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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: [Co(DOTAM)]Cl₂•3H₂O, [Ni(DOTAM)]Cl₂•4H₂O, and [Cu(DOTAM)](ClO₄)₂•H₂O. Solid state and solution IR spectroscopic features for a series of [M(DOTAM)]²⁺ complexes (M=Mn, Co, Cu, Ni, Ca, Zn) correlate with solid state and solution coordination numbers. [Co(DOTAM)]²⁺, [Ni(DOTAM)]²⁺, and [Zn(DOTAM)]²⁺ are demonstrated to be six-coordinate in both the solid state and in solution, while [Mn(DOTAM)]²⁺ and [Ca(DOTAM)]²⁺ are eight-coordinate in the solid state and remain so in solution. [Cu(DOTAM)]²⁺, which is five-coordinate by X-ray crystallography, is shown to increase its coordination number in solution to six-coordinate.

GRAPHICAL ABSTRACT SYNOPSIS

Solid state and solution IR spectroscopic features for the series [M(DOTAM)]²⁺ (M=Mn, Co, Cu, Ni, Ca, Zn) correlate with solid state and solution coordination numbers.

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SUPPLEMENTARY DATA

CCDC 1415820, 1415821, and 1415822 contain the supplementary crystallographic data for this paper. These data may be obtained free of charge via <http://www.ccdc.cam.ac.uk/contents/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Additional supplementary data associated with this article is available free of charge via the journal website.

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Keywords

DOTAM; X-ray structure; infrared spectroscopy; coordination complex

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 [2–4]. In particular, the lanthanide complexes of DOTAM and its derivatives have been the subject of structural, dynamics, and reactivity studies [5–14]. More recently, complexes of DOTAM and its derivatives have found potential application as contrast agents in a variety of magnetic resonance imaging techniques [15–20]. 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 [21]. 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+} [21]. 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 $\text{DMF}-d_7$ solution [21]. 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 [22].

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.

MATERIALS AND METHODS

Materials

DOTAM was either synthesized [21] or purchased from Macrocyclics, 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 Microlit 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 minutes 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).

Synthesis

[Co(DOTAM)]Cl₂•3H₂O: DOTAM (0.0904mmol) was dissolved in deionized water (5 mL). CoCl₂•6H₂O (0.0904mmol) was added and the solution was stirred at room temperature for 30 minutes. 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. Calcd 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⁻¹cm⁻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 two hours. 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. Calcd for $C_{16}H_{40}N_8O_4NiCl_2 \cdot 4H_2O$: 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 $\nu(NH_2)$, 1656 $\nu(C=O)$, 1604 $\nu(C=O)$; IR (cm^{-1}) (D_2O solution): 1649 $\nu(C=O)$, 1634 $\nu(C=O)$; Mass spectrum (ESI-MS $m/z = 229.27$, $[Ni(DOTAM)]^{2+}$); UV-Vis: $\lambda_{max} = 540$ nm, $\epsilon = 23$ M $^{-1}cm^{-1}$.

$[Cu(DOTAM)](ClO_4)_2 \cdot H_2O$: DOTAM (0.5020 mmol) in 80% methanol (20 mL) was heated to reflux and $Cu(ClO_4)_2 \cdot 6H_2O$ (0.552 mmol) in 6 mL methanol was added dropwise throughout a five hour 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. Calcd for $C_{16}H_{32}N_8O_{12}Cl_2Cu \cdot H_2O$: 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 $\nu(C=O)$, 1629 $\nu(C=O)$; IR (cm^{-1} D_2O solution): 1679 $\nu(C=O)$; Mass spectrum (ESI-MS $m/z = 232.13$, $[Cu(DOTAM)]^{2+}$); UV-Vis: $\lambda_{max} = 734$ nm, $\epsilon = 136$ M $^{-1}cm^{-1}$.

RESULTS AND DISCUSSION

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 Figure 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 $[Zn(DOTAM)]^{2+}$ [21]. 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 $[Co(DOTAM)]Cl_2 \cdot 3H_2O$ are very similar to those for $[Co(DOTAM)]Cl_{1.83}Br_{0.17} \cdot 3H_2O$, which has recently been published [23], although there are some slight differences in the bond distances and angles.

