



Contents lists available at SciVerse ScienceDirect

## International Journal of Mass Spectrometry

journal homepage: [www.elsevier.com/locate/ijms](http://www.elsevier.com/locate/ijms)

## Mass spectrometric characterization of a dinuclear terbium phthalocyaninato complex

Oliver Hampe<sup>a,b,\*</sup>, Svetlana Klyatskaya<sup>a</sup>, Tatjana Karpuschkin<sup>a</sup>, Matthias Vonderach<sup>b</sup>, Patrick Weis<sup>b</sup>, Mario Ruben<sup>a,c</sup>, Manfred M. Kappes<sup>a,b</sup><sup>a</sup> Institut für Nanotechnologie, Karlsruher Institut für Technologie (KIT) – Campus Nord, P.O. Box 3640, D-76021 Karlsruhe, Germany<sup>b</sup> Institut für Physikalische Chemie, Karlsruher Institut für Technologie (KIT) – Campus Süd, Kaiserstr. 12, D-76128 Karlsruhe, Germany<sup>c</sup> IPCMS-CNRS UMR 7504, Université de Strasbourg, 23 Rue du Loess, F-67034 Strasbourg, France

## ARTICLE INFO

## Article history:

Received 2 May 2012

Received in revised form 14 June 2012

Accepted 15 June 2012

Available online xxx

## Keywords:

High-resolution mass spectrometry

Collision induced dissociation ion-mobility spectrometry

## ABSTRACT

A newly synthesized heteroleptic bis-terbium-tris-phthalocyaninato sandwich complex has been studied using negative-ion electrospray ionization mass spectrometry. Intense ion signals corresponding to the singly and doubly negatively charged complex were observed upon chemical reduction in solution using tetrakis(dimethylamino)ethylene (TDAE) as an electron transfer reagent. Ion mobility mass spectrometry and collision induced dissociation using Fourier transform ion cyclotron resonance and Orbitrap mass spectrometers were employed to determine the stacking order of the triple-decker complex and to characterize the electronic stability of the isolated singly and doubly charged anions.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

Single molecule magnets (SMMs) are of current importance in many fields of chemistry and chemical physics. Metal organic compounds are good candidates for SMMs. In particular the open-shell electronic configurations of d- and/or f-elements can lead to (large) magnetic spin moments. In this context there are indications that (multi)lanthanide phthalocyanine complexes may serve as a particularly useful toolbox for assembling new SMM systems.

Recently, the synthesis and electronic characterization of bis(phthalocyaninato) complexes with trivalent holmium [1,2] as well as terbium and dysprosium metal centers [3] have been reported. Characterization of magnetic properties and the associated spin dynamics has been successfully performed in ensemble measurements in condensed phase by way of solid state NMR [4,5] or for isolated molecules supported on various host surfaces. More specifically, the latter gave important insight into the possible quenching of the magnetic moment due to coupling between metal center and substrate, e.g. for Cu(111) or Cu(100), the ligand field and hence magnetic properties of the Tb complex remains unaltered. The Tb ion presents its full orbital and spin magnetic moment as expected for a  $J=6$  ground state along

the easy axis, i.e. the axis perpendicular to the Pc plane, and vanishing magnetization in the hard Pc plane [6,7]. Moreover, it has been shown that TbPc<sub>2</sub> couples antiferromagnetically to ferromagnetic Ni substrates. This coupling is strongly anisotropic and can be manipulated by doping the interface with electron acceptor or donor atoms [8]. Functionalized Pc<sub>2</sub>Tb-SMMs grafted onto sp<sup>2</sup>-carbon materials like single-walled carbon nanotube (SWCNT) and graphene weakly interact through charge transfer [9–11].

In this context it is natural to explore larger SMM congeners comprising multiple metal centers whose metal–metal coupling allows variation of overall magnetic properties [12,13]. In order to relate the optical and magnetic properties of such systems to their underlying electronic structure it can be helpful to transfer them into gas-phase [14,15] where measurements in the absence of solvent, substrate or other matrices can be performed [16,17]. This is the subject of the present study.

Herein we report the synthesis and detailed mass spectrometric analysis of a novel phthalocyaninato (Pc) complex hosting two terbium metal centers. This molecule may be considered the next larger homologue of the single terbium bis-phthalocyaninato complex recently described by Klyatskaya et al. [18]. The present study comprises experiments using collisional induced dissociation giving insight into the structure of the complex as well as ion-mobility experiments and a first quantum chemical assessment of the structure at a semi-empirical level.

\* Corresponding author at: Institut für Nanotechnologie, Karlsruher Institut für Technologie (KIT) – Campus Nord, P.O. Box 3640, D-76021 Karlsruhe, Germany.

E-mail address: [oliver.hampe@kit.edu](mailto:oliver.hampe@kit.edu) (O. Hampe).

