Metal Ion Binding by a Bicyclic Diamide: Deep UV Raman Spectroscopic Characterization

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Deep UV resonance Raman spectroscopy was used for characterizing ligand−metal ion complexes. The obtained results demonstrated a strong intrinsic sensitivity and selectivity of a Raman spectroscopic signature of a bicyclic diamide, a novel chelating agent for lanthanides and actinides (Lumetta, G. J.; Rapko, B. M.; Garza, P. A.; Hay, B. P.; Gilbertson, R. D.; Weakley, T. J. R.; Hutchison, J. E. *J. Am. Chem. Soc*. **2002**, *124*, 5644). Molecular modeling, which included structure optimization and calculation of Raman frequencies and resonance intensities, allowed for assigning all strong Raman bands of the bicyclic diamide as well as predicting the band shifts observed because of complex formation with metal ions. A comparative analysis of Raman spectra and the results of the molecular modeling could be used for elucidating the structure of complexes in solution.

Introduction

A molecular sensor is commonly composed of a selective chelating agent conjugated with a reporting element, which provides a spectroscopic or electrochemical readout.[1] Although probing the chelating group directly is most desirable, it is often limited by the sensitivity of a detection system. Herein, we report on the first application of deep UV resonance Raman spectroscopy (UVRR) for probing ligand−metal ion complexes. The results obtained demonstrate a strong sensitivity and intrinsic selectivity of resonance Raman spectroscopic detection with respect to metal ions. Molecular modeling was utilized to predict the Raman spectroscopic response.

The development of chelating agents for lanthanides and actinides has important industrial and environmental implication.[2,3,4] Various spectroscopic methods have been used for studying lanthanide and actinide complexes. Luminescence and absorption spectroscopies have relied on narrow emission and absorption bands possessed by a majority of lanthanides because of Laporte-forbidden transitions.[5] A long fluorescence lifetime (∼1 ms) and sensitivity to H_2O−D_2O exchange have allowed studying the stoichiometry of aqueous Eu(III), Nd(III), and Yb(III) complexes from Stern Volmer experiments.[5,6] Competition between Eu(III) and other lanthanides for complex formation with polyoxometalates has been used to determine the stability constants of the lanthanide complexes using laser-induced fluorescence technique.[7] Sensitized near-infrared and visible luminescence has been exploited for studying different lanthanide complexes aimed at their application as light-emitting materials.[6,8] Nonabsorbing metal ions, such as La and Lu, have been reported to induce noticeable changes in the absorption spectrum of binding ligands that allows for determining the stability constants of complex formation.[9]

Electrochemical methods have also been proven useful for the determination of formation constants of lanthanide complexes.[10] The most recent advances in the methodology have allowed for characterizing the electronic structure of the complexes on the basis of the voltammetric data.[11,12] In particular, a series of sandwich lanthanide−phthalocyaninato complexes have been studied by means of cyclic voltammetry and differential pulse voltammetry.[13,14] The HOMO−LUMO gaps have been evaluated from the half-wave potentials of oxidations and have been directly related to the ionic radii of a coordinating metal.

X-ray, the most powerful structural method,[15] has been extensively employed for studying lanthanide complexes.[16−19] The technique is invaluable for the deliberate synthesis of the ligands selectively coordinating certain f-elements.[20] However, the applicability of X-ray data for solution structures needs to be established.

Various NMR methods have been utilized for structural and dynamic studies of lanthanide and actinide complexes.[21−23] Thus, ^{1}H and ^{13}C and ^{11}B have been used to deduce the correct structures and stoichiometries of several complexes of para- and diamagnetic lanthanides and 1,2-phenylenedioxoborylcyclopentadienyl.[24] Symmetry of the ligands and their helical conformation in chiral macrocyclic lanthanide complexes have been established by means of ^{1}H and ^{13}C NMR.[25]