The most significant difference between the structures of $[Co(DOTAM)]Cl_2 \cdot 3H_2O$ and $[Ni(DOTAM)]Cl_2 \cdot 4H_2O$ 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.[24] 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 $[\text{Ni}(\text{DOTAM})]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ 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 $[\text{Ni}(\text{DOTAM})]^{2+}$ 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 atoms displaying 6-coordinate geometries and larger atoms preferring 8-coordinate geometries. There is no evidence of specific electronic structural effects on the $\text{M}-\text{O}_{\text{bonded}}$ 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 likely reflects a sterically controlled maximum coordination number for each ion, with ions less than 0.745 Å in radius unable to accommodate more than six ligands.

H_4DOTA is a carboxylic acid analogue of DOTAM (see Scheme 1) and several of the complexes in Table 4 have $\text{M}(\text{H}_2\text{DOTA})$ analogues. For $\text{M}=\text{Mn}, \text{Co}, \text{Ni},$ and Cu , the $\text{M}(\text{H}_2\text{DOTA})$ complexes are exclusively six coordinate with distorted octahedral geometries. Only one seven-coordinate transition metal H_4DOTA complex has been reported ($[\text{Na}[\text{Fe}(\text{DOTA})]\cdot 5\text{H}_2\text{O}$ [33]) and no eight coordinate transition metal complexes are currently known. These observations may be rationalized in terms of the differences in electrostatic contributions to bonding in $[\text{H}_x\text{DOTA}]^{x-4}$ compared to DOTAM. The carboxylic acid groups on $[\text{H}_x\text{DOTA}]^{x-4}$ must first be deprotonated to bind to the metal and the bound carboxylates carry a full negative charge near the metal ion. This would lead to unfavorable electrostatic interactions with additional carboxylate groups in a higher coordination number complex. It appears that once the charge of the ion has been neutralized, binding of further carboxylates is thermodynamically disfavored. Thus $[\text{H}_x\text{DOTA}]^{x-4}$ is expected to bind to M(II) ions as a hexadentate ligand and to M(III) ions as a heptadentate ligand, consistent with the experimental observations. The amide pendant arms in DOTAM will, however, experience much weaker mutual electrostatic interactions and the coordination number will be determined primarily by steric considerations, *i.e.*, the ionic radius of the metal ion. Table 5 compares the observed M-O bond lengths between $[\text{M}(\text{DOTAM})]^{2+}$ complexes and their $[\text{M}(\text{H}_2\text{DOTA})]$ analogues.

In general, even if both $[\text{M}(\text{DOTAM})]^{2+}$ and $[\text{M}(\text{H}_2\text{DOTA})]$ have the same coordination number (*e.g.*, $\text{M}=\text{Co}, \text{Zn}, \text{Ni}$) the M-O bond lengths in the $[\text{H}_x\text{DOTA}]^{x-4}$ complexes are approximately 0.07 Å shorter than those of the DOTAM analogues. For $[\text{Mn}(\text{DOTAM})]^{2+}$ and $[\text{Mn}(\text{H}_2\text{DOTA})]$, in which there is a difference in coordination number, the difference in bond lengths is even larger (0.15 Å).

Solid State IR

The solid state IR spectroscopy (KBr pellet) of the carbonyl region for the complexes are summarized in Table 6. The free ligand DOTAM exhibits a strong peak at 1678 cm^{-1} , which

is assigned to the $\nu(\text{C}=\text{O})$ stretch of the amide group. A shoulder at 1632 cm^{-1} is also apparent. This shoulder may be assigned to the characteristic amide II band which corresponds to an NH_2 bending mode [34].

