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Unusual bridging of three nitrates with two bridgehead protons in an octaprotonated azacryptand

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Abstract

Structural analysis of the nitrate complex of a thiophene-based azacryptand suggests that three nitrates are bridged with two bridgehead protons which play the topological role of two transition metal ions in a classical Werner type coordination complex bridging three anions.

Anion bridging is often observed in dinuclear Werner type coordination compounds incorporating one, two or three anions between the two metal centers (**a-c**).¹ Macrocyclic based homodinuclear complexes are known to bridge an anion including halide, carbonate, sulfate and perchlorate with the coordinating metal ions located at two subunits composed of multibinding sites in a macrocycle (**d**).² Indeed the anion bridging was seen in the first synthetic bicyclic anion receptors termed as *katapinands*, in which one chloride was linearly hydrogen-bonded with two bridgehead nitrogens (**e**).^{3,4} To our knowledge, the bridging of multiple anions has not been observed previously in a synthetic receptor.

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[†]Electronic Supplementary Information (ESI) available: One crystallographic data in CIF format, ORTEP view of the complex, all data of hydrogen bonding interactions, N-O bond distances, explanation of disorder model and complete list of authors in Ref. ²⁰ in pdf format. See DOI: 10.1039/b000000x/

Octaazacryptands are analogous to the *katapinands* in terms of dimensionality, but contain six additional secondary amine contributing major binding sites for negatively charged anions.⁵ Such receptors are known to complex anionic guests with the diverse binding modes ranging from monotopic⁶ to ditopic,⁷ and tritopic complexes.^{8,9} In the case of tritopic binding, guest species can be either inside the cavity in a cascade fashion⁸ or in the pockets formed by the linking arms of an azacryptand.⁹ The later mode of binding is known as ‘cleft binding’ that was introduced by Whitlock for a molecular tweezer with a guest in its pocket without complete encapsulation.¹⁰ The cleft binding in pyridine-based cryptand for perchlorates^{9a} and perhenates^{5b} as well as *p*-xylyl cryptand for sulfates, is reported previously, in which the anions are hydrogen bonded with the protonated secondary amines of the corresponding

cryptand. In these complexes, the bridgehead amines remain unprotonated. Therefore, it is unclear if the charged bridgehead amines could qualify in bridging the pocket bound anions (**f**). This communication reports the first structural evidence of unusual bridging of three nitrates by both bridgeheads in an octaprotonated azacryptand, where the protonated bridgehead protons play the topological role of two transition metal ions in a classical Werner type coordination complex bridging three anions.

The cryptand **L** was previously reported by Nelson as dicopper and disilver complexes¹¹ and later by Fabbrizzi as dicopper complex.¹² In this study, the neutral **L** was prepared from the Schiff base derived reaction following the literature procedure.¹³ The nitrate salt was obtained by titrating **L** dissolved in methanol with HNO₃.¹⁴

Structural analysis of the first example of a triply bridged anion cryptate, [H₈**L**(NO₃)₃](NO₃)₅·HNO₃·6H₂O indicates that the complex is an octahydronitrate adduct of **L**, with six molecules of water and one molecule of nitric acid.[‡] As shown in Fig. 1, the protons on the central nitrogen atoms, N1 and N4 point towards the cavity and each site acts as three hydrogen bond donors for three nitrates, forming a bridged nitrate complex with a total of six hydrogen bonds. With the exception of one proton on N7 that forms a secondary N...O5(cavity) hydrogen bond (N...O = 3.113(9) Å), all secondary nitrogen protons are directed outward from the cavity and involved in coordinating external nitrates. It is interesting to note that no other secondary amine except N7 is involved in interacting with internal nitrates. Each of the internal nitrates is bridged through one oxygen with two *endo*-oriented protons on the bridgehead nitrogens with N...O distances ranging from 3.099(10) to 3.370 (8) Å (Table 1), forming a trigonal bipyramidal coordination geometry of the three oxygen atoms sitting inside the cavity (Fig. 2). Both of the bridgehead nitrogen protons act as trifurcated (four-center) H-bond acceptors.¹⁵ Therefore, the observed bond distances in N...O's are relatively longer than those observed in the normal N...O' bonds with one acceptor.^{6,16}

The bridging oxygens are separated by 2.494 (12), 2.602(11), and 3.000(8) Å. The remaining two oxygen atoms in the nitrates lie between the arms of the macrocycle to minimize anion-anion repulsion. The shortest O...O distance between O4 and O8A made us curious to investigate for a possible proton between the three internal oxygen atoms. However, the difference of the electron density at the midpoint that was nearly zero, ruled out the existence of any proton between the bridging nitrates in [NH(NO₃)₃HN]⁺.

