Inorganic Chemistry
COMMUNICATION
pubs.acs.org/IC

$[U(Tp^{Me2})_2(bipy)]^+$: A Cationic Uranium(III) Complex with Single-Molecule-Magnet Behavior

Maria A. Antunes,[†] Laura C. J. Pereira,[†] Isabel C. Santos,[†] Marinella Mazzanti,[‡] Joaquim Marçalo,[†] and Manuel Almeida*,[†]

[†]Unidade de Ciências Químicas e Radiofarmacêuticas, Instituto Tecnológico e Nuclear/CFMCUL, P-2686-953 Sacavém, Portugal
[‡]Laboratoire de Reconnaissance Ionique et Chimie de Coordination, Service de Chimie Inorganique et Biologique, UMR-E 3 CEA/UJF, FRE3200 CNRS, INAC, CEA-Grenoble, F-38054 Grenoble Cedex 09, France

S *Supporting Information*

ABSTRACT: The addition of 2,2′-bipyridine to $[U(Tp^{Me2})_2I]$ (**1**) results in the displacement of the iodide and the formation of the cationic uranium(III) complex $[U(Tp^{Me2})_2(bipy)]I$ (**2**). This compound was isolated as a dark-green solid in good yield and characterized by IR and NMR spectroscopies, and its molecular structure was determined by single-crystal X-ray diffraction. Studies of its magnetic properties revealed a frequency dependence of magnetization with a blocking temperature of 4.5 K and, at lower temperatures, a slow relaxation of magnetization with an energy barrier of 18.2 cm^{-1}, characteristic of single-molecule-magnet behavior.

The study of the magnetic properties of actinide molecular compounds has received increased attention in recent years, owing to the unique characteristics revealed by these systems when compared to lanthanide and transition-metal compounds.[1] Those characteristics are related to the 5f electrons, which are more extended than the 4f electrons in the lanthanides and can give rise to larger magnetic spin−orbit coupling and enhanced magnetic anisotropy. Recent studies on the magnetic properties of uranium compounds have focused on multinuclear systems, uranium−lanthanide and uranium−transition metal complexes, and uranium complexes with redox-active ligands.[1a,2] Although the interpretation of their magnetism remains challenging because of the complexity of these systems, strong efforts to produce compounds as discrete molecules are being done to better understand the role of such 5f electrons in stronger magnetic exchange environments. A few years ago a new class of mononuclear compounds based on lanthanides was identified in which, at low temperatures, the magnetization presents slow relaxation, the so-called single-molecule-magnet (SMM) behavior, which arises from the magnetic anisotropy generated from the metal−ligand interaction.[3] Very recently, a few systems based on actinides have been identified.[4] In particular, the Long group showed that the simple uranium(III) complex $[U(Ph_2BPz_2)_3]$ with axial coordination,[4a] first isolated in our laboratory,[5] exhibits SMM behavior. In this respect, the actinides, due to higher spin−orbit coupling, larger magnetocrystalline anisotropy, and enhanced covalency, are better candidates to provide SMMs than the lanthanides.[1a,4c]

Inspired by these results and based on our previous work on the coordination chemistry of uranium(III) with the hydrotris(3,5-dimethylpyrazolyl)borate ligand (Tp^{Me2}),[6] we set out to investigate the magnetic properties of the cationic complex $[U(Tp^{Me2})_2(bipy)]I$ (**2**). Here we report the synthesis and characterization of a new uranium complex without axial symmetry presenting SMM behavior.

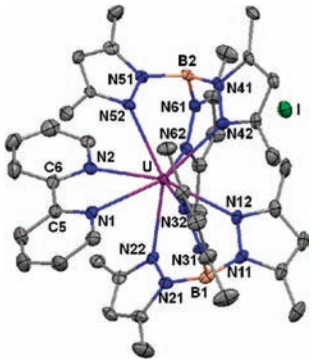

Figure 1. Molecular structure of $2 \cdot 1.5MeC{\equiv}N$ with 40% probability ellipsoids. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): U−N1 2.729(4), U−N2 2.691(4), U−N(Tp) 2.524(4)−2.653(4), C5−C6 1.478(7); N(Tp)−U−N(Tp) 69.15(11)−86.03(12), N1−U−N2 61.21(13). The shortest intermolecular U···U distance is 9.4550(4) Å.

