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## Synthesis and structure of $[\text{Na}_4(\text{DMSO})_{15}][(\text{I}_3)_3(\text{I})]$ . Self-assembly of hexacoordinated sodium $\ddagger$

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**A new complex with the molecular formula  $[\text{Na}_4(\text{DMSO})_{15}][(\text{I}_3)_3(\text{I})]$  represents the first example of  $\text{Na}^+$  coordinated solely by DMSO. The triiodide ( $\text{I}_3^-$ ) and iodide ( $\text{I}^-$ ) anions form an infinite linear chain running throughout the crystal.**

Currently, alkali and alkaline earth metals are used in the synthesis of coordination polymers including remarkable ‘edible’ species.<sup>1</sup> These materials are of interest for their potential applications in the pharmaceutical industry, rechargeable batteries and the fabrication of porous materials.<sup>2</sup> The final structure of a coordination polymer network depends on the building blocks, *i.e.* organic ligands, metal ions, counter ions and solvent molecules. It also depends on complementary, reversible and directional interactions such as coordination bonds, hydrogen bonding,  $\pi$ – $\pi$  stacking and van der Waals interactions.<sup>3</sup> Metal–ligand coordination is a directional interaction that can induce different supramolecular architectures. Depending on the number of donor atoms, their orientation in the ligand and the coordination number of the metal, different one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) structures can be produced.<sup>4</sup> Another key factor in the design of coordination polymers is the charge balance in the structure. Counter ions are present in structures to allow neutral ligands to bind to metal ions and to give overall electrical neutrality. They can serve as a template for the observed form and topology of the network. They are also relevant because in some cases, a solid product can be isolated when a large counter ion is used.<sup>5</sup> The hydrophilic nature of particularly the smaller alkali metal ions means that they are frequently coordinated to water, and there are no

examples of sodium surrounded entirely by DMSO, DMF or other related solvents. However, the tendency of alkali metal cations to form a solvated hydrophilic layer can result in interesting layered compounds in which the polar, solvated cations separate from ‘softer’ anions.<sup>6</sup>

Recently, the coordination chemistry of DMSO has been the subject of several review articles, focusing on the use of transition metal DMSO complexes as precursors for the synthesis of new organometallic and coordination compounds. By contrast, the CSD contains only 19 examples of  $\text{Na}^+$  coordinated to one or two molecules of DMSO,<sup>7</sup> as well as a few of DMSO coordinated anionic transition metal complexes with alkali metal ions as counter ions.<sup>8</sup>

In this study, we report the synthesis of a new supramolecular compound with the molecular formula  $[\text{Na}_4(\text{DMSO})_{15}][(\text{I}_3)_3(\text{I})]$  (**1**), where the sodium ions interact directly with DMSO, an electrically neutral ligand, to give a unique tetrameric DMSO-bridged cluster  $[\text{Na}_4(\text{DMSO})_{15}]^{4+}$  based on octahedral metal cations. The cation layer is fully separated from the infinite polyiodide layer  $[(\text{I}_3)_3(\text{I})]^{4-}$  resulting in crystals with a greenish metallic lustre. The synthesis was performed at room temperature with DMSO, iodomethane ( $\text{CH}_3\text{I}$ ) and sodium hydroxide ( $\text{NaOH}$ ) using a simple combination of reagents. $\S$

The infrared (IR) spectrum of **1** presented the characteristic bands of the ligand. However, the band at  $1017\text{ cm}^{-1}$ , assigned to the sulfur–oxygen vibration,  $\nu(\text{S}=\text{O})$ , appears at a lower wave number compared to the free ligand ( $1026\text{ cm}^{-1}$ ). These data suggest that the coordination occurs through the oxygen atom of DMSO with the  $\text{Na}^+$ , but this decrease is not as remarkable as in the study of DMSO complexes with transition metals by Cotton *et al.*<sup>9</sup> The chemical shifts ( $\delta$ ) obtained by the proton and carbon nuclear magnetic resonances ( $^1\text{H}$  and  $^{13}\text{C}$  NMR), in different solvents, indicate the presence of DMSO<sup>10</sup> and are not significantly affected by the coordination with the  $\text{Na}^+$  ion.

