The triethanolamine complexes
of calcium azide and strontium azide

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Bis(triethanolamine) strontium diazide

Abstract. The two isotypic compounds bis(triethanolamine) calcium diazide and bis(triethanolamine) strontium diazide $[N(CH_2CH_2OH)_3]_2M(N_3)_2$, $M = Ca[Sr]$, were obtained by reacting triethanolamine with the corresponding metal azides in aqueous solution. Their crystal structures were determined by single-crystal X-ray techniques. Both compounds crystallize in the space group $R32$: $a = 8.136(3)$ [8.232(1)], $c = 27.254(13)$ [27.377(12)] Å, N = 3, $R = 0.064$ [0.078]. Calcium [strontium] forms complex cations with two triethanolamine molecules, whose central atoms are surrounded by six OH-oxygen atoms and two amino-N atoms. The azide ions are located between these complex cations and they are not coordinated to the metal atoms.

Introduction

In the course of investigations on the coordinative behaviour of calcium and strontium in azide compounds, we chose triethanolamine (TEA) as complex-forming molecule. It is well known, that TEA forms multiply coordinated chelate-complexes of high stability, involving the three OH groups and the central N atom in metal-atom coordination. To our knowledge, three complexes of TEA with alkaline or alkaline earth metal atoms

have so far been subjected to single crystal structure analysis. These three structures show interesting features, which shall be briefly summarized.

With NaJ, TEA forms a complex compound of composition (TEA)NaJ, which crystallizes in space group $P\bar{1}$ with N = 2. Sodium shows a coordination number of seven, being surrounded by the four heteroatoms of one TEA molecule, by two oxygen atoms of a neighbouring molecule and by one iodine anion. The coordination polyhedra are linked to chains running along (110) (Voegele et al., 1974a).

$Sr(NO_3)_2$ and TEA react to form the compound $(TEA)_2Sr(NO_3)_2$, which crystallizes in $C2/c$ with N = 4. Strontium is surrounded by the eight heteroatoms of two TEA molecules, with approximately cubic coordination polyhedra. The two nitrate groups are not coordinated to Sr, and they are involved in hydrogen bonding (Voegele et al., 1974b).

Barium acetate and TEA form the compound $[TEA]_2Ba(CH_3CO_2)_2$, which crystallizes in $P\bar{1}$ with N = 2. Barium shows the coordination number nine, being surrounded by the eight heteroatoms of two TEA molecules and one acetate-O atom. The compound thus consists of $(TEA_2 \cdot CH_3COOBa)^+$ cations and CH_3COO^- anions (Voegele et al., 1974).

The present communication describes experiments to obtain complexes between TEA and calcium [strontium] azide and to determine their crystal structures.

Experimental

1 ml of TEA was added to 20 ml of saturated aqueous calciumazide [strontiumazide] solution. The precipitates were redissolved by heating to 338 [353] K and crystallized by slowly cooling to 283 K. Both compounds form colourless crystals which are stable at ambient conditions. The TEA compound with $Ca(N_3)_2$ crystallizes in regular hexagonal platelets, the crystals of the strontium compound are of irregular shape.

The elemental analysis yielded a molar ratio of $Ca(N_3)_2[Sr(N_3)_2]$ to TEA of 1:2; the compounds thus have the composition bis (triethanolamine) calcium [strontium]-diazide, $[N(CH_2CH_2OH)_3]_2M(N_3)_2$ with M = Ca [Sr].

The crystal structures were determined at room temperature on a four-circle diffractometer. The lattice constants and other relevant experimental parameters are collected in Table 1.

All calculations were carried out on a UNIVAC 1100/81 computer at the Rechenzentrum Graz. The computer programs SHELXS (Sheldrick, 1986), SHELX (Sheldrick, 1976) and XRAY (Stewart, 1976) were used. A list of observed and calculated structure factors was deposited [1].

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[1] Further details about the structure analysis can be obtained from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2. Please, specify the deposition number CSD 51369, the authors and the literature reference.

Table 1. Experimental parameters and data.