The synthesis of complex **2** is presented in Scheme in the SI. The addition of a stoichiometric amount of 2,2′-bipyridine to a solution of $[U(Tp^{Me2})_2I]^7$ (**1**) in toluene afforded the cationic uranium(III) complex **2** as a dark-green solid in 88% yield.

At room temperature, the ^1H NMR spectrum of **2** in an acetonitrile-d_3 solution displayed six resonances for the methyl groups and three resonances for the 4H of the pyrazolyl rings. The resonances corresponding to coordinated 2,2′-bipyridine were shifted to low field compared to the free ligand and appeared as four signals between 19.56 and 9.88 ppm. This pattern is consistent with C_2 symmetry of the solution species in which both Tp^{Me2} ligands as well as the two pyridyl rings are equivalent. In the IR spectrum of **2**, the band assigned to the B−H stretching vibration appeared at 2516 cm^{-1}. The existence of only one band above 2500 cm^{-1} is indicative of a κ^3-coordination mode for both Tp^{Me2} ligands.[6] The presence of a neutral 2,2′-bipyridine ligand in **2** was confirmed by the IR spectrum, which presents a strong band at 1595 cm^{-1} and no bands between 900 and 1000 cm^{-1}, as observed for other reported compounds.[8]

Received: April 6, 2011
Published: September 14, 2011

dx.doi.org/10.1021/ic200705p | *Inorg. Chem.* 2011, 50, 9915–9917

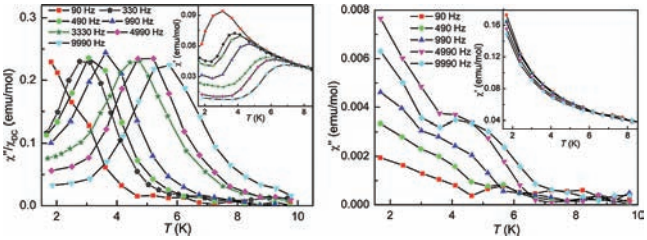

Figure 2. Temperature dependence of the real (χ', insets) and imaginary (χ'') components of the ac susceptibility of **2** under 0 T (left) and 0.05 T (right) dc fields, collected at different ac frequencies. The χ'' data at 0.05 T are normalized by the corresponding values of χ_{dc} at each temperature.

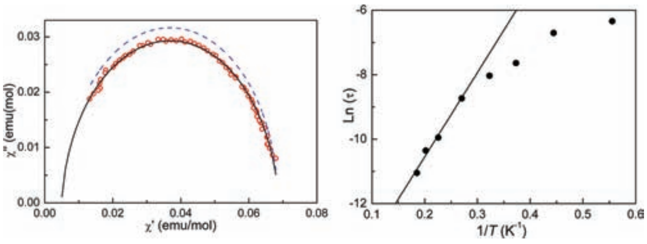

Figure 3. (Left) Cole–Cole plot for complex **2** at 4.5 K and 0.05 T. The dashed and solid lines represent the least-squares fits with a generalized Debye model to a single relaxation model and to a distribution of single relaxation modes, respectively. (Right) Plot of ln(τ) vs T^{-1} with a fitting to the Arrhenius law.

