). The organic layer was filtered and dried over $MgSO_4$, and the solvent was removed. The secondary amine was purified by silica gel column chromatography using 95:5 CH_2Cl_2/MeOH. Characterization data for all new compounds are presented below.

*2-((2-Phenylquinolin-8-ylamino)methyl)phenol (**1d**).* R_f = 0.80 (95:5 CH_2Cl_2/MeOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.66 (d, J = 3.8, 2H; CH_2), 6.67 (brs, 1H; NH), 6.90−6.98 (m, 3H; ArH), 7.21−7.26 (m, 2H; ArH), 7.34 (t, J = 7.8, 1H; ArH), 7.42−7.52 (m, 3H; ArH), 7.88 (d, J = 8.5, 1H; ArH), 7.11−7.16 (m, 3H; ArH), 8.31 (brs, 1H; OH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 48.2 (d), 109.7 (s), 116.6 (s), 117.4 (s), 119.3 (s), 120.1 (s), 123.4 (q), 127.1 (s), 127.2 (q), 127.4 (s), 128.5 (s), 128.8 (s), 128.9 (s), 129.3 (s), 137.0 (s), 138.8 (q), 139.3 (q), 144.6 (q), 154.7 (q), 156.7 (q). IR: ν (cm^{-1}) 1585, 1515, 1490, 1460, 1346, 1329, 1292, 1249, 1215, 767, 752, 740. HRMS calcd for $C_{29}H_{23}N_3O_4$ (MH^+): 478.1761. Found: 478.1756 (ESI+). MP = 136−137 °C.

*Methyl 3-(2-Hydroxybenzylamino)propanoate (**1f**).* R_f = 0.29 (95:5 CH_2Cl_2/MeOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.59 (t, J = 6.1, 2H; CH_2), 2.96 (t, J = 6.1, 2H; CH_2), 3.72 (s, 3H; CH_3), 4.02 (s, 2H; CH_2), 6.80 (td, J = 1.0, 7.3, 1H; ArH), 6.85 (dd, J = 1.0, 8.1, 1H; ArH), 7.01 (d, J = 6.7, 1H; ArH), 7.18 (td, J = 1.0, 7.4, 1H; ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 33.6 (d), 43.6 (d), 51.8 (t), 52.4 (d), 116.3 (s), 119.0 (s), 122.2 (q), 128.4 (s), 128.8 (s), 158.1 (q), 172.8 (q). IR: ν (cm^{-1}) 1593, 1492, 1460, 1335, 1091, 751. LRMS for $C_{11}H_{15}NO_3$ (MH^+): 210.61. Anal. Calcd for $C_{11}H_{15}NO_3 \cdot 0.4H_2O$ (216.45): C, 61.04; H, 7.36; N, 6.47. Found: C, 60.96; H, 7.10; N, 6.69.

*General Procedure for Tertiary Amines **2a**−**f**.* The appropriate secondary amine **1a**−**g** (2.95 mmol), 2-(chloromethyl)-4-nitrophenol (2.95 mmol), and triethylamine (23.6 mmol) were refluxed together in $CHCl_3$ (20 mL) for 2 h. The reaction was diluted with CH_2Cl_2 (200 mL) and washed with water (200 mL). The organic layer was filtered and dried over $MgSO_4$. The product was purified by silica gel column chromatography using 98:2 CH_2Cl_2/MeOH. The sticky residue was isolated as a powder by dissolution in a minimum volume of CH_2Cl_2, precipitating with hexane addition, decanting, and drying in vacuo. Characterization data for all new compounds are presented below.

*2-(((2-Hydroxybenzyl)(pyridin-2-ylmethyl)amino)methyl)-4-nitrophenol (**2a**).* R_f = 0.29 (95:5 CH_2Cl_2/MeOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.89 (s, 2H; CH_2), 3.91 (s, 2H; CH_2), 3.99 (s, 2H; CH_2), 6.80−6.97 (m, 3H; ArH), 7.07−7.22 (m, 3H; ArH), 7.35 (t, J = 6.5, 1H; ArH), 7.79 (dt, J = 1.6, 7.7, 1H; ArH), 8.06 (d, J = 2.8, 1H; ArH), 8.12 (dd, J = 2.8, 8.9, 1H; ArH), 8.68 (d, J = 4.9, 1H; ArH) 9.97 (brs, 2H; OH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 56.0 (d), 56.3 (d), 56.8 (d), 117.0 (s), 117.6 (s), 119.5 (s), 120.8 (q), 122.0 (q), 123.0 (s), 123.4 (s), 126.0 (s), 126.6 (s), 129.8 (s), 130.3 (s), 138.2 (s), 140.0 (q), 148.0 (s), 155.5 (q), 157.0 (q), 163.9 (q). IR: ν (cm^{-1}) 1585, 1478, 1453, 1436, 1330, 1271, 1151, 1088, 750. LRMS for $C_{20}H_{19}N_3O_4$(MH^+): 366.72. Anal. Calcd for $C_{20}H_{19}N_3O_4$ (379.41): C, 65.74; H, 5.24; N, 11.50. Found: C, 65.79; H, 5.20; N, 11.49. MP = 102−104 °C.

