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Hg(II) and Cd(II) complexes with mixed donor macrocyclic thioethers: The oxophobicity of mercury(II)

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ABSTRACT

A series of Hg(II) and Cd(II) homoleptic complexes with mixed donor (O,S and N,S) macrocycles is reported. The macrocyclic oxa thiacrowns 9S2O (1-oxa-4,7-dithiacyclononane) and 18S4O2 (1,10-dioxa-4,7,13,16-tetrathiacyclooctadecane) bind to Hg(II) to form distorted tetrahedral S4 geometries without coordination of the oxygen atoms. In contrast, the two macrocycles coordinate to Cd(II) through all ligand donors to form S4O2 environments. We also report the structure of bis(9N2S (1,4-diaza-7-thiacyclononane))cadmium(II), $[Cd(9N2S)_2]^{2+}$ which shows octahedral coordination in a *trans* N4S2 environment. Furthermore, two new homoleptic Cd(II) complexes with the related hexadentate macrocycles 18N6 (1,4,7,10,13,16-hexaazacyclooctadecane) and 18S6 (1,4,7,10,13,16-hexathiaycloоctadecane) are described. Among the Cd(II) complexes, we highlight a trend in ^{113}Cd NMR that shows progressive upfield chemical shifts as secondary amine donors replace thioether S donors.

1. Introduction

The coordination chemistry of mercury and cadmium has received considerable attention, in part due to concerns regarding their impact on the environment and on health [1,2]. Complexes of mercury(II) and cadmium(II) with macrocyclic ligands have been used in two key roles – for the detection of heavy metals and also for their removal. For example, Baumann and co-workers reported a pentathiacrown system appended to a polystyrene resin that resulted in the removal of Hg(II) in aqueous systems [3,4]. Prodi, Savage, and co-workers have used a modified 18N2O4 macrocycle (1,10-diaza-4,7,13,16-tetraoxacyclooctadecane) for the detection of both Cd(II) and Hg(II) by fluorescence [5]. Our research group has been interested in the development of correlations between the coordination sphere environment surrounding the heavy metal and ^{199}Hg NMR and ^{113}Cd NMR chemical shifts [6,7]. In that regard, we have published two recent reports which deal largely with homoleptic thiacrown complexes of mercury(II) and cadmium(II), and we observed definite relationships between the heavy metal NMR chemical shift and the complex structure. Our hope is that such structure-spectroscopic correlations will assist in the further development of remediation and detection agents for these insidious metal ions. We feel that accumulation of additional ^{199}Hg and ^{113}Cd shift data will prove beneficial in the continued development of heavy metal NMR spectroscopy as a structural probe for the study of their complexes [8–10].

We now wish to extend this coordination chemistry to include mixed donor azathia and oxathia macrocyclic complexes containing two heavy metal ions and to examine their NMR properties. The ligands examined in this report are shown in Scheme 1. Several reviews of heavy metal complexes with mixed N,S and O,S donor macrocyclic systems have appeared [11,12]. There are additional reports describing a series of Cd(II) complexes with four coordinate aza-thioether macrocycles [13], the bis 9N2S (1-thia-4,7-diazacyclononane) Hg(II) complex [14], and both the Hg(II) and Cd(II) homoleptic complexes of the macrocycle 18S4N2 (1,10-diaza-4,7,13,16-tetrathiacyclooctadecane) [7,15]. Furthermore, several other studies which use modified azathia macrocycles as chemosensors for mercury(II) and cadmium(II) have appeared. The detection of the heavy metal ion is based upon fluorescence [16–18], emission [19], or absorption [20] properties of the complex. We report here the synthesis and characterization of several new homoleptic complexes of Hg(II) and Cd(II) with mixed donor N,S and O,S macrocycles including 9S2O (1-oxa-4,7-dithiacyclononane), 18S4O2 (1,10-dioxa-4,7,13,16-tetrathiacyclooctadecane), and 9N2S.

