

Radium Revisited: Revitalization of the Coordination Chemistry of Nature's Largest 2+ Cation

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Abstract

The crystallization, single crystal structure, and Raman spectroscopy of $\text{Ra}(\text{NO}_3)_2$ have been investigated by experiment and theory, which represent the first, pure radium compound characterized by single crystal X-ray diffraction. The Ra^{2+} centers are bound by six chelating nitrate anions to form an anticuboctahedral geometry. The Raman spectrum acquired from a single crystal of $\text{Ra}(\text{NO}_3)_2$ generally occurs at a lower frequency than found in $\text{Ba}(\text{NO}_3)_2$ as expected. Computational studies on $\text{Ra}(\text{NO}_3)_2$ provide an estimation of the bond orders *via* Wiberg bond indices and indicate that Ra–O interactions are weak with values of 0.025 and 0.026 for Ra–O bonds. Inspection of natural bond orbitals and natural localized molecular orbitals suggest negligible orbital mixing. However, second-order perturbation interactions show that donation from the lone pairs of the nitrate oxygen atoms to the 7s orbitals of Ra^{2+} stabilize each Ra–O interaction by *ca.* 5 kcal mol⁻¹.

Main Body

Marie and Pierre Curie's discovery of radium is one of the key denotations of the dawn of the Atomic Age.^{1,2} Despite its historic importance in laying the foundation of nuclear sciences including Rutherford's gold foil experiment,³ early cancer treatments,⁴ the discovery of fission,⁵ and countless other transformations of our understanding of atomic structure,⁶ the structural chemistry of radium is poorly understood by modern standards. In fact, no single crystal structure of a radium compound has been reported.

Given the low solubility of RaSO_4 , which renders it useful in cancer treatment, as well as its geologic and historic significance, it remains the best studied radium compound. X-ray powder diffraction and EXAFS studies of RaSO_4 with high isotopic purity have been reported.^{7,8} However, the largest contributions to the structural chemistry of radium were report by Weigel and Trinkl, who using a combination of micro-scale synthesis and photographic powder X-ray diffraction techniques established the close correspondence between the structural chemistry of Ba^{2+} and Ra^{2+} as well as the first experimental determination of the ionic radius of Ra^{2+} .⁹⁻¹¹ In addition, in the light of the fact that Ra^{2+} exists in the form of hydrated ions in both environmental and medical scenarios, the hydration and dynamics of Ra^{2+} have been probed to reveal Ra^{2+} is more labile than Ba^{2+} .¹² Further applications of modern characterization techniques are needed to provide a more precise understanding radium and will likely demonstrate that its larger atomic/ionic radius can yield chemistry that is not accessible with barium. This is aptly illustrated by computational studies of radium fluoride compounds that predict higher oxidation states than 2+ should be accessible at high pressures, although experimental validation of this is needed.¹³

The dearth of modern studies on radium has many origins. First, the only moderately long-lived isotope that is potentially available is ^{226}Ra ($t_{1/2} = 1620$ years). A half-life of this timescale renders the specific activity of even microgram samples quite high and makes manipulation of samples challenging. Second, ^{226}Ra decays *via* an α -emission to short-lived ^{222}Rn ($t_{1/2} = 3.8$ days) and a series of other short-lived daughters, and thus preventing contamination of facilities and, more importantly, protecting researchers, requires well-planned and executed experimental procedures and specialized facilities. Lastly, characterizing compounds containing ^{226}Ra would require rapid collection of data before radiation damage alters the integrity and even composition of the samples.

Given these challenges, one might ask if the chemistry of radium is worth pursuing. From both basic and applied perspectives, the answer is most certainly yes. From an application point of view of the palliative, Xofigo® is being successfully used to address metastatic prostate and other cancers. This drug is in fact a solution of $^{223}\text{RaCl}_2$ and relies on the propensity of Ra^{2+} to localize in bone; the exact property that makes radium so hazardous for researchers. From a fundamental perspective, Ra^{2+} is the largest, redox stable 2+ cation in the periodic table, and offers opportunities to understand how coordination chemistry evolves in heavy elements.