Chemical formula	$[N(C_2H_4OH)_3]_2Ca(N_3)_2$	$[N(C_2H_4OH)_3]_2Sr(N_3)_2$
Molecular weight	422.50	470.04
Cell constants	$a = 8.136(3)$ Å	$a = 8.232(1)$ Å
	$c = 27.254(13)$ Å	$c = 27.377(12)$ Å
	$V = 1562.5$ Å^3	$V = 1606.5$ Å^3
Space group	$R32$	
Z	3	
$F(000)$	672.01	726.00
Observed/calculated density	$1.304/1.347$ Mg $\cdot$ m^{-3}	$1.311/1.457$ Mg $\cdot$ m^{-3}
Crystal dimensions	$0.30 \times 0.30 \times 0.30$ m^3	$0.12 \times 0.08 \times 0.10$ mm^3
Temperature	$20 \pm 3°C$	$20 \pm 4°C$
Data collection limits	$0° \le 2\theta \le 70°$	$0° \le 2\theta \le 60°$
	$-13 \le h \le 13; 0 \le k \le 13; 0 \le l \le 43$	$-11 \le h \le 11; 0 \le k \le 11; 0 \le l \le 32$
Scan mode	ω scan, $\Delta\omega = 1.6°$	
Independent reflections	814	411
$F_o \ge 4\sigma|F_o|$	648	303
Absorption coefficient	0.306 mm^{-1}, no correction applied	2.452 mm^{-1}, no correction applied
Extinction coefficient	0.0001	0.0001
Extinction correction	five reflections omitted	no correction applied
Atomic scattering factors	International Tables (1974)	
Least squares parameters	57	
$R_1: \Sigma(|F_o| - |F_{cl}|)/\Sigma|F_o|$	0.0638	0.0783
$R_w: \{\Sigma \sqrt{w}(|F_o| - |F_{cl}|)/\Sigma|\sqrt{w}|F_o|$	0.0654	0.0704
Weighting function	$4.0871/(\sigma^2|F_o| + 5.16 \times 10^{-4}|F_o|^2)$	$1.2924/(\sigma^2|F_o| + 1.19 \times 10^{-3}|F_o|^2)$
Max. peak in last difference map	0.64 eÅ^{-3}	0.91 eÅ^{-3}

Table 2. Atomic coordinates ($\times 10^4$) and equivalent temperature coefficients ($\text{Å}^2 \times 10^3$) for $[N(C_2H_4OH)_3]_2Ca(N_3)_2$ (left) and $[N(C_2H_4OH)_3]_2$-$Sr(N_3)_2$ (right).

Atom	x	y	z	U_{eq}	x	y	z	U_{eq}
Ca(Sr)	0	0	0	27(1)	0	0	0	21(2)
N11	6667	3333	61(2)	38(2)	6667	3333	23(7)	44(11)
N12	6667	3333	498(2)	37(2)	6667	3333	457(7)	47(12)
N13	6667	3333	917(2)	70(4)	6667	3333	875(10)	88(18)
N1	0	0	1013(1)	27(2)	0	0	1022(7)	35(9)
C1	425(7)	−1464(7)	1180(1)	46(4)	418(27)	−1447(28)	1205(5)	49(25)
H11	−894(7)	−2798(7)	1197(1)	237(41)	−872(27)	−2781(28)	1206(5)	161(87)
H12	1030(7)	−1073(7)	1543(1)	91(17)	946(27)	−1087(28)	1574(5)	74(36)
C2	1721(21)	−1731(21)	883(1)	61(6)	1759(53)	−1670(56)	910(6)	68(27)
H21	1496(21)	−3135(21)	954(1)	226(47)	1693(53)	−2973(56)	1008(6)	12(34)
H22	3150(21)	−685(21)	986(1)	215(48)	3134(53)	−511(56)	996(6)	48(41)
O	1537(14)	−1552(14)	382(1)	62(5)	1524(58)	−1647(53)	426(3)	63(22)
H3	2286(117)	−2009(136)	196(15)	74(19)	2656(93)	−1530(158)	261(39)	23(37)

Table 3. Selected values of bond lengths (Å) and bond angles (°).

		$[N(C_2H_4OH)_3]_2Ca(N_3)_2$	$[N(C_2H_4OH)_3]_2Sr(N_3)_2$
Bond lengths			
Ca(Sr)	−O	2.412(31) 6 ×	2.544(66) 6 ×
	N1	2.761(4) 2 ×	2.798(18) 2 ×
N12	−N11	1.192(6)	1.188(29)
	N13	1.143(8)	1.143(34)
N1	−C1	1.468(17) 3 ×	1.482(27) 3 ×
C2	−C1	1.429(26) 3 ×	1.452(51) 3 ×
	O	1.389(10) 3 ×	1.341(21) 3 ×
N11	−H3	1.81(12) 3 ×	1.99(19) 3 ×
Bond angles			
O−Ca(Sr)−O		179.7(3)	177.7(10)
N11−N12−N13		180.0(0)	180.0(1)
C1−N1−C1		110.9(3)	109.2(18)
N1−C1−C2		116.0(7)	114.2(19)
C1−C2−O		114.4(14)	115.0(41)
Ca(Sr)−N1−C1		108.0(2)	109.7(9)
Ca(Sr)−O−C2		126.2(11)	125.0(37)

Structure determination

The structure was solved with Patterson techniques (subprogram PATT of program SHELXS, Sheldrick, 1986) and difference Fourier syntheses. All non-H atoms were refined with anisotropic libration coefficients. In the terminal refinement cycles, the methylene protons were fixed at calculated positions; the O−H distances were constrained to 1.00(2) Å. The refinement converged at $R = 0.064$ [0.078] and $R_w = 0.065$ [0.070]. Atom coordinates and equivalent isotropic temperature coefficients are collected in Table 2, selected interatomic distances and angles are given in Table 3.