The latest hardware development has allowed for applying ^{1}H NMR for solutions with ligand concentrations in the millimolar range[26] and the sample amount of less than 10 nanomoles.[27] Coordinated lanthanides act as an additional magnetic field source in the sample and dramatically change the chemical shifts of the signals, especially for nuclei in the vicinity of the complexation site.[28] In addition, band splitting may occur in the case of coupling with NMR active f-elements.[29] Bovens et al. studied the dynamics of formation of Dy(III) and Eu(III) complexes with cy(DTPA-EN) using ^{17}O NMR technique.[22] Among the trivalent lanthanide ions, ^{139}La(III) has the most favorable NMR properties, including a high natural abundance (99.91%), high NMR receptivity, sensitivity of the chemical shift to the lanthanide coordination, and dependence of the resonance line width on the environment.[22] Coordination compounds of other lanthanides have been explored as well.[21,23] Several 2D NMR techniques (ROESY, TOCSY, $^{1}H - ^{13}C$) have

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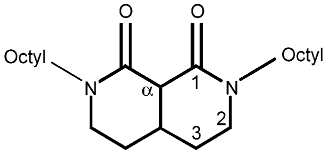
been invoked to identify two different conformers and coordination geometries of Y(III)-DOTA-Tyr^3-octreotide complexes.[30] The distances between specific moieties in the conformers, which served later as a starting point for molecular dynamics simulations, had been evaluated from the NOE (nuclear Overhauser effect) cross peaks. The accurate measurement of long-range ^{13}C−^{1}H coupling constants has been discussed to be a powerful tool for determining the 3D structure of carbohydrates and lanthanide complexes.[24,27]

Vibrational (IR and Raman) spectroscopy has been widely utilized in coordination chemistry.[31] Frequency shift in normal modes of solvent molecules upon coordination with metal ions has been used for developing a novel titration Raman spectroscopic methodology.[32] In particular, the solvation shell structure has been characterized for *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide complexes with many metals including lanthanides. Detailed analysis of Raman spectra has allowed for elucidating the reaction pathways for complex formation between lanthanides and large anions.[33] Force constants as well as other characteristics of various transition metal and lanthanide clusters have been determined using Raman spectroscopy.[34] The strengths of metal−oxygen bonds have been probed with Raman and IR spectroscopies for europium and terbium pyridine-carboxylates and pyridine-dicarboxylates.[35]

Deep UV excitation allows for a dramatic increase in the sensitivity of Raman spectroscopy for molecular systems, which do not possess absorption in the near UV and visible regions.[36,37] The analysis of resonant enhancement found for UV Raman bands of cyclic compounds has allowed for characterizing the conformational changes in saturated hydrocarbon rings on complex formation in solution.[38,39]

A bicyclic diamide **1** has been specifically designed to enhance lanthanide and actinide ion affinity by chemically stabilizing a free-ligand conformation suitable for metal binding.[40] Complex formation with metal cations occurs through coordination with two amide oxygen atoms of bicyclic diamides.[40] X-ray analysis of **1**−Eu complex in a crystal form has determined the conformation adopted by **1** upon complex formation, including bond lengths and the geometry of hydrocarbon rings.[40] Substantial changes in ^{13}C and ^{1}H NMR spectra have indicated the formation of **1**−Eu complex in solution.[40]

Complex formation of **2** (the methyl derivative instead of octyl one) with Nd(III), Am(III), Pu(IV), Np(V), U(VI), and Pu(VI) ions has been investigated using UV−vis absorption spectroscopy.[41] The absorption of the metal ions has been found to change because of complex formation. Stoichiometry of complexes and their stability constants have been determined using singular value decomposition followed by nonlinear fitting of absorption spectra.[41]



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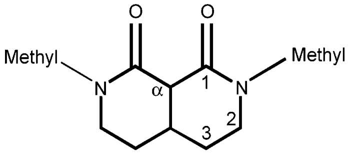

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Experimental Section

Materials and Sample Preparation. Ligand-octyl **1** was rendered by James Hutchison, University of Oregon. La(CF_3SO_3)$_3$ and Lu(CF_3SO_3)$_3$ (Aldrich) and **1** were dehydrated in a vacuum centrifuge and then were dissolved in acetonitrile (Aldrich, spectrophotometric grade) dried priorly with silica gel (Davisil 633).