The thermal stability of **1** was studied by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). In Fig. 1 (TG curve), within the temperature range of 50–200 °C, **1** lost 74.82% (calcd 76.33%) of its mass. The total mass lost was due to the loss of  $\text{I}_2$  (calcd 30.06%) and of DMSO (calcd 46.27%) in a number of well-defined various stages. This stepwise loss suggests that the sodium–DMSO cluster can

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$\ddagger$  Dedicated to Prof. Luis Echegoyen on the occasion of his 60<sup>th</sup> birthday.

$\S$  Electronic supplementary information (ESI) available: Further details about the synthesis methods, the IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, the TG-DSC thermograms and the crystallographic data are given in the form of a CIF file. CCDC 820376. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc11898f

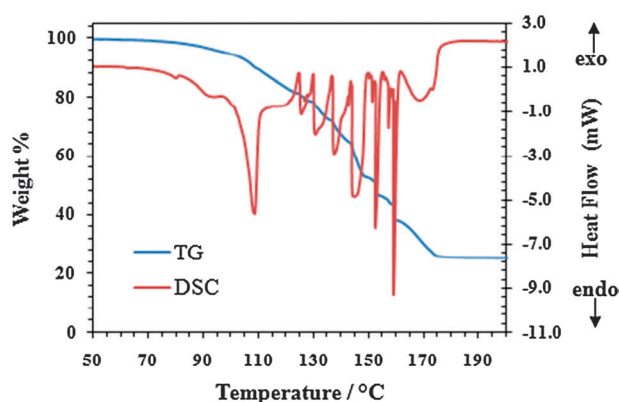


Fig. 1 Curve TG/DSC of compound 1.



Scheme 1 Thermal decomposition of compound 1.

stabilise a variety of polyiodide anions, perhaps because of the separate, layered structure. Eventually it is likely that compound **1** probably completely decomposes to sodium iodide (NaI) 24.50% (calcd 23.67%) (Scheme 1).

Compound **1** has a melting point of 108.7 °C, which corresponds to an endothermic peak found in Fig. 1 (DSC curve). The DSC curve in this region overlaps with other peaks, suggesting that the fusion of the compound is accompanied by its decomposition.

Crystals of complex **1** obtained during the synthesis were analyzed by single-crystal X-ray diffraction (XRD).<sup>¶</sup> In the structure of complex **1** (Fig. 2), coordination around the Na<sup>+</sup> is octahedral. This result is in accordance with other studies, where the usual coordination number for metal ion complexes bound to the oxygen atom of DMSO is six,<sup>11</sup> although it is unique for sodium. The structure has two types of anions: I<sub>3</sub><sup>-</sup>

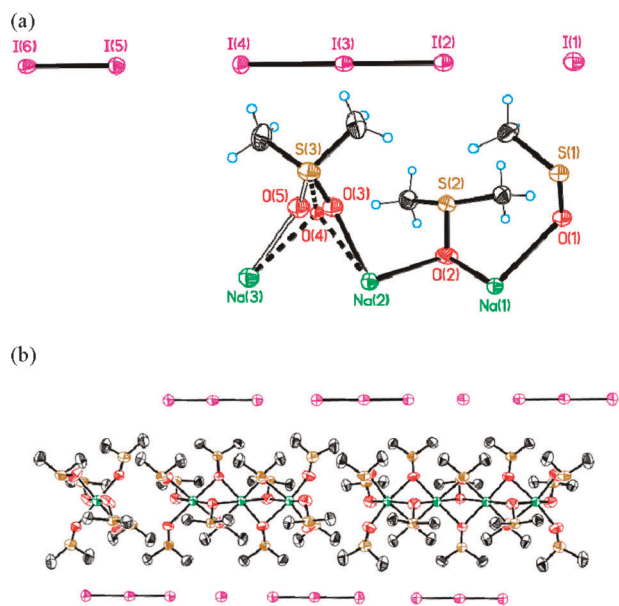


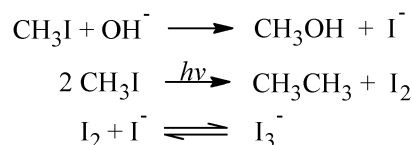
Fig. 2 (a) Asymmetric unit of **1**. (b) An example of an oligomeric alignment of a monomer, a trimer and a tetramer cation along the *c*-axis. Thermal ellipsoids are drawn with a 30% probability level.

