The Crystal and Molecular Structure of Tetrakis(biuret)strontium(II) Perchlorate

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Crystals of tetrakis(biuret)strontium(II) perchlorate, $[Sr((NH_2CO)_2NH)_4](ClO_4)_2$, are monoclinic with $a = 11.21(1)$, $b = 7.30(1)$, $c = 14.52(1)\,Å$, $\beta = 98.2(2)°$, $D_{obs} = 1.976$, $D_{calcd}(Z = 2) = 1.973\,g/cm^3$, space group $P2/c$. 1526 independent reflections recorded photographically by the equi-inclination Weissenberg technique using $CuK\alpha$, the intensities of which were estimated visually, were used in the structure determination. The structure was solved by Patterson and Fourier methods and refined anisotropically by diagonal least squares to an R factor of 0.094. The strontium atoms are located at special positions related by inversion. The perchlorate moieties are ionic although extensive hydrogen bonding exists between them and the primary and secondary amines of biuret. The two biuret ligands in the asymmetric unit are bonded to strontium as bidentates via the carbonyl oxygens with a small twist (10.9, 12.0°) about the oxygen–oxygen line. The six membered rings formed by the chelate ligands with strontium are folded (49.6, 1.8°) about the oxygen–oxygen line. This is attributed to packing considerations. The co-ordination polyhedron is best described as approximately D_2–222 distorted square antiprism with the bidentate ligands spanning opposite edges of the rectangular faces. To our knowledge this complex presents the first case of an eight co-ordinate non-transition metal complex, characterized by x-rays, where all of the ligands are non-ionic chemically identical oxygen donor bidentates.

Introduction

Biuret, $NH_2CONHCONH_2$, has been reported to complex with transition metals as a neutral bidentate via the oxygens, a dianionic bidentate via the nitrogens, or as a monodentate ligand via one of the two oxygens.[1–5] The x-ray structural determination of the α-form of biuret hydrate[6], potassium bis(biureto)cuprate(II) tetrahydrate[7], bis(biuret)copper (II) chloride[8], bis(biuret)zinc(II) chloride[9], and bis(biuret)cadium(II) chloride[10], have been carried out. Diacetamide, $CH_3CONHCOCH_3$, like biuret can behave as a neutral bidentate ligand forming complexes of high co-ordination number with the alkaline earth perchlorates[11]. The structure of one, pentakis(diacetamide)barium(II) perchlorate[12] shows ten co-ordinate barium(II) with the ligands bonded through the oxygens as bidentates. The perchlorate moieties were not co-ordinated although the infrared showed significant deviation towards C_{3v} symmetry[13].

On the other hand, the alkaline earth perchlorate complexes with strongly basic neutral nitrogen donor ligands such as diethylenetriamine suggest a possible co-ordination number of 9^{14} and with weakly basic 1,10-phenanthroline and 2,2-bipyridine a co-ordination number of 8^{15}. However with ligands of smaller bite such as 1,8-naphthyridine and 2,7-dimethyl-1,8-naphthyridine the co-ordination number of the alkaline earth perchlorates rarely exceeds 4^{16} while with the lanthanide perchlorates it reaches 12^{17}.

We have recently undertaken the study of biuret complexes with the alkaline earths, the lanthanides and actinides which is a natural extension of the work on diacetamide with the alkaline earth. The infrared of most of the perchlorate complexes obtained show biuret to be the only ligand and to be bonded as a neutral bidentate via the oxygens[18]. However, significant variations in the CO stretching region and the NH_2 deformation region would indicate deviations in the biuret configuration from the α-form[2]. Systematic distortion of the perchlorate moiety from T_d symmetry with changes in cationic size were also observed. The crystal structure of $Sr(biuret)_4(ClO_4)_2$ was carried out in order to establish "standards" to be used in the interpretation of the infrared spectra and the study of the effect of cationic size and charge on the co-ordination number and the disposition of the neutral bidentate ligands.

Experimental

Preparation

Reagent grade hydrated strontium perchlorate and biuret in the molar ratio 1:6 were refluxed for six hours in minimum acetone then absolute ethanol was added to salt out the complex. Large crystals suitable

for x-ray work developed as a second crop from the mother liquor upon leaving it to evaporate slowly at room temperature. The air stable crystals were collected and washed with dry acetone. M.p. 205–6 °C. *Anal.* Calcd. for $Sr(NH_2CONHCONH_2)_4(ClO_4)_2$: Sr, 12.53; C, 13.71; N, 24.04; H, 2.86. Found: Sr, 12.50; C, 13.79; N, 23.96; H, 2.83.