The molecular structure of **2**·1.5MeC≡N determined by X-ray diffraction analysis confirms the ionic character of this compound and the coordination modes of both $\mathrm{Tp^{Me2}}$ ligands and bipyridine (Figure 1).[9] The metal coordination geometry can be best described as distorted dodecahedral (Figure SI2 in the Supporting Information), and the arrangement of the donor atoms around the uranium atom approximates a C_2 symmetry, which is consistent with the solution NMR data. The U–N($\mathrm{Tp^{Me2}}$) distances range from 2.524(4) to 2.653(4) Å and are within the range found for other $[\mathrm{U(Tp^{Me2})_2X}]$ compounds previously reported by us [2.500(16)–2.802(6) Å].[6] The two pyrazolyl rings nearest the bipyridine ligand are very twisted about their B–N bonds, with B–N–N–U torsion angles of 45(1)° and 40(1)°. The U–N(bipy) distances [2.729(4) and 2.691(4) Å] are longer than those found for other uranium(III) complexes, which range from 2.626(7) to 2.694(9) Å.[2g,8b,10] This is probably due to an increased steric congestion about the uranium center in complex **2** imposed by the two $\mathrm{Tp^{Me2}}$ ligands. The bipyridine ligand is not planar, as expected for a neutral bipyridine upon coordination to a metal,[8a] presenting a torsion angle between the two pyridyl rings of 20(1)°, much higher than those observed for other reported uranium(III) complexes,[8b,10b] which reflects once more the more crowded coordination sphere of complex **2**. The C–C bond distance linking the two pyridyl rings is 1.478(7) Å, comparable with those of free bipyridine[11] and other related compounds,[2g,10a] further confirming the neutral character of bipyridine in **2**.

Complex **2** is paramagnetic, as expected for a uranium(III) compound, and its χT product drops monotonically from 0.8 emu K mol^{-1} at 300 K to 0.32 emu K mol^{-1} at 1.8 K (Figure SI4). The effective magnetic moment at 300 K is 2.53 μ_B, rather lower than the calculated moment for an isolated $\mathrm{U^{III}}$ ion (3.58 μ_B) but well within the range observed for uranium(III) coordination compounds.[1b,2g]

Below 5 K, there is a minimum in the χT curve (see the inset in Figure SI4). Below this temperature, the magnetization shows slow relaxation, as is more clearly revealed by the alternating-current (ac) susceptibility measurements, shown in Figure 2, by the temperature dependence of the real, χ', and imaginary, χ'', components of the ac susceptibility under zero applied direct-current (dc) field. Below 6 K and for the lowest frequencies, χ' increases monotonically upon cooling, as expected for a paramagnetic system. A similar slow relaxation of the magnetization in discrete molecules has been previously observed for some lanthanide systems[3] and more recently described in the trigonal-prismatic uranium(III) complexes $[\mathrm{U(Ph_2BPz_2)_3}]$[4a] and $[\mathrm{U(H_2BPz_2)_3}]$,[4b] classified as SMMs. Similarly to what happens in these latter cases, the application of small dc magnetic fields drastically changes the relaxation dynamics and a considerable increase of the χ' to χ'' ratio is observed. The χ'' curves at 0.05 T dc field in Figure 2 (right) were divided by the dc susceptibility, χ_{dc}, measured at 0.05 T in order to match the relaxation time τ with the inverse of the angular frequency ω of the applied ac field exactly at the peak of the corresponding curve.[3e,4c]

The magnetization relaxation rate was probed in the temperature range from 1.8 to 6 K. At fixed temperatures, χ' and χ'' were measured, while the frequency ω of the ac field was varied from 10 Hz to 10 kHz under applied dc fields from 0 to 0.1 T. These data provided Cole–Cole plots (χ'' vs χ' plots) for temperatures different from the one obtained at 4.5 K and B = 0.05 T, shown in Figure 3 (left). The ac susceptibility data show a very good agreement with the generalized Debye model,[12] $\chi(\omega) = \chi_S + (\chi_T + \chi_S)/(1 + i\omega\tau)^{1-\alpha}$, where χ_S and χ_T are the adiabatic and isothermal susceptibilities, τ is the average magnetization relaxation time, and α is a parameter ranging from 0 to 1 that quantifies the width of the relaxation time distribution (α = 0 corresponds to the ideal Debye model, with a single relaxation time). The fit obtained at 4.5 K is represented by the solid line, giving parameters of χ_S = 0.005 emu mol^{-1}, χ_T = 0.07 emu mol^{-1}, α = 0.173, and $\tau = 5 \times 10^{-5}$ s. The rather small α values obtained along with the nearly semicircular and symmetrical shape of the Cole–Cole plots are consistent with only one single magnetization relaxation process with a narrow distribution of these relaxation times.

