

The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R&D No. 190-9609-2801. KC thanks the Universiti Sains Malaysia for a Visiting Postdoctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1228). Services for accessing these data are described at the back of the journal.

References

- Anagnostopoulos, A. (1976). *J. Inorg. Nucl. Chem.* **38**, 435–437.
 Bagley, M. J., Nicholls, D. & Warburton, B. A. (1970). *J. Chem. Soc. A*, **16**, 2694–2697.
 Maslejkova, A., Uhrinova, S., Mrozinski, J., Zurowska, B., Munoz, M. C. & Julve, M. (1997). *Inorg. Chim. Acta*, **255**, 343–349.
 Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
 Sheldrick, G. M. (1996). *SADABS. Siemens Area Detector Absorption Correction Software*. University of Göttingen, Germany.
 Siemens (1996a). *SHELXTL*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Siemens (1996b). *SMART and SAINT. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1999). **C55**, 24–26

Bis(triethanolamine)strontium(II) bis(2,4-dinitrophenolate)

NARINDER SINGH POONIA,^a NEERA CHHABRA,^a W. S. SHELDRIK,^b GEETA HUNDAL,^c SANGEETA OBRAI^c AND MANINDER SINGH HUNDAL^c

^aDepartment of Chemistry, Devi Ahilya University, Khandwa Road, Indore, India, ^bLehrstuhl für Analytische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany, and ^cDepartment of Chemistry, Guru Nanak Dev University, Amritsar 143 005, India. E-mail: gndu@rocketmail.com

(Received 12 September 1997; accepted 24 July 1998)

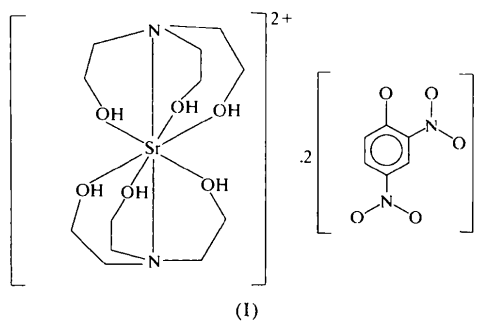
Abstract

In the title compound, bis(2,2',2''-nitrotriethanol-N,O,O',O'') strontium(II) bis(2,4-dinitrophenolate), [Sr(C₆H₁₅NO₃)₂](C₆H₃N₂O₅)₂, the coordination number around the cation is eight, and it is effectively sandwiched by the two tetradentate triethanolamine ligands, which coordinate through all three hydroxyl O atoms and the amine N atom. The Sr—O distances are in the range 2.574 (7)–2.586 (6) Å, and the Sr—N distance is 2.777 (7) Å. The two 2,4-dinitrophenolate anions are charge separated in the lattice. The shortest Sr···O

distance to the 2,4-dinitrophenolate anions is Sr···O1 [4.268 (8) Å].

Comment

The role of 'double-action' ligands, such as triethanolamine, is to stabilize the cation by coordination and the anion by hydrogen bonding (Poonia & Bajaj, 1979; Bajaj & Poonia, 1988), which results in a reduction in the nucleophilic properties of the latter. The title complex, (I), has been studied to investigate the role of hydrogen bonding in complexes of the type M(DNP)₂(TEA)_n, where M = Ca²⁺, Sr²⁺ or Ba²⁺, DNP = 2,4-dinitrophenolate and TEA = triethanolamine. The structures of Ca(DNP)₂(TEA) and Ba(DNP)₂(TEA)₂ have already been reported (Hundal *et al.*, 1995; Kanters *et al.*, 1984). It appears that hydrogen bonding is a dominant factor in decreasing cation–anion interactions in the above series. The Sr²⁺ ion is present on a crystallographic centre of symmetry and is eightfold coordinated by two TEA molecules. The coordination around Sr²⁺ is bicapped trigonal antiprismatic. Both of the DNP counter-anions are excluded from the coordination cluster, resulting in the formation of a charge-separated complex. Important bond distances and angles are given in Table 1. The Sr—O distances are in the range 2.574 (7)–2.586 (6) Å, and the Sr—N1 distance is 2.777 (7) Å. The N—C—O torsion angles [−51.3 (13) to −54.6 (13)°] are comparable to the values of 46.8 (4) and 67.4 (4)° reported earlier (Hundal *et al.*, 1995, 1996; Kanters *et al.*, 1984), producing nearly *gauche* conformations of the terminal OH groups with respect to the C—N bonds. There are three nearly planar C—N—C—C fragments with torsion angles ranging from 160.2 (9) to 169.5 (8)°, which are comparable to the values found in the literature.