and iodide (I<sup>-</sup>) ions. Both ions form linear chains near the carbon atom of the DMSO ligand. There is a large body of experimental and theoretical evidence on the interaction stability of iodide ions with the carbon atom of DMSO.<sup>12,13</sup>

The compound crystallizes as a hexagonal space group *P*6<sub>3</sub>/*m* with a well-ordered chain of anionic I<sub>3</sub><sup>-</sup> and I<sup>-</sup> units along the *c*-axis, but occupation disorders were observed for the Na<sup>+</sup> cations at positions Na(2) and Na(3). This disorder can only be interpreted as an oligomeric mixture of the general formula [Na<sub>*x*</sub>(DMSO)<sub>3*x*+3</sub>]<sup>x+</sup>, where the tetramer is the major cation. Fig. 2a shows the asymmetric unit with the Na positions lying on the center of symmetry for the 6<sub>3</sub> screw axis. The multiplicities/occupation factors for Na(1) and Na(2) that build-up the tetrameric structure are normally 0.3333 and 0.1666 for Na(3), which lie within the symmetry center of the axis. The disorder above leads to an occupation factor of around 0.2833 for Na(2) and 0.0500 for Na(3), which means that position Na(2) is only 85% occupied and Na(3) is 30% occupied. Normally, Na(3) is the position for a monomer, but by filling this position only with monomers implies that the occupation of Na(2) should be 70%. Therefore, larger oligomers, such as pentamers, must be included in the chain; this situation is shown by the oxygen position at S(3). Anisotropic refinement of the oxygen leads to a cigar-like ellipsoid and indicates disorder. Fortunately, the position may be split into three parts: O3 (70% for dimer, trimer and tetramer), O4 (15% for pentamer or higher, connecting Na(2) and Na(3)) and O5 (15% for monomer).

In the synthesis of **1** occurs simultaneously a side reaction between iodomethane and dimethyl sulfoxide in which trimethylsulfoxonium iodide (**2**) is formed, the characterization of this compound coincides with those reported in the literature<sup>14</sup> (see ESI<sup>†</sup>).

The anion triiodide I<sub>3</sub><sup>-</sup> was formed during the synthesis of complex **1**, probably due to the formation of iodide ion and iodine in the reaction medium<sup>15</sup> (Scheme 2). In the synthesis of complex **1** using a molar ratio of 33.2/1 (solvent to Na<sup>+</sup> ion), the solvent, DMSO, acts as a ligand; its action involves both the solvation and the coordination of the Na<sup>+</sup> ion. The nucleophilic character and high dielectric constant ( $\epsilon_r = 46.6$ ) of DMSO allow it to coordinate strongly with the cation Na<sup>+</sup> through its oxygen atom (ion–dipole interaction), to act as an electron donor and to form the general formula of a solvated ion [Na<sub>*x*</sub>(DMSO)<sub>3*x*+3</sub>]<sup>x+</sup>. On the periphery of the solvated ion, the clustering of solvent molecules produces a spherical, hydrophobic layer of alkyl groups. This layer encases the Na<sup>+</sup> ion inside the resulting structure, and the electrostatic attractions (ion–ion) between the Na<sup>+</sup> ions and the I<sup>-</sup>/I<sub>3</sub><sup>-</sup> ions decrease. In other words, complex **1** is formed through a self-assembly process driven by ion–dipole interactions, where DMSO molecules are connected with the Na<sup>+</sup> ions to form a 1D



Scheme 2 Proposed mechanism of the formation of the anion triiodide I<sub>3</sub><sup>-</sup> in the reaction medium.

oligomeric structure. Furthermore, based on the structure formed, the linear arrangement of triiodide and iodide ions stabilizes the oligomeric structure in the first dimension.