For temperatures above 3.5 K, this single relaxation time follows an activated Arrhenius law, $\tau(T) = \tau_0 \exp(E_{\mathrm{eff}}/k_BT)$. The temperature dependence of the parameter τ extracted from ac susceptibility data in the frequency range of 100 Hz to 10 kHz, under a field of 0.05 T, is shown in Figure 3 (right). At lower temperatures below 3 K, a deviation from the Arrhenius law is observed, which can be attributed to the onset of a magnetic relaxation regime with quantum tunneling effects similar to the other examples of SMMs with actinides.[4] The fit to the Arrhenius law gives $\tau_0 = 1.4 \times 10^{-7}$ s, which is consistent with a slow magnetic relaxation[3a] and on the same order of magnitude as other well-known SMMs such as $\mathrm{Fe_8}$[13] and a few recently described lanthanide compounds.[14] The effective relaxation barrier of E_{eff} = 18.2 cm^{-1} was found to be comparable with the one obtained for $[\mathrm{U(Ph_2BPz_2)_3}]$ ($\tau_0 = 1 \times 10^{-9}$ s; E_{ff} = 20 cm^{-1})[4a] but slightly higher than that of $[\mathrm{U(H_2BPz_2)_3}]$.[4b]

Interestingly, the relaxation energy barrier in **2** is only slightly smaller than that in $[\mathrm{U(Ph_2BPz_2)_3}]$. This could arise from a slightly weaker axial ligand field interacting with uranium(III), less effective in pinning the electron density and magnetic moments in one direction. The Tp* ligand in **2** presents nitrogen coordinating atoms of nature similar to those found in the (Ph_2BPz_2) ligands. However, the U−N distances in **2** (2.524−2.653 Å) are larger than those in [$U(Ph_2BPz_2)_3$] (2.487−2.568 Å). Moreover, the two additional nitrogen atoms of the bipy ligand, of softer nature with respect to the pyrazolyl nitrogen atom, probably contribute to creating a less anisotropic ligand field.

Spin−spin relaxation effects are unlikely to be significant in view of the relatively large U···U distances, with the shortest being 9.4550(4) Å. This process of the quantum tunneling magnetization effect is being investigated by detailed lower temperature measurements, which will be reported in a subsequent publication.

In conclusion, a new mononuclear uranium compound exhibiting SMM behavior has been identified. This is only the third example of a uranium compound with such behavior. The observed variation in the relaxation barrier with respect to the previously reported compound of uranium showing SMM behavior suggests that a small variation in the uranium coordination sphere can significantly affect the relaxation behavior. Further experimental and theoretical studies of this complex and of related compounds will be important to more clearly establish magnetostructural correlations, namely, revealing the factors that govern the blocking temperature and enlightening the relaxation mechanisms. This should allow for the design of new uranium compounds showing higher relaxation barriers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental and crystallographic details, a CIF file for **2**, Scheme SI1, Figures SI1−SI5, and Tables SI1−SI4. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: malmeida@itn.pt.

■ ACKNOWLEDGMENT

M.A.A. is grateful to FCT (Portugal) for support through Grant SFRH/BPD/74194/2010. The support of Dr. N. Marques in the initial stages of this work is also acknowledged.

■ REFERENCES

(1) (a) Rinehart, J. D.; Harris, T. D.; Kozimor, S. A.; Bartlett, B. M.; Long, R. J. *Inorg. Chem.* **2009**, *48*, 3382–3395. (b) Edelstein, N. M.; Lander, G. H. In *The Chemistry of the Actinide and Transactinide Elements*, 3rd ed.; Morss, L. R., Edelstein, N. M., Fuger, J., Eds.; Springer: Dordrecht, The Netherlands, 2006; Vol. 4, Chapter 20. (c) Lukens, W. W.; Walter, M. D. *Inorg. Chem.* **2010**, *49*, 4458–4465.