In the case of (I), the counter-anion does not interact with the cation but it is strongly hydrogen bonded to the TEA ligands. The phenolic O atom forms two hydrogen bonds with the hydroxyl O atoms; it has an intramolecular hydrogen bond [O7···O1 2.70 (1) Å] and is also attached to O8 of the centrosymmetrically related molecule, forming an intermolecular bond [O1···O8 2.65 (1) Å]. Thus, the phenolic O atom acts as a double hydrogen-bond acceptor towards two hydroxyl groups,

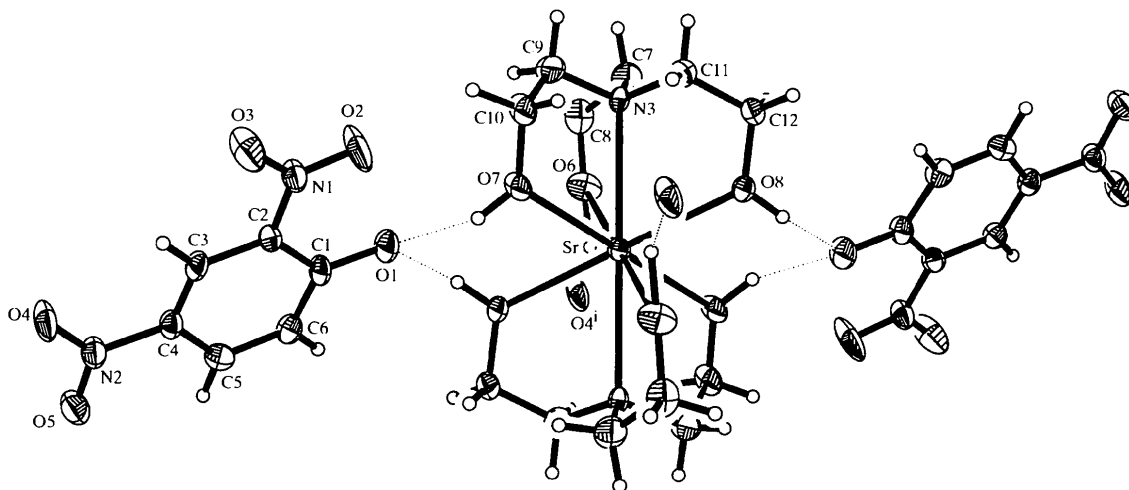


Fig. 1. The molecular structure of (I), showing the atom-labelling scheme and the hydrogen bonding in the molecule. Displacement ellipsoids are drawn at the 30% probability level.

forming a bridge between the two groups. The third hydroxyl O atom behaves as a donor towards one O atom of the *para*-nitro group of the DNP residue, resulting in an intermolecular hydrogen bond [O6...O4ⁱ 2.85 (1) Å; symmetry code: (i) $x, y, z + 1$]. Extensive hydrogen bonding between triethanolamine and DNP has also been observed in the case of Ba(DNP)₂(TEA)₂ and, to a lesser extent, in the case of Ca(DNP)₂(TEA). It appears that this hydrogen bonding is responsible for the formation of charge-separated complexes. In the Ca²⁺ complex, only two hydrogen-bonding interactions were observed, namely, between two of the three hydroxyl groups and between two phenolic O atoms of the two counter-anions, whereas in the present case all the hydroxyl groups are involved in the hydrogen bonding to DNP, *i.e.* a total of six hydrogen-bonding interactions are observed. In the Ba²⁺ complex, seven hydrogen-bonding interactions are observed, involving all the hydroxyl groups of TEA; one group is a double donor. In both the latter cases, the respective complexes are either completely or partially charge separated.