## 2. Experimental methods

### 2.1. Synthesis of the heteroleptic tris(phthalocyaninato)bis-terbium (III) complex (**1**)

A step-wise divergent strategy was used to synthesize the heteroleptic tris(phthalocyaninato)bis-terbium (III) complex **1** (see Scheme 1) using two different phthalocyaninato lithium salts (**2** and **3**, see Scheme 1) as well as [Tb(acac)<sub>3</sub>·2H<sub>2</sub>O] (acac = acetylacetonato) in an overall 1:1:1 ratio. Refluxing first PCl<sub>2</sub> (**2**) and Tb(acac)<sub>3</sub>·2H<sub>2</sub>O in 1-chloronaphthalene leads to the formation of mononuclear half-decker. By then adding (A<sub>3</sub>B)Li<sub>2</sub> (**3**) we tried to force the reaction towards symmetric stacking for a Tb<sub>2</sub>(A<sub>3</sub>B)<sub>2</sub>Pc. The formation of mono- and binuclear complexes was monitored during the course of the corresponding reactions by thin-layer chromatography and matrix-assisted laser desorption/ionization-time of flight (MALDI-ToF) mass spectrometry (Applied Biosystems Voyager DE Pro). The isolation of the target complex (A<sub>3</sub>B)<sub>2</sub>Tb<sub>2</sub>Pc (**1**) was achieved via column chromatography on basic alumina oxide followed by reprecipitation from a CH<sub>2</sub>Cl<sub>2</sub>–hexane mixture. The material obtained was then subjected to a detailed mass spectrometric analysis as described in the next section.

Reactions requiring an inert gas atmosphere were conducted under argon, and the glassware was oven dried (140 °C). All reagents were purchased from commercial sources and used as received. PCl<sub>2</sub> (**2**) [19] and the asymmetrically substituted phthalocyanine compound (A<sub>3</sub>B)Li<sub>2</sub> (**3**) [18] were prepared according to the literature procedures. Complex **1** was prepared as follows: under a slow stream of Ar, a mixture of PCl<sub>2</sub> (**2**) (68 mg, 0.13 mmol) and Tb(acac)<sub>3</sub>·2H<sub>2</sub>O (59 mg, 0.13 mmol) in 1-chloronaphthalene (5 mL) percolated through a basic alumina column just before being used was heated to 185–195 °C for 1 h until the absence of free **2**. The resulting dark blue solution was cooled down and **3** (160 mg, 0.11 mmol) was added. The mixture was heated up to 200–210 °C for 1 h until the disappearance of free **3** as checked by MALDI-ToF mass spectrometry. The mixture was then subjected to column chromatography (basic alumina oxide, 60 g), eluting with CH<sub>2</sub>Cl<sub>2</sub>/hexane (7/4, v/v). 1-Chloronaphthalene eluted first, then a greenish-blue band which was collected and concentrated to yield a raw material containing a mixture of (A<sub>3</sub>B)<sub>2</sub>PcTb<sub>2</sub> and several by-products: [(A<sub>3</sub>B)PcTb]<sup>0/-</sup>, [(A<sub>3</sub>B)<sub>2</sub>Tb]<sup>0/-</sup>, and [PcTb]<sup>0/-</sup> as a dark blue-green powder (150 mg). The complex **1** was separated from the crude mixture by column chromatography (basic alumina oxide), eluting with CH<sub>2</sub>Cl<sub>2</sub> followed by reprecipitation from the n-hexane/CH<sub>2</sub>Cl<sub>2</sub> mixture to afford a deep green solid of **1** (12 mg, 8% yield from **2**; R<sub>f</sub> = 0.5; CH<sub>2</sub>Cl<sub>2</sub>). Complex **1** is stable at ambient conditions in solid state as well in solutions.

### 2.2. Mass spectrometry

Mass spectra and collision-induced dissociation (CID) data were acquired using a 7T Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (APEX II, Bruker Daltonics, Billerica, MA, USA) employing an electrospray ion source (Analytica of Branford) described recently in more detail [20,21] and on a hybrid linear quadrupole ion trap/Orbitrap mass spectrometer (LTQ Orbitrap XL, Thermo Fisher Scientific, San Jose, CA, USA). For MS/MS experiments, CID with argon as the collision gas was pulsed into the FT-ICR mass spectrometer to typical peak partial pressures of ~2 × 10<sup>-7</sup> mbar. For MS/MS experiments in the linear Q trap of the LTQ Orbitrap instrument, helium was used as the buffer and collision gas (and maintained at a pressure ~2 × 10<sup>-5</sup> mbar). The possibility to vary the type and pressure of the collision gas in the FT-ICR

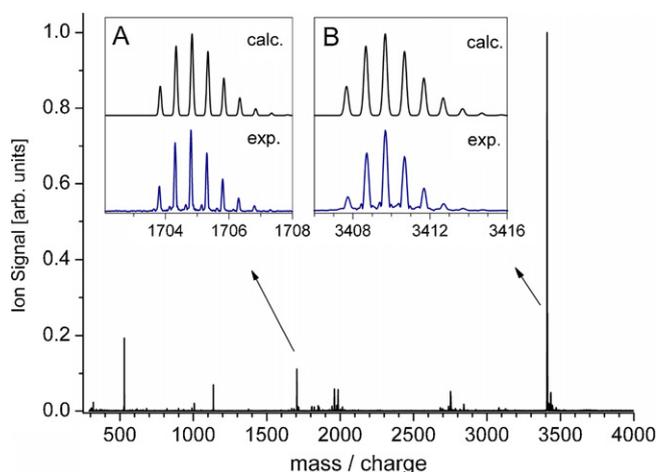


Fig. 1. FT-ICR negative ion mass spectrum of **1** and TDAE in ortho-dichlorobenzene. The insets show an enlarged view of the *m/z* ranges corresponding to the singly and doubly charged anions of **1** (labelled B and A, respectively) – as evidenced by the comparison with the calculated isotopomere distribution.