Discussion

The two crystal structures are approximately isomorphous; the description given below therefore applies to both, the calcium and the strontium compound.

The metal atom is located at the origin of the coordinate system (point symmetry 32), and it is coordinated to two TEA molecules whose N atoms are located at the threefold axis (Fig. 1). Their six symmetry-equivalent O atoms form a slightly distorted octahedron around the metal atom. The M−O distances agree well with corresponding distances in related compounds; the distances between metal atom and the amine nitrogen atoms are 2.76(1) [2.80(2)] Å, significantly longer than the M−O distances.
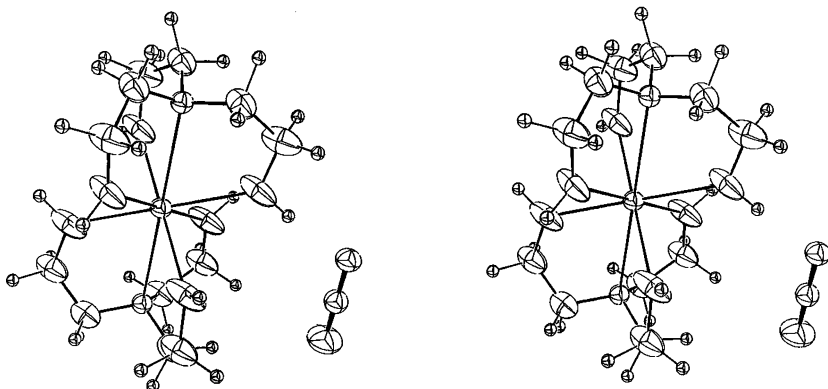
Fig. 1. The coordination of calcium with thermal ellipsoids (50% probability non-hydrogen atoms) in $[N(CH_2CH_2OH)_3]_2Ca(N_3)_2$.
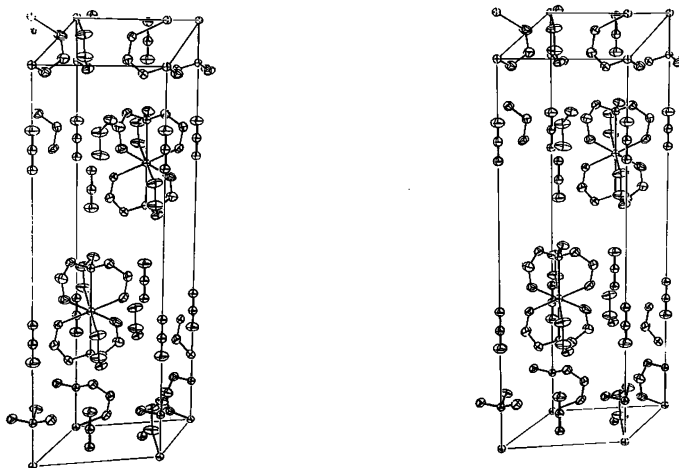
Fig. 2. ORTEP-drawing of the crystal structure (non-hydrogen atoms) of $[N(CH_2CH_2OH)_3]_2Ca(N_3)_2$.

The geometry of the TEA molecule is as expected from its chemical consitution.

The azide ions also lie on threefold axes and are therefore constrained to be linear; however, the two $N-N$ distances are significantly non-equivalent (Table 3). The azide ions are not coordinated to the metal atom; the terminal azide nitrogen atom N11 is involved in three H bonds to the surrounding OH groups. Figure 2 gives a stereoscopic ORTEP-representation of the crystal structure of the calcium compound. Both structures consist of doubly-charged complex cations, surrounded by azide anions.

The two structures have strong analogies to the structure of $(TEA)_2Sr(NO_3)_2$ mentioned in the introduction: in this compound, Sr is similarly surrounded by two TEA molecules, with the nitrate anions not involved in metal coordination.

The two crystal structures are among the few known metal azides, whose azide ions are not coordinated to a metal atom; so far, only two such crystal structures have been described. In $[(N_3)Co(NH_3)_5](N_3)_2$, two of the three azide groups are not coordinated to cobalt (Palenik, 1964), and in the recently determined crystal structure of $[Mg(H_2O)_6](N_3)_2$, none of the azide groups interacts directly with magnesium (Mautner et al., 1986).

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