In the entire series, the preferences of the cations indicate that as one moves down the group the attraction between the cation and counter-anion decreases. The attraction is highest for Ca²⁺, because of the high charge density of the cation and also because the anion is highly nucleophilic. Thus, in the case of Ca²⁺, the hydrogen-bonding interactions are not sufficient to cause charge separation and an ion-paired complex is formed. The charge density of Sr²⁺ is less than that of Ca²⁺; the cation–anion interactions are weakened and the hydrogen-bonding interactions are sufficiently strong to give a charge-separated complex. Accordingly, it is expected that Ba(DNP)₂(TEA)₂ should also be a charge-separated complex. However, what is actually observed is a partially charge-separated complex, probably because

Ba²⁺, being the largest cation in the series, prefers a higher coordination number in comparison to Ca²⁺ and Sr²⁺.

Experimental

The title complex was prepared by dropwise addition of triethanolamine (1:1 ratio) to a warm solution of Sr(DNP)₂ in acetone. Complexation was indicated by a change in colour of the solution from yellow to orange. Crystals were obtained by slow evaporation of the solution after 30 d.

Crystal data

[Sr(C₆H₁₅NO₃)₂]-
(C₆H₃N₂O₅)₂

$M_r = 752.21$

Monoclinic

$P2_1/c$

$a = 7.826 (2) \text{ \AA}$

$b = 17.069 (3) \text{ \AA}$

$c = 11.578 (2) \text{ \AA}$

$\beta = 93.09 (3)^\circ$

$V = 1544.4 (5) \text{ \AA}^3$

$Z = 2$

$D_x = 1.618 \text{ Mg m}^{-3}$

$D_m = 1.625 \text{ Mg m}^{-3}$

D_m measured by flotation

Data collection

Siemens P4 diffractometer

$2\theta/\theta$ scans

Absorption correction:

ψ scan (North *et al.*,
1968)

$T_{\min} = 0.577$, $T_{\max} = 0.638$

2183 measured reflections

2011 independent reflections

1305 reflections with

$I > 2\sigma(I)$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25
reflections

$\theta = 10.0\text{--}12.5^\circ$

$\mu = 1.831 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Prismatic

$0.30 \times 0.25 \times 0.25 \text{ mm}$

Orange

$R_{\text{int}} = 0.087$

$\theta_{\text{max}} = 22.4^\circ$

$h = 0 \rightarrow 8$

$k = 0 \rightarrow 18$

$l = -12 \rightarrow 12$

3 standard reflections

every 50 reflections

intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} = 0.006$
$R[F^2 > 2\sigma(F^2)] = 0.078$	$\Delta\rho_{\max} = 0.421 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.279$	$\Delta\rho_{\min} = -1.190 \text{ e } \text{\AA}^{-3}$
$S = 1.077$	Extinction correction: none
1770 reflections	Scattering factors from
214 parameters	<i>International Tables for</i>
H atoms not refined	<i>Crystallography</i> (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.1520P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Selected geometric parameters (\AA , $^\circ$)

Sr—O6	2.574 (7)	C1—C2	1.440 (12)
Sr—O7	2.586 (6)	C2—C3	1.369 (13)
Sr—O8	2.583 (6)	C3—C4	1.361 (13)
Sr—N3	2.777 (7)	C4—C5	1.417 (13)
C1—C6	1.422 (13)	C5—C6	1.363 (13)
O6—Sr—O7	95.7 (2)	O6—Sr—N3	63.0 (2)
O6—Sr—O8	101.4 (2)	O7—Sr—N3	63.7 (2)
O7—Sr—O8	107.2 (2)	O8—Sr—N3	63.6 (2)
C11—N3—C7—C8	165.3 (8)	N3—C9—C10—O7	-54.6 (13)
C9—N3—C7—C8	-72.9 (11)	C9—N3—C11—C12	169.5 (8)
N3—C7—C8—O6	-51.3 (13)	C7—N3—C11—C12	-69.8 (10)
C11—N3—C9—C10	-78.7 (10)	N3—C11—C12—O8	-52.6 (11)
C7—N3—C9—C10	160.2 (9)		