X-Ray
Data collection and reduction
Crystal data are listed in Table I. The unit cell translations were determined from rotation photographs about each axis by extrapolation to a Bragg angle of 90°. The error reported is the standard deviation of the intercept. The monoclinic angle, β, was determined from a Weissenberg photograph of the h0l zone. The error reported is the standard deviation of the mean. The density was measured by flotation. Oscillation and Weissenberg photographs showed systematic absences in the general set h0l when $l = 2n + 1$. In this light two space groups were possible Pc(No. 7), and $P2/c$(No. 13 if the heavy atoms are located at centers of inversion related by translation $c/2$. The solution and consequent refinement of the structure established unequivocally the space group as $P2/c$. No attempts were made to choose the space group on the basis of morphology, etch figures, piezoelectric or other effects, however, stoichiometry and infrared spectroscopy would indicate that such a proposed chelate would have higher symmetry than that present in the space group Pc.

The external morphology showed elongation along the c-axis. The single crystal used for the collection of intensity data was cut from a larger crystal to have the dimensions $0.06 \times 0.09 \times 0.2$ mm^3 ($c \times a \times b$), and was mounted about the b-axis. Equiinclination Weissenberg levels, h0l–h6l were recorded on multiple films using nickel filtered copper radiation. The intensity of 1526 observable independent reflections were estimated visually and corrected for Lorentz, polariza-

tion and cylindrical absorption effects[19, 20]. Interlayer scales were tentatively set at unity. Final values for the interlayer scales were obtained by comparing ΣF_o and ΣF_c within each level (h0l–h6l) after all of the atoms were located and the structure refined isotropically to R of 0.14[21]. The approximate absolute scale factor and the overall isotropic thermal parameter ($\bar{B} = 3.16$ A^2) were determined by a Wilson plot[22]. Scattering curves for hydrogen, carbon, nitrogen, oxygen and chlorine were obtained from self-consistent wave functions[23], while that for strontium from the Thomas–Fermi–Dirac statistical model[24]. Scattering factors for strontium and chlorine were corrected for real, $\Delta f'$, and imaginary, $\Delta f''$, dispersion[25].

Solution and refinement of structure
The structure was determined by the heavy atom method. The space group was assumed to be $P2/c$ rather than Pc. A three dimensional Patterson summation[26] reavealed a major peak at the Harker line 0, v, $^1/_2$ that corresponds to the fractional co-ordinates for the heavy atoms 0, 0.1517, $^1/_4$ and 0, –0.1517, $^3/_4$. A three dimensional Fourier summation[26,27] phased on the strontium atom revealed the approximate positions of the other nineteen non-hydrogen atoms in the asymmetric unit. Few other peaks were also observed. The R-factor at this point was 0.44. The inclusion in the Fourier summation of the nineteen non-hydrogen atoms followed by five cycles of diagonal matrix least squares refinement of the co-ordinates and the individual isotropic temperature factors reduced R to 0.116. Subsequent allowance for the anisotropic vibration of all of the atoms followed by five cycles of further least squares refinement converged to a final R value of 0.094. The observed and calculated structure amplitudes are reported in Table II. The maximum shift in the last cycle of refinement was less than $.03\sigma$ for the co-ordinates (Table III) and less than $.1\sigma$ for the anisotropic thermal parameters (Table IV). A difference electron density map run at this point revealed several residual peaks of intensity less than $.4e/A^3$ some of which corresponds to likely hydrogen positions, the peak height of an average carbon atom being $8e/A^3$. No attempts however were made to deduce the hydrogen atom positions. The least squares refinement was carried out on F with the function minimized being $\Sigma w(|F_o|-|F_c|)^2$. The residual, $R = \Sigma||F_o|-|F_c|| /\Sigma|F_o|$ and the weighted residual, $wR = (\Sigma w||F_o|-|F_c||^2/\Sigma wF_o^2)^{1/2}$. Empirical weighting schemes outlined in the structural factor least squares program[27] were tried but all gave worse values of wR than simply weighing all observations equally. All observations were therefore given unit weight. Reflections were not excluded from refinement because of extinction effects. The unobserved planes were not included in the calculation of the residual. Interatomic distances (Table V) and bond angles (Table VI) were

TABLE I. Crystallographic Data for $[Sr(biuret)_4](ClO_4)_2$.