To develop the chemistry of Ra^{2+} one must first synthesize and characterize benchmark compounds for comparison with Ba^{2+} analogs. Herein we report the crystallization, structure, and vibrational spectroscopy of $\text{Ra}(\text{NO}_3)_2$, the first, pure radium compound characterized by single crystal X-ray diffraction. Given the aforementioned challenges for manipulating radium samples, only 1.0 mg of ^{226}Ra was used for the recrystallization of $\text{Ra}(\text{NO}_3)_2$. Compared with the crystallization of $\text{Ba}(\text{NO}_3)_2$, which can be accomplished by the vapor diffusion of most

common alcohols, including methanol, ethanol, and isopropanol into aqueous solutions of barium nitrate, crystals of $\text{Ra}(\text{NO}_3)_2$ could only be grown when isopropanol was employed owing to the lower solubility of $\text{Ra}(\text{NO}_3)_2$. Other alcohols rapidly yield powders. Photographs of the resultant $\text{Ra}(\text{NO}_3)_2$ crystals are shown in **Figure S1**.

Single crystal X-ray diffraction analysis reveals that $\text{Ra}(\text{NO}_3)_2$ is isostructural with $\text{Ba}(\text{NO}_3)_2$ and crystallizes in the cubic space group $Pa\bar{3}$ (No. 205), $a = 8.2268(1)$ Å at 100 K. The radium cation is located on a $4b$ Wyckoff position with $\bar{3}$ site symmetry and is coordinated by six chelating nitrate anions with the nitrogen atom located on a C_3 symmetric site. The $[\text{Ra}(\text{NO}_3)_6]^{4-}$ moiety is shown in **Figure 1**. The resulting RaO_{12} polyhedron is shown in **Figure S2** and best described as an anticuboctahedron (Johnson solid, J_{27}) with slight distortions away from a regular prism¹⁴ as indicated by two distinct Ra–O distances of 2.937(4) Å and 2.979(4) Å. Both of these distances are longer than the Ba–O distances of 2.8667(5) and 2.9259(5) Å found in $\text{Ba}(\text{NO}_3)_2$ (as shown in **Table 1**) corresponding well with the larger ionic radius of Ra^{2+} . In addition, each $[\text{Ra}(\text{NO}_3)_6]^{4-}$ moiety is linked with twelve crystallographically-equivalent Ra^{2+} cations, forming a 3D network as shown in **Figure S3**. Additional crystallographic details for $\text{Ra}(\text{NO}_3)_2$ are provided in the supporting information.

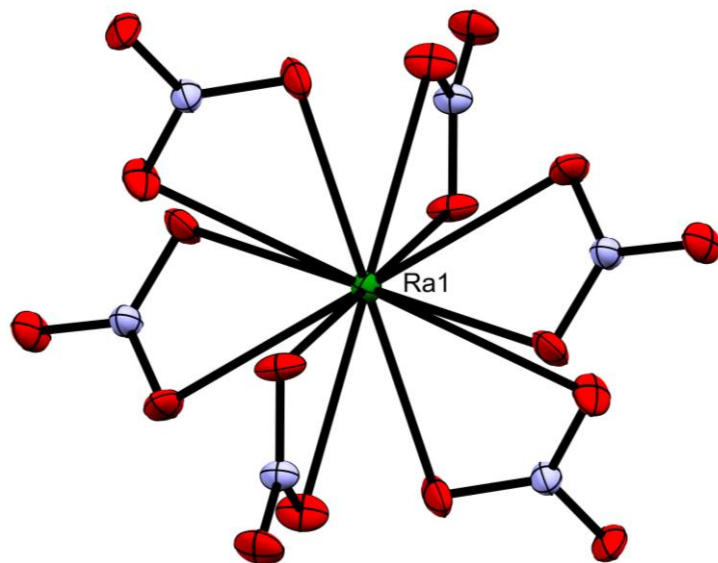


Figure 1. Coordination environment of Ra^{2+} in $\text{Ra}(\text{NO}_3)_2$. 50% probability ellipsoids are depicted at 100 K.