*2-(((2-Hydroxybenzyl)(pyridin-2-ylethyl)amino)methyl)-4-nitrophenol (**2b**).* R_f = 0.29 (95:5 CH_2Cl_2/MeOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.94 (t, J = 6.7, 2H; CH_2), 3.14 (t, J = 6.7, 2H; CH_2), 3.49 (brs, 2H; OH), 3.85 (s, 4H; CH_2), 6.69−6.82 (m, 3H; ArH), 7.05−7.24 (m, 4H; ArH), 7.64 (dt, J = 1.7, 7.8, 1H; ArH), 7.94 (d, J = 2.2, 1H; ArH), 8.00 (dd, J = 2.8, 8.9, 1H; ArH), 8.54 (d, J = 5.0, 1H; ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 33.9 (d), 53.7 (d), 55.2 (d), 55.7 (d), 116.5 (s), 116.6 (s), 119.7 (s), 121.6 (q), 122.1 (s), 122.4 (s), 123.7 (s), 125.5 (s), 126.2 (q), 129.6 (s), 130.9 (s), 137.6 (s), 139.7 (q), 148.8 (s), 156.1 (q), 158.6 (q), 163.9 (q). IR: ν (cm^{-1}) 1589, 1478, 1456, 1438, 1332, 1272, 1150, 1086, 751. LRMS for $C_{21}H_{21}N_3O_4$ (MH^+): 380.84. Anal. Calcd for $C_{21}H_{21}N_3O_4 \cdot 0.35H_2O$ (385.72): C, 65.39; H, 5.67; N, 10.89. Found: C, 65.40; H, 5.48; N, 10.84. MP = 108−110 °C.

*2-(((2-Hydroxybenzyl)(quinolin-8-yl)amino)methyl)-4-nitrophenol (**2c**).* R_f = 0.82 (95:5 CH_2Cl_2/MeOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.48 (s, 4H; CH_2), 6.80−6.85 (m, 2H; ArH), 6.90 (d, J = 9.1, 1H; ArH), 7.12−7.22 (m, 2H; ArH), 7.47 (d, J = 5.0, 2H; ArH), 7.59 (q, J = 4.1, 2H; ArH), 8.05 (dd, J = 3.2, 8.6, 1H; ArH), 8.17 (d, J = 2.7, 1H; ArH), 8.31 (dd, J = 1.4, 8.6, 1H; ArH), 9.01 (dd, J = 1.4, 4.6, 1H; ArH), 10.46 (brs, 1H; OH), 12.59 (brs, 1H; OH). ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.6 (d), 56.7 (d), 117.1 (s), 117.7 (s), 119.5 (s), 120.9 (q), 121.4 (s), 121.8 (s), 122.2 (q), 124.4 (s), 125.9 (s), 126.8 (s), 127.0 (s), 129.7 (s), 130.1 (q), 130.6 (s), 138.9 (s), 140.0 (q), 141.8 (q), 143.6 (q), 148.3 (s), 156.9 (q), 163.7 (q). IR: ν (cm^{-1}) 1580, 1514, 1486, 1390, 1340, 1281, 1262, 1250, 1233, 1088, 792, 759. LRMS for $C_{23}H_{19}N_3O_4$ (MH^+): 402.82. Anal. Calcd for $C_{23}H_{19}N_3O_4$ (401.41): C, 68.82; H, 4.77; N, 10.47. Found: C, 69.03; H, 4.69; N, 10.50. MP = 184−185 °C.

*2-(((2-Hydroxybenzyl)(2-phenylquinolin-8-yl)amino)methyl)-4-nitrophenol (**2d**).* R_f = 0.82 (95:5 CH_2Cl_2/MeOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.48 (s, 2H; CH_2), 4.51 (s, 2H; CH_2), 6.77−6.85 (m, 3H; ArH), 7.12−7.22 (m, 2H; ArH), 7.46−7.64 (m, 6H; ArH), 7.80 (d, J = 8.7, 1H; ArH), 7.86 (m, 2H; ArH), 8.03 (dd, J = 2.4, 9.0, 1H; ArH), 8.17 (d, J = 2.4, 1H; ArH), 8.32 (d, J = 8.7, 1H; ArH), 10.59 (brs, 2H, OH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 56.6 (d), 57.4 (d), 117.2 (s), 117.7 (s), 119.6 (s), 121.2 (s), 121.7 (s), 122.4 (s), 124.5 (s), 125.7 (s), 126.4 (s), 126.5 (s), 128.5 (s), 128.5 (s), 128.9 (q), 129.2 (s), 129.2 (s), 129.6 (s), 129.7 (s), 130.5 (s), 138.8 (q), 138.9 (q), 140.2 (q), 142.6 (q), 144.1 (q), 156.5 (q), 156.8 (q), 159.8 (q), 163.1 (q). IR: ν (cm^{-1}) 1584, 1515, 1490, 1459, 1342, 1327, 1290, 1246, 1217, 765, 752, 740. LRMS for $C_{29}H_{23}N_3O_4$ (MH^+): 478.88. Anal. Calcd for $C_{29}H_{23}N_3O_4$ (477.52): C, 72.94; H, 4.85; N, 8.80. Found: C, 71.76; H, 4.55; N, 8.67. MP = 175−176 °C.

*2-(((2-Hydroxybenzyl)(2-hydroxyphenyl)amino)methyl)-4-nitrophenol (**2e**).* R_f = 0.54 (95:5 CH_2Cl_2/MeOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.22 (s, 2H; CH_2), 4.36 (s, 2H; CH_2), 6.77 (d, J = 9.0, 1H; ArH), 6.87−6.95 (m, 4H; ArH), 7.03−7.08 (m, 1H; ArH), 7.11 (brs, 3H; OH) 7.20−7.26 (m, 3H; ArH), 8.00 (dd, J = 2.8, 9.0, 1H; ArH), 8.05 (d, J = 2.8, 1H; ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 54.0 (d), 57.9 (d), 116.1 (s), 116.5 (s), 116.9 (s), 120.9 (s), 121.2 (s), 121.6 (q), 121.6 (s), 122.4 (q), 125.7 (s), 126.2 (s), 127.1 (s), 130.3 (s), 131.6 (s), 133.8 (q), 140.5 (q), 151.0 (q), 154.5 (q), 163.4 (q). IR: ν (cm^{-1}) 1587, 1490, 1458, 1334, 1271, 1227, 1173, 1086, 747. LRMS for $C_{20}H_{18}N_2O_5$ (MH^+): 367.72. Anal. Calcd for $C_{20}H_{18}N_2O_5$ (366.37): C, 65.57; H, 4.95; N, 7.65. Found: C, 65.61; H, 4.97; N, 7.50. MP = 158−159 °C.