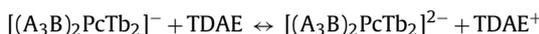
instrument on one hand and the somewhat higher sensitivity of the latter instrument was decisive for our experimental findings.

Arrival time distributions of gas-phase ions were measured on a home-built ion mobility quadrupole mass spectrometer system [22]. The setup comprises a 60 cm long drift cell filled with 2–4 mbar of helium or nitrogen, followed by a quadrupole mass filter (4 kDa mass range, 9.5 mm diameter rods, 880 kHz radio frequency, Extrel Inc.) and allows for separation of isomeric species on the basis of differences in their collision cross sections.

All instruments are equipped with electrospray ionization sources. Freshly prepared solutions in *o*-dichlorobenzene/acetonitrile were used at ~0.1 mM concentration and sprayed after adding a ~10 fold stoichiometric excess of tetrakis-(dimethyl amino)ethylene (TDAE). TDAE has been shown to be able to act as electron donor and to enhance negative ion formation of molecules in electrospray mass spectrometry [23].

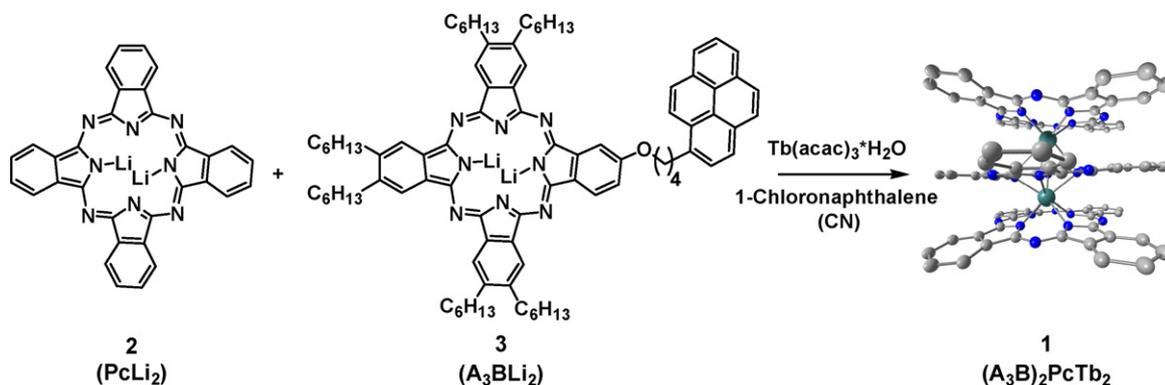
## 3. Results and discussion

Fig. 1 displays an electrospray FT-ICR mass spectrum obtained from a solution of **1** and TDAE dissolved in *o*-dichlorobenzene – as obtained in negative-ion mode. The neutral target molecule **1** is detected both as a singly and doubly charged anion (see insets labelled A and B in Fig. 1 and masses given in Table 1) with only minor fragmentation/contamination visible – mostly in the form of the mononuclear complex. Observation of intact gas-phase (di-)anions therefore proves the successful synthesis and isolation of **1** as a complex with the composition (A<sub>3</sub>B)<sub>2</sub>PcTb<sub>2</sub> (i.e. comprising two terbium atoms, two derivatized phthalocyanine units (A<sub>3</sub>B, C<sub>88</sub>H<sub>104</sub>N<sub>8</sub>O) and one unsubstituted phthalocyanine (Pc, C<sub>32</sub>H<sub>16</sub>N<sub>8</sub>) – corresponding to a total stoichiometry of C<sub>208</sub>H<sub>224</sub>N<sub>24</sub>O<sub>2</sub>Tb). The efficient formation of the (di-)anion may be rationalized by a sequential electron transfer reaction (=reduction) involving TDAE in solution [24] which can be formally written as:



The detailed assignment of the observed ionic species is summarized in Table 1.

After establishing the molecular formula and composition of the dinuclear complex **1**, its structure and in particular its stacking configuration next become of interest. In principle, such a



**Scheme 1.** Schematic representation of the synthesis of the heteroleptic complex **1**. (The metal complex **1** is shown without side groups; hydrogen atoms are omitted for clarity.)

**Table 1**

Summary of the molecular masses<sup>a</sup> from MS and MS/MS experiments of  $(A_3B)_2PcTb_2$ .