M. W. = 698.85
Crystallographic system: monoclinic
Space group: $P2/c$

Unit cell parameters:	$a = 11.21(1)$ A^a	
	$b = 7.30(1)$ A	
	$c = 14.52(1)$ A	
	$\beta = 98.2$ (2)°	
	V = 1176.1 A^3	
$d_{calcd} = 1.973$ g/cm^3	Z = 2	$\mu_{CuK\alpha} = 63.3$ cm^{-1}
$d_{obs} = 1.976$ g/cm^3		$\lambda = 1.5418$ A
$F_{000} = 704$		

^{a} Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit in the preceeding number.

TABLE II. Observed and Calculated Structure Amplitudes × 10 (F_{000} = 704).

TABLE II. (Cont.)

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
H=	1, K=	6	5	89	112	-10	266	-284	H=	4, K=	6	-8	195	230	-1	363	-356	9	105	118	3	319	296	-12	72	118				0	142	150
			6	313	-316	-11	125	-119				-9	136	-173	-2	92	-94	10	204	-207	5	202	170				H=	9, K=	6	2	196	-203
-1	200	160	7	329	-219	-14	77	-174	0	118	140	-10	297	-322	-3	93	97				6	149	-145	H=	8, K=	6				4	82	124
-3	365	518	8	98	150				2	152	-172	-14	59	-104	-4	94	113	H=	6, K=	6	7	114	-157				0	85	94			
-5	177	-327	9	96	91	H=	3, K=	6	3	351	-312				-4	96	-135							2	129	-143	4	243	247	H=	10, K=	6
-6	499	-482	12	247	274				-4	333	318	H=	5, K=	6	-6	168	-210	-1	136	-124	H=	7, K=	6	3	89	-119	6	211	-235			
-13	96	-146	13	120	110	0	337	281	-5	177	-186				-8	193	193	-2	441	-376				6	176	208	H=	9, K=	6	-1	125	-143
-11	129	130				1	107	114	-6	424	-195	0	470	477	-11	117	133	-3	218	198	-2	381	-346							-2	73	-69
-12	187	201	H=	2, K=	6	2	450	-438	-7	234	259	1	229	221	-12	127	163	-4	381	390	-3	168	176	H=	8, K=	6	-1	121	-134	-3	125	133
-13	102	-136				3	84	-65	-8	98	149	2	509	-517	-13	118	-128	-5	333	-333	-3	215	-231				-2	214	-256	-6	149	-238
			-1	218	-209	4	178	153	-9	97	-123	3	165	-171				-10	218	-246	-7	92	101	-1	94	-108	-1	185	159			
H=	2, K=	6	-2	337	-360	5	132	131	-10	211	-222	H=	4, K=	6	8	215	233	H=	6, K=	6	-12	92	121	-8	211	266	-4	194	179	H=	11, K=	6
			-3	430	476	6	96	-133	-12	194	238				9	119	99				-13	45	-101	-2	163	-147						
3	440	401	-4	78	115	7	296	-287	-13	70	-67	-2	321	-333				-8	211	266				-3	162	173	H=	10, K=	6	-1	64	-84
1	110	128	-5	209	-193	8	310	339	-14	114	-124	-4	352	302	H=	5, K=	6	-9	84	-107	H=	7, K=	6	-4	230	292				-2	164	-191
2	150	-124	-6	282	-254	9	133	144				-7	310	309				-10	78	-124				-6	125	-180				-4	190	152
4	144	135	-8	367	341	10	262	-266							2	295	-257	-11	67	85	5	240	218									
															5	135	163															

TABLE III. Fractional Atomic Coordinates.[a]