The distance between the two bridgehead nitrogens is 5.528(6) Å, which is shorter than that observed in the *katapinand* chloride complex (6.20 Å).⁴ Three bridging oxygens are positioned at the corner of a triangle bisecting the N...N axis. The remaining seven nitrates and one molecular nitric acid are associated with electrostatic and hydrogen bonding interactions outside the macrocyclic cavity. The external nitrates are linked to the macrocycle with one to four N-H...O bonds in the range of 2.763(7) to 3.113(9) Å. All N—O bonds in nitrate groups with the exception of one labeled N(17), are of similar length ranging from 1.2041 (13) to 1.294 (8) Å, consistent with an even negative charge distribution as expected from an unprotonated nitrate with N=O bonds. However, the bond length in N17—O26, that is equal to 1.366 (10) Å as opposed to N17—O27, 1.167 (10) and N17—O25, 1.180 (9) Å in the same nitrate, that is close to 1.41 Å observed in undissociated N—O—H bond in HNO₃.¹⁷ Therefore, the nitro group containing N17 is deduced to be a molecular nitric acid, which is also required

[‡]Crystal data for [H₈**L**(NO₃)₃](NO₃)₅·HNO₃·6H₂O: C₃₀H₆₉N₁₇S₃O₃₃, *M* = 1292.20, crystal size 0.25 × 0.12 × 0.10 mm³, Monoclinic, *P*2₁/*c*, *a* = 17.394 (2), *b* = 13.713 (2), *c* = 23.772 (3) Å, β = 106.553 (6)°, *V* = 5435.2 (12) Å³, *Z* = 4, *d*_{calc} = 1.579 g cm⁻³, *T* = 100.0 (5) K, Nonius KappaCCD diffractometer, μ(Mo-Kα) = 0.25 mm⁻¹, 9562 independent reflections (6444 observed), 775 parameters, *R*_{int} = 0.040, *R* = 0.088, *wR*(*F*²) = 0.278. CCDC 713455.

for charge balance. Nitric acid coexisting with water molecules in the solid state is not unprecedented, and has been well documented by others.¹⁸

It should be noted that in solution the ligand formed a 1:1 complex even in the presence of excess nitrate, with strong affinity ($\log K = 4.30$ in D₂O at pD 2.5) for nitrate studied by ¹H NMR titrations, failing to correlate the structural data in solid state. Such behaviour is not unusual in water that may be solvated inside the cavity, as seen in the related cryptands.^{5a,8b}

In order to understand the energy involved in the complex formation of the ligand with nitrate, density functional theory (DFT) calculations were carried out using hybrid density functional B3LYP19 with a 6-311G** basis set, implemented in Gaussian 03.20 The stabilization energies (enthalpies) of complexation were calculated as, $E_s = \Delta H (\text{Ligand} + \text{guests}) - \Delta H (\text{Ligand}) - \Delta H (\text{guests})$ from the fully optimized structures. Harmonic vibrational frequencies were also calculated at the B3LYP/6-311G** level. The thermal corrections were made using the ideal gas, rigid rotor, and harmonic oscillator approximations. The initial geometry was modelled from the crystallographic coordinates of the nitrate complex with eight charges. Within the optimized geometry, the stabilization energy of macrocycle was found to be -964 kcal/mol for a single nitrate, resulting from strong electrostatic interactions with the highly charged macrocycle. The calculated stabilization energy was found to be as $E_{s1} = -964$ for the first nitrate, $E_{s2} = -428$ for the second nitrate and $E_{s3} = -368$ kcal/mol for the third nitrate, giving the total energy, $E_{s1} + E_{s2} + E_{s3} = -1760$ kcal/mol for 1:3 complex. The gradual decrease of the stabilization energy in nitrate binding is perhaps due to the nitrate-nitrate repulsion within the cavity. DFT calculations thus support the formation of both 1:1 and 1:3 complexes, indicating energetically favourable binding for three nitrates as observed in solid phase.