On coordination to a metal ion, the spectrum changes in a manner consistent with the new geometry. Figure 2, left, shows representative solid state IR spectra for eight-coordinate (Mn), six-coordinate (Ni), and five-coordinate (Cu) complexes. Spectra for four other complexes are provided in the Supplementary Data. For eight-coordinate $[\text{M}(\text{DOTAM})]^{2+}$ complexes ($\text{M}=\text{Mn}, \text{Ca}$), two peaks are observed. Since the pendant arms are all bound to the metal ion and are therefore essentially equivalent, the peaks in each spectrum are assigned as the $\nu(\text{C}=\text{O})$ stretch and the amide II band. This assignment was confirmed by a deuterium exchange experiment. Incubation of $[\text{Mn}(\text{DOTAM})]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ in D_2O and subsequent isolation of the solid complex resulted in the replacement of all exchangeable protons with deuterium. The IR spectrum of this solid gave only one carbonyl peak, at 1648 cm^{-1} , which was assigned as the $\nu(\text{C}=\text{O})$ stretch. The peak at 1618 cm^{-1} was thus attributed to the amide II band. In both the fully protonated and deuterated forms, there is an approximate shift of 12 cm^{-1} of the $\nu(\text{C}=\text{O})$ stretch to lower energy relative to the free ligand. These results are consistent with the transfer of some electron density to the metal and a small lowering of the net $\text{C}=\text{O}$ bond order.

For each of the six-coordinate complexes ($\text{M}=\text{Co}, \text{Ni}, \text{Zn}$), three peaks were observed in the solid state IR spectrum (see Figure 2 and Supplementary Data). In each case, the highest energy peak is at a higher wavenumber than that observed for the free ligand. This peak is, however, shifted out of the carbonyl region upon incubation in D_2O , and is thus assigned as an amide II peak. The remaining two peaks were assigned to the bound and unbound pendant arm $\nu(\text{C}=\text{O})$ stretches. The higher energy peak is similar in energy to the $\nu(\text{C}=\text{O})$ for the free ligand and likely corresponds to the unbound pendant arms. The lower energy peak is therefore assigned to the $\nu(\text{C}=\text{O})$ of the bound arms. Thus, in each six-coordinate complex, two $\nu(\text{C}=\text{O})$ peaks are observed, which correspond to the two types of amide groups (bound and unbound) present.

The only five-coordinate complex, $[\text{Cu}(\text{DOTAM})]^{2+}$, is structurally unique with one bound pendant arm, one long contact, and two unbound arms in the solid state. Two distinct peaks are observed in the IR spectrum, a broad, asymmetrical peak at 1679 cm^{-1} and a much weaker peak at 1628 cm^{-1} (see Figure 2). Upon incubation with D_2O , the 1628 cm^{-1} peak is shifted out of the carbonyl region and is thus assigned as the amide II band, while the 1679 cm^{-1} band is resolved into three components. On the basis of the relative energies of the peaks, they are assigned as the unbound pendant arms (1678 cm^{-1}), the long contact pendant arm (1656 cm^{-1}), and the bound pendant arm (1627 cm^{-1}). The $\nu(\text{C}=\text{O})$ stretches in the complex are apparently much closer in energy and overlap extensively, accounting for the broad carbonyl peak.

Solution IR

Solution structures may be considerably different from solid state structures and since solution properties depend on structure it is useful to develop protocols for defining coordination number in solution. Solution IR spectroscopy can provide insights into

coordination by carbonyl-based ligands. Representative spectra of the carbonyl regions of $[M(\text{DOTAM})]^{2+}$ ($M=\text{Mn, Ni, Cu}$) in D_2O are given in Figure 2, right, and the observed peak frequencies for all species are summarized in Table 6. Spectra of the other species are given in the Supplementary Data.

For the DOTAM free ligand one peak is observed, which is again consistent with the equivalence of all four amide groups. The peak is, however, considerably shifted from its solid state value. This likely reflects both a small contribution from deuteration of the amide nitrogens and a larger effect due to hydrogen (*i.e.*, deuterium) bonding with the solvent. In all cases, the amide II band has been shifted out of the carbonyl region.

Each of the complexes exhibits strong $\nu(\text{C}=\text{O})$ bands with no other peaks apparent in the region. For the eight-coordinate complexes, only one peak is observed at $\sim 1643\text{ cm}^{-1}$, consistent with a solution structure in which all the pendant arms are bound and thus equivalent. The six-coordinate complexes exhibit two peaks, one of which is observed between 1634 cm^{-1} and 1640 cm^{-1} and is assigned to the unbound amide group by comparison to the free ligand in solution. The other peak, which is assigned to the bound pendant arms, is at higher frequency. Binding to the metal ion presumably decreases the strength of hydrogen bonding interaction with the solvent and the peaks are not shifted as much as those of the free ligand.