Compound	Molecular formula	Ionic species	$m/z$		
			Calculated	Experimental	Deviation
$(A_3B)_2PcTb_2$	$C_{208}H_{224}N_{24}O_2Tb_2$	$M^-$	3407.668	3407.686	0.018
$(A_3B)_2PcTb_2$	$C_{208}H_{224}N_{24}O_2Tb_2$	$M^{2-}$	1703.834	1703.846	0.012
$(A_3B)_2Tb$	$C_{176}H_{208}N_{16}O_2Tb$	$M^-$	2736.625	2736.593	0.032
$(A_3B)PcTb$	$C_{120}H_{120}N_{16}OTb$	$M^-$	1959.909	1959.928	0.019
$[(A_3B)_2PcTb_2-R]^b$	$C_{188}H_{207}N_{24}O_2Tb_2$	$M^{2-}$	1575.268	1575.276	0.008
$[(A_3B)_2PcTb_2-R]^b$	$C_{188}H_{207}N_{24}O_2Tb_2$	$M^-$	3150.534	3150.543	0.009
$[(A_3B)_2PcTb_2-2R]^b$	$C_{168}H_{190}N_{24}O_2Tb_2$	$M^-$	2893.401	2894.412	0.011

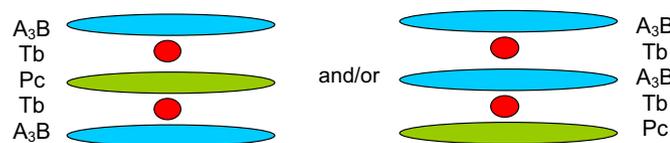
<sup>a</sup> Given are the values of the monoisotopic peak.

<sup>b</sup>  $R = C_{20}H_{17}$ .

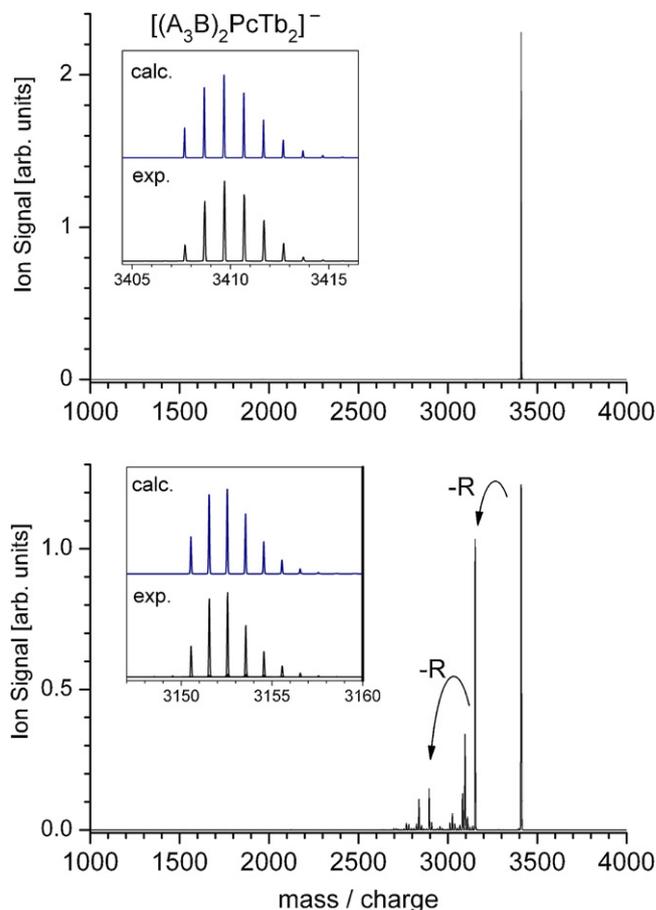
heteroleptic triple-decker complex can occur either as a symmetric and/or asymmetric variant as displayed in Scheme 2. In an attempt to resolve this, mass-selected collision induced dissociation (CID) experiments were performed on both the singly and doubly charged molecular anions.

Fig. 2 displays the outcome of the CID experiments carried out in the LTQ instrument: after isolation in the linear Q trap (shown in the top panel) the molecular monoanion was kinetically excited and subjected to collisions with helium (with an ion excitation strength of ~14%). Charged fragments were subsequently detected in the Orbitrap analyzer. The primary dissociation channel (see lower panel and inset of Fig. 2) was observed to be the formation of ions consistent with the loss of a  $R = C_{20}H_{17}$  unit, i.e. the side chain  $(CH_2)_4$  pyrene of the  $A_3B$  ligand is lost by homolytically cleaving a carbon–oxygen bond. This first dissociation step is followed by the subsequent loss of  $R$  from the second  $A_3B$  unit. Further fragmentation taking place at the phthalocyanine side chains follows these initial steps.