In summary, we presented a very unusual feature that three nitrates are arranged in space with three oxygen atoms from each of the nitrates in a close-fitting triangle between the two tertiary N-H groups, resulting in a trigonal bipyramidal substructure. Stabilization of this critical trigonal bipyramidal $[\text{NH}(\text{NO}_3)_3\text{HN}]^+$ arrangement might be the result of the specific conformation of the cryptand in which all the secondary protonated amines except N7 were utilized in coordinating external nitrates and water molecules. The amine N7 was only available secondary protonated nitrogen to interact an internal nitrate. The protonated amines provided enough electrostatic potential to bring the three nitrates into the three clefts of the macrocycle. The absence of the appreciable hydrogen bonds with secondary amines helped to anchor the three oxygen atoms in the cavity where the both *endo*-oriented protons shared their charges with the three oxygen atoms forming two trifurcated hydrogen bonds. It appears that the participation of the two bridgehead protons in hydrogen binding was due to the lack of free secondary protonated amines. This argument is also supported by our recent report with this ligand in its octaprotonated form, showing an encapsulated chloride which was stabilized by only two bridgehead protons without the involvement of secondary protons.²¹ As compared with normal or bifurcated hydrogen bonds, the trifurcated H-bonds are less common in synthetic complexes,¹⁵ however they exist in many natural systems, for example, in enzyme-peptide interactions²² and protein α -helices.²³ The structure, reported herein, represents the first crystallographic evidence of triply bridged anions as $[\text{NH}(\text{NO}_3)_3\text{HN}]^+$ in a synthetic macrocycle, showing a surprising corollary²⁴ to a dinuclear metal complex $[\text{MA}_3\text{M}]^2$, where the bridgehead protons in the cryptand play the topological role of two transition metal ions in a classical Werner type coordination complex bridging three anions.

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Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Notes and references

1. a Housecroft, A.; Sharpe, AG. *Inorganic Chemistry*. 3rd Ed.. Prentice Hall; 2008. p. 694-701. b Malinkin S, Penkova L, Pavlenko VA, Haukka M, Fritsky IO. *Acta Cryst* 2009;E65:m1247–m1248. c Meijboom R. *Acta Cryst* 2006;E62:m3511–m3513. d Cavigliasso G, Stranger R. *Inorg. Chem* 2005;44:5081–5091. [PubMed: 15998037]
2. a Lehn J-M, Pine SH, Watanabe EI, Willard AK. *J. Am. Chem. Soc* 1977;99:6766–6768. b Lehn J-M. *Pure Appl. Chem* 1980;52:2441–2459. c Amendola V, Bastianello E, Fabbrizzi L, Mangano C, Pallavicini P, Perotti A, Lanfredi AM, Ugozzoli F. *Angew. Chem. Int. Ed* 2000;39:2917–2920. d Lehn J-M. *Science* 1985;227:849–856. [PubMed: 17821215] e Harding CJ, Mabbs FE, MacInnes EJJ, McKee V, Nelson J. *J. Chem. Soc., Dalton Trans* 1996:3227–3230. f Amendola V, Fabbrizzi L, Mangano C, Pallavicini P, Poggi A, Taglietti A. *Coord. Chem. Rev* 2001;219-221:821–837. g Dussart Y, Harding C, Dalgaard P, McKenzie C, Kadirvelraj R, McKee V, Nelson J. *J. Chem. Soc., Dalton Trans* 2002:1704–1713.
3. Park CH, Simmons HE. *J. Am. Chem. Soc* 1968;90:2431–2432.
4. Bell RA, Christoph GG, Fronczek FR, Marsh RE. *Science* 1975;190:151–152.
5. a Hynes MJ, Maubert B, McKee V, Town RM, Nelson J. *J. Dalton Trans* 2000:2853–2859. b McKee V, Nelson J, Town RM. *Chem. Soc. Rev* 2003;32:309–325. [PubMed: 14518184] c Hossain MA. *Curr. Org. Chem* 2008;12:1231–1256. d Ravikumar I, Lakshminarayanan PS, Suresh E, Ghosh P. *Inorg. Chem* 2008;47:7992–7999. [PubMed: 18710222]
6. Hossain MA, Llinares JM, Miller C, Seib L, Bowman-James K. *Chem. Commun* 2000:2269–2270.
7. a Mason S, Seib L, Bowman-James K. *J. Am. Chem. Soc* 1998;120:8899–8900. b Mason S, Llinares JM, Morton M, Clifford T, Bowman-James K. *J. Am. Chem. Soc* 2000;122:1814–1015.
8. a Hossain MA, Llinares JM, Mason S, Morehouse P, Powell D, Bowman-James K. *Angew. Chem. Int. Ed. Engl* 2002;41:2335–2338. [PubMed: 12203584] b Hossain MA, Morehouse P, Powell PD, Bowman-James K. *Inorg. Chem* 2005;44:2143–2149. [PubMed: 15792448]
9. a McKee V, Morgan GG. *Acta Cryst* 2003;C59:o150–o152. b Li Y, Jiang L, Feng X-L, Lu T-B. *Cryst. Growth Des* 2008;8:3689–3694. c Arunachalam M, Ravikumar I, Ghosh P. *J. Org. Chem* 2008;73:9144–9147. [PubMed: 18937408]
10. Chen C-W, Whitlock HW Jr. *J. Am. Chem. soc* 1978;100:4921–4922.
11. Drew MGB, Harding CJ, Howarth OW, Lu Q, Marrs DJ, Morgan GG, McKee V, Nelson J. *J. Chem. Soc., Dalton Trans* 1996:3021–3030.
12. Amendola V, Fabbrizzi L, Mangano C, Pallavicini P, Zema M. *Inorg. Chim. Acta* 2002;337:70–74.
13. a Chen D, Martell AE. *Tetrahedron* 1991;47:6900–6901. b Drew GB, Marrs D, Hunter J, Nelson J. *J. Chem. Soc., Dalton Trans* 1992:11–18.
14. $\text{H}_8\text{L}(\text{NO}_3)_3[\text{NO}_3]_5 \cdot \text{HNO}_3 \cdot 6\text{H}_2\text{O}$: This salt was obtained by titrating the neutral ligand **L** (20 mg, 32 μmol) with conc. HNO_3 in MeOH (2mL) to pH 2. The white precipitate thus formed was redissolved in water, which was recrystallized to give X-ray quality crystals. Yield: 25 mg, 60%. ^1H NMR (300 MHz, D_2O , TMS): 7.27 (s, 6H, ArH), 4.52 (s, 12H, ArCH₂), 3.36 (t, 12H, NCH₂), 2.87 (t, 12H, NCH₂CH₂). X-ray quality crystals were grown from solutions of the salt in MeOH and H₂O (10:1 v/v) under slow diffusion of Et₂O.
15. Steiner T. *Angew. Chem. Int. Ed* 2002;41:48–76.
16. Hazari SKS, Roy TG, Barua KK, Tiekink ERT. *J. Chem Cryst* 2008;38:1–8.
17. Housecroft, A.; Sharpe, AG. *Inorganic Chemistry*. 3rd Ed.. Prentice Hall; 2008. p. 450
18. a Toriumi K, Yamashita M, Ito H. *Acta Cryst* 1986;C42:963–968. b Young VG Jr, Sykes AG. *Inorg. Chem* 1998;37:376–378. c Calleja M, Mason SA, Prince PD, Steed JW, Wilkinson C. *New J. Chem*