$[\text{Cu}(\text{DOTAM})]^{2+}$ is five-coordinate in the solid state and exhibits only one distinct peak in D_2O solution, but the peak is broad and asymmetrical, suggesting that it may represent several overlapping bands. Deconvolution of the peak (see Supplementary Data) gives two contributing bands, at 1669 cm^{-1} and 1642 cm^{-1} , indicating the presence of only two distinct amide environments in the complex. It thus appears that the structure of $[\text{Cu}(\text{DOTAM})]^{2+}$ in solution is different from the solid state structure and is most likely a six-coordinate distorted octahedron similar to, for example, $[\text{Ni}(\text{DOTAM})]^{2+}$.

It should be noted that the solution structure of $[\text{Zn}(\text{DOTAM})]^{2+}$ in $\text{DMF-}d_7$ has been previously investigated with temperature dependent ^{13}C NMR spectroscopy [21]. In that work, only two peaks were observed near room temperature, corresponding to a single peak for each of the pendant arm carbons and a single peak for the ring carbons. On cooling to 218K, the ring carbon peaks decoalesced into two peaks, but the pendant arm peaks remained unchanged. These results were interpreted in terms of an effectively eight-coordinate structure in $\text{DMF-}d_7$ solution with a dynamic process resulting in a change in the helicity of the complex.

The IR data in Table 6 support a six-coordinate structure in D_2O solution, but ^1H NMR spectroscopy at 400 MHz gives only one peak for the pendant arms [22]. We interpret these results and the previous study [21] in terms of the dynamic process shown in Scheme 2 which involves both linkage isomerization and changes in helicity. In Scheme 2, horizontal arrows connect species related by the linkage isomerization while vertical arrows connect species related by helicity inversion. An interpretation consistent with both the IR and NMR results is that the helicity inversion is occurring with a rate similar to the frequency difference between the two peaks for ring carbons and can therefore be decoalesced at low

temperatures. The linkage isomerism involving randomization of the pendant arms appears, however, to occur on a much faster timescale and the resonances are not decoalesced at temperatures above 218K. The IR timescale, however, is on the order of a molecular vibration and can therefore distinguish between the two different types of carbonyl groups in the six-coordinate geometry. Further studies on $[\text{Zn}(\text{DOTAM})]^{2+}$ and related complexes are underway to more fully define the nature of the dynamic processes occurring in solution.

CONCLUSION

DOTAM is a versatile ligand which forms $[\text{M}(\text{DOTAM})]^{2+}$ complexes with transition metal and main group ions that can display a variety of solid state and solution structures. IR spectroscopy, both in the solid state and in solution, is a valuable tool for determining the metal coordination number in DOTAM complexes. In general, a carbonyl peak is observed for each distinct type of carbonyl. For eight-coordinate complexes with only one type of carbonyl (*i.e.*, bound) only one peak is observed. For six-coordinate complexes, two carbonyl peaks are observed in both the solid state and solution, one for the bound carbonyls and one for the unbound carbonyls. $[\text{Cu}(\text{DOTAM})]^{2+}$ has a more complex five-coordinate geometry in the solid state and several overlapping IR peaks are observed. In solution, however, the structure appears to be six-coordinate with only two overlapping peaks. For the other complexes the evidence indicates that the solid state coordination number is maintained in solution.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Two views of the $[M(\text{DOTAM})]^{2+}$ ions (top $M=\text{Co}$; middle $M=\text{Ni}$; bottom $M=\text{Cu}$), red=O; blue=N; grey=C. Hydrogen atoms have been omitted for clarity. The long Cu-O contact in $[\text{Cu}(\text{DOTAM})]^{2+}$ has been rendered as a white bond.

Figure 2. Solid State (Left) and Solution (D₂O, Right) IR of the Carbonyl Region for [M(DOTAM)]²⁺ (M = Mn, top; Ni, middle; Cu, bottom).