Spectral Measurements. Deep UV Raman instrumentation has been described in detail elsewhere.[42] Briefly, 197-nm laser beam (~1 mW, Indigo-S laser system from Coherent) was focused into a spinning Suprasil NMR tube (5-mm outer diameter, 0.38-mm wall thickness) containing 150 μL solution. To avoid sample heating, the solution was additionally mixed using a magnetic stirrer. Scattered radiation was collected in backscattering geometry, dispersed using a home-built double monochromator, and detected with a liquid-nitrogen cooled CCD camera (Roper Scientific). The accumulation time for every spectrum was 6 min. Absorption spectra were recorded in 1-mm cell using HP 8452A spectrophotometer.

Data Processing. GRAMS/AI(7.01) software was used for Raman spectroscopic data processing. Raman spectra were normalized using acetonitrile as an internal standard. The contribution of Suprasil and acetonitrile was quantitatively subtracted.

Theoretical Calculations. The molecular geometry was estimated initially for **2** at the molecular mechanics level within MM3 force field[43] followed by the quantum mechanics conformation search at the UHF/3-21G, UHF/6-31G*, and UHF/6-31+G(d)[44,45] for a gas phase. The obtained frequencies were scaled by a factor of 0.8929.[46] For Hartree−Fock calculations, solvent effect was taken into account using Onsager reaction field model.[47] DFT modeling of the ligand structure was performed at the B3LYP/6-31G* and B3LYP/6-311G* treating solvent at polarizable continuum model (PCM).[48] Frequencies for the latter model were multiplied by a factor of 0.98 to correct for the anharmonicity missing from the harmonic frequency calculations.[49] To deduce the modes that gave rise to strong UVRR bands, resonance Raman intensities were calculated using time-dependent density-functional theory (TD-DFT)[50] as implemented in Gaussian'03.

Geometry optimization of the [**2**−La]Cl_3 and [**2**−Lu]Cl_3 complexes (brackets mark the first coordination sphere) at the UHF 6-31G* level for both the gas phase and acetonitrile solution were followed by Raman frequency calculations with the same model chemistry. Stuttgart/Dresden effective-core potentials (ECP)[51] were used for La and Lu atoms while the ligand atoms were treated at 6-31G* basis set to allow for comparing the results with those of the free ligand.[52]

Results and Discussion

The UV absorption of **1** is dominated by a strong $\pi-\pi^*$ transition of two amide chromophores at ~207 nm with a minor contribution from $n-\pi^*$ transition at ~290 nm (Figure 1). Complexation with La(III) and Lu(III) red-shifted and enhanced the low-wavelength band while the absorbance above 250 nm became weaker. These changes were quite similar for La and Lu salts. Our hypothesis was that the vibrational signature of the amide groups involved in ion binding would be ion-sensitive. We probed the amide vibrational modes by monitoring a 197-nm Raman scattering, which was resonantly enhanced because of the $\pi-\pi^*$ electronic transition of the amide chromophore. Figure 2 shows the UVRR spectra of a free-ligand **1** and its complexes with La(III) and Lu(III) in acetonitrile. The presented spectra of complexes were obtained at metal salt

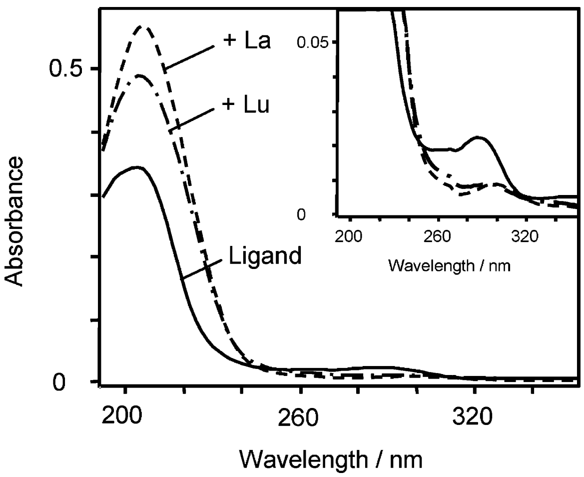


Figure 1. Absorption spectra of **1** (0.4 mM, solid) and its mixture with La$(CF_3SO_3)_3$ (1.0 mM, dashed) and Lu$(CF_3SO_3)_3$ (1.0 mM, dash–dot) in acetonitrile.