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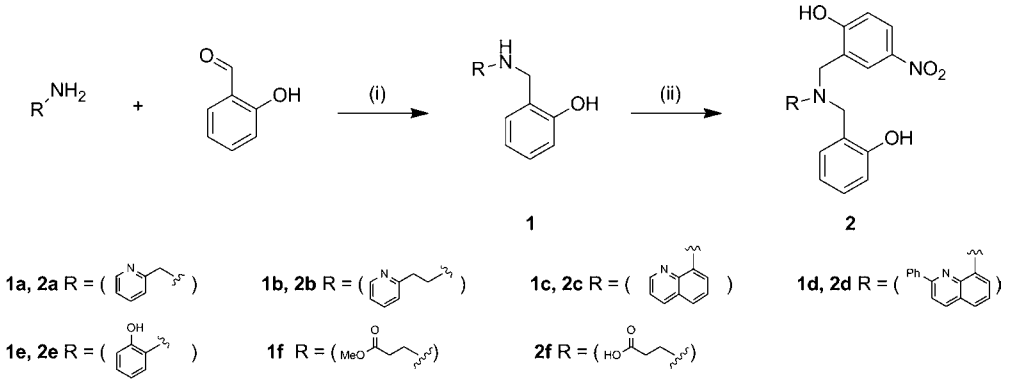
Scheme 1. Synthesis of Tertiary Amine Ligands, 2a−f[a]



[a](i) (a) 2-Hydroxybenzaldehyde, MeOH, RT, 30 min or 6 h or 7days. (b) $NaBH_4$, NaOH, H_2O, RT, 1h (yields **1a** = 68%, **1b** = 72%, **1c** = 83%, **1d** = 89%, **1e** = 87%, **1f** = 84%). (ii) (a) 2-Chloromethyl-4-nitrophenol, $CHCl_3$, triethylamine, reflux, 2 h. (b) **2f** only 6 M HCl, 110 °C, 4 h (yields **2a** = 69%, **2b** = 53%, **2c** = 51%, **2d** = 39%, **2e** = 68%, **2f** = 46%). Isolated yields are after chromatography.

*Methyl 3-((2-Hydroxy-5-nitrobenzyl)(2-hydroxybenzyl)amino)-propanoate (**2f-Me**).* R_f = 0.50 (95:5 CH_2Cl_2/MeOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.73 (t, *J* = 7.4, 2H; CH_2), 3.02 (t, *J* = 7.4, 2H; CH_2), 3.69 (s, 3H; CH_3), 3.85 (s, 2H; CH_2), 3.89 (s, 2H; CH_2), 6.77−6.81 (m, 2H; Ar*H*), 6.88 (t, *J* = 7.4, 1H; Ar*H*), 7.13−7.20 (m, 2H; Ar*H*), 8.00 (d, *J* = 2.3, 1H; Ar*H*), 8.05 (dd, *J* = 2.7, 8.9, 1H; Ar*H*), 8.20 (brs, 2H; O*H*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 31.2 (d), 49.2 (d), 52.1 (t), 55.0 (d), 56.2 (d), 116.0 (s), 116.5 (s), 120.5 (s), 121.0 (q), 121.7 (q), 125.9 (s), 130.0 (s), 131.1 (s), 139.7 (q), 155.4 (s), 157.0 (q), 164.4 (q), 172.3 (q). IR: ν (cm^{-1}) 1593, 1496, 1458, 1336, 1284, 1090, 753. LRMS for $C_{18}H_{20}N_2O_6$ (MH^+): 361.73. Anal. Calcd for $C_{18}H_{20}N_2O_6$ (360.36): C, 59.99; H, 5.59; N, 7.77. Found: C, 59.84; H, 5.53; N, 7.70.

*3-((2-Hydroxy-5-nitrobenzyl)(2-hydroxybenzyl)amino)propanoic Acid (**2f**).* **2f-Me** (0.100 g, 0.417 mmol) in 6 M HCl (2 mL) was refluxed for 4 h at 110 °C. The reaction mixture was diluted with water (200 mL) and washed with CH_2Cl_2 (200 mL). The aqueous layer was separated and neutralized with 1 M NaOH to pH 7, and **2f** was transferred into an organic layer of 9:1 CH_2Cl_2/MeOH (200 mL). The organic layer was separated, filtered, and dried over $MgSO_4$, and the solvent was removed. The pale yellow solid **2f** was dissolved in CH_2Cl_2 and precipitated upon addition of hexane and then filtered (0.047 g, 49%). R_f = 0.36 (90:10 CH_2Cl_2/MeOH). ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.53 (t, *J* = 7.4 Hz, 2H; CH_2), 2.74 (t, *J* = 7.4 Hz, 2H, CH_2), 3.50 (brs, 1H; COO*H*), 3.70 (s, 2H; CH_2), 3.78 (s, 2H; CH_2), 6.77 (m, 2H; Ar*H*), 6.89 (t, *J* = 9.0, 1H; Ar*H*), 7.10 (td, *J* = 1.5, 7.4, 1H; Ar*H*), 7.17 (dd, *J* = 1.5, 7.4, 1H; Ar*H*), 8.03 (dd, *J* = 2.8, 9.0, 1H; Ar*H*), 8.14 (d, *J* = 2.8, 1H; Ar*H*). ^{13}C NMR (125 MHz, DMSO-d_6): δ 31.0 (d), 48.6 (d), 53.2 (d), 53.6 (d), 115.7 (s), 116.2 (q), 119.3 (s), 123.1 (s), 124.7 (q), 125.3 (q), 126.3 (s), 129.0 (s), 130.7 (s), 139.5 (q), 156.8 (s), 164.2 (q), 173.6 (q). IR: ν (cm^{-1}) 1596, 1495, 1460, 1335, 1283, 1089, 752. HRMS calcd for $C_{17}H_{18}N_4O_6$ (MH^+): 347.1238. Found: 347.1228 (ESI+).