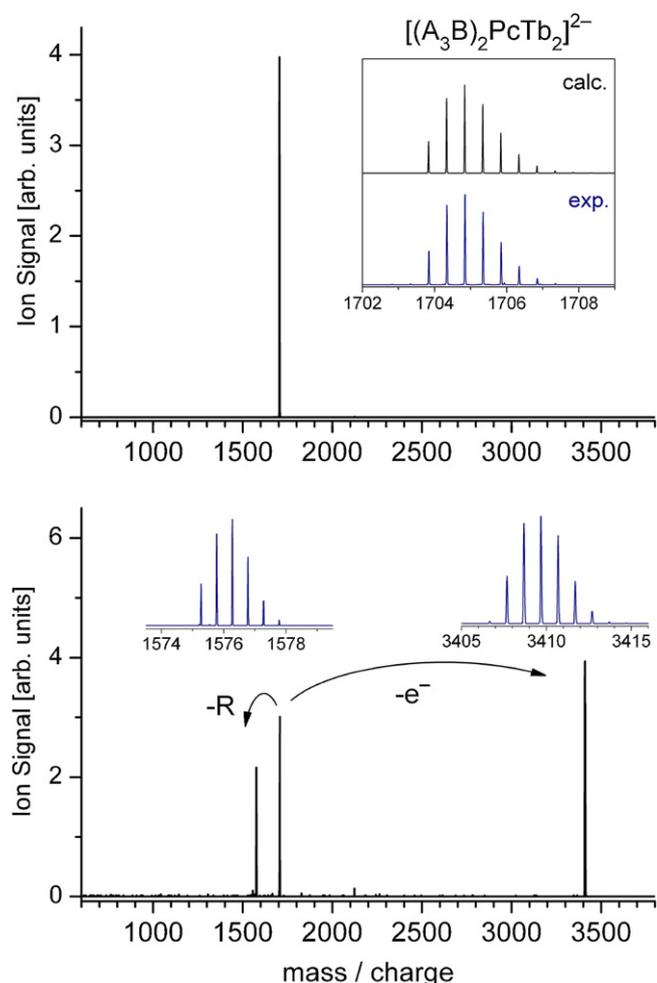
Further MS/MS experiments were conducted to investigate the behavior and stability of the doubly charged molecular anion  $[(A_3B)_2PcTb_2]^{2-}$  following the same protocol as for the singly charged ion. Fig. 3 shows the fragmentation mass spectrum. Two distinct dissociation channels are observed: (i) loss of a neutral  $C_{20}H_{17}$  leading to the corresponding dianion (see inset around  $m/z = 1576$ ), and (ii) emission of an electron leading to the formation of  $[(A_3B)_2PcTb_2]^-$ . Such decay behavior is remarkable as one



**Scheme 2.** Schematic structures of the two possible stacking configurations for a  $Tb_2(A_3B)_2Pc$  complex: a symmetric one (on the left) and an asymmetric one (on the right).



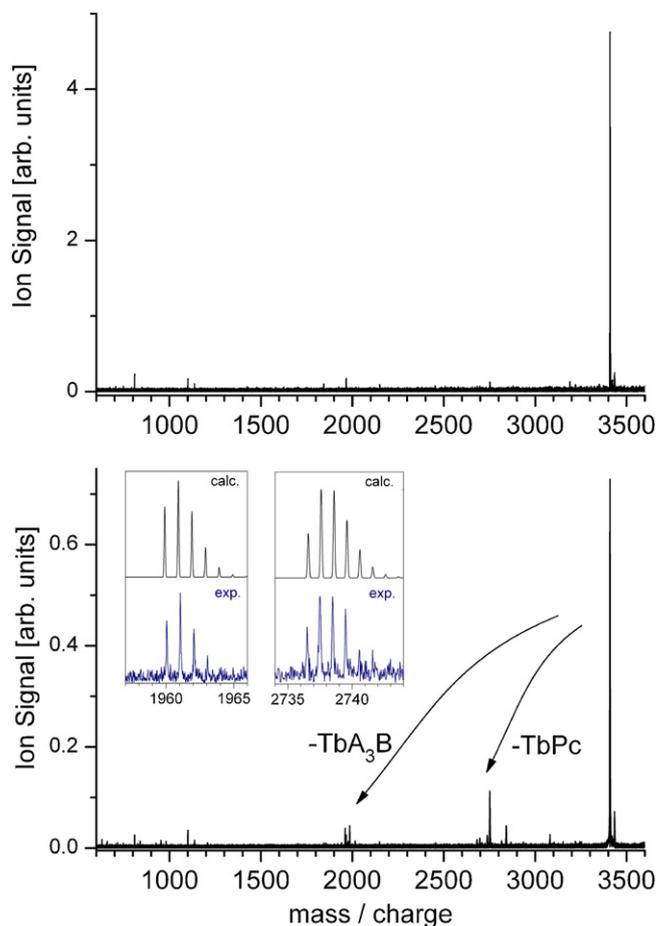
**Fig. 2.** MS/MS data acquired in the LTQ-Orbitrap mass spectrometer showing the singly charged precursor anion of **1** after isolation (top panel) and after collision induced dissociation with helium (bottom panel).  $R$  denotes the neutral fragment ( $C_{20}H_{17}$ ) from the  $A_3B$  ligand.



**Fig. 3.** MS/MS data acquired in the LTQ-Orbitrap mass spectrometer showing the doubly charged anion of **1** after isolation (top panel) and after collision induced dissociation with helium (bottom panel). R denotes the neutral fragment ( $C_{20}H_{17}$ ) from the  $A_3B$  ligand.

might instead have intuitively expected fission into two singly charged anions. However, in multiply charged anions the emission of an electron is often found to be favored over ionic fragmentation – particularly in cases where the electron binding energy is negative. Early examples of such metastable multianions include  $PtCl_4^{2-}$  [25,26] or  $CuPc(SO_3)_4^{4-}$  [27,28]. Our fragmentation observation may then be indicative of a very low (or even negative) electron binding energy of  $[(A_3B)_2PcTb_2]^{2-}$ , although spontaneous electron autodetachment as probed under collision-free conditions in the FT-ICR instrument at room temperature was not observed.