DMSO is an ambidentate ligand, and its bonding mode has been well rationalized through Pearson's concepts for the hardness and softness of acids and bases. According to these concepts, coordination occurs through sulfur (a soft donor) with metal ions that are soft Lewis acids, and it occurs through oxygen (a hard donor) with metal ions that are hard acids.<sup>12,16</sup> Therefore, in the synthesis of complex **1**, the Na<sup>+</sup> ion (a hard acid) prefers to coordinate to the oxygen atom of DMSO instead of forming NaI because the I<sup>-</sup> ion is a soft Lewis base.<sup>17</sup>

To obtain similar complexes to **1** with other hard acids, such as a lithium ion (Li<sup>+</sup>), potassium ion (K<sup>+</sup>), rubidium ion (Rb<sup>+</sup>) and cesium ion (Cs<sup>+</sup>), additional experiments were conducted using similar conditions to the synthesis of **1**. Unfortunately, we did not obtain the complexes containing these cations. However, by adding NaI to the final solutions of these experiments and keeping the solution at 4 °C, **1** resulted. This compound likely formed because K<sup>+</sup> (138 pm),<sup>18</sup> Rb<sup>+</sup> (166 pm) and Cs<sup>+</sup> (181 pm) have ionic radii greater than Na<sup>+</sup> (102 pm) and because Li<sup>+</sup> has an ionic radius (76 pm) smaller than Na<sup>+</sup>. In other words, the intermediate ionic radius of the Na<sup>+</sup> ion is optimal for the self-assembly process. Similar results have also been reported by Chen *et al.*<sup>19</sup> for the synthesis of 2D hybrid transition metal–alkali complexes, where only the Na<sup>+</sup> ion induces the organization.

In conclusion, a novel supramolecular compound with the formula [Na<sub>4</sub>(DMSO)<sub>15</sub>][(I<sub>3</sub>)<sub>3</sub>(I)] has been synthesized. In this structure, the sodium is hexacoordinated, and there is an arrangement of two linearly alternating anions. Future work within our group will focus on the application of this novel compound and the collateral reactions in the synthesis.

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## Notes and references

§ Synthesis of **1**. NaOH powder (0.170 g, 4.24 mmol) was added to a DMSO (11.010 g, 140.91 mmol) and distilled water (0.130 g, 7.20 mmol) solution. The mixture was ultrasonicated for 30 min, CH<sub>3</sub>I (3.420 g, 24.09 mmol) was added, and ultrasonication was continued for 1.5 h. The obtained yellow solution was maintained at 20 °C for 6 d, with continuous agitation. The color of the solution changed from yellow to red, and a white precipitate formed. The precipitate was filtered, washed with ethanol and identified as [(CH<sub>3</sub>)<sub>3</sub>SO]I (**2**) (0.694 g, 13%) (see ESI†). The filtrate was kept refrigerated at 4 °C for 8 d, where green crystals formed with metallic luster for **1**.

The crystals of **1** were filtered and dried in a vacuum. The yield obtained was 0.762 g, 28%.

¶ Crystal data for **1**: C<sub>30</sub>H<sub>90</sub>I<sub>10</sub>Na<sub>4</sub>O<sub>15</sub>S<sub>15</sub>, *M* = 2532.88, hexagonal, Space group *P6<sub>3</sub>/m*, *a* = 12.0292(4), *b* = 12.0292(3), *c* = 32.9777(7) Å, *V* = 4132.61(19) Å<sup>3</sup>, *Z* = 2, *d*<sub>calcd</sub> = 2.035 Mg m<sup>-3</sup>, crystal size 0.35 × 0.15 × 0.08 mm<sup>3</sup>, *T* = 233(2) K, λ = 0.71073 Å, 16891 reflections collected, 2729 independent reflections (*R*<sub>int</sub> = 0.0499), *R*<sub>1</sub> = 0.0352 [*I* > 2σ(*I*)], *wR*<sub>2</sub> = 0.0902 (all data), GOF = 1.081. CCDC 820376.