DOTAM: R = NH₂

H₄DOTA: R = OH

SCHEME 1.

SCHEME 2.

Crystallographic Data and Structural Refinement for the Complexes [Co(DOTAM)]Cl₂•3H₂O, [Ni(DOTAM)]Cl₂•4H₂O, and [Cu(DOTAM)](ClO₄)₂•H₂O.

Table 1

Crystal	[Co(DOTAM)]Cl ₂ •3H ₂ O	[Ni(DOTAM)]Cl ₂ •4H ₂ O	[Cu(DOTAM)](ClO ₄) ₂ •H ₂ O
Crystal color, habit,	pink block	purple block	blue block
Crystal size (mm ³)	0.320 × 0.230 × 0.200	0.22 × 0.12 × 0.10	0.20 × 0.20 × 0.20
Crystal system	triclinic	triclinic	triclinic
Space group	<i>P</i> 1̄	<i>P</i> 1̄	<i>P</i> 1̄
<i>a</i> (Å)	8.769(4)	9.3488(18)	9.391(4)
<i>b</i> (Å)	11.585(5)	11.388(2)	12.288(4)
<i>c</i> (Å)	13.995(6)	13.703(3)	12.999(4)
<i>α</i> (°)	95.590(8)	70.756(5)	99.487(5)
<i>β</i> (°)	96.316(8)	71.195(5)	108.167(5)
<i>γ</i> (°)	108.640(8)	78.755(5)	106.764(5)
<i>V</i> (Å ³)	1325.8(10)	1297.3(4)	1310.1(8)
<i>Z</i>	2	2	2
Radiation (λ, Å)	Mo <i>Kα</i> (0.71073)	Mo <i>Kα</i> (0.71075)	Mo <i>Kα</i> (0.71073)
<i>μ</i> (mm ⁻¹)	0.899	1.118	1.118
<i>T</i> (K)	298	223	173
<i>θ</i> (°) (completeness to <i>θ</i>)	25.242 (99.7 %)	25.242 (99.7 %)	25.12 (99.1 %)
Reflections collected	22082	13639	11186
Independent reflections (<i>R</i> _{int})	5780 (0.0329)	5906 (0.0465)	4046 (0.041)
Data/restraints/parameters	5780/0/361	5906/0/348	4635/90/380
Goodness-of-fit on <i>F</i> ²	1.058	1.104	1.089
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0348 w <i>R</i> 2 = 0.0764	<i>R</i> 1 = 0.0657 w <i>R</i> 2 = 0.1328	<i>R</i> 1 = 0.0389 w <i>R</i> 2 = 0.1022
Final <i>R</i> indices (all data)	<i>R</i> 1 = 0.0426 w <i>R</i> 2 = 0.0793	<i>R</i> 1 = 0.0956 w <i>R</i> 2 = 0.1452	<i>R</i> 1 = 0.0453 w <i>R</i> 2 = 0.1082
CCDC Number	1415821	1415820	1415822

Table 2

Structural Parameters for the Metal Coordination Spheres of [Co(DOTAM)]Cl₂•3H₂O, [Ni(DOTAM)]Cl₂•4H₂O, and [Cu(DOTAM)](ClO₄)₂•H₂O.

	[Co(DOTAM)] ²⁺	[Ni(DOTAM)] ²⁺	[Cu(DOTAM)] ²⁺
Bond Distances(Å)			
M-N	2.2580(16)	2.109(3)	2.057(2)
	2.2710(18)	2.111(3)	2.096(2)
	2.2942(16)	2.159(3)	2.131(2)
	2.3061(16)	2.166(3)	2.282(2)
M-O	2.1120(14)	2.003(2)	2.077(2)
	2.1238(14)	2.033(3)	2.486(2)
Bond Angles(deg)			
N-M-N	79.75(6)	84.89(12)	84.99(9)
	77.75(6)	84.12(12)	82.00(9)
O-M-N	76.56(6)	82.00(11)	76.00(8)
	75.67(6)	81.95(11)	