Atom	x/a	y/b	z/c
Sr	0.0000	−0.1517(3)	−0.2500
O_1	0.0227(8)	0.1235(14)	−0.3478(6)
O_2	0.1407(10)	−0.2058(14)	−0.3668(7)
C_1	0.0753(11)	0.1672(22)	−0.4106(9)
C_2	0.1800(12)	−0.1241(21)	−0.4311(9)
N_1	0.0714(12)	0.3463(20)	−0.4412(9)
N_2	0.1421(11)	0.0527(17)	−0.4585(8)
N_3	0.2602(13)	−0.1943(21)	−0.4814(10)
O_3	−0.2207(9)	−0.0917(13)	−0.3445(7)
O_4	−0.0986(9)	−0.4179(14)	−0.3490(7)
C_3	−0.3053(14)	−0.1977(24)	−0.3329(10)
C_4	−0.1888(12)	−0.4814(20)	−0.3249(8)
N_4	−0.4212(11)	−0.1371(21)	−0.3385(11)
N_5	−0.2932(10)	−0.3844(15)	−0.3170(8)
N_6	−0.1976(11)	−0.6648(17)	−0.3037(9)
Cl	0.4202(3)	0.3331(6)	−0.3896(2)
O_5	0.3394(11)	0.3510(22)	−0.4763(8)
O_6	0.5375(11)	0.2725(18)	−0.4029(10)
O_7	0.4302(12)	0.5153(19)	−0.3438(10)
O_8	0.3695(11)	0.2054(18)	−0.3277(9)

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit in the preceeding number.

calculated without correction for thermal motion using NRC-12 computer program[28]. Pertinent least squares planes and deviations therefrom and dihedral angles between[29] are reported in Table, VII. Figure 1 shows the molecular unit, [Sr (biuret)₄](ClO₄)₂. Figure 2 is a packing diagram showing the contents of the unit cell. Figure 3 shows distances in the strontium(II) co-ordination polyhedron.

Discussion

The crystal structure consists of well separated monomeric units. The molecular unit, [Sr(NH₂ CONHCONH₂)₄](ClO₄)₂, shows C_2 symmetry (Figure 1, 2). The four bonded biuret oxygens in the asymmetric unit, Sr/2(NH₂CONHCONH₂)₂(ClO₄), will complete the co-ordination polyhedron upon π rotation (Figure 3).

The co-ordination polyhedron is best described as being closer to square antiprismatic (D_{4d}) than cubic (O_h). Such co-ordination is expected for this tetrakis biuret complex with strontium(II) considering that the ligand is a neutral bidentate[30,31]. The $\bar{8}$ axis of the idealized D_{4d}–$\bar{8}2m$ square antiprism should be taken
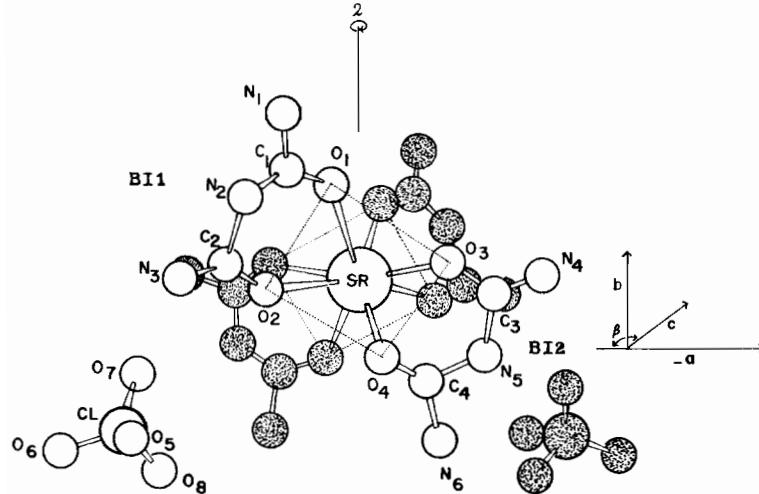
Figure 1. Molecular unit. Atoms at x, y, z and x̄, y, 1/2−z viewed perpendicular to the *ab*-face. The shaded atoms at x̄, y, 1/2−z are related to the unshaded atoms at x, y, z by the two-fold rotation axis. Strontium at fractional co-ordinates 0.0, −0.1517, −0.25.

TABLE IV. Anisotropic Thermal Parameters as Mean Square Amplitude (A^2).[a]