- R. A. Smaldone, R. S. Forgan, H. Furukawa, J. J. Gassensmith, A. M. Z. Slawin, O. M. Yaghi and J. F. Stoddart, *Angew. Chem., Int. Ed.*, 2010, **49**, 8630.
- (a) K. M. Fromm, *Coord. Chem. Rev.*, 2008, **252**, 856; (b) M. P. Suh, Y. E. Cheon and E. Y. Lee, *Coord. Chem. Rev.*, 2008, **252**, 1007.
- (a) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995; (b) S. Kitagawa and S. Noro, *Compr. Coord. Chem. II*, 2004, **7**, 231; (c) A. Y. Robin and K. M. Fromm, *Coord. Chem. Rev.*, 2006, **250**, 2127.
- A. K. Bar, R. Chakrabarty and P. S. Mukherjee, *Inorg. Chem.*, 2009, **48**, 10880.
- J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, Wiley, United Kingdom, 2009.
- A. W. Coleman, S. G. Bott, S. D. Morley, C. M. Means, K. D. Robinson, H. Zhang and J. L. Atwood, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1361.
- CSD v5.32 Nov 2010 + 2 updates.
- (a) M. Calligaris, *Coord. Chem. Rev.*, 2004, **248**, 351; (b) M. Calligaris and O. Carugo, *Coord. Chem. Rev.*, 1996, **153**, 83.
- (a) F. A. Cotton and R. Francis, *J. Am. Chem. Soc.*, 1960, **82**, 2986; (b) M. J. Bennett, F. A. Cotton, D. L. Weaver, R. J. Williams and W. H. Watson, *Acta Crystallogr.*, 1967, **23**, 788; (c) F. A. Cotton, R. Francis and W. D. Horrocks, *J. Phys. Chem.*, 1960, **64**, 1534.
- H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512.
- H. H. Szmant, in *Chemistry of Dimethyl Sulfoxide*, in *Dimethyl Sulfoxide*, ed. S. W. Jacob, E. E. Rosenbaum and D. C. Wood, Marcel Dekker Inc., New York, 1971, pp. 1–97.
- K. Wakabayashi, Y. Maeda, K. Ozutsumi and H. Ohtaki, *J. Mol. Liq.*, 2004, **110**, 43.
- T. Megyes, I. Bakó, T. Radnai, T. Grósz, T. Kosztolányi, B. Mroz and M. Probst, *Chem. Phys.*, 2006, **321**, 100.
- (a) R. Kuhn, *Angew. Chem.*, 1957, **17**, 570; (b) R. Kuhn and H. Trischmann, *Justus Liebigs Ann. Chem.*, 1958, **611**, 117; (c) O. Knop, A. Linden, B. R. Vincent, S. C. Choi, S. T. Cameron and R. J. Boyd, *Can. J. Chem.*, 1989, **67**, 1984; (d) S. G. Smith and S. Winstein, *Tetrahedron*, 1958, **3**, 317.
- N. Davidson and T. Carrington, *J. Am. Chem. Soc.*, 1952, **74**(24), 6277.
- N. S. Panina and M. Calligaris, *Inorg. Chim. Acta*, 2002, **334**, 165.
- (a) R. G. Pearson, *Inorg. Chem.*, 1988, **27**, 734; (b) R. G. Pearson, *J. Am. Chem. Soc.*, 1985, **107**, 6801.
- R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Crystallogr.*, 1976, **A32**, 751.
- G. J. Chen, F. X. Gao, F. P. Huang, J. L. Tian, W. Gu, X. Liu, S. P. Yan and D. Z. Liao, *Cryst. Growth Des.*, 2009, **9**, 2662.