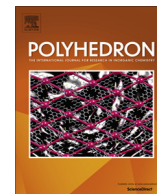




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Correlation of solid state and solution coordination numbers with infrared spectroscopy in five-, six-, and eight-coordinate transition metal complexes of DOTAM

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ABSTRACT

Three new DOTAM (1,4,7,10-tetrakis(acetamido)-1,4,7,10-tetraazacyclododecane) complexes have been synthesized and characterized by X-ray crystallography: $[\text{Co}(\text{DOTAM})]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$, $[\text{Ni}(\text{DOTAM})]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, and $[\text{Cu}(\text{DOTAM})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$. Solid state and solution IR spectroscopic features for a series of $[\text{M}(\text{DOTAM})]^{2+}$ complexes (M = Mn, Co, Cu, Ni, Ca, Zn) correlate with solid state and solution coordination numbers. $[\text{Co}(\text{DOTAM})]^{2+}$, $[\text{Ni}(\text{DOTAM})]^{2+}$, and $[\text{Zn}(\text{DOTAM})]^{2+}$ are demonstrated to be six-coordinate in both the solid state and in solution, while $[\text{Mn}(\text{DOTAM})]^{2+}$ and $[\text{Ca}(\text{DOTAM})]^{2+}$ are eight-coordinate in the solid state and remain so in solution. $[\text{Cu}(\text{DOTAM})]^{2+}$, which is five-coordinate by X-ray crystallography, is shown to increase its coordination number in solution to six-coordinate.

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1. Introduction

The multidentate macrocyclic ligand DOTAM (1,4,7,10-tetrakis(acetamido)-1,4,7,10-tetraazacyclododecane (Scheme 1) forms complexes with a wide variety of metal ions [1–3]. In particular, the lanthanide complexes of DOTAM and its derivatives have been the subject of structural, dynamics, and reactivity studies [4–13]. More recently, complexes of DOTAM and its derivatives have found potential application as contrast agents in a variety of magnetic resonance imaging techniques [14–19]. In these complexes, DOTAM and related derivatives typically function as eight-coordinate chelates and are generally stable to dissociation. Main group and transition metal complexes of DOTAM, however, exhibit significant structural diversity in the solid state. In all main group and transition metal complexes that have been structurally characterized, the metal ion binds to the four amine nitrogens of the 12-membered ring and to either two or four oxygen donor atoms of the pendant arm amide groups. For example, $[\text{Ca}(\text{DOTAM})](\text{ClO}_4)_2 \cdot 2.5\text{H}_2\text{O}$ has been crystallographically characterized as 8-coordinate while $[\text{Zn}(\text{DOTAM})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ is six

coordinate in the solid state [20]. Reported $\log K$ values for binding to M^{2+} ions span a range from 5.4 for Ba^{2+} to >19 for Cd^{2+} and Pb^{2+} [20]. The structures of the complexes in solution, however, may be very different from those in the solid state and may exhibit dynamic behavior. One study of $[\text{Zn}(\text{DOTAM})]^{2+}$ reports evidence from variable temperature ^{13}C NMR spectroscopy for an effectively 8-coordinate structure in DMF-d_7 solution [20]. Variable temperature ^1H NMR spectroscopy of the same complex in D_2O demonstrates that dynamic processes involving the ring protons as well as the pendant arm methylene protons are also evident [21].

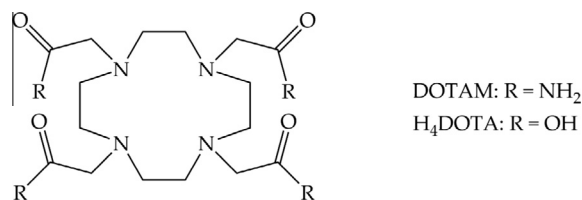
We have been interested in developing relatively straightforward methods for characterizing the solution structures of these and related species, particularly with respect to the coordination number of the central atom. Standard NMR techniques are usually not very useful. Many of the complexes are paramagnetic and the diamagnetic complexes exhibit a variety of fluxionalities on the NMR timescale that obscure the underlying structures. Few of the complexes exhibit visible absorptions and the ligand field spectra are not particularly diagnostic of coordination number. We have explored more general approaches to defining both solid state and solution structures and report that infrared spectroscopy in the carbonyl stretching region provides a means of correlating a relatively simple physical measurement with the solid state coordination number. Further, the infrared spectrum in solution indicates that the solid state coordination numbers are usually maintained in aqueous solutions.

