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Sodium Thioether Macrocyclic Chemistry: Remarkable Homoleptic Octathia Coordination to Na^+

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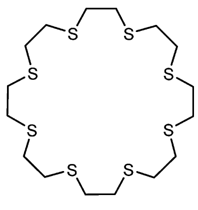
Ⓢ *Supporting Information*

ABSTRACT: Unprecedented homoleptic octathioether macrocyclic coordination to Na^+ in $[Na([24]aneS_8)]^+$ has been achieved by using $Na[B\{3,5\text{-}(CF_3)_2\text{-}C_6H_3\}_4]$ as a source of "naked" Na^+ ions and confirmed crystallographically, with $d(Na-S) = 2.9561(15)-3.0524(15)$ Å. Density functional theory calculations show that there is electron transfer from the S 3p and C 2p valence orbitals of the ligand to the 3s and 3p orbitals of the Na^+ ion upon complexation.

Macrocyclic ligands have been exploited extensively within transition-metal chemistry because of the typically higher stabilities of their complexes caused by the macrocyclic effect.[1−3] The capacity to vary the number and type of donor groups (Lewis bases) and overall ring size (binding cavity) renders them extremely versatile ligands. Thioether macrocycles have been studied intensively. Their ability to stabilize unusual transition-metal oxidation states and geometries has been established, as well as their coordinative flexibility, enabling ready interchange between oxidation states during electron-transfer reactions.[4] A diverse chemistry of these ligands toward p-block acceptors has also emerged more recently.[2,5] In contrast, examples of thioether coordination toward s-block cations are much rarer. It is well-known that these hard, labile cations have a very high affinity for crown ethers, and examples of coordination of the heavier chalcogenoether donor groups in the s block are limited to a very small number of mixed thia−oxa and selena−oxa macrocyclic complexes.[6−8] Within group 2, we recently reported Ca^{II} and Sr^{II} species, $[CaI_2([18]aneO_2S_4)]$ ($[18]aneO_2S_4$ = 1,10-dioxa-4,7,13,16-tetrathiacyclooctadecane), $[MI_2([18]aneO_4E_2)]$ (M = Ca, Sr; E = S, Se; $[18]aneO_4S_2$ = 1,4,10,13-tetraoxa-7,16-dithiacyclooctadecane; $[18]aneO_4Se_2$ = 1,4,10,13-tetraoxa-7,16-diselenacyclooctadecane), that show distorted eight-coordination through the six macrocyclic donor atoms and two mutually cis iodide ligands, with $d(Ca-S/Se)$ of ca. 3.0 Å.[7] The alkaline-earth diiodides (MI_2) were found to be better suited as precursors for this chemistry than MCl_2 or $M(CF_3SO_3)_2$, etc., because of their higher solubilities in noncompetitive solvents. This was linked to their lower lattice energies. However, group 1 complexes containing soft donor ligands such as thioethers are extremely rare. Structural evidence from $[18]aneO_4S_2$ species containing K^+ and Na^+ ions shows that, in this O-rich ligand, the $K/Na\cdots S$ distances are *extremely* long, with macrocycle coordination undoubtedly dominated by the presence of several short, favorable K/Na−O bonds.[8a] s-Block complexes containing thioether-only coordination are completely unknown.

Very recent work[9] on Na^+ complexes with aza macrocycles led to isolation of the distorted octahedral sandwich cation $[Na(Me_3\text{-}tacn)_2]^+$ and the distorted five-coordinate cation $[Na(THF)(Me_4\text{-}cyclam)]^+$ (Me_3-tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane; Me_4-cyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; THF = tetrahydrofuran) using $Na[BAr^F]\cdot 2THF$ ($[BAr^F]^- = [B\{3,5\text{-}(CF_3)_2\text{-}C_6H_3\}_4]^-$),[10] which has good solubility in weak donor solvents such as CH_2Cl_2 and toluene. These results led to the intriguing prospect that an entirely new coordination chemistry of the hard, oxophilic group 1 cations with very soft donor ligands might be within reach. We therefore sought to establish whether it would be possible to induce coordination of much softer, neutral thioether ligands toward very hard group 1 cations by taking advantage of the large, weakly coordinating $[BAr^F]^-$ anion.[11] We report here the first examples of group 1 complexes containing S(thioether)-only macrocycles, including the very unexpected homoleptic octathia cation, $[Na([24]aneS_8)]^+$ ($[24]aneS_8$ = 1,4,7,10,13,16,19,22-octathiacyclotetracosane).