*General Procedure for Beryllium Complexes **3a−g**.* All Be^{II} complexes were prepared by adding ligands **2a−g** (30 μmol), $BeSO_4$ (30 μmol, as a 1 M solution in H_2O), and triethylamine (300 μmol) to 1 mL of four different solvents (DMF, DMSO-d_6, MeOH, or D_2O) and mixed at 50 °C for 16 h to aid complexation. Resulting solutions (28 mmol L^{-1}) were cooled to 298 K and analyzed via ^{9}Be NMR spectroscopy. **Caution!** Beryllium salts are extremely toxic and should be handled with appropriate care. All beryllium solid manipulations were handled in a Plas-Laboratories 818 Series, HEPA filtered (0.4 lm prefilter), reversed-pressure glove box. All beryllium solution work was performed in a dedicated HEPA-filtered chemical hood.

Computational Details. Density functional theory (DFT) calculations were carried out using the Gaussian09 package of programs.[25] Becke's three-parameter hybrid exchange correlation function containing the nonlocal gradient correction of Lee, Yang, and Parr (B3LYP)[26] in conjunction with the 6-311G++(2d,p) basis set were used to obtain the optimized geometries. NMR shieldings for beryllium were evaluated at the minima using B3LYP with 6-311G++(2d,p) as the basis set and the GIAO (gauge including atomic orbital) NMR method[27,28] as implemented by Cheeseman et al.[29] in the Gaussian09 package. Complex $Be(H_2O)_4^{2+}$ is the standard reference for ^{9}Be NMR spectroscopy and defined as 0.00 ppm. Structure determination for this complex 6-311++G(2d,p) followed by calculation of the magnetic shielding 6-311++G(2d,p) gave a value of 109.10 ppm. The calculated chemical shift reported in this study is in relation to $Be(H_2O)_4^{2+}$ using the expression $\delta_{complex} = \sigma_{reference} - \sigma_{complex}$. Time-dependent DFT (TD-DFT) calculations were carried out using B3LYP/6-311G++(2d,p) in a *N*,*N*-dimethylformaldehyde (DMF) solvent field using the SCRF-PCM method,[30] which creates the solvent cavity via a set of overlapping spheres. Geometry optimizations were not carried out in a solvent field as this displayed little increase in NMR accuracy despite the significant increase in computational expense. However, TD-DFT calculations were found to be more accurate with solvent contributions included than without.[31,32]

RESULTS AND DISCUSSION

Synthesis. The secondary amines **1a−f** were synthesized in 68−89% yields by a Schiff base condensation between the appropriate amine and 2-hydroxybenzaldehyde in methanol followed by an in situ reduction with sodium borohydride, sodium hydroxide, and water (Scheme 1i).[33] Condensations for the alkyl-linked **1a**, **1b**, and **1f** required 30 min stirring at RT, while the aryl-linked **1e** required 6 h, and **1c−d** were stirred at RT for 7 days. The secondary amines **1a**,[34] **1b**,[35] **1c**,[36] and **1e**[37] are known compounds, and characterization data agreed with the literature, while **1d** and **1f** had not been previously reported and were therefore fully characterized. The final tertiary amines **2a−f** were synthesized in 39−69% yields by refluxing the appropriate secondary amine **1a−f**, 2-chloromethyl-4-nitrophenol, and triethylamine in chloroform for 2 h (Scheme 1(ii)(a)), the carboxylic acid on **1f** was isolated by heating the methyl ester in hydrochloric acid (Scheme 1(ii)(b)). We chose the substituted 2-chloromethyl-4-nitrophenol as it was commercially available which meant tertiary amines **2a−f** were all new compounds (owing to the nitro substituent) and hence fully characterized; several structurally analogous ligands are known which do not have this nitro substituent.[38−40] In addition to the six new ligands **2a−f**, 2-(bis(2-hydroxy-3,5-dimethylbenzyl)amino)acetic acid, **2g**, was synthesized via a one-pot Mannich reaction[41] which had a structurally analogous donor set to **2f** with the exception that one of the donor arms

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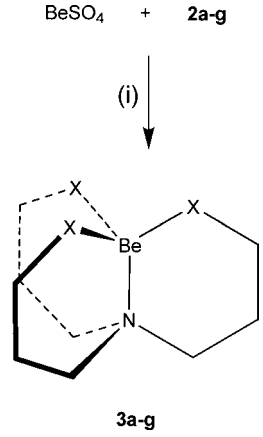
on **2g** had a methyl-linked carboxylic acid rather than the analogous ethyl-linked carboxylic acid of **2f**.

Be^{II} complexes were prepared according to Scheme 2. To avoid potential exposure to hazardous beryllium solids the resulting complexes **3a−g** were left in solution and not isolated. Instead, ^{9}Be NMR spectra of the reaction mixtures were directly recorded, and the results are summarized in Table 1.

Scheme 2. Generalized Structure for the Be^{II} Tetracoordinate Complexes 3a−g[a]



[a](i) 1 M $BeSO_{4(aq)}$, triethylamine, 50 °C, 16 h.