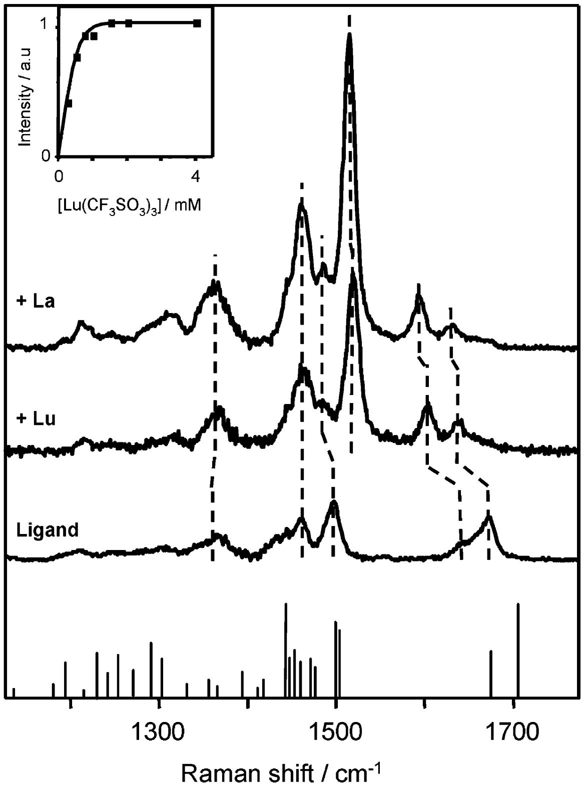


Figure 2. 197-nm excited resonance Raman spectra of **1** (1.5 mM) and its complexes with Lu$(CF_3SO_3)_3$ (4 mM) and La$(CF_3SO_3)_3$ (4 mM) in acetonitrile. The contributions of salts and acetonitrile were subtracted. Solid vertical lines represent calculated Raman modes of **1** in acetonitrile (see text). Inset: The intensity of **1**–Lu Raman band at 1602 cm^{-1} as a function of Lu$(CF_3SO_3)_3$ concentration.

concentrations exceeding the ligand concentration; a further increase in the salt concentrations did not result in any noticeable changes in the Raman spectra (Figure 2, inset). At low salt concentrations, there was an indication that higher order ligand-to-ion complexes formed.[41,42] Experimentally observed and calculated Raman frequencies for a free ligand and its complexes with La(III) and Lu(III) in acetonitrile are summarized in Table 1.

Only two theoretical modes were found for **2** in the high-frequency region, in-phase (1708 cm^{-1}) and out-of-phase (1678 cm^{-1}) C═O stretching vibrations, which were assigned to 1672 and 1643 cm^{-1} Raman bands. A similar splitting of 30 cm^{-1} has been observed for the C═O stretching vibrations in Fe$(oxalate)_3^{3-}$ complexes.[53] A smaller splitting of amide I band has been reported recently for cyclic diamides, diketopiperazine, and its derivatives, with C═O groups in the para-position in a six-membered ring.[54,55] The relative positioning of C═O moieties in **1** is closer to that in oxalic acid than in diketopiperazine derivatives. Consequently, the kinematics and dipole–dipole interaction between C═O stretching vibrations are expected to be similar for **1** and oxalic acid resulting in a similar splitting pattern. The resonance enhancement was stronger for the in-phase stretching mode of **1** than for the out-of-phase one that is consistent with results reported for $Cr(CO)_4$(bipyridine) complex.[56] As our calculations showed, C═O stretching frequencies found for acetonitrile solution are substantially downshifted as compared to the gas-phase modes. Exceeding sensitivity of amide I band toward solvent has been reported previously.[57,58] Specifically, acetonitrile downshifts the calculated C═O stretching modes by up to 70 cm^{-1}.[58]

Several vibrational modes were calculated to involve C_1–N stretching coupled with various motions of carbon atoms in the 1400–1500-cm^{-1} frequency range. Several cyclic amide compounds have exhibited a strong resonance Raman band around 1500 cm^{-1} assigned to amide II mode involving significant C–N stretching and small C–C stretching.[39,59] Very strong calculated modes involving C_1–N stretching coupled with small ring stretching and H–C_2–H scissoring vibrations were assigned to an intense Raman band at 1498 cm^{-1}. Strong resonance enhancement of the C_1–N stretching coupled with ring stretching has been reported for cyclic amides, δ-vareloctam, and diketopiperazine.[39,59]