(2) (a) Newell, B. S.; Rappe, A. K.; Shores, M. P. *Inorg. Chem.* **2010**, *49*, 1595–1606. (b) Chadwick, F. M.; Ashley, A.; Wildgoose, G.; Goicoechea, J. M.; Randall, S.; O'Hare, D. *Dalton Trans.* **2010** 6789–6793. (c) Fortier, S.; Wu, G.; Hayton, T. W. *J. Am. Chem. Soc.* **2010**, *132*, 6888–6889. (d) Arnold, P. L.; Potter, N. A.; Magnani, N.; Apostolidis, C.; Griveau, J. C.; Colineau, E.; Morgenstern, A.; Caciuffo, R.; Love, J. B. *Inorg. Chem.* **2010**, *49*, 5341–5343. (e) Rinehart, J. D.; Kozimor, S. A.; Long, J. R. *Angew. Chem., Int. Ed.* **2010**, *49*, 2560–2564. (f) Schelter, E. J.; Wu, R. L.; Scott, B. L.; Thompson, J. D.; Cantat, T.; John, K. D.; Batista, E. R.; Morris, D. E.; Kiplinger, J. L. *Inorg. Chem.* **2010**, *49*, 924–933. (g) Kraft, S. J.; Fanwick, P. E.; Bart, S. C. *Inorg. Chem.* **2010**, *49*, 1103–1110. (h) Schelter, E. J.; Wu, R. L.; Veauthier, J. M.; Bauer, E. D.; Booth, C. H.; Thomson, R. K.; Graves, C. R.; John, K. D.; Scott, B. L.; Thompson, J. D.; Morris, D. E.; Kiplinger, J. L. *Inorg. Chem.* **2010**, *49*, 1995–2007. (i) Minasian, S. G.; Krinsky, J. L.; Rinehart, J. D.; Copping, R.; Tyliszczak, T.; Janousch, M.; Shuh, D. K.; Arnold, J. *J. Am. Chem. Soc.* **2009**, *131*, 13767–13783. (j) Salmon, L.; Thuéry, P.; Rivière, E.; Ephritikhine, M. *Inorg. Chem.* **2006**, *45*, 83–93. (k) Bart, S. C.; Anthon, C.; Heinemann, F. W.; Bill, E.; Edelstein, N. M.; Meyer, K. *J. Am. Chem. Soc.* **2008**, *130*, 12536–12546. (l) Lam, C. P.; Anthon, C.; Heinemann, F. W.; O'Connor, J. M.; Meyer, K. *J. Am. Chem. Soc.* **2008**, *130*, 6567–6576. (m) Monreal, M. J.; Diaconescu, P. L. *Organometallics* **2008**, *27*, 1702–1706. (n) Nocton, G.; Burdet, F.; Pecaut, J.; Mazzanti, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 7574–7578. (o) Nocton, G.; Horeglad, P.; Pécaut, J.; Mazzanti, M. *J. Am. Chem. Soc.* **2008**, *130*, 16633–16645. (p) Mougel, V.; Horeglad, P.; Nocton, G.; Pecaut, J.; Mazzanti, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 8477–8480. (q) Nocton, G.; Horeglad, P.; Vetere, V.; Pecaut, J.; Dubois, L.; Maldivi, P.; Edelstein, N. M.; Mazzanti, M. *J. Am. Chem. Soc.* **2010**, *132*, 495–508.

(3) (a) Gatteschi, D.; Sessoli, R.; Villain, J. *Molecular Nanomagnets*; Oxford University Press: Oxford, U.K., 2006. (b) Winpenny, R. E. P. *Struct. Bonding (Berlin)* **2006**, 122. (c) Sessoli, R.; Powell, A. K. *Coord. Chem. Rev.* **2009**, *252*, 2328–2341. (d) Ishikawa, N.; Sugita, M.; Ishikawa, T.; Koshihara, S.; Kaizu, Y. *J. Am. Chem. Soc.* **2003**, *12*58694–8695. (e) Ishikawa, N.; Sugita, M.; Ishikawa, T.; Koshihara, S.; Kaizu, Y. *J. Phys. Chem B* **2004**, *108*, 11265–11271. (f) Ishikawa, N.; Mizuno, Y.; Takamatsu, S.; Ishikawa, T.; Koshihara, S. y. *Inorg. Chem.* **2008**, *47*, 10217–10219.