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Scheme 1.

2. Materials and methods

2.1. Materials

DOTAM was either synthesized [20] or purchased from Macro-cyclics, Inc. D₂O (99.9% D) was purchased from Cambridge Isotope Laboratories, Inc. All other materials were purchased from commercial sources and used as received.

Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA or Robertson Microлит Laboratories, Ledgewood, NJ. IR spectra were obtained using a Perkin-Elmer Spectrum BX FT-IR System. Solid state IR spectra were obtained as KBr pellets. Deuterium exchange experiments were performed by dissolving 5–10 mg of the complex in 2 mL of D₂O and allowing 15 min for H/D exchange to occur. The D₂O was removed by rotary evaporation to yield a sample in which the exchangeable protons were deuterated. Solution IR spectra were obtained in D₂O using a cell mounted with CaF₂ plates and a path length of 0.1 mm. Deconvolution of the [Cu(DOTAM)]²⁺ solution IR spectrum was carried out using the fitting routines in Origin version 9.0. UV-Vis measurements were obtained using a Hitachi U 2900 Double-Beam Ultraviolet-Visible Spectrophotometer. ESI-MS data were obtained in H₂O:MeOH solutions using a Finnigan LCQ Advantage Max spectrometer. X-ray crystallographic analyses were carried out by Dr. Brandon Mercado, X-ray Crystallographic Facility, Department of Chemistry, Yale University ([Co(DOTAM)]Cl₂·3H₂O), Dr. Christopher Incarvito, X-ray Crystallographic Facility, Department of Chemistry, Yale University ([Ni(DOTAM)]Cl₂·4H₂O), and Drs. Neil R. Brooks and Victor G. Young, Jr., X-ray Crystallographic Laboratory, Department of Chemistry, University of Minnesota ([Cu(DOTAM)](ClO₄)₂·H₂O).

2.2. Synthesis

[Co(DOTAM)]Cl₂·3H₂O: DOTAM (0.0904 mmol) was dissolved in deionized water (5 mL). CoCl₂·6H₂O (0.0904 mmol) was added and the solution was stirred at room temperature for 30 min. The solution was then allowed to evaporate slowly to a final volume of 1.5 mL. Pink cubic crystals suitable for X-ray crystallographic analysis were obtained by the slow diffusion of acetone into this solution. *Anal. Calc.* for C₁₆H₃₆N₈O₄CoCl₂·3H₂O: C, 32.99; H, 6.25; N, 19.24. Found: C, 33.19; H, 6.55; N, 19.27%. IR (cm⁻¹; KBr pellet): 1699 ν(NH₂), 1657 ν(C=O), 1607 ν(C=O); IR (cm⁻¹; D₂O solution): 1665 ν(C=O), 1640 ν(C=O); Mass spectrum (ESI-MS *m/z* = 229.73, [Co(DOTAM)]²⁺); UV-Vis: λ_{max} = 519 nm, ε = 438 M⁻¹ cm⁻¹.

[Ni(DOTAM)]Cl₂·4H₂O: DOTAM (0.1 mmol) and NiCl₂ (0.11 mmol) were dissolved in 6 mL of 80% methanol/water and heated at reflux for 2 h. 8 mL ethanol was added to the cooled solution to precipitate the product. Crystals suitable for X-ray crystallographic analysis were obtained by slow diffusion of acetone into an aqueous solution of the purple product. *Anal. Calc.* for C₁₆H₄₀N₈O₄NiCl₂·4H₂O: C, 31.91; H, 6.65; N, 18.62. Found: C, 32.93; H, 7.00; N, 18.97%. IR (cm⁻¹) (KBr pellet): 1681 ν(NH₂), 1656 ν(C=O), 1604 ν(C=O); IR (cm⁻¹) (D₂O solution): 1649 ν(C=O), 1634 ν(C=O); Mass spectrum (ESI-MS *m/z* = 229.27, [Ni(DOTAM)]²⁺); UV-Vis: λ_{max} = 540 nm, ε = 23 M⁻¹ cm⁻¹.