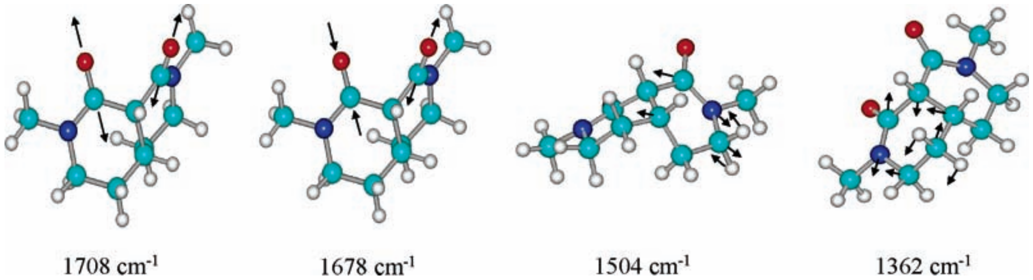
A strong band at 1460/1462 cm^{-1} is evident in the resonance Raman spectra of **1** and its complexes with La(III) and Lu(III). Caswell and Spiro[60] reported a strong enhancement of the 1465-cm^{-1} polyproline trans-imide II band for a cyclic compound with C(O)N–$(CH_2)_2$ moiety. Several strong UV resonance bands in the region of 1400–1500 cm^{-1} have been assigned to various conformers of six-membered amides.[39] Our preliminary evaluation of the resonance Raman enhancement for ligand **2** (Supporting Information) did not show a strong band around 1460 cm^{-1}. This might be because the calculations were made only for a single conformer resulting from the ab initio structure optimization (Supporting Information). The search for other stable conformers and the calculation of their resonance Raman spectra are in progress in our laboratory.

Several normal modes were found in the region of a broad low-intensity band (1362 cm^{-1}). The most intense band in the calculated resonance Raman spectrum involving C–N stretching, ring deformation, and H–C_2–H and H–C_3–H rocking motions was found at 1362 cm^{-1}. Several calculated normal modes involve C_α–H bending vibrations. There was no evidence, however, for the resonance enhancement of these bands, which are normally strong in the deep UVRR spectra of peptides in random coil and β-sheet conformations and weak for those in the α-helical form. Asher et al.[61] have shown that C_α–H bending is enhanced when coupled with the adjacent N–H bending vibration, however, the structure of **1** would not allow for such coupling.

The optimized geometry of the complex showed the elongation of C═O bonds and contraction of C–N bonds upon complex formation (Supporting Information, Table 7). As a result, mixing between downshifted C═O and upshifted C–N stretching vibrations became more efficient. As seen from Table 1, C═O stretching frequencies of both complexes were smaller than those of the free ligand. Although C═O bonds for the Lu

TABLE 1: Experimental (ligand 1) and Calculated (ligand 2) Raman Frequencies for a Free Ligand and Complexes with La(III) and Lu(III)[a]

ligand			complex with La(III)		complex with Lu(III)	
exp	calc	predominant modes	exp	calc	exp	calc
1672	1708	C═O in-phase stretching	1632	1603	1636 (+4)	1610 (+7)
1643	1678	C═O out-of-phase stretching	1594	1575	1602 (+8)	1581 (+6)
		coupling of C═O + C−$\mathrm{C_\alpha H}$ stretching	1515	1515	1518 (+3)	1518 (+3)
1498	1504	C−N stretching + ring stretching + H−$\mathrm{C_2}$−H scissoring	1486	1487	1485 (−1)	1486 (−1)
1460		C−N stretching + $\mathrm{CH_3}$ out-of-plane bending	1462		1462 (0)	
1362	1362	C−N stretching + $\mathrm{CH_3}$ umbrella motion + H−$\mathrm{C_2}$−H rocking	1362	1357	1362 (0)	1358 (+1)
				1366		1367 (+1)


1708 cm^{-1} 1678 cm^{-1} 1504 cm^{-1} 1362 cm^{-1}

[a] The shift of **1**-Lu Raman bands relative to those of **1**-La is shown in parentheses. The major calculated vibrational modes are shown schematically for the calculated conformation of the free ligand.

complex were longer than those for the La complex, the high-frequency Lu-complex normal modes were upshifted compared to those of the La-complex. The latter might be assigned to a strong contribution of the C−N stretching to the high-frequency modes dominated by the C═O stretching. Remarkably, the downshift of the high-frequency modes predicted for the La complex in comparison with the Lu complex was also observed in Raman spectra (Table 1).