Table 1. M–O (M = Ba and Ra) Interatomic Distances and effective ionic radii r_{ionic} of twelve-coordinated M^{II} (M = Ba and Ra).¹⁵

Compound	$r_{\text{ionic}} / \text{\AA}$	$d(\text{M–O}) / \text{\AA}$	$d(\text{M–O}) / \text{\AA}$
Ba(NO₃)₂	1.61	2.8667(5)	2.9259(5)
Ra(NO₃)₂	1.70	2.937(4)	2.979(4)

In order to further characterize $\text{Ra}(\text{NO}_3)_2$, a single crystal Raman spectroscopic study was performed. Low-intensity bands on the low-frequency side of ν_1 , ν_2 , and ν_4 observed in most spectra of cubic alkaline metal and Pb^{2+} nitrates were also be detected in the spectrum of $\text{Ra}(\text{NO}_3)_2$.¹⁶ Specifically, $\text{Ra}(\text{NO}_3)_2$ is isomorphous with $\text{Ca}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, and $\text{Pb}(\text{NO}_3)_2$,¹⁷ and displays a ν_1 mode at 1044.8 cm^{-1} corresponding to the stretch of the D_{3h} symmetric nitrate and dominates all other vibrational modes.^{18,19} Much less intense ν_2 and ν_4

stretches at 821 cm^{-1} and 728.7 cm^{-1} , respectively, were also observed.²⁰ Two low-energy peaks at 73.0 and 119.8 cm^{-1} are designated as the Raman-active librational and translational lattice modes, respectively.²¹ In comparing the Raman spectra of $\text{Ra}(\text{NO}_3)_2$ and $\text{Ba}(\text{NO}_3)_2$, it is observed that the Raman peaks shift from 83 and 133 cm^{-1} in $\text{Ba}(\text{NO}_3)_2$ to 73.0 and 119.8 cm^{-1} as shown in **Figure 2**. The ν_4 and ν_1 modes are also lower in energy by approximately 3 cm^{-1} , while the ν_2 is at the same energy in both compounds. The Raman spectra of $\text{Ca}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, and $\text{Ra}(\text{NO}_3)_2$ are summarized in the SI. A general decrease in energy of the vibrational modes of the nitrate ion are observed across the series and $\text{Ra}(\text{NO}_3)_2$ continues this trend. This is most likely the result of the increasing ionic radius causing a more diffuse +2 charge and slightly weaker bonding between the metal and nitrate ions.

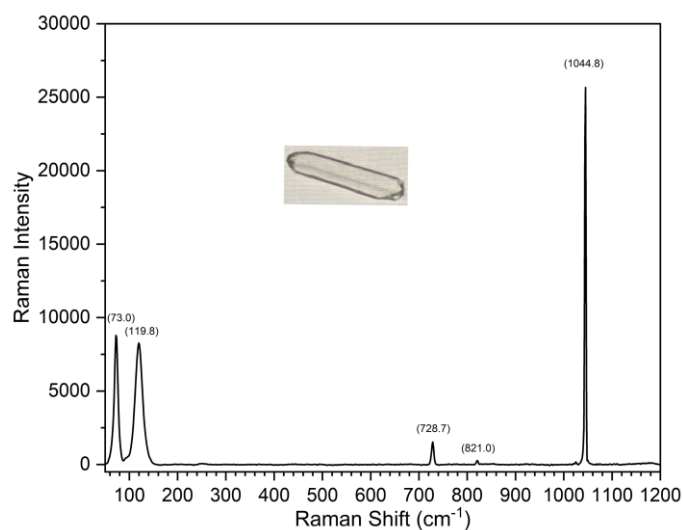


Figure 2. Raman spectrum of $\text{Ra}(\text{NO}_3)_2$ acquired from a single crystal (see inset for picture of the crystal).