The reaction of $Na[BAr^F]\cdot 2THF$ with 1 mol equiv of $[24]aneS_8$ in anhydrous CH_2Cl_2 affords $[Na([24]aneS_8)][BAr^F]$ as a white crystalline solid. The product is moderately stable in solution and can be stored as a solid for several months without degradation. Microanalysis and ^1H NMR spectroscopy confirm the 1:1 $[24]aneS_8/[BAr^F]^-$ ratio, without retention of THF. The ligand resonances are little shifted from those of the ligand itself. ^{23}Na NMR spectroscopy shows a singlet at +4.0 ppm, to a high frequency of Na^+ in water ($[Na(THF)_x][BAr^F]$: $\delta(^{23}Na) = -4.8$).[9]



$[24]aneS_8$

The coordination environment was established unambiguously by X-ray crystallography. The structure (Table S1 in the

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Supporting Information, SI) of [Na([24]aneS$_8$)][BAr^F] contains discrete Na$^+$ cations coordinated to all eight S-donor atoms from the macrocycle in a distorted dodecahedral environment (Figure 1), with discrete [BAr^F]$^-$ anions providing charge balance. The Na−S bonds [2.9561(15)−3.0524(15) Å] are very significantly longer than the sum of the ionic radius of Na$^+$ (1.32 Å for CN = 8) and the covalent radius of S (1.05 Å).[12]

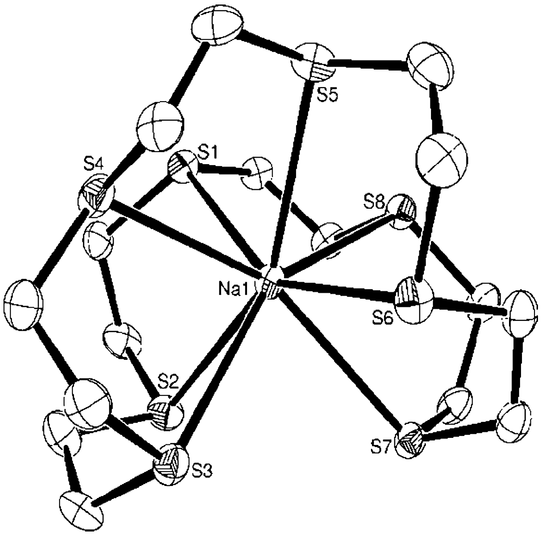
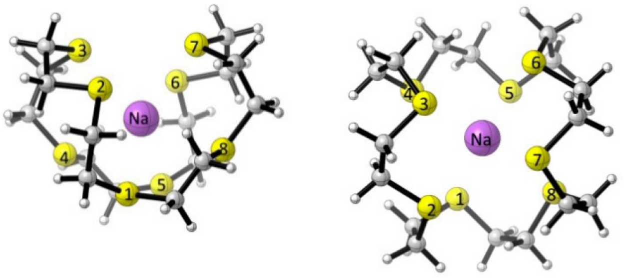


Figure 1. View of the crystal structure of the [Na([24]aneS$_8$)]$^+$ cation with numbering scheme. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

Attempts to isolate Na$^+$ complexes with [9]aneS$_3$ (1,4,7-trithiacyclononane) by analogous reaction of Na[BAr^F]·2THF with 2 mol equiv of the macrocycle gave the half-sandwich complex [Na([9]aneS$_3$)(THF)$_2$][BAr^F]. ^{1}H NMR, IR, and microanalysis data support this formulation, with retention of two THF ligands and tridentate coordination of the thiamacrocycle, which was confirmed by crystallographic analysis (Table S1 in the SI). Although both the cation and anion are disordered (as is often observed for [BAr^F]$^-$ salts[9,13]), the cation (Figure S1 in the SI) is clearly based on five-coordination at Na$^+$ via an O$_2$S$_3$ donor set, with no close Na···F(BAr^F) contacts.

Isolation of the homoleptic octathia-coordinated sodium cation [Na([24]aneS$_8$)]$^+$, without stabilization from other ligands, is highly unexpected given the extreme hard−soft metal−ligand mismatch. In order to probe the electronic structure of this complex, density functional theory (DFT) calculations were performed on the [M([24]aneS$_8$)]$^+$ cations (M = Li, Na, K, Rb, Cs), using the BP86 and B3LYP functionals with a 6-311G(d,p) basis set and the *Gaussian 09* package.[14] Details of the computational methodology are given in the SI. In general, good agreement was obtained between the BP86 and B3LYP results, so only a summary of the main results of the BP86 calculations is presented here, with all of the results obtained with both functionals given in the SI. The computed minimum-energy geometry for [Na([24]aneS$_8$)]$^+$ has S_4 symmetry (Figure 2), whereas in the experimental (solid-state) [Na([24]aneS$_8$)]-[BAr^F] structure, the cation occupies a general position in the unit cell with a distorted dodecahedral geometry. The computed bond lengths of [Na([24]aneS$_8$)]$^+$ are in good agreement with the corresponding crystallographic parameters (Table 1), with the former being generally slightly longer. The acuteness of the S−Na−S bond angles is also reproduced by the BP86/6-311G(d,p) calculations, which give S−Na−S bond angles in the range 68.3−70.4°, compared to those derived experimentally, 67.85(4)−71.10(4)°. This suggests that the DFT calculations are sufficient to allow qualitative analysis of the electronic structure in this complex.