The strongest Raman band at 1498 cm^{-1} loses its intensity in the spectra of complexes most probably because of the constrained C−N stretching. Instead, a new strong band at 1518 cm^{-1} arises from the coupling of C═O and C−$\mathrm{C_\alpha H}$ stretchings in both rings in an in-phase manner. The out-of-phase counterpart calculated at 1475 cm^{-1} was not observed in the Raman spectra because of its low intensity. Vibrational coupling strengthened in a cyclic compound has been reported to result in frequency splitting and strong resonance enhancement of the higher frequency band.[39] In particular, a strong C−N stretching band observed in the UVRR spectrum of cyclo-(glycine-proline) at 1515 cm^{-1} has been attributed to the vibrational coupling.[39] Although C═O stretching vibrations are normally expected for higher frequencies, the 1519-cm^{-1} C═O stretching band has been observed in an $\mathrm{Fe(acac)_3}$ complex.[62] Because of the complexity and low symmetry of the ligand and its metal complexes, the ultimate assignment of the observed bands would require resolving the normal mode problem in nonredundant symmetry coordinates.[63]

Conclusions

This study demonstrated that deep UV resonance Raman spectroscopy was a powerful tool for studying complex formation of a bicyclic diamide **1**, a novel chelating agent for lanthanides and actinides, with La(III) and Lu(III) in acetonitrile. A comparative analysis of Raman spectra and the results of molecular modeling allowed for elucidating the complex structures in solution. Molecular modeling, which included structure optimization and calculation of Raman frequencies and resonance intensities, allowed for assigning all strong Raman bands of the bicyclic diamide as well as predicting the band shifts observed because of complex formation with metal ions. The highest frequency Raman bands observed at 1672 and 1643 cm^{-1} (free ligand **1**) were assigned to mainly C═O in-phase and out-of-phase stretching, respectively. These bands showed the largest downshift on complex formation with metal cations. Remarkably, the larger shift found for La-**1** complex than that for Lu-**1** was predicted quantitatively by the modeling (Table 1). This intrinsic selectivity of deep UV resonance Raman spectroscopic detection in combination with its high sensitivity because of resonance enhancement opens a great opportunity for developing a new method for sensing applications.

A strengthened coupling of C═O stretching vibrations because of ring formation in **1**−La and **1**−Lu complexes was shown to result in the resonance enhancement of a strong band around 1515 cm^{-1} assigned to mainly the combination of C═O and C−$\mathrm{C_\alpha H}$ stretching modes. The 3D structure of ligand **2** and its complexes with La(III) and Lu(III) in acetonitrile was evaluated by ab initio calculations on DFT level. The conformational changes due to coordination of lanthanum and lutetium were verified by comparing the calculated changes in the normal modes with experimentally observed changes in Raman shifts on complex formation.

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Supporting Information Available: Optimized Cartesian and internal coordinates for a free ligand **2**, La-**2** and Lu-**2** complexes, and calculated resonance Raman intensities. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Lehn, J.-M.; Ball, P. *New chemistry*; Hall, N., Ed.; Cambridge University Press: Cambridge, U.K., 2000; pp 300−351.

(2) Gorden, A. E. V.; Xu, J. D.; Raymond, K. N.; Durbin, P. *Chem. Rev.* **2003**, *103*, 4207.

(3) Kaltsoyannis, N. *Chem. Soc. Rev.* **2003**, *32*, 9.

(4) Mathur, J. N.; Murali, M. S.; Nash, K. L. *Solvent Extr. Ion Exch.* **2001**, *19*, 357.

(5) Moreau, J.; Guillon, E.; Pierrard, J.-C.; Rimbault, J.; Port, M.; Aplincourt, M. *Chem. Eur. J.* **2004**, *10*, 5218.

(6) Hebbink, G. Ph.D. Thesis, University of Twente, 2002.

(7) VanPelt, C. E.; Crooks, W. J., III; Choppin, G. R. *Inorg. Chim. Acta* **2003**, *346*, 215.