- 2003;27:28–31. d Bivian-Castro EY, Roltzsch M, Gupta D, Lippert B. *Inorg. Chim. Acta* 2005;358:2395–2402.
19. a Becke AD. *Phys. Rev* 1988;A38:3098–3100. b Lee C, Yang W, Parr RG. *Phys. Rev. B* 1988;37:785–789.
20. Frisch, MJ., et al. Gaussian 03, Revision B.03. Gaussian, Inc.; Pittsburgh PA: 2003.
21. Saeed MA, Fronczek FR, Hossain MA. *Chem. Commun* 2009:6409–6411.
22. Betzel C, Singh TP, Visanji M, Peters K, Fittkau S, Saenger W, Wilson KS. *J. Biol. Chem* 1993;268:15854–15858. [PubMed: 8340410]
23. Fain AV, Ukrainskii DL, Dobkin SA, Galkin AV, Esipova NG. *Biophysics* 2008;53:125–133.
24. Bowman-James K. *Acc. Chem. Res* 2005;38:671–678. [PubMed: 16104690]

Fig. 1. ORTEP view of the nitrate complex of **L** with 30% probability factor for the thermal ellipsoid. (External nitrates and water molecules are omitted for clarity).

A **B**

Fig. 2. Three nitrates bridged with two bridgehead protons. (A) side-on view of the $[\text{NH}(\text{NO}_3)_3\text{HN}]^+$ motif and (B) three fold axis view of $[\text{H}_8\text{L}(\text{NO}_3)_3]^{5+}$.

Table 1Selected interatomic distances for hydrogen bonding interactions in $[\text{H}_8\text{L}(\text{NO}_3)_3]^{5+}$.

atoms	distances (Å)	atoms	distances (Å)
N1–H1...O1	3.156 (7)	N4–H4...O1	3.290 (6)
N1–H1...O8A	3.122 (12)	N4–H4...O4	3.370 (8)
N1–H1...O4	3.370 (8)	N4–H4...O8A	3.099 (10)