At this point it is informative to discuss the possible “localization” of the additional electron(s) of **1** in terms of a simple valence electron picture (“oxidation state”) of the constituents. The electronic structure of metal phthalocyanines (and derivatives thereof) may be thought of as resulting from the metal center donating two of its valence electrons to the phthalocyanine moiety. For the corresponding double-decker complex comprising a typically trivalent metal center like terbium, this leads to a situation in which the neutral complex  $[TbPc_2]^0$  exists, but can easily be reduced to the negatively charged  $[TbPc_2]^-$ . The electronic structure of the neutral triple-decker compound would then correspond to a situation in which the two terbium metal atoms (formally assigned as Tb(III)) have donated their six valence electrons to satisfy the stability of the closed shell  $\pi$  electron system of each phthalocyanine ( $Pc^{2-}$ ).



**Fig. 4.** MS/MS experiment showing the mass spectrum of the anion of **1** as isolated in the ICR cell (top panel) and after collision induced dissociation using argon as collision gas. The two dominant fragment ions (shown enlarged in the insets) are  $[(A_3B)PcTb]^-$  and  $[(A_3B)_2Tb]^-$ , respectively.

For the singly and doubly charged anion of **1** it is then conceivable that the extra electron occupies a  $\pi^*$  orbital (though it cannot be completely ruled out that the metal atom would be reduced to Tb(II)). Note that electrochemical reduction/oxidation of similar complexes in condensed phase by cyclic voltammetry is typically interpreted as taking place at the Pc ligands [29]. In future, it may prove interesting to investigate this redox behavior with light spectroscopic probes in order to learn about the pertaining oxidation states in more detail.

In a further CID experiment the singly charged anion  $[(A_3B)_2PcTb]^-$  was probed in the ICR cell of an FTMS instrument using argon as collision gas. Several dissociation products were observed, of which the two dominant ones – see insets in Fig. 4 – were assigned to the fragment anions  $[(A_3B)PcTb]^-$  and  $[(A_3B)_2Tb]^-$ , respectively. These fragmentation pathways correspond to a cleavage of the Tb–Pc and Tb– $A_3B$  bonds, respectively. The apparent difference in fragmentation behavior observed between the two CID experiments (CID with helium in a linear trap at  $\sim 10^{-5}$  mbar vs. CID with argon at  $\sim 10^{-7}$  mbar) may be attributed to the higher energy collisions (and energy transfers) associated with argon in the ICR cell. The observed fragment pattern also allows for structural assignment: the *asymmetric* stacking configuration appears to be dominant (see Scheme 2), although a mixture of both cannot be ruled out completely.

In order to shed some more light on this question we also performed ion-mobility experiments in order to isolate/distinguish multiple isomers. As can be seen from Fig. 5, a bimodal arrival time

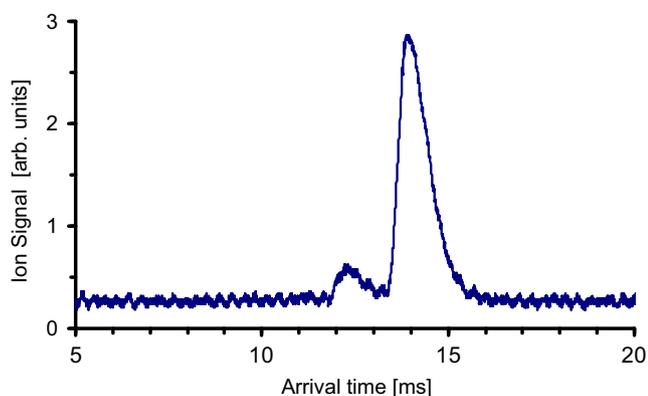


Fig. 5. IMS arrival time distribution of the anion of **1** indicating the presence of two different isomers.

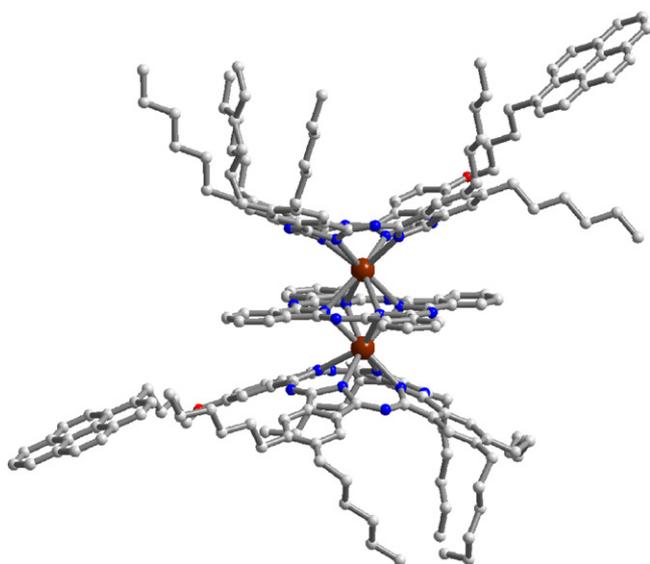


Fig. 6. Calculated structure of  $(A_3B)_2PcTb_2$  (symmetric stacking) at the PM6 level as implemented in the MOPAC2009 package [30]. Note that since the atom type Tb is not implemented in PM6, La was used instead (color code: dark red – Tb(La); red – oxygen; blue – nitrogen; grey – carbon; hydrogen atoms are omitted for clarity). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

distribution is measured, which indeed implies that two groups of isomers/conformers are present which do not interconvert on the experimental time scale. Together with the fragmentation behavior, it is therefore tempting to assign the more intense isomer to the asymmetric stack (whereas the minor isomer would then in turn correspond to the symmetrically stacked double-decker molecule). Unfortunately, a quantitative comparison of computed collision cross-sections with experiment is not feasible given current computational resources. However we did succeed in finding one (local?) minimum structure for the di-lanthanide triple-decker complex in its symmetric stacking configuration based on a PM6 level computation [30]. As can be seen from Fig. 6, in this computed structure the two  $A_3B$  moieties are bent strongly out of the plane whereas the central phthalocyanine unit remains essentially planar.