Side view Top view

Figure 2. Optimized geometry of the [Na([24]aneS$_8$)]$^+$ system obtained at the BP86/6-311G(d,p) level of theory.

Table 1. Bond Lengths (Å) for [Na([24]aneS$_8$)]$^+$

	distance/Å	
bond	computed	experimental
Na−S1	3.077	2.9800(15)
Na−S2	3.096	3.0009(16)
Na−S3	3.077	3.0524(15)
Na−S4	3.096	2.9728(15)
Na−S5	3.077	3.0261(16)
Na−S6	3.096	2.9957(16)
Na−S7	3.077	2.9561(15)
Na−S8	3.096	3.0269(15)

Zero-point-corrected computed bond dissociation energies for [M([24]aneS$_8$)]$^+$ → M$^+$ + [24]aneS$_8$ decrease on going from Li to Cs (Table 2). This correlates with the increase in the radius/charge ratio down group 1 and suggests that the Li$^+$ and Na$^+$ complexes would be the easiest to form. However, attempts to isolate the corresponding Li$^+$ (and K$^+$) complex using an analogous method have so far proved unsuccessful.

Table 2. Zero-Point-Corrected Bond Dissociation Energies (kJ mol^{-1}) for [M([24]aneS$_8$)]$^+$ → M$^+$ + [24]aneS$_8$ (M = Li, Na, K, Rb, Cs) Using the BP86 Functional

Li	410.6[a]	Rb	226.0
Na	346.9	Cs	196.0
K	273.0		

[a] Values corrected for basis set superposition error.

It is notable that the [Na([24]aneS$_8$)]$^+$ cation, together with the uncoordinated [24]aneS$_8$ ligand (which adopts a similar conformation in the gas phase; see Figure S3 in the SI), has an unusual charge distribution. The charge densities on each center are presented in Table S5 in the SI and show that, upon formation of [M([24]aneS$_8$)]$^+$ from [24]aneS$_8$ and M$^+$, the electron density is transferred from the S 3p and C 2p valence orbitals of the ligand to the 3s and 3p orbitals of the Na$^+$ center. As a result, the charge density on each S atom becomes more positive, while the charge density on each C atom becomes less negative. A domino effect is observed, insofar as the positively charged Na$^+$ attracts the lone-pair electrons from the S atoms, which then pull electrons from the C−C and C−H bonds.

In the uncomplexed ligand, the charge densities on each center are somewhat unexpected given that the electronegativities of S and C are similar, with that of S slightly greater than that of C and greater than that of H (Table S5 in the SI). The result of the DFT calculations on the ligand indicates positive charges on the S atoms and negative charges on the C atoms (with the expected small positive charges on the H atoms).

The highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of the optimized structure of $[Na([24]aneS_8)]^+$ (Figure 2) are shown in Figure 3. The HOMO is composed of S 3p orbitals, which show little interaction with orbitals on other centers. This molecular orbital is therefore nonbonding in character. The LUMO is antibonding because it shows antibonding interactions between the valence p orbitals on S atoms that are close to each other (namely, between S2 and S7, S1 and S4, S3 and S6, and S5 and S8) and antibonding interactions between the valence orbitals in the C−C units. Population analysis of the frontier molecular orbitals clearly shows that electron transfer takes place from the HOMO and a group of closely packed occupied orbitals lying below the HOMO, into the 3s and 3p valence orbitals of the Na^+ ion.

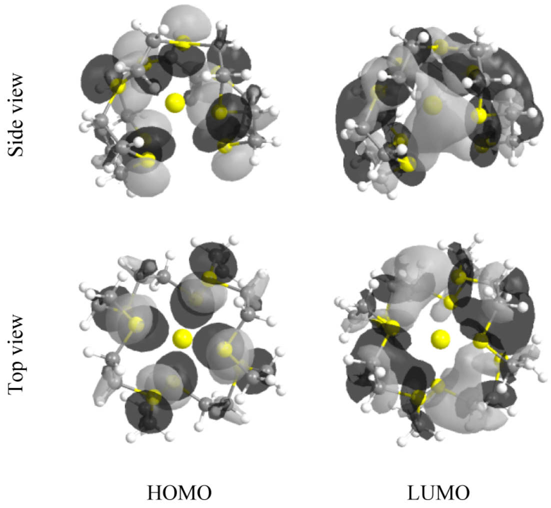


Figure 3. Representative orbital plots for the $[Na([24]aneS_8)]^+$ cation obtained using the BP86 functional. The dark (+) and gray (−) lobes represent the signs of the angular part of the atomic orbital contributing to a molecular orbital.