Table 1. ^{9}Be NMR Shifts and Line Widths of Be^{II} Chelated to 3a−g

	^{9}Be NMR shift, ppm (line width, Hz)			
Be^{II} complex	DMF	DMSO-d_6	MeOH	D_2O
3a	4.51 (67)	no complex	4.18 (188)	insoluble
3b	2.77 (62)	3.18 (123)	2.94 (150)	insoluble
3c	5.15 (89)	no complex	no complex	insoluble
3d	no complex	no complex	no complex	insoluble
3e	4.40 (59)	5.10 (106)	5.28 (159)	Insoluble
3f	not measured	2.11 (174)	2.33 (151)	2.60 (175)
3g	4.06 (66)	4.64 (130)	insoluble	5.15 (104)

With the exception of **3d**, all reactions showed new ^{9}Be NMR shifts within the range expected for a four-coordinate Be^{II} complex (e.g., Figure 1).[22] The phenyl substituent at the 2-position on the quinoline of **2d** coupled with poor solubility likely hindered chelation to Be^{II}. Use of several different solvents allowed the ^{9}Be NMR shifts and line widths (width at 1/2 heights) to be measured despite the variable solubility of this series of ligands and their corresponding Be^{II} complexes; unfortunately, no single solvent could be used to directly compare all ^{9}Be NMR shifts. Control reactions in the absence of all ligands gave ^{9}Be NMR shifts centered around 0 ppm (as expected), suggesting ligand chelation rather than simple Be^{II} speciation with the solvent or triethylamine was the cause of the shifts. The line width is related to the symmetry of a complex, and for highly symmetrical four-coordinate species, line widths of less than 50 Hz have been observed.[22] Typical line widths are generally greater than this, especially when beryllium is coordinated to form unsymmetrical four-coordinate species, such as those reported by Niemeyer and Power.[42] Ligands **3a−g** each provide four different donor arms and are therefore expected to exhibit broad line widths, yet given the method of sample preparation (nonisolated products) the potential existence of fluxional minor Be^{II} products contributing (at least partially) to the line width broadening cannot be excluded. Evidence for tetracoordinate chelation to Be^{II} was therefore further investigated via computational methods.

^{9}Be NMR Computational. Structures of the six potential Be^{II} complexes **3a−c** and **3e−g** (**3d** was excluded from further study) were computationally optimized and their ^{9}Be NMR shifts calculated (Table 2). Complexes **3a−c** contained two ionizable donor atoms and were optimized as neutral Be^{II} species, while **3e−g** contained three ionizable donor atoms and were optimized as anionic Be^{II} species. It was possible to optimize two different conformers which were very close in energy for the complexes for **3a**, **3c**, **3e**, and **3g**, as all contained one five-membered chelate which "lock" these conformations. The conformers will be herein be designated "syn" and "anti" conformers according to the orientation of aligned aromatic rings and equatorial protons on the CH_2 directly adjacent the central amine upon Be^{II} chelation; an example is given for **3g** in Figure 2. The syn and anti conformer for **3a**, **3c**, **3e**, and **3g** typically differed in energy by 10 kJ mol^{-1} or less. These energy differences are equivalent to the torsional energy barrier in simple bond rotations, which suggest that upon coordination to Be^{II} both conformations exist in solution. Complexes **3b** and **3f** only had six-membered chelates within their structures, and this lead to only one possible minimized structure. For simplicity, enanantiomers brought about by having four different donor groups around the Be^{II} core in all complexes (except **3g**) were not considered as they would given energetically identical models. As shown in Table 1, the experimental shift data shows some variation when measured in different solvents; therefore, for convenience, the closest experimental ^{9}Be NMR shift value (regardless of solvent) was chosen for comparison with the gas-phase-calculated values of the modeled complexes. It has recently been shown that DFT NMR calculations tend to overestimate the experimental ^{9}Be values by approximately 10%, and it may be possible to obtain more accurate values from using the CCSD(T) level of theory.[43]

The calculated ^{9}Be NMR shifts for the beryllium complexes with ligands **2b**, **2e**, **2f**, and **2g** correlated reasonably well with the experimental shifts, providing good evidence that the expected four-coordinate species formed in solution. A $\Delta\delta$ of approximately 0.5 ppm or less is considered an acceptable deviation for these types of calculations.[22] These four ligands all offered one tertiary amine donor and two phenol groups, and each differed by one donor group (Figure 3). Be^{II} coordinated

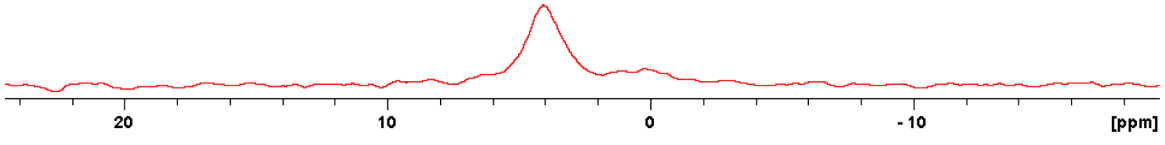


Figure 1. ^{9}Be NMR shift of **3g** coordinated to beryllium in DMF.

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Table 2. Calculated ^{9}Be NMR Shifts for Tetracoordinate Ligands[a]

complex	δ_{ref}	$\delta_{model[a]}$	$\delta_{(ref-model)}$	δ_{exptl}	$\lvert\Delta_{exptl-calcd}\rvert$
$Be(H_2O)_4^{2+}$	109.10	109.10	0.00	0.00	0.00
3a-syn		102.89	6.21	4.51 (DMF)	1.70
3a-anti		103.12	5.98		1.47
3b		105.19	3.91	3.18 (DMSO-d_6)	0.73
3c-syn		102.65	6.45	5.15 (DMF)	1.30
3c-anti		102.81	6.29		1.14
3e-syn		103.28	5.82	5.28 (MeOH)	0.54
3e-anti		103.57	5.53		0.25
3f		106.63	2.47	2.60 (D_2O)	0.13
3g-syn		103.92	5.18	5.15 (D_2O)	0.03
3g-anti		103.97	5.13		0.02

[a]Gas-phase model utilized as inclusion of solvent models had negligible influence on the ^{9}Be shielding tensors.

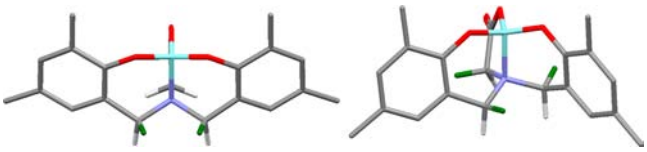

Figure 2. Geometry-optimized syn conformer (left) and anti conformer (right) of **3g**. Be^{II} is light blue, O is red, N is blue, and C is gray. Equatorial protons are shown in green for clarity.