#### 4. Conclusions

A new heteroleptic phthalocyaninato complex with two terbium metal centers ( $Tb_2Pc(A_3B)_2$ ) has been synthesized and investigated by several mass-spectrometric methods. Singly and

doubly charged anions generated by electrospray ionization have been subjected to collision induced dissociation experiments. The preliminary experimental results suggest that: (i) the doubly charged anion is only weakly bound with respect to loss of an excess electron after modest collisional excitation with helium and (ii) the structure of the sandwich complex is primarily that of an asymmetric stack with respect to the two types of phthalocyanine ligands although ion-mobility experiments indicate the coexistence of two isomeric species.

#### Acknowledgments

Financial support from the Karlsruhe Institute of Technology (KIT) is gratefully acknowledged. P.W., O.H., M.R., and M.M.K. thank the Deutsche Forschungsgemeinschaft (DFG) for funding through projects C5, C6 and C7 of the collaborative research centre SFB/TRR 88 “3MET” (Kooperative Effekte in homo- und hetero-metallischen Komplexen).

#### References

- [1] N. Ishikawa, M. Sugita, W. Wernsdorfer, Nuclear spin driven quantum tunneling of magnetization in a new lanthanide single-molecule magnet: bis(phthalocyaninato)holmium anion, *Journal of the American Chemical Society* 127 (2005) 3650–3651.
- [2] N. Ishikawa, M. Sugita, W. Wernsdorfer, Quantum tunneling of magnetization in lanthanide single-molecule magnets: bis(phthalocyaninato)terbium and bis(phthalocyaninato)dysprosium anions, *Angewandte Chemie International Edition* 44 (2005) 2931–2935.
- [3] N. Ishikawa, M. Sugita, N. Tanaka, T. Ishikawa, S.-y. Koshihara, Y. Kaizu, Upward temperature shift of the intrinsic phase lag of the magnetization of bis(phthalocyaninato)terbium by ligand oxidation creating an  $S = 1/2$  spin, *Inorganic Chemistry* 43 (2004) 5498–5500.
- [4] F. Branzoli, P. Carretta, M. Filibian, G. Zoppellaro, M.J. Graf, J.R. Galan-Mascaros, O. Fuhr, S. Brink, M. Ruben, Spin dynamics in the negatively charged terbium(III) bis-phthalocyaninato complex, *Journal of the American Chemical Society* 131 (2009) 4387–4396.
- [5] F. Branzoli, P. Carretta, M. Filibian, M.J. Graf, S. Klyatskaya, M. Ruben, F. Coneri, P. Dhakal, Spin and charge dynamics in  $[TbPc(2)](0)$  and  $[DyPc(2)](0)$  single-molecule magnets, *Physical Review B* 82 (2010).
- [6] L. Vitali, S. Fabris, A.M. Conte, S. Brink, M. Ruben, S. Baroni, K. Kern, Electronic structure of surface-supported bis(phthalocyaninato) terbium(III) single molecular magnets, *Nano Letters* 8 (2008) 3364–3368.
- [7] S. Stepanow, J. Honolka, P. Gambardella, L. Vitali, N. Abdurakhmanova, T.C. Tseng, S. Rauschenbach, S.L. Tait, V. Sessi, S. Klyatskaya, M. Ruben, K. Kern, Spin and orbital magnetic moment anisotropies of monodispersed bis(phthalocyaninato)terbium on a copper surface, *Journal of the American Chemical Society* 132 (2010) 11900–11901.
- [8] A.L. Rizzini, C. Krull, T. Balashov, J.J. Kavich, A. Mugarza, P.S. Miedema, P.K. Thakur, V. Sessi, S. Klyatskaya, M. Ruben, S. Stepanow, P. Gambardella, Coupling single molecule magnets to ferromagnetic substrates, *Physical Review Letters* 107 (2011).
- [9] M. Urdampilleta, S. Klyatskaya, J.P. Cleuziou, M. Ruben, W. Wernsdorfer, Supramolecular spin valves, *Nature Materials* 10 (2011) 502–506.
- [10] A. Candini, S. Klyatskaya, M. Ruben, W. Wernsdorfer, M. Affronte, Graphene spintronic devices with molecular nanomagnets, *Nano Letters* 11 (2011) 2634–2639.
- [11] M. Lopes, A. Candini, M. Urdampilleta, A. Reserbat-Plantey, V. Bellini, S. Klyatskaya, L. Marty, M. Ruben, M. Affronte, W. Wernsdorfer, N. Bendib, Surface-enhanced Raman signal for terbium single-molecule magnets grafted on graphene, *ACS Nano* 4 (2010) 7531–7537.
- [12] K. Katoh, T. Kajiwara, M. Nakano, Y. Nakazawa, W. Wernsdorfer, N. Ishikawa, B.K. Breedlove, M. Yamashita, Magnetic relaxation of single-molecule magnets in an external magnetic field: an ising dimer of a terbium(III)-phthalocyaninate triple-decker complex, *Chemistry - A European Journal* 17 (2011) 117–122.
- [13] K. Takahashi, M. Itoh, Y. Tomita, K. Nojima, K. Kasuga, K. Isa, Preparation, characterization, and electrochemical properties of tris(2,3,9,10,16,17,23,24-octabutoxyphthalocyaninato)dijtterbium(III) and -didysprosium(III), *Chemistry Letters* 22 (1993) 1915–1918.
- [14] J.Z. Jiang, R.C.W. Liu, T.C.W. Mak, T.W.D. Chan, D.K.P. Ng, Synthesis, spectroscopic and electrochemical properties of substituted bis(phthalocyaninato)lanthanide(III) complexes, *Polyhedron* 16 (1997) 515–520.
- [15] R.L.C. Lau, J.Z. Jiang, D.K.P. Ng, T.W.D. Chan, Fourier transform ion cyclotron resonance studies of lanthanide(III) porphyrin-phthalocyanine heteroleptic sandwich complexes by using electrospray ionization, *Journal of the American Society for Mass Spectrometry* 8 (1997) 161–169.