Further similarities between $\text{Ba}(\text{NO}_3)_2$ and $\text{Ra}(\text{NO}_3)_2$ are found from computational studies of the $[\text{Ra}(\text{NO}_3)_6]^{4-}$ and $[\text{Ba}(\text{NO}_3)_6]^{4-}$ fragments. Through localization of the canonical molecular orbitals using the Natural Bond Orbital (NBO) approximation,²² it is suggested that in the nitrate environment, Ba^{2+} and Ra^{2+} cations have electronic structures close to that of their

isolated ions by examining their natural electron configurations, $[\text{core}]5s^25p^66s^{0.13}$ and $[\text{core}]6s^26p^67s^{0.13}$, respectively.²³ An estimation of the bond orders *via* the Wiberg bond indices (WBI), indicates that the Ra–O interactions are rather weak with values of 0.032 and 0.034 for Ba–O bonds and 0.025 and 0.026 for Ra–O bonds. Interestingly, the slight difference favoring Ba–O bonds correlates with the observation from the Raman spectra suggesting slightly weaker bonds for the Ra–nitrate interactions. Furthermore, while inspection of natural bond orbitals (NBOs)²² and natural localized molecular orbitals (NLMOs) in both complexes suggest negligible metal–nitrate orbital mixing, second-order perturbation interactions show that donation from the lone pairs of the nitrate oxygen atoms to the 7s (6s) orbitals of Ra (Ba) stabilize each Ra (Ba)–O interaction by *ca.* 5 (6) kcal mol⁻¹.

Another useful set of metrics to assess the nature of the metal-ligand interactions is the Quantum Theory of Atoms in Molecules (QTAIM).²⁴ Particularly, the accumulation of electron density, $\rho(r)$, and kinetic $G(r)$, potential $V(r)$, and total $H(r)$ energy densities at the bond critical point (BCP). Comparison between these metrics show that Ra–O and Ba–O bonds display very similar topologies as provided in **Table 2**. The predominance of kinetic over potential energy densities suggests that electrostatic interactions in M–O bonds drive the bond formation as well as the observed (low) accumulation of electron density at their BCPs. This is reflected in the positive values of the total energy densities that is commonly associated with purely ionic interactions.

Table 2. QTAIM metrics of the radium nitrate bonds in $[\text{Ra}(\text{NO}_3)_6]^{4-}$ and $[\text{Ba}(\text{NO}_3)_6]^{4-}$. Parameters were obtained from molecular DFT/PBE0 calculations. Electron densities are

expressed in $e \text{ \AA}^{-3}$, while kinetic (G), potential (V), and total (H) energy densities are given in $\text{kcal mol}^{-1} \text{ \AA}^{-3}$.

	$\rho(r)$	G(r)	V(r)	H(r)
Ba–O1	0.1396	77.1	-67.5	9.6
Ba–O2	0.1235	67.5	-57.6	9.9
Ra–O1	0.1353	76.9	-65.2	11.7
Ra–O2	0.1232	68.9	-57.2	11.7

In conclusion, the vapor-diffusion crystallization, single-crystal structure, vibrational spectroscopy, chemical bonding in $\text{Ra}(\text{NO}_3)_2$ have been examined. The comparison of $\text{Ra}(\text{NO}_3)_2$ with other alkaline earth metal compounds offers guidance for future coordination chemistry of radium.

ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic files (CIF). Experimental details, crystal pictures, additional crystal structure figures, additional Raman data, crystallographic data tables, and computational details and References.

Access Codes. CSD 2253091 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing interests.

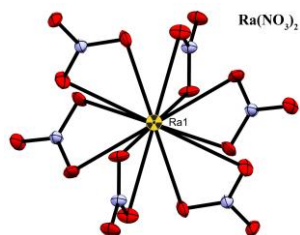
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TOC Synopsis: The synthesis, structure, and Raman spectrum of $\text{Ra}(\text{NO}_3)_2$ have been investigated by experiment and theory. Single crystal X-ray diffraction analysis reveals that radium nitrate is isomorphous with $\text{Ba}(\text{NO}_3)_2$ and crystallizes in the cubic space group $P\bar{a}3$ (No. 205) with $a = 8.2268(1) \text{ \AA}$ at 100 K. $\text{Ba}(\text{NO}_3)_2$ has been further characterized with the use of Raman spectroscopy.