Atom	$U_{11} \times 10^3$	$U_{22} \times 10^3$	$U_{33} \times 10^3$	$U_{23} \times 10^3$	$U_{13} \times 10^3$	$U_{12} \times 10^3$
Sr	26(1)[b]	20(1)	26(1)	−00(1)	08(1)	06(1)
O_1	41(5)	33(6)	29(5)	03(5)	09(4)	−03(5)
O_2	51(8)	33(7)	39(5)	05(4)	20(5)	11(5)
C_1	26(6)	45(9)	27(6)	−02(5)	−05(5)	−09(7)
C_2	29(7)	38(9)	34(7)	−08(7)	06(5)	−04(6)
N_1	55(8)	38(9)	48(7)	18(7)	13(6)	15(7)
N_2	38(7)	33(8)	31(6)	10(5)	14(5)	08(5)
N_3	51(8)	62(11)	57(9)	−07(8)	25(7)	05(7)
O_3	38(5)	24(6)	51(6)	09(5)	04(4)	−04(4)
O_4	31(5)	30(6)	53(6)	−04(5)	10(4)	−01(4)
C_3	39(8)	56(12)	36(8)	−07(7)	01(6)	00(7)
C_4	31(7)	31(9)	21(6)	00(5)	07(5)	−03(6)
N_4	27(6)	44(9)	84(10)	00(8)	03(6)	05(6)
N_5	38(6)	15(7)	41(6)	03(5)	13(5)	00(5)
N_6	42(7)	17(7)	60(8)	03(6)	07(6)	−04(6)
Cl	30(2)	39(2)	35(2)	−01(2)	03(1)	−03(2)
O_5	57(7)	114(12)	36(6)	20(8)	−18(5)	−33(9)
O_6	42(7)	55(9)	103(11)	−01(8)	34(7)	12(6)
O_7	69(9)	49(9)	93(10)	−27(8)	23(8)	02(7)
O_8	54(8)	62(9)	67(8)	17(7)	10(6)	−13(6)

[a] The form of the anisotropic thermal parameter is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* \ 2U_{13}hla^*c^* + U_{12}hka^*b^*)]$. [b] Estimated standard deviation, shown in parentheses, are right-adjusted to the least significant digit in the preceeding number.
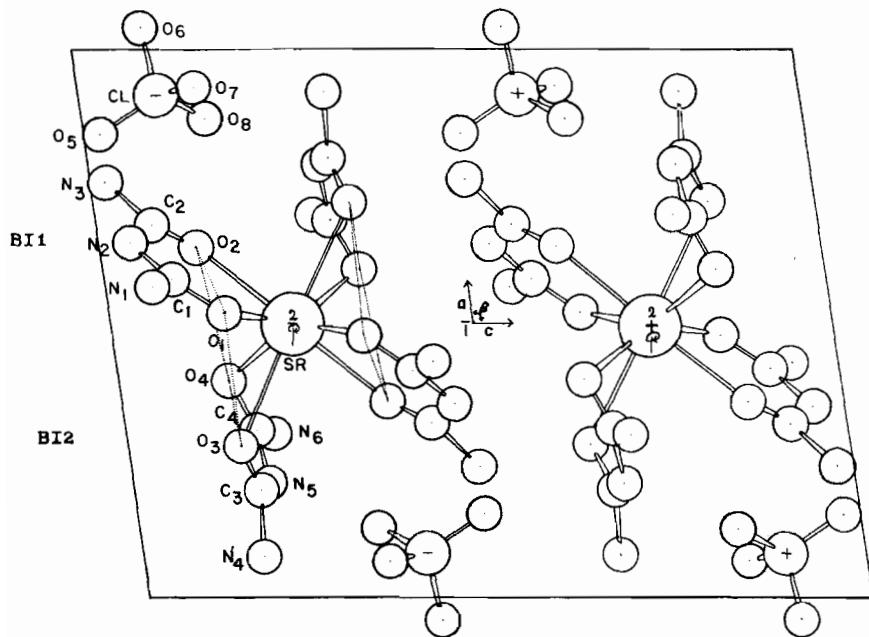
Figure 2. Packing diagram showing contents of the unit cell viewed down *b*-axis.

TABLE V. Interatomic Distances (A).

Bond distances in co-ordination sphere

Sr—O_1	2.494(10)[a]	Sr—O_3	2.689(10)
Sr—O_2	2.506(10)	Sr—O_4	2.571(10)

Distances within ligands

C_1—O_1	1.198(16)	C_3—O_3	1.253(19)
C_2—O_2	1.240(17)	C_4—O_4	1.209(17)
C_1—N_2	1.375(18)	C_3—N_5	1.386(21)
C_2—N_2	1.399(20)	C_4—N_5	1.386(18)
C_1—N_1	1.380(22)	C_3—N_4	1.364(20)
C_2—N_3	1.339(20)	C_2—N_6	1.380(19)