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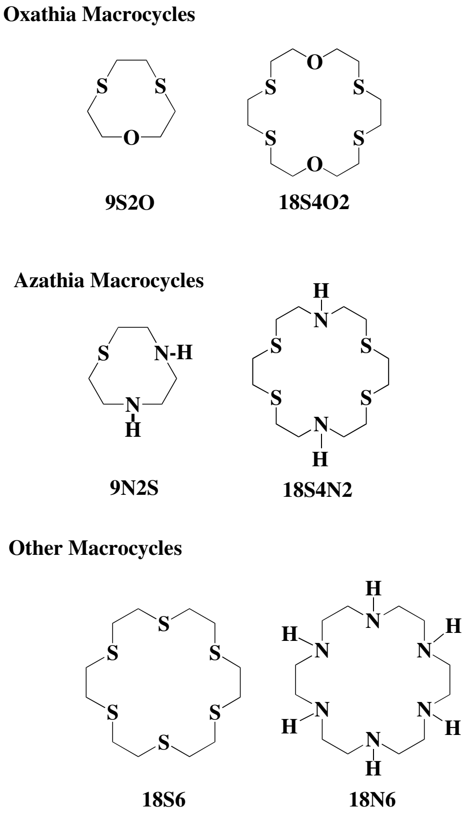

Scheme 1. Macrocyclic ligands discussed in this report.

2. Experimental

2.1. Materials and measurements

The ligands 9S2O, 18S4O2, and 9N2S were prepared by their respective literature methods [21–24]. All other reagents and solvents were purchased commercially and used as received. An aqueous solution containing 45% by weight of $Cd(BF_4)_2$ was used as the source of that reagent in aqueous syntheses. *Caution!!! Although the perchlorate salts prepared in this report do not appear to be shock-sensitive, they should be handled with caution and only in very small quantities*. Mercury and cadmium are toxic metals, and their compounds should be handled accordingly.

Elemental analyses were performed by Atlantic Microlab, Inc., of Atlanta, Georgia. Fourier Transform Infrared spectra were obtained on a Nicolet FT-IR using dry pre-weighed KBr powder and an ATR accessory. All $^{13}C\{^1H\}$ and ^1H NMR spectra were recorded on a JEOL ECX-400 NMR spectrometer using either the residual deuterated organic solvent (CD_3NO_2, CD_3CN, etc.) peaks for the internal reference or an internal reference of d-6-acetone for $^{13}C\{^1H\}$ NMR spectra obtained in D_2O. The $^{113}Cd\{^1H\}$ NMR spectra were collected at 25 °C and 88.66726 MHz using a 75° pulse, a 0.5 s acquisition time, and a relaxation delay time of 5.0 s. Referencing was done using a 0.10 M solution of $Cd(ClO_4)_2$ in D_2O at 0 ppm. The $^{113}Cd\{^1H\}$ NMR spectra were collected until a minimum signal/noise ratio of 20/1 was obtained. Data collection on one sample typically required 10 000–12 000 transients and took 24–30 h to complete.

2.2. Complexes with oxathiacrown ligands

2.2.1. Synthesis of $[Hg(9S2O)_2](ClO_4)_2$

A solution containing 107 mg of $Hg(ClO_4)_2 \cdot 3H_2O$ (0.236 mmol) and 10 drops of acetic anhydride in 10 mL of CH_3NO_2 was added dropwise to a solution containing a mass of 76.9 mg of 9S2O (0.468 mmol) in 5 mL of CH_3NO_2 and cooled at 0°C for about 15 min. A volume of 40 mL of diethyl ether was added dropwise to the cold solution which was left at 0° overnight. White crystals of $[Hg(9S2O)_2](ClO_4)_2$ had formed which were filtered, washed with diethyl ether (3 × 15 mL) to yield 126 mg of product (73.9%). *Anal.* calc. for $C_{12}H_{24}Cl_2HgO_{10}S_4$: C, 19.80; H, 3.32; S, 17.62; Cl, 9.74. Found: C, 19.63; H, 3.27; S, 17.34, Cl, 9.73%. FT-IR (cm^{-1}): 2991 (C–H), 2939 (C–H), 2904(C–H), 2866 (C–H), 1628, 1543, 1469, 1409, 1297, 1111–1081 s, (ClO_4^-), 904, 813, 624, 409. ^1H NMR (CD_3NO_2) δ (ppm): complex AA′BB′ symmetrical pattern at 4.09–4.01 (4H) and 3.86–3.78 (4H) (–O–C*H*$_2$–CH$_2$–S–); broad, overlapping multiplets at 3.49–3.26 (16H, –O–CH$_2$–C*H*$_2$–S– and –S–C*H*$_2$–C*H*$_2$–S–). $^{13}C\{^1H\}$ NMR (CD_3CN) δ (ppm): 62.11 (4C, –O–CH$_2$–CH$_2$–S–), 32.94 (4C, –O–CH$_2$-*C*H$_2$–S–), 29.87 (–S-(*C*H$_2$)$_2$–S–). No ^{199}Hg NMR signal in CD_3NO_2 was observed after 12 000 transients. Slow evaporation of a nitromethane solution produced large rods suitable for single crystal X-ray analysis.