[Cu(DOTAM)](ClO₄)₂·H₂O: DOTAM (0.5020 mmol) in 80% methanol (20 mL) was heated to reflux and Cu(ClO₄)₂·6H₂O (0.552 mmol) in 6 mL methanol was added dropwise throughout a 5 h period. A blue solid precipitated when the solution was allowed to cool. Recrystallization from water gave crystals that were suitable for X-ray crystallographic analysis. *Anal. Calc.* for C₁₆H₃₂N₈O₁₂Cl₂Cu·H₂O: C, 28.21; H, 4.99; N, 16.45. Found: C, 28.72; H, 4.95; N, 16.65%. IR (cm⁻¹ KBr pellet): 1663 ν(C=O), 1679 ν(C=O); IR (cm⁻¹ D₂O solution): 1649 ν(C=O); Mass spectrum (ESI-MS *m/z* = 232.13, [Cu(DOTAM)]²⁺); UV-Vis: λ_{max} = 734 nm, ε = 136 M⁻¹ cm⁻¹.

3. Results and discussion

3.1. X-ray crystal structures

The key parameters of the crystal structure solutions are given in Table 1. The [M(DOTAM)]²⁺ ions (M = Co, Ni, and Cu) are shown in Fig. 1 and fully labeled figures are available in the Supplementary Data. The structural parameters of the coordination spheres of the ions are given in Table 2. The [Co(DOTAM)]²⁺ and [Ni(DOTAM)]²⁺ ions in the crystals exhibit a six-coordinate distorted octahedral geometry similar to other previously reported six-coordinate DOTAM complexes such as [Zn(DOTAM)]²⁺ [20]. In each case, the metal ion is coordinated to the four ring nitrogen atoms and two oxygen atoms of the pendant arm amide groups. The cell constants and structural parameters for [Co(DOTAM)]Cl₂·3H₂O are very similar to those for [Co(DOTAM)]Cl_{1.83}Br_{0.17}·3H₂O, which has recently been published [22], although there are some slight differences in the bond distances and angles.

The most significant difference between the structures of [Co(DOTAM)]Cl₂·3H₂O and [Ni(DOTAM)]Cl₂·4H₂O is in the orientation of the unbound pendant arms in the lattice. For the cobalt complex, the unbound amides are oriented similarly to the bound arms, but with a longer distance to the metal to give a fairly compact structure for the cation. In contrast, for the nickel cation the unbound pendant arms are extended away from the metal center and the planes of their amide groups are nearly perpendicular to each other. This extended structure seems to be stabilized by a number of hydrogen bonds in the lattice (see below).

The copper complex has a five-coordinate geometry and is significantly different from the other metal complexes. On the basis of the Addison τ value (0.043) it is best described as a distorted square pyramid with the nitrogen atoms occupying the equatorial positions. [23] The Cu—O distance is 2.077(2) Å which is consistent with the ionic radius of Cu(II). In addition there is a long-range interaction at 2.486(2) Å with the oxygen atom of another amide.

Extensive hydrogen bonding interactions with the pendant arm nitrogens as donors are evident in each of the crystal structures and are summarized in Table 3. The crystal of [Ni(DOTAM)]Cl₂·4H₂O exhibits more, and stronger, hydrogen bonds involving both the bound and unbound amide groups than either the cobalt or the copper analogues. These hydrogen bonds link the [Ni(DOTAM)]²⁺ cations to form supramolecular layers within the crystal.

Table 4 summarizes the bond distances and angles for the coordination spheres of crystallographically characterized main group and transition metal complexes of DOTAM. In general, the metal ligand distances follow the trends in ionic radius of the M(II) cations with smaller ions displaying 6-coordinate geometries and larger ions preferring 8-coordinate geometries. There is no evidence of specific electronic structural effects on the M—O_{bonded} distances for these metal ions. For ions with a radius of 0.96 Å or greater, eight coordinate geometries are observed. For ions with radii less than or equal to 0.745 Å, six coordinate distorted octahedral geometries are formed (except for Cu(II)). This trend most

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