Pertinent non-bonded approaches

$Sr \cdots N_2$	3.913(11)	$Sr \cdots N_5$	3.704(12)
$O_1 \cdots O_2$	2.776(14)	$O_3 \cdots O_4$	2.752(14)

Distances within anion

Cl—O_5	1.450(12)
Cl—O_6	1.426(13)
Cl—O_7	1.484(14)
Cl—O_8	1.465(13)

Hydrogen-bonded atoms

$N_1 \cdots O_4$(I)[2]	3.019(17)	$N_4 \cdots O_7$(III)	3.030(20)
$N_3 \cdots O_6$(II)	3.062(19)	$N_5 \cdots O_5$(IV)	2.981(16)
		$N_5 \cdots O_7$(V)	3.061(18)
		$N_6 \cdots O_1$(VI)	3.058(16)
		$N_6 \cdots O_8$(V)	3.050(18)

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit in the preceeding number. [b] Roman numerals refer to the following transformations of the atoms, relative to the assymetric unit at x,y,z

I	x, 1 + y, z	IV	$\bar{x}, \bar{y}, \bar{z} - 1$
II	$1 - x, \bar{y}, \bar{z} - 1$	V	$\bar{x}, y - 1, \bar{z} - 1/2$
III	x - 1, y - 1, z	VI	x, y - 1, z

TABLE VI. Bond Angles (deg.).

Angles involving cation cluster

Sr—O_1—C_1	138.5(9)[a]	Sr—O_3—C_3	119.3(9)
Sr—O_2—C_2	139.4(9)	Sr—O_4—C_4	116.0(9)
O_1—C_1—N_2	126(1)	O_3—C_3—N_5	125(1)
O_2—C_2—N_2	122(1)	O_4—C_4—N_5	125(1)
C_1—N_2—C_2	125(1)	C_3—N_5—C_4	123(1)
O_1—C_1—N_1	120(1)	O_3—C_3—N_4	122(1)
O_2—C_2—N_3	124(1)	O_4—C_4—N_6	122(1)
N_1—C_1—N_2	114(1)	N_4—C_3—N_5	114(1)
N_3—C_2—N_2	113(1)	N_6—C_4—N_5	113(1)
O_1—Sr—O_2	67.4(3)	O_3—Sr—O_4	63.1(3)

Angles about chlorine in anion

O_5—Cl—O_6	112.6(8)
O_5—Cl—O_7	107.8(8)
O_5—Cl—O_8	110.0(8)
O_6—Cl—O_7	109.1(8)
O_6—Cl—O_8	109.4(8)
O_7—Cl—O_8	107.9(8)

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit in the preceeding number.

TABLE VII. Planes of Best Fit and Deviations Therefrom.[a]

Plane (A): $O_1, O_2, C_1, C_2, N_1, N_2, N_3$
$-0.687X -0.295Y -0.664Z = 2.373$
Deviation (A) from plane
O_1 0.010, O_2 −0.037, C_1 0.20, C_2 0.006, N_1 −0.087 N_2 0.140, N_3 −0.052
Distance (A) of other atoms from plane
Sr −0.017

Plane (B): O_1, C_1, N_1, N_2
$-0.730X -0.206Y -0.652Z = 2.362$
Deviation (A) from plane
O_1 0.001, C_1 −0.002, N_1 0.001, N_2 0.001

Plane (C): O_2, C_2, N_3, N_2
$-0.658X -0.382Y -0.649Z = 2.458$
Deviation (A) from plane
O_2 0.002, C_2 −0.004, N_3 0.001, N_2 0.001

Plane (D): O_1, Sr, O_2
$-0.680X -0.310Y -0.664Z = 2.377$

Plane (E): $O_3, O_4, C_3, C_4, N_4, N_5, N_6$
$-0.126X -0.158Y -0.979Z = 5.299$
Deviation (A) from plane
O_3 −0.123, O_4 0.143, C_3 −0.041, C_4 0.012, N_4 0.130, N_5 −0.063, N_6 −0.058
Distance (A) of other atoms from plane
Sr −1.671

Plane (F): O_3, C_3, N_4, N_5
$-0.011X -0.177Y -0.984Z = 5.006$
Deviation (A) from plane
O_3 0.004, C_3 −0.012, N_4 0.004, N_5 0.004

Plane (G): O_4, C_4, N_6, N_5
$-0.217X-0.200Y-0.956Z=5.483$
Deviation (A) from plane
O_4 0.002, C_4 −0.005, N_6 0.002, N_5 0.002

Plane (H): O_3, Sr, O_4
$0.529X + 0.328Y -0.783Z = 2.722$

Plane (I): O_5, Cl, O_6
$0.302X + 0.950Y -0.076Z = 4.400$

Plane (J): O_7, Cl, O_8
$-0.868X + 0.229Y -0.441Z = - 1.765$

Dihedral angles between planes (deg.)