The poor quality of the available crystals limited the resolution of the data to 22.5° , which led in turn to the low data/parameter ratio of 8.27. The structure was solved by direct methods using *SHELXTL/PC* (Sheldrick, 1995) and refined using full-matrix least-squares methods. Refinement was carried out on F^2 for all reflections, except for 241 with very negative F^2 . All H atoms were fixed, except for the three hydroxyl group H atoms, which were located in a difference Fourier map. The H atoms were not refined and all non-H atoms were treated anisotropically.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC*. Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

NSP thanks DST (New Delhi) for financial support (Sanction SP/S1/F-45/90, dated 25 May 1992). MSH thanks the Guru Nanak Dev University for providing a grant for the purchase of the diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1079). Services for accessing these data are described at the back of the journal.

References

- Bajaj, A. V. & Poonia, N. S. (1988). *Coord. Chem. Rev.* **87**, 55–213.
 Hundal, G., Ripoll, M. M., Hundal, M. S. & Poonia, N. S. (1995). *Acta Cryst.* **C51**, 1788–1791.
 Hundal, G., Ripoll, M. M., Hundal, M. S. & Poonia, N. S. (1996). *Acta Cryst.* **C52**, 789–792.
 Kanters, J. A., Smeets, W. J. J., Venkatasubramanian, K. & Poonia, N. S. (1984). *Acta Cryst.* **C40**, 1701–1704.
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
 Poonia, N. S. & Bajaj, A. V. (1979). *Chem. Rev.* **79**, 389–444.
 Sheldrick, G. M. (1995). *SHELXTL/PC*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994). *XSCANS. X-ray Single Crystal Analysis System*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1999). **C55**, 26–28

(2,5,8,11,14-Pentaoxapentadecane- $\kappa^5\text{O}$)-bis(2,4,6-trinitrophenolato- O^1,O^2)-calcium(II)

NARINDER SINGH POONIA,^a GEETA HUNDAL,^b SANGEETA OBRAI^b AND MANINDER SINGH HUNDAL^b

^aDepartment of Chemistry, Devi Ahilya University, Khandwa Road, Indore, India, and ^bDepartment of Chemistry, Guru Nanak Dev University, Amritsar 143 005, India. E-mail: cse@gndu.ernet.in

(Received 16 October 1997; accepted 20 April 1998)

Abstract

In the title complex, $[\text{Ca}(\text{C}_6\text{H}_2\text{N}_3\text{O}_7)_2(\text{C}_{10}\text{H}_{22}\text{O}_5)]$, the tetraglyme ligand coordinates with Ca^{2+} through all five O atoms to form an equatorial arrangement around the cation. Both the picrate counter-anions chelate through their phenolic O atom and one of the O atoms of an *o*-nitro group. The anions are on opposite sides of the plane formed by the tetraglyme ligand. The Ca^{2+} coordination number is nine. The geometry around the cation is of the monocapped square antiprism type.

Comment

The structures of complexes of the *s*-block metal ions, $[\text{M}(\text{anion})_x(\text{ligand})_y(\text{solvent})_z]$, where the ligand is an electrically neutral molecule with O- and N-donor atoms, appear to depend strongly on whether or not a polar or polarizable hydrogen(s) is present on the ligand. A ligand such as the glyme molecule, which lacks polarizable H atoms, interacts with the cation resulting in the formation of ion-paired complexes only (Poonia & Bajaj, 1979), whereas ligands carrying polarizable hydrogen(s), such as glycols, diamines and ethanolamines, coordinate with the cation and also bond to the counter-anion. This latter case usually leads to a decrease in the cation–anion interaction, maybe to the extent that the cation and one or more counter-anions no longer remain within a bonding distance of each other (Bajaj & Poonia, 1987; Poonia & Bajaj, 1979; Fenton, 1987). The title compound, (I), has been investigated in order to gain a deeper insight into systems lacking polar or polarizable H atoms.