(4) (a) Rinehart, J. D.; Long, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 12558–12559. (b) Rinehart, J. D.; Meihaus, K. R.; Long, J. R. *J. Am. Chem. Soc.* **2010**, *132*, 7572–7573. (c) Magnani, N.; Apostolidis, C.; Morgenstern, A.; Colineau, E.; Griveau, J. C.; Bolvin, H.; Walter, O.; Caciuffo, R. *Angew. Chem., Int. Ed.* **2011**, *50*, 1696–1698.

(5) Maria, L.; Campello, M. P.; Domingos, A.; Santos, I.; Andersen, R. *J. Chem. Soc., Dalton Trans.* **1999**, *43*, 2015–2018.

(6) (a) Antunes, M. A.; Ferrence, G. M.; Domingos, A.; McDonald, R.; Burns, C. J.; Takats, J.; Marques, N. *Inorg. Chem.* **2004**, *43* 6640–6643. (b) Antunes, M. A.; Domingos, A.; Santos, I. C.; Marques, N.; Takats, J. *Polyhedron* **2005**, *24*, 3038–3045.

(7) Sun, Y.; McDonald, R.; Takats, J.; Day, V. W.; Eberspacher, T. A. *Inorg. Chem.* **1994**, *33*, 4433–4434.

(8) (a) Schultz, M.; Boncella, J. M.; Berg, D. J.; Yilley, T. D.; Andersen, R. A. *Organometallics* **2002**, *21*, 460–472. (b) Maria, L.; Domingos, A.; Galvão, A.; Ascenso, J.; Santos, I. *Inorg. Chem.* **2004**, *43*, 6426–6434.

(9) Crystallographic data for **2**·1.5MeC≡N: $C_{86}H_{113}B_4I_2N_{31}U_2$, monoclinic, 0.24 × 0.16 × 0.03 mm^3, $C2/c$, $a = 27.2210(7)$ Å, $b = 18.1835(5)$ Å, $c = 22.9469(7)$ Å, $\beta = 118.3710(10)°$, $V = 9993.9(5)$ Å^3, $Z = 4$, $T = 150(2)$ K, R1 = 0.0318 and wR2 = 0.0660. Additional selected bond lengths and angles (Table SI1), crystallographic details (Table SI2), and a more detailed discussion are given in the Supporting Information.

(10) (a) Mehdoui, T.; Berthet, J. C.; Thuéry, P.; Salmon, L.; Rivière, E.; Ephritikhine, M. *Chem.—Eur. J.* **2005**, *11*, 6994–7006. (b) Rivière, C.; Nierlich, M.; Ephritikhine, M.; Madic, C. *Inorg. Chem.* **2001**, *40*, 4428–4435.

(11) Chisholm, M. H.; Huffman, J. C.; Rothwell, I. P.; Bradley, P. G.; Kress, N.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 4945–4947.

(12) (a) Cole, K. S.; Cole, R. H. *J. Chem. Phys.* **1941**, *9*, 341. (b) Aubin, S. M. J.; Sun, Z.; Pardi, L.; Krzystek, J.; Folting, K.; Brunel, L. C.; Rheingold, A. L.; Christou, G.; Hendrickson, D. N. *Inorg. Chem.* **1999**, *38*, 5329–5340.

(13) (a) Bal, M.; Friedman, J. R.; Rumberger, E. M.; Shah, S.; Hendrickson, D. N.; Avraham, N.; Myasoedov, Y.; Shtrikman, H.; Zeldov, E. *J. Appl. Phys.* **2006**, *99*, 08D103. (b) Harman, W. H.; Harris, T. D.; Freedman, D. E.; Fong, H.; Chang, A.; Rinehart, J. D.; Ozarowski, A.; Sougrati, M. T.; Grandjean, F.; Long, G. J.; Long, J. R.; Chang, C. J. *J. Am. Chem. Soc.* **2010**, *132*, 18115–18126.

(14) Wang, X. L.; Li, L. C.; Liao, D. Z. *Inorg. Chem.* **2010**, *49*, 4735–4737.