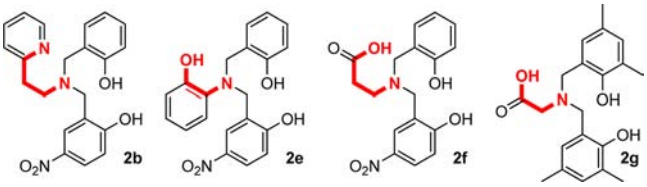

Figure 3. Tetracoordinate ligands with well-correlated ^{9}Be NMR shifts upon Be^{II} coordination.

to the central amine and the two phenols would form two unstrained six-membered chelate rings. The remaining arm on **2e**, **2f**, and **2g** offered a strongly coordinating oxygen donor. Once fully enveloped around beryllium, ligands **2e** and **2g** would generate an additional five-membered chelate ring and **2f** a third six-membered chelate ring (red outline, Figure 3). Ligand **2b** with a weaker coordinating nitrogen donor would also give an unstrained six-membered chelate ring upon coordination to Be^{II}.

The calculated ^{9}Be NMR shifts for the beryllium complexes of **2a** and **2c** did not correlate as well with the experimental shifts. This suggested full encapsulation via tetradentate chelation was perhaps not occurring. In both ligands, the fourth donor in both cases is neutral, weakly coordinating nitrogen atoms which if coordinated would form a strained five-membered chelate ring (Figure 4). Combination of both of these factors appears to not favor tetradentate coordination.

In an effort to explore this further, the syn and anti conformations of the beryllium complex [Be^{II}(**2a**)(DMF)] were optimized containing a DMF molecule in place of the pyridine arm (Figure 5). The calculated ^{9}Be NMR shift values for each of these conformers were 3.30 ($\Delta_{exptl-calcd}$ = 1.21 ppm) and 3.40 ppm ($\Delta_{exptl-calcd}$ = 1.11 ppm), respectively. Both values are in better agreement to the experimental ^{9}Be NMR shift obtained in DMF (4.51 ppm) than those obtained for the two conformers of the modeled tetracoordinated species, namely, 6.21 (Δ 1.70) and 5.98 ppm (Δ 1.47), respectively, thus providing evidence that tetrachelation of beryllium by all four

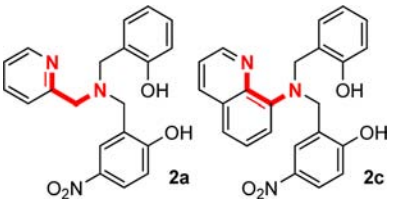

Figure 4. Tetracoordinate ligands with poorly correlating calculated vs experimental ^{9}Be NMR shifts.

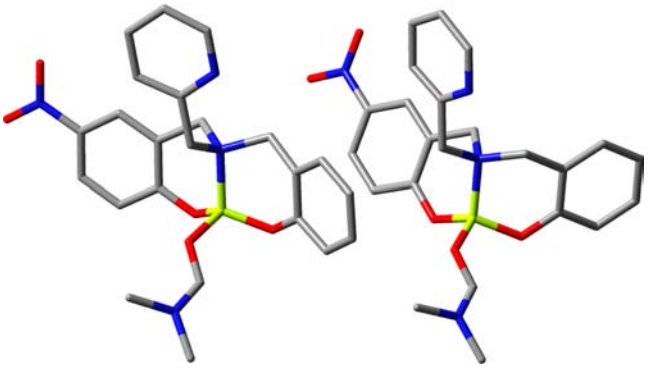

Figure 5. Optimized models of the syn (left) and anti (right) [Be(**2a**)(DMF)] complexes. Be^{II} is yellow, O is red, N is blue. and C is gray. Hydrogen atoms have been removed for clarity.

donor atoms of the ligand is unlikely. NMR calculations were also performed on similar beryllium-coordinated DMF adducts of the syn and anti conformers of the quinoline ligand **2c**, again showing an improvement in accuracy between the modeled and experimental NMR values (syn calculated = 4.01 ppm (Δ 1.14) and anti calculated = 4.98 ppm (Δ 0.17)). A two-coordinate beryllium complex of [Be^{II}(**2a**)$(DMF)_2$] with the beryllium bound as a bischelate through both phenolate groups of the ligand and with two coordinated DMF solvent molecules was also tested (syn conformer), but the resulting high $\Delta_{exptl-calcd}$ value of 3.28 ppm indicated that this species was not likely to be present. Other untested possibilities for the observed ^{9}Be NMR shift present in solution may include polymeric or μ-hydroxy cluster complexes,[44−47] for example, the $Be_3(OH)_3$ core is well known.[48−52]

Electronic Spectroscopy. Electronic spectra of Be^{II} complexes (**3b**, **3e**, **3f**, and **3g**) were recorded by making an appropriate dilution to the DMF-solvated reaction mixtures so as to avoid manipulation of beryllium-containing solid samples. Spectra of the associated ligands (**2b**, **2e**, **2f**, and **2g**) were

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recorded by preparing "blank" reaction mixtures, i.e., in the absence of $BeSO_{4(aq)}$ and making the appropriate dilution. The strongest transitions are summarized in Table 3, and the first 5

Table 3. Electronic Absorption Data for Ligands and Their Associated Be^{II} Chelates in DMF

	experimental				experimental		
ligand	$c/10^{-5}$ M L^{-1}	λ/ nm	ε/L M $^{-1}$ cm^{-1}	Be^{II} complex	$c/10^{-5}$ M L^{-1}	λ/ nm	ε/L M $^{-1}$ cm^{-1}
2b	5.28	428	9600	**3b**	5.28	367	14 700
2e	5.96	418	24 500	**3e**	5.96	385	15 400
2f	5.78	390	8800	**3f**	5.78	351	12 000
2g	5.83	289	4000	**3g**	5.83	302	6200

calculated transitions with nonzero oscillator strengths can be found in the Supporting Information (Tables S1.1−S1.4). The similarity between the measured calculated electronic spectra (Figure S1.1, Supporting Information) further supports the proposed computational models for **3b**, **3e**, **3f**, and **3g**.