Plane (A) and Plane (D)	1.8
Plane (B) and Plane (C)	10.9
Plane (E) and Plane (H)	49.6
Plane (F) and Plane (G)	12.0
Plane (A) and Plane (E)	38.4
Plane (I) and Plane (J)	90.6

[a] Equations are expressed in the cosine form $lX + mY + nZ = p$ where X, Y and Z are cartesian co-ordinates related to the cell co-ordinates by $X = xa$, $Y = yb$, $Z = zc$.
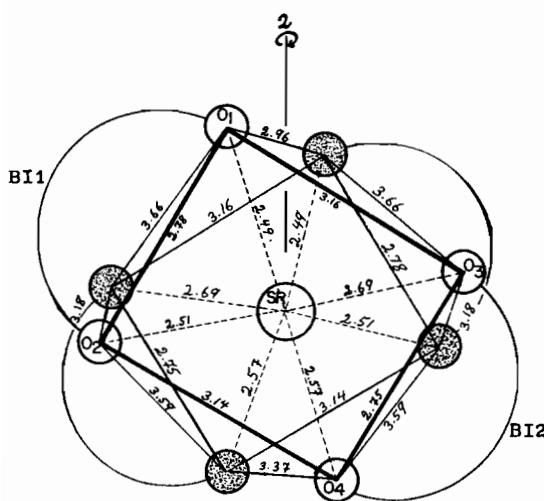
Figure 3. Antiprismatic co-ordination polyhedron viewed perpendicular to the *ab*-face showing distances (A). The shaded atoms are related to the unshaded atoms by the two-fold rotation axis.

as perpendicular to the *ab*-face and the 2 axis parallel to the *b*-axis. The bidentate ligands span opposite edges of the square faces of the antiprism (Figure 3). Deviation from idealized square antiprismatic geometry is towards the quasi-symmetry D_2–222. Such a quasi-symmetry has been achieved in the tetrakis complex $[Zr(CH_3COCHCOCH_3)_4]$[32] where, with an average zirconium–oxygen distance of 2.198 A, the edge length (2.675 A) of an equilateral antiprism is just the average intra-ring oxygen–oxygen distance (2.674 A). In $[Sr(NH_2CONHCONH_2)_4]^{++}$, the Sr(II) antiprismatic polyhedron exhibits significant deviation from D_2 symmetry. This deviation is attributed to a smaller average intra-ring O–O distance (2.76 A) than is required to span the edge of the equilateral antiprism with an average Sr–O bond distance of 2.55 A. The co-ordination polyhedron in $[Ce(CH_3COCHCOCH_3)_4]$[33] is also approximately square antiprismatic with symmetry approximating D_2 but with more deviation from D_2 than in the Zr(IV) case and less deviation than in the Sr(II) case. Since in the three cases the chelate bite is nearly the same, deviation from D_2 symmetry will be greatest with the largest cation, namely Sr(II) (ionis radius[34] for Sr(II) = 1.13 A, Ce(IV) = 1.01 A, and Zr(IV) = 0.80 A). The intra-ring O–O separation is 2.81 A along square face edges, while the inter-ring O–O separation is 2.97 A along square face edges, and 2.95 A along triangular faces in the Ce(IV) complex. However, the intra-ring O–O distance is 2.76 A along square face edges, while the inter-ring O–O distance is 3.15 A along square face edges, and 3.45 A along triangular faces in the Sr(II) complex. In contrast, the co-ordination polyhedron in the charged complex

anion $[Y(CF_3COCHCOCF_3)_4]^{-}$[35] is, as expected[30], best described as D_2 dodecahedral rather than antiprismatic.

The strontium–oxygen bond distances (2.49, 2.51, 2.69, 2.57 A) average 0.03 A longer than the sum of the ionic radii (Sr^{++} = 1.13 A, O^{2-} = 1.40 A)[34], indicating weak metal–oxygen bonding. This was previously found to be the case in the similar alkaline earth complex $[Ba(CH_3CONHCOCH_3)_5](ClO_4)_2$[12], where the metal–oxygen bond distance average 0.06 A longer than the sum of the ionic radii.