(8) Bellusci, A.; Barberio, G.; Crispini, A.; Ghedini, M.; La Deda, M.; Pucci, D. *Inorg. Chem.* **2005**, *44*, 1818.

(9) Comby, S.; Imbert, D.; Chauvin, A.-S.; Bünzli, J.-C. G.; Charbonnière, L. J.; Ziessel, R. F. *Inorg. Chem.* **2004**, *43*, 7369.

(10) Laurie, S. H.; Byrne, R. H. *Polyhedron* **1995**, *14*, 1759.

(11) Sato, O.; Hayami, S.; Einaga, Y.; Gu, Z.-Z. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 443.

(12) Özkan, S. A.; Uslu, B.; Aboul-Enein, H. Y. *CRC Crit. Rev. Anal. Chem.* **2003**, *33*, 155.

(13) Zhu, P.; Lu, F.; Pan, N.; Arnold, D. P.; Zhang, S.; Jiang, J. *Eur. J. Inorg. Chem.* **2004**, *3*, 510.

(14) Zhu, P.; Pan, N.; Ma, C.; Sun, X.; Arnold, D. P.; Jiang, J. *Eur. J. Inorg. Chem.* **2004**, *3*, 518.

(15) van Grieken, R. E.; Markowicz, A. A. *Handbook of X-ray spectrometry*; Marcel Dekker Inc.: New York, 2002.

(16) Cendrowski-Guillaume, S. M.; Le Gland, G.; Lance, M., Nierlich M.; Ephritikhine, M. *C. R. Chim.* **2002**, *5*, 73.

(17) Villiers, C.; Thuéry, P.; Ephritikhine, M. *J. Coord. Chem.* **2003**, *56*, 1537−1547.

(18) Yi-Shan, S.; Bing, Y.; Zhen-Xia, C. *J. Solid State Chem.* **2004**, *177*, 3805.

(19) Petriček, S. *Polyhedron* **2004**, *23*, 2293.

(20) Kannappan, R.; Tanase, S.; Tooke, D. M.; Spek, A. L.; Mutikainen, I.; Turpeinen, U.; Reedijk, J. *Polyhedron* **2004**, *23*, 2285.

(21) Wang, Y.-W.; Liu, W.-S.; Tang, N.; Tan, M.-Y. *Spectrochim. Acta, A* **2004**, *60*, 2459.

(22) Bovens, E.; Hoefnagel, M. A.; Boers, E.; Lammers, H.; van Bekkum, H.; Peters, J. A. *Inorg. Chem.* **1996**, *35*, 7679.

(23) Zitha-Bovens, E.; Muller, R. N.; Laurent, S.; Vander Elst, L.; Geraldes, C. F. G. C.; van Bekkum, H.; Peters, J. A. *Helv. Chim. Acta* **2005**, *88*, 618.

(24) Cassani, M. C.; Davies, M. J.; Hitchcock, P. B.; Lappert, M. F. *Inorg. Chim. Acta* **2005**, *358*, 1595.

(25) Lisowski, J. *Magn. Reson. Chem.* **1999**, *37*, 287.

(26) Taylor, D. P.; Choppin, G. R. *Inorg. Chim. Acta* **2005**, *358*, 459.

(27) Duus, J. Ø.; Gotfredsen, C. H.; Bock, K. *Chem. Rev.* **2000**, *100*, 4589.

(28) Braun, S.; Kalinowski, H.-O.; Berger, S. *150 and more basis NMR experiments: a practical course;* Wiley-VCH: Weinheim, 1998.

(29) Lambert, J. B.; Mazzola, E. P. *Nuclear magnetic resonance spectroscopy: an introduction to principles, applications, and experimental methods;* Pearson/Prentice Hall: Upper Saddle River, NJ, 2004.

(30) Deshmukh, M. V.; Voll, G.; Kühlewein, A.; Mäcke, H.; Schmitt, J.; Kessler, H.; Gemmecker, G. *J. Med. Chem.* **2005**, *48*, 1506.

(31) Nakamoto, K. *Infrared and Raman spectra of inorganic and coordination compounds;* John Wiley & Sons, Ltd: New York, 1997.