From the TD-DFT calculations, the strongest transitions of **2b**, **2e**, and **2f** were assigned as being $\pi \rightarrow \pi^*$ localized on the nitrated phenol. Upon coordination this transition is blue shifted from 33 (**3e**) to 61 nm (**3b**), which is explained by changes in the electron density of the now inhibited resonance delocalized form of the 4-nitrophenolate group upon coordination to the Be^{II} cation (Figure 6).

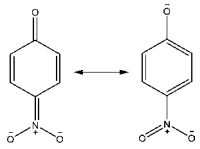

Figure 6. Reasonance structures of 4-nitrophenolate.

Ligand **2g**, with only methyl groups substituted on the phenol rings, acts as a more strongly electron-donating ligand. As a result, upon coordination to Be^{II} to form **3g**, the $\pi \rightarrow \pi^*$ transition is red shifted by 13 nm due to the electron-withdrawing effect of the Be^{II} cation.

Fluorescence Spectroscopy. The fluorescence spectra of the Be^{II} complexes (**3b**, **3e**, **3f**, and **3g**) were recorded by making the appropriate dilution to the DMF-solvated reaction mixtures. Spectra of the associated ligands (**2b**, **2e**, **2f**, and **2g**) were also recorded by preparing "blank" reaction mixtures containing no $BeSO_{4(aq)}$ and making the appropriate dilution. The ligands did not exhibit appreciable fluorescence; see, for example a comparison of ligand **2g** with the beryllium-coordinated complex analogue **3g** (Figure 7). Upon coordination of Be^{II}, two of the complexes, **3e** and **3g**, displayed fluorescence emission (at 425 and 335 nm respectively); however, no fluorescence was detected for **3b** and **3f**. This is consistent with the fact that **3b** and **3f** can only form the anticonformer, whereas **3e** and **3g** are capable of forming either syn or anti confomers. We propose that when either **3e** or **3g** is locked in the syn conformer that two of the phenols of each complex are rigidly held in a plane, allowing electron density to be distributed by an extended π system across both of these phenol rings and Be^{II} (Figure S1.2, Supporting Information).

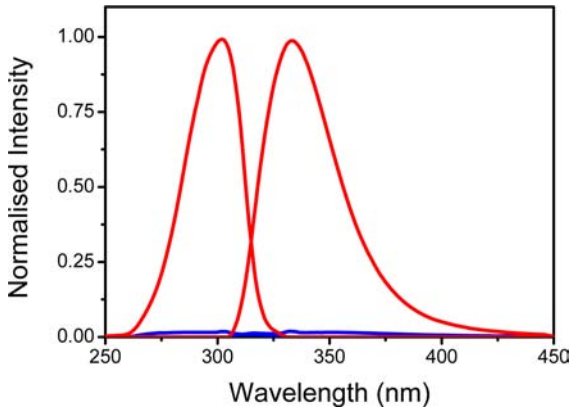

Figure 7. Normalized absorption and emission spectra at 10^{-5} M of ligand **2g** (blue) and Be^{II} complex **3g** (red) in DMF and triethylamine.

CONCLUSIONS

Studies in experimental Be^{II} coordination chemistry have waned in the past decade, largely due to the associated toxicity of the element. We have shown that it is possible to explore the coordination chemistry of this element without isolation of the resulting complexes. As the greatest hazard when working with beryllium is inhalation of the particulate matter, this method minimizes the risk associated with this hazard by decreasing the amount of exposure to beryllium-containing solids. To this end, we studied a series of tetracoordinate Be^{II} complexes and gained valuable insight into the coordination of these complexes through spectroscopic assessment, complimented with computational modeling. Several of the complexes studied gave rise to unexpected fluorescence, which may give rise to applications as Be^{II} detectors.

ASSOCIATED CONTENT

Supporting Information

Tables containing a summary of the first five transitions calculated for the cationic complexes **3b**, **3e-syn**, **3f**, and **3g-syn**. Figures of the calculated and measured ultraviolet spectra for **3b** and the molecular orbitals associated with the main transition for **3g-syn** obtained from theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) *Toxicological profile for beryllium*; Agency toxic Substances Disease Registry: 1993; 153.