These results demonstrate that highly unusual soft thioether donor complexes of the Na^+ cation can be readily accessed by using macrocyclic architectures. The higher denticity rings are better suited for ensuring complete displacement of competitive ligands such as THF. DFT calculations show good agreement with the experimentally determined Na−S bond distances and S−Na−S angles. The similar conformations in the "free" and coordinated rings predicted by DFT suggest that preorganization of $[24]aneS_8$ may contribute to the stability of the Na^+ complex. The charge density change in the ligand on each center on going from Na^+ + $[24]aneS_8$ to $[Na([24]aneS_8)]^+$ has been investigated and the nature of the HOMO and LUMO in this complex established. The DFT calculations on $[Na([24]aneS_8)]^+$ show that there is electron transfer from the S 3p and C 2p valence orbitals of the ligand to the 3s and 3p orbitals of the Na^+ ion upon complex formation, which plays a key role in stabilizing the complex.

These results open up new possibilities for a rich chemistry of other soft donor complexes with s-block acceptors and are expected to lead to new types of reaction chemistry.

■ ASSOCIATED CONTENT

Supporting Information

Details of the preparation and characterization of the complexes, together with the crystallographic details for $[Na([24]aneS_8)][BAr^F]$ and $[Na([9]aneS_3)(THF)_2][BAr^F]$ (CCDC 1034573 and 1034574). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Kim, S.; Lindoy, L. F.; Lee, S. S. *Coord. Chem. Rev.* **2014**, *280*, 176.

(2) Levason, W.; Reid, G. In *Supramolecular Chemistry: From Molecules to Nanomaterials*; Gale, P. A., Steed, J. W., Eds.; Wiley: New York, 2012; p 785.

(3) Lindoy, L. F. *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge University Press: Cambridge, U.K., 1989.

(4) (a) Blake, A. J.; Schröder, M. *Adv. Inorg. Chem.* **1990**, *35*, 1. (b) Cooper, S. R.; Rawle, S. C. *Struct. Bonding (Berlin)* **1990**, *72*, 1. (c) Stephen, E.; Blake, A. J.; Davis, E. S.; McMaster, J.; Schröder, M. *Chem. Commun.* **2008**, 5707. (d) Shaw, J. L.; Wolowska, J.; Collison, D.; Howard, J. A. K.; McInnes, E. J. L.; McMaster, J.; Blake, A. J.; Wilson, C.; Schröder, M. *J. Am. Chem. Soc.* **2006**, *128*, 13827. (e) Ihlo, L.; Kampf, M.; Bottcher, R.; Kirmse, R. *Z. Naturforsch., Teil B* **2002**, *57*, 171. (f) Huang, D.; Zhang, X.; McInnes, E. J. L.; McMaster, J.; Blake, A. J.; Davies, E. S.; Wolowska, J.; Wilson, C.; Schröder, M. *Inorg. Chem.* **2008**, *47*, 9919.

(5) (a) Levason, W.; Reid, G. *J. Chem. Soc., Dalton Trans.* **2001**, 2953. (b) Levason, W.; Reid, G.; Zhang, W. *Dalton Trans.* **2011**, *40*, 8491.

(6) Park, H.; Park, K.-M.; Lee, S. S. *Dalton Trans.* **2010**, *39*, 9696.

(7) Farina, P.; Levason, W.; Reid, G. *Dalton Trans.* **2013**, *42*, 89.

(8) (a) Röttgers, T.; Sheldrick, W. S. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1976. (b) Röttgers, T.; Sheldrick, W. S. *J. Solid State Chem.* **2000**, *152*, 271.

(9) Everett, M.; Jolleys, A.; Levason, W.; Pugh, D.; Reid, G. *Chem. Commun.* **2014**, *50*, 5843.

(10) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.

(11) (a) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927. (b) Krossing, I.; Raabe, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066.

(12) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832.

(13) Chaplin, A. B.; Weller, A. S. *Eur. J. Inorg. Chem.* **2010**, 5124.

(14) Frisch, M. J.; et al. *Gaussian 09*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.

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