(32) Ishiguro, S.-i.; Umebayashi, Y.; Kanzaki, R. *Anal. Sci.* **2004**, *20*, 415.

(33) Tramšek, M.; Benkič, P.; Turičnik, A.; Tavčar, G.; Žemva, B. Z. *J. Fluorine Chem.* **2002**, *114*, 143.

(34) Lombardi, J. R.; Davis, B. *Chem. Rev.* **2002**, *102*, 2431.

(35) Zolin, V. F. *J. Alloys Compd.* **2004**, *380*, 101.

(36) Asher, S. A. *Anal. Chem.* **1993**, *65*, 59A.

(37) Asher, S. A. *Anal. Chem.* **1993**, *65*, 201A.

(38) Mukerji, I.; Sokolov, L.; Mihailescu, M.-R. *Biopolymers* **1998**, *46*, 475.

(39) Wang, Y.; Spiro, T. G. *Biophys. Chem.* **2003**, *105*, 461.

(40) Lumetta, G. J.; Rapko, B. M.; Garza, P. A.; Hay, B. P.; Gilbertson, R. D.; Weakley, T. J. R.; Hutchison, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 5644.

(41) Sinkov, S. I.; Rapko, B. M.; Lumetta, G. J.; Hay, B. P., Hutchison J. E., Parks B. W. *Inorg. Chem.* **2004**, *43*, 8404.

(42) Lednev, I. K.; Ermolenkov, V. V.; He., W.; Xu, M. *Anal. Bioanal. Chem.* **2005**, *381*, 431.

(43) Hay, B. P.; Clement, O.; Sandrone, G.; Dixon, D. A. *Inorg. Chem.* **1998**, *37*, 5887.

(44) Montgomery, J. A., Jr.; Frish, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1999**, *110*, 2822.

(45) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(46) Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*; Gaussian, Inc.: Pittsburgh, PA, 1996.

(47) Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 523.

(48) Cossi, M.; Scalmani, G.; Rega, N.; Barone, V. *J. Chem. Phys.* **2002**, *117*, 43.

(49) Chua, Y. T.; Stair, P. C.; Nicholas, J. B.; Song, W.; Haw, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 866.

(50) Neugebauer, J.; Hess, B. A. *J. Chem. Phys.* **2004**, *120*, 11564.

(51) Leininger, T.; Nicklass, A.; Küchle, W.; Stoll, H.; Dolg, M.; Bergner, A. *Chem. Phys. Lett.* **1996**, *255*, 274.

(52) Maron, L.; Eisenstein, O. *New J. Chem.* **2001**, *25*, 255.

(53) Ohrstrom, L.; Michaud-Soret, I. *J. Phys. Chem. A* **1999**, *103*, 256.

(54) Hirst, J. D.; Persson, B. J. *J. Phys. Chem. A* **1998**, *102*, 7519.

(55) Besley, N. A.; Brienne, M.-J.; Hirst, J. D. *J. Phys. Chem. B* **2000**, *104*, 12371.

(56) Vičck Jr., A.; Grevels, F.-W.; Snoeck, T. L.; Stufkens, D. J. *lnorg. Chim. Acta* **1998**, *278*, 83.

(57) Markham, L. M.; Hudson, B. S. *J. Phys. Chem.* **1996**, *100*, 2731.

(58) Wong, M. W.; Wiberg, K. B.; Frisch, M. *J. Chem. Phys.* **1991**, *95*, 8991.

(59) Song, S.; Asher, S. A., Krimm, S.; Shaw, K. D. *J. Am. Chem. Soc*. **1991**, *113*, 1155.

(60) Caswell, D. S.; Spiro, T. G. *J. Am. Chem. Soc.* **1987**, *109*, 2796.

(61) Asher, S. A.; Ianoul, A.; Mix, G.; Boyden, M. N.; Karnoup A.; Diem, M.; Schweitzer-Stenner, R. *J. Am. Chem. Soc.* **2001**, *123*, 11775.

(62) Teleb, S. M.; Refat, M. S. *Spectrochim. Acta A* **2004**, *60*, 1579.

(63) Studt, F.; MacKay, B. A.; Fryzuk, M. D.; Tuczek, F. *J. Am. Chem. Soc.* **2004**, *126*, 280.