2.2.2. Synthesis of $[Hg(18S4O2)](ClO_4)_2$

A mixture containing 88.8 mg of $Hg(ClO_4)_2 \cdot 3H_2O$ (0.196 mmol), 10 drops of acetic anhydride, and 57.5 mg of 18S4O2 (0.175 mmol) in 15 mL of CH_3NO_2 was refluxed for 1.5 h. After cooling in an ice bath, 20 mL of diethyl ether was slowly added to precipitate a white crystalline solid. The solid was isolated by filtration and washed with diethyl ether (3 × 15 mL) to yield 57.7 mg (45.3%) of $[Hg(18S4O2)](ClO_4)_2$. *Anal.* calc. for $C_{12}H_{24}Cl_2HgO_{10}S_4$: C, 19.80; H, 3.32; S, 17.62; Cl, 9.74. Found: C, 19.78; H, 3.29; S, 17.40; Cl, 9.59%. FT-IR (cm^{-1}): 2987 (C–H), 2939 (C–H), 2870 (C–H), 2793 (C–H), 1559, 1464, 1409, 1357, 1271, 1111–1081 s, (ClO_4^-), 1020, 913, 775, 693, 624. ^1H NMR (CD_3CN) δ (ppm): sharp multiplet at 3.73 (8H, –O–C*H*$_2$–CH$_2$–S–), broad mutliplet at 3.33–3.05 (16H, –O–CH$_2$–C*H*$_2$–S– and –S–C*H*$_2$–C*H*$_2$–S–). $^{13}C\{^1H\}$ NMR (CD_3CN) δ (ppm): 66.21 (4C, –O–*C*H$_2$–CH$_2$–S–), 34.24 (4C, –O–CH$_2$-*C*H$_2$–S–), 31.76 (4C, –S-(*C*H$_2$)$_2$–S–). No ^{199}Hg NMR signal in CD_3CN was observed after 40 000 transients. Two consecutive crystallizations using diethyl ether diffusion into acetonitrile resulted in X-ray quality colorless prisms.

2.2.3. Synthesis of $[Cd(9S2O)_2](ClO_4)_2$ and $[Cd(18S4O2)](ClO_4)_2$

The two known Cd(II) complexes $[Cd(9S2O)_2](ClO_4)_2$ and $[Cd(18S4O2)](ClO_4)_2$ were prepared by the published methods [25]. Verification of complex formation was accomplished by ^1H and $^{13}C\{^1H\}$ NMR spectra which matched the prior results.

For $[Cd(9S2O)_2](ClO_4)_2$: ^1H NMR (CD_3NO_2), δ (ppm): multiplet at 3.99 (8H, –OC*H*$_2$–CH$_2$S–), singlet at 3.29 (8H, –SC*H*$_2$–C*H*$_2$S–), multiplet at 3.24 (8H, –OCH$_2$–C*H*$_2$S–). $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ (ppm): 63.91, 31.37, 29.52. Data collection for the $^{113}Cd\{^1H\}$ NMR spectrum of the complex was attempted, but no ^{13}Cd NMR peak was observed. Data collection on one sample typically required 10 000–12 000 transients and 24–30 h to complete. Colorless plates of the complex, suitable for X-ray diffraction studies, were obtained from diethyl ether diffusion into a nitromethane solution.

For $[Cd(18S4O2)](ClO_4)_2$: ^1H NMR (CD_3NO_2), δ (ppm): multiplets at 3.97 (8H, –OC*H*$_2$–CH$_2$S–), 3.41 (8H, –OCH$_2$–C*H*$_2$S–), 3.28 (8H, –SC*H*$_2$–C*H*$_2$S–). $^{13}C\{^1H\}$ NMR (CD_3NO_2) δ (ppm): 66.89, 32.79, 31.28. The $^{113}Cd\{^1H\}$ NMR spectra were collected, but again no ^{113}Cd NMR peak for the complex was observed. Data collection on one sample typically required 10 000–12 000 transients and 24–30 h to complete. Colorless plates of the complex were obtained from diethyl ether diffusion into a nitromethane solution.

2.3. Complexes with azathiacrown ligands

2.3.1. Synthesis of $[Cd(9N2S)_2](ClO_4)_2$

A solution containing 91.0 mg of $Cd(ClO_4)_2 \cdot 6H_2O$ (0.217 mmol) dissolved in 10 mL of MeOH was slowly added to a stirred solution