- [16] M. Kordel, D. Schooss, S. Gilb, M.N. Blom, O. Hampe, M.M. Kappes, Photodissociation of trapped metastable multiply charged anions: a routine electronic spectroscopy of isolated large molecules? *Journal of Physical Chemistry A* 108 (2004) 4830–4837.
- [17] O.T. Ehrler, J.P. Yang, A.B. Sugiharto, A.N. Unterreiner, M.M. Kappes, Excited state dynamics of metastable phthalocyanine-tetrasulfonate tetra-anions probed by pump/probe photoelectron spectroscopy, *Journal of Chemical Physics* 127 (2007).
- [18] S. Klyatskaya, J.R. Galan-Mascaros, L. Bogani, F. Hennrich, M. Kappes, W. Wernsdorfer, M. Ruben, Anchoring of rare-earth-based single-molecule magnets on single-walled carbon nanotubes, *Journal of the American Chemical Society* 131 (2009) 15143–15151.
- [19] P.A. Barrett, D.A. Frye, R.P. Linstead, 213. Phthalocyanines and associated compounds. Part XIV. Further investigations of metallic derivatives, *Journal of the Chemical Society (Resumed)* (1938) 1157–1163.
- [20] M.N. Blom, O. Hampe, S. Gilb, P. Weis, M.M. Kappes, Tunneling electron loss from isolated platinum tetrahalide dianions, *Journal of Chemical Physics* 115 (2001) 3690–3697.
- [21] B. Concina, M. Neumaier, O. Hampe, M.M. Kappes, Electron emission from laser-heated fullerene dianions: probing the repulsive Coulomb barrier, *Journal of Chemical Physics* 128 (2008) 1134306.
- [22] M. Vonderach, O.T. Ehrler, P. Weis, M.M. Kappes, Combining ion mobility spectrometry, mass spectrometry, and photoelectron spectroscopy in a high-transmission instrument, *Analytical Chemistry* 83 (2011) 1108–1115.
- [23] O. Hampe, M. Neumaier, M.N. Blom, M.M. Kappes, On the generation and stability of isolated doubly negatively charged fullerenes, *Chemical Physics Letters* 354 (2002) 303–309.
- [24] M. Fujitsuka, C.P. Luo, O. Ito, Electron-transfer reactions between fullerenes (C-60 and C-70) and tetrakis(dimethylamino)ethylene in the ground and excited states, *Journal of Physical Chemistry B* 103 (1999) 445–449.
- [25] P. Weis, O. Hampe, S. Gilb, M.M. Kappes, Metastability of isolated platinum and palladium tetrahalide dianions and the role of electron tunneling, *Chemical Physics Letters* 321 (2000) 426–432.
- [26] X.B. Wang, C.F. Ding, L.S. Wang, Photodetachment spectroscopy of a doubly charged anion: direct observation of the repulsive Coulomb barrier, *Physical Review Letters* 81 (1998) 3351–3354.
- [27] X.B. Wang, L.S. Wang, Observation of negative electron-binding energy in a molecule, *Nature* 400 (1999) 245–248.
- [28] K. Arnold, T.S. Balaban, M.N. Blom, O.T. Ehrler, S. Gilb, O. Hampe, J.E. van Lier, J.M. Weber, M.M. Kappes, Electron autodetachment from isolated nickel and copper phthalocyanine-tetrasulfonate tetraanions: isomer specific rates, *Journal of Physical Chemistry A* 107 (2003) 794–803.
- [29] K. Katoh, K. Yamamoto, T. Kajiwara, J. Takeya, B.K. Breedlove, M. Yamashita, Magnetic properties of lanthanoid(III) phthalocyaninato triple-decker complexes in an external magnetic field and electronic transport properties for molecular spintronics, *Journal of Physics: Conference Series* 303 (2011) 012035.
- [30] J.J.P. Stewart, *Stewart Computational Chemistry*, MOPAC 2009, Colorado Springs, CO, USA, 2008.