Octaco-ordination for strontium perchlorate complexes with neutral ligands is not unusual. It was suggested for the similar oxygen chelate with diacetamide, $Sr(CH_3CONHCOCH_3)_4(ClO_4)_2$[11], and for complexes with the weakly basic nitrogen bidentates 1,10-phenanthroline and 2,2′-bipyridine[14]. It seems however that the bidentate bite is a critical factor in determining the co-ordination number. The weakly basic nitrogen bidentates 1,8-naphthyridine, and 2,7-dimethyl-1,8-naphthyridine form four membered rings with the metal and exhibit an unexpected co-ordination number of four[16]. Since the biuret bite (2.75, 2.78 A) is shown to be equal to that of diacetamide in $[Ba(CH_3CONHCOCH_3)_5](ClO_4)_2$[12] (2.72–2.79 A), both neutral ligands are expected to yield complexes of similar co-ordination numbers with the alkaline earth perchlorates. This was found to be generally true except for barium where the biuret complex was found to be $1.5Ba(ClO_4)_2(biuret)_3 \cdot 1solvent$[18] and its infrared spectrum indicated bridging ligands in the α-form[2]. The x-ray structure of $1.5Ba(ClO_4)_2(biuret)_3 \cdot 1butanol$ awaits determination.

The two biuret ligands (BI1 and BI2 Figure 2, 3) in the asymmetric unit span opposit edges of the square face of the antiprism with BI2 folded in such a way as to make it approximately coplanar with the square antiprismatic face (Figure 2). BI1 makes with strontium an overall flat six membered ring except for some puckering. The flatness of the ring is exhibited as a 1.8° dihedral angle (Table VII) between the ligand best fit plane (O_1, O_2, C_1, C_2, N_1, N_2, N_3) and the (O_1, Sr, O_2) plane, and is supported by a long Sr–N_2 separation (Table V) and a short Sr to ligand plane distance (0.017 A, Table VII). BI2, on the other hand, makes with strontium a folded and puckered six membered ring. The folding about the O–O line is exhibited as a 49.6° dihedral angle between the ligands best fit plane (O_3, O_4, C_3, C_4, N_4, N_5, N_6) and the (O_3, Sr, O_4) plane, and is supported by a short Sr–N_5 separation (Table V) and a long Sr to ligand plane distance (1.671 A, Table VII). Ring puckering is exhibited mainly by twisting about the O–O line, the magnitude of which is indicated by the dihedral angle between the ligands two (N, O, C, N) best fit planes (10.9° for BI1 and 12.0° for BI2). Some twisting about the O–O lines has been anticipated from the infrared spectrum

since a remnant band in the NH_2 deformation region suggests deviation from the β-form of biuret towards the α-form[2]. The difference in the disposition of the two ligands has been suspected from the numerous carbonyl stretching bands in the infrared spectrum.

Variations in intra-ligand dimensions, which add to the complexity of the infrared spectrum, are obvious from Tables V and VI. The carbonyl entry angles in BI1 are significantly larger than in BI1 (138.5, 139.4° in BI1 compared to 119.3, 116.0° in BI2, Table VI). This is expected considering the planarity of the first chelate ring. This large variation in the entry angle would tend to support an electrostatic metal–oxygen bonding model over a covalent hybrid orbitals model. The larger bite and bite angle of BI1 over BI2 (2.776 A, 67.4° in BI1 compared to 2.752 A, 63.1° in BI2, Table V, VI) are again consistant with the planarity of the first chelate ring.

The perchlorate moiety is ionic but with obvious deviation from T_d symmetry (Table V, VI). This deviation, which is apparent from the infrared, is caused by packing considerations as well as extensive hydrogen bonding, in particular with the primary and secondary amines of BI2 (Table V). In fact this hydrogen bonding might have been the driving force behind BI2 chelate ring's folding (Figure 2). The amine stretching region in the infrared shows weaker amine–perchlorate hydrogen bonding than amine–carbonyl hydrogen bonding in crystalline biuret.

The thermal vibrations of the atoms (Table IV) are not highly anisotropic. Allowance for anisotropy reduced the R-factor by only 0.022. The thermal parameters are generally low in agreement with the air stability and non-hygroscopy of this perchlorate complex.

Acknowledgements

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