Table 3

Hydrogen Bonds Involving Pendant Arm Nitrogen Atoms.^{a,b}

[Cu(DOTAM)]Cl ₂ •3H ₂ O		[Ni(DOTAM)]Cl ₂ •4H ₂ O		[Cu(DOTAM)](ClO ₄) ₂ •H ₂ O	
Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
N7-O4	2.925	N5-O1'	2.928	N21-O51'	2.836
Bound		N5-O3'	2.998		
pendant		N5-Cl1'	3.245		
arms		N7-Cl2''	3.312		
		N7-Cl1'''	3.263		
N6-O6	2.974			N51-O21'	2.965
				N31-O31'	2.910
Unbound				N31-O1W	2.997
pendant		N6-Cl1	3.410		
arms		N8-Cl2	3.458		
		N6-Cl1'	3.320		
		N8-Cl1''	3.346		

^a Hydrogen bonds were defined on the basis of bond length criteria in ref [25].

^b Hydrogen bonds to unprimed atoms are intramolecular, while those involving primed atoms are intermolecular.

Table 4
Structurally Characterized Main Group and Transition Metal [M(DOTAM)]²⁺ Complexes.

Complex	C,N ^a	<i>r</i> _{ionic} (Å) ^b	ave. <i>r</i> _{M-O} (Å)	ave. <i>r</i> _{M-N} (Å)	Reference
[Cu(DOTAM)](ClO ₄) ₂ •H ₂ O	5	0.65	2.077	2.142	this work
[Ni(DOTAM)]Cl ₂ •4H ₂ O	6	0.69	2.018	2.136	this work
[Zn(DOTAM)](ClO ₄) ₂ •H ₂ O	6	0.74	2.099	2.247	21
[Co(DOTAM)]Cl ₂ •3H ₂ O	6	0.745	2.117	2.282	this work
[Mn(DOTAM)]Cl ₂ •2H ₂ O	8	0.96	2.310	2.428	27
[Cd(DOTAM)](ClO ₄) ₂ •1.5H ₂ O	8	1.10	2.491	2.439	21
[Ca(DOTAM)](ClO ₄) ₂ •2.5H ₂ O	8	1.12	2.407	2.592	21
[Hg(DOTAM)](ClO ₄) ₂ •0.5CH ₃ OH•1.5H ₂ O	8	1.14	2.593	2.442	28
[Pb(DOTAM)][(NO ₃) ₂ •3.5H ₂ O]	8	1.29	2.754	2.625	29

^aSolid state metal coordination number.

^bfrom reference [26].

Table 5

Comparison of M-O Bond Distances for [M(DOTAM)]²⁺ and [M(H₂DOTA)] Analogues.

Ave M-O Bond Distance (Å)				
M	[M(DOTAM)] ²⁺	Reference	[M(H ₂ DOTA)]	Reference
Cu ²⁺	2.077	this work	1.965	30
Ni ²⁺	2.018	this work	2.025	30
Zn ²⁺	2.099	21	2.037	31
Co ²⁺	2.117	this work	2.038	32
Mn ²⁺	2.310	27	2.160	27

Table 6Solid State and Solution IR Results for DOTAM and [M(DOTAM)]²⁺ Complexes^a

	Solid State		Solution	
	$\nu(\text{C=O})$ Unbound (cm ⁻¹)	$\nu(\text{C=O})$ Bound (cm ⁻¹)	$\nu(\text{C=O})$ Unbound (cm ⁻¹)	$\nu(\text{C=O})$ Bound (cm ⁻¹)
DOTAM	1678		1637	
[Cu(DOTAM)] ²⁺		1679	1642	1669
	<i>1678, 1656^b</i>	<i>1627</i>		
[Ni(DOTAM)] ²⁺	1656	1604	1634	1649
	<i>1670</i>	<i>1625</i>		
[Zn(DOTAM)] ²⁺	1671	1618	1636	1670
[Co(DOTAM)] ²⁺	1657	1607	1640	1665
	<i>1665</i>	<i>1639</i>		
[Mn(DOTAM)] ²⁺		1667		1642
		<i>1648</i>		

^a Entries in italics represent solid state IR peaks after deuterium substitution of all exchangeable protons.^b Assigned to the long contact amide.