(2) Puchta, R. *Nat. Chem.* **2011**, *3*, 416.
(3) Taylor, T. P.; Ding, M.; Ehler, D. S.; Foreman, T. M.; Kaszuba, J. P.; Sauer, N. N. *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* **2003**, *A38*, 439−469.
(4) McCleskey, T. M.; Buchner, V.; Field, R. W.; Scott, B. L. *Rev. Environ. Health* **2009**, *24*, 75−115.
(5) Eisenbud, M. *Appl. Occup. Environ. Hyg.* **1998**, *13*, 25−31.
(6) Reeves, A. L. *Handb. Met.-Ligand Interact. Biol. Fluids: Bioinorg. Med.* **1995**, *2*, 772−9.
(7) Saltini, C.; Amicosante, M.; Franchi, A.; Lombardi, G.; Richeldi, L. *Eur. Respir. J.* **1998**, *12*, 1463−1475.
(8) Wang, Y.; Dai, S. *Immunol. Res.* **2013**, *55*, 83−90.
(9) Strupp, C. *Ann. Occup. Hyg.* **2011**, *55*, 43−56.
(10) Strupp, C. *Ann. Occup. Hyg.* **2011**, *55*, 30−42.
(11) Strupp, C. *Ann. Occup. Hyg.* **2011**, *55*, 558−559.
(12) Stefaniak, A. B. *Ann. Occup. Hyg.* **2011**, *55*, 556−557.
(13) Boffetta, P.; Fryzek, J. P.; Mandel, J. S. *Crit. Rev. Toxicol.* **2012**, *42*, 107−118.
(14) Stefaniak, A. B.; Virji, M. A.; Day, G. A. *Arch. Environ. Occup. Health* **2012**, *67*, 219−228.
(15) Schuler, C. R.; Virji, M. A.; Deubner, D. C.; Stanton, M. L.; Stefaniak, A. B.; Day, G. A.; Park, J. Y.; Kent, M. S.; Sparks, R.; Kreiss, K. *Scand. J. Work, Environ. Health* **2012**, *38*, 270−281.
(16) Plieger, P. G.; Ehler, D. S.; Duran, B. L.; Taylor, T. P.; John, K. D.; Keizer, T. S.; McCleskey, T. M.; Burrell, A. K.; Kampf, J. W.; Haase, T.; Rasmussen, P. G.; Karr, J. *Inorg. Chem.* **2005**, *44*, 5761−5769.
(17) Plieger, P. G.; John, K. D.; Burrell, A. K. *Polyhedron* **2007**, *26*, 472−478.
(18) Minogue, E. M.; Ehler, D. S.; Burrell, A. K.; McCleskey, T. M.; Taylor, T. P. *ASTM Spec. Tech. Publ.* **2006**, *STP 1473*, 92−101.
(19) Diyabalanage, H. V. K.; Ganguly, K.; Ehler, D. S.; Collis, G. E.; Scott, B. L.; Chaudhary, A.; Burrell, A. K.; McCleskey, T. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7332−7334.
(20) McCleskey, T. M.; Ehler, D. S.; Keizer, T. S.; Asthagiri, D. N.; Pratt, L. R.; Michalczyk, R.; Scott, B. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 2669−2671.
(21) Scott, B. L.; McCleskey, T. M.; Chaudhary, A.; Hong-Geller, E.; Gnanakaran, S. *Chem. Commun.* **2008**, 2837−2847.
(22) Plieger, P. G.; John, K. D.; Keizer, T. S.; McCleskey, T. M.; Burrell, A. K.; Martin, R. L. *J. Am. Chem. Soc.* **2004**, *126*, 14651−14658.
(23) Chinea, E.; Dominguez, S.; Mederos, A.; Brito, F.; Arrieta, J. M.; Sanchez, A.; Germain, G. *Inorg. Chem.* **1995**, *34*, 1579−87.
(24) Collis, G. E.; Burrell, A. K.; John, K. D.; Plieger, P. G. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2003**, *C59*, o443−o444.
(25) R. A.; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision A.1*; Gaussian, Inc.: Wallingford, CT, 2009.
(26) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter* **1988**, *37*, 785−9.
(27) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789−807.
(28) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251−60.
(29) Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996**, *104*, 5497−509.
(30) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999−3093.
(31) Charlot, M.-F.; Aukauloo, A. *J. Phys. Chem. A* **2007**, *111*, 11661−11672.
(32) Vlcek, A., Jr.; Zalis, S. *J. Phys. Chem. A* **2005**, *109*, 2991−2992.
(33) Tandon, S. S.; Chander, S.; Thompson, L. K.; Bridson, J. N.; McKee, V. *Inorg. Chim. Acta* **1994**, *219*, 55−65.
(34) Biswas, S.; Mitra, K.; Chattopadhyay, S. K.; Adhikary, B.; Lucas, C. R. *Transition Met. Chem.* **2005**, *30*, 393−398.
(35) Yajima, T.; Shimazaki, Y.; Ishigami, N.; Odani, A.; Yamauchi, O. *Inorg. Chim. Acta* **2002**, *337*, 193−202.
(36) Usatyuk, V. G.; Yalchin, B.; Aydin, A.; Medzhidov, A. A. *Azerb. Khim. Zh.* **2004**, 129−136.
(37) Abreu, A.; Jesus, A. S.; Beltran, H. I.; Santillan, R.; Farfan, N. *J. Organomet. Chem.* **2006**, *691*, 337−348.
(38) Mukherjee, A.; Lloret, F.; Mukherjee, R. *Inorg. Chem.* **2008**, *47*, 4471−4480.
(39) Philibert, A.; Thomas, F.; Philouze, C.; Hamman, S.; Saint-Aman, E.; Pierre, J.-L. *Chem.—Eur. J.* **2003**, *9*, 3803−3812.
(40) Whitelaw, E. L.; Jones, M. D.; Mahon, M. F.; Kociok-Kohn, G. *Dalton Trans.* **2009**, 9020−9025.
(41) Short, J. H.; Ours, C. W. *J. Heterocycl. Chem.* **1975**, *12*, 869−76.
(42) Niemeyer, M.; Power, P. P. *Inorg. Chem.* **1997**, *36*, 4688−4696.
(43) Kraus, F.; Baer, S. A.; Buchner, M. R.; Karttunen, A. J. *Chem.—Eur. J.* **2012**, *18*, 2131−2142.
(44) Alderighi, L.; Gans, P.; Midollini, S.; Vacca, A. *Adv. Inorg. Chem.* **2000**, *50*, 109−172.
(45) Mederos, A.; Dominguez, S.; Chinea, E.; Brito, F.; Midollini, S.; Vacca, A. *Bol. Soc. Chil. Quim.* **1997**, *42*, 281−295.
(46) Wong, C. Y.; Woolins, J. D. *Coord. Chem. Rev.* **1994**, *130*, 243−73.
(47) Puchta, R.; Neumueller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2011**, *637*, 67−74.
(48) Faure, R.; Bertin, F.; Loiseleur, H.; Thomas-David, G. *Acta Crystallogr., Sect. B* **1974**, *30*, 462−7.
(49) Puchta, R.; Neumuller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2009**, *635*, 1196−1199.
(50) Carell, B.; Olin, A. *Acta Chem. Scand.* **1961**, *15*, 1875−84.
(51) Kakihana, H.; Sillen, L. G. *Acta Chem. Scand.* **1956**, *10*, 985−1005.
(52) Ohtaki, H. *Inorg. Chem.* **1967**, *6*, 808−13.