

Fig. 1. Molecular structure and numbering scheme.

the mean Os—O distance of 2.148 Å reported by Behling, Capparelli, Skapski & Wilkinson (1982), for the bidentate acetate found in the Os^{VI} complex $K[OsO_2(O_2CMe)_3] \cdot 2MeCO_2H$. Least-squares cal-

culations reveal a near-perfect central plane composed of the Os atom, the acetate ligand, and two Br atoms. Triphenylphosphine ligands reside on either side of the central plane and exhibit a P(1)—Os—P(2) bond angle of 175.1 (1)°. The central plane forms a dihedral angle of 89.70° with the plane defined by P(1)—Os—P(2).

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Structure of Tetrakis(biuret)samarium(III) Nitrate, $[Sm(NH_2CONHCONH_2)_4](NO_3)_3$

BY SALIM F. HADDAD

Department of Chemistry, The University of Jordan, Amman, Jordan

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Abstract. $[Sm(C_2H_5N_3O_2)_4](NO_3)_3$, $M_r = 748.69$, monoclinic, $C2/c$, $a = 17.256(2)$, $b = 7.090(1)$, $c = 20.545(2)$ Å, $\beta = 109.6(5)^\circ$, $V = 2368(8)$ Å³, $Z = 4$, $D_m = 2.090$, $D_x = 2.100$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 26.4$ cm⁻¹, $F(000) = 1484$, ambient temperature, $R = 0.0185$, $wR = 0.0252$ for 1526 reflections with $I_o > 3.0\sigma(I_o)$. Sm is located at site of symmetry 2. The two biuret ligands in the asymmetric unit are samarium-bonded as bidentates *via* the carbonyl O atoms with a twist (15.1, 15.7°) about the oxygen–oxygen line. One of the three nitrates in the molecular unit is centred at $\bar{1}$ and is disordered. The three O atoms of the disordered nitrate are distributed at eight positions, four with occupancy $\frac{1}{2}$ and four with occupancy $\frac{1}{4}$. The eight O-atom positions are imposed in part by hydrogen bonding. The CN = 8 coordination polyhedron is found by shape-parameter analysis to be closer to the square antiprism D_{4d} than the dodecahedron D_{2d} or the cube O_h . The twist angles, ϕ , in the dodecahedral *BAAB* trapezoids are 30.6 and 26.3°. The bidentate ligands span opposite edges of the rectangular faces of the square antiprism.

Introduction. Biuret (NH₂CONHCONH₂) was first reported as a decomposition product of urea and of urea nitrate (Wiedemann, 1848). Wiedemann also noted the formation of a characteristic red–violet colour as biuret is added to copper(II) sulfate in alkaline media, an observation which is the basis of the well known biuret reaction, where a violet–red colour is produced when cupric salts are added to proteins or polypeptides in alkaline media (Brücke, 1883; Schiff, 1898). With biuret, the colour is believed to be due to the violet hydroxy-bridged dimeric $K_2[Cu(NHCONHCONH)OH]_2 \cdot 4H_2O$ complex (McLellan & Melson, 1967), or due to the red $K_2[Cu(NHCONHCONH)_2] \cdot 4H_2O$ complex (Freeman, Smith & Taylor, 1961). In both the violet and the red complexes biuret behaves as a bidentate dianion bonding to Cu^{II} *via* the amide N atoms in a *cis–cis* configuration. In the solid state free biuret assumes a *trans–cis* configuration as found in the crystal structure of biuret hydrate (Hughes, Yakel & Freeman, 1961). It also assumes the *trans–cis* configuration in the crystal structure of bis(biuret)cadmium(II) chloride

(Cavalca, Nardelli & Fava, 1960) as it bonds to Cd^{II} *via* one of the carbonyl O atoms. In the crystal structures of bis(biuret)copper(II) chloride (Freeman, Smith & Taylor, 1961), and bis(biuret)zinc(II) chloride (Nardelli, Fava & Giraldi, 1963) biuret assumes a *trans-trans* configuration as the neutral ligand chelates to the metal *via* both carbonyl O atoms.

Series of complexes of biuret with alkaline-earth and lanthanide perchlorates, nitrates and halides were prepared by us and the crystal structures of [Sr(NH₂CONHCONH₂)₄](ClO₄)₂ reported (Haddad & Gentile, 1975). Biuret was found to behave in this complex as a neutral bidentate ligand bonding *via* the carbonyl O atoms to Sr^{II} in the *trans-trans* configuration with a small twist (10.9, 12.0°) about the oxygen-oxygen lines. We wish to report the crystal structure of the complex obtained on reacting samarium(III) nitrate with biuret in alcohol as a prototype of lanthanide(III) nitrate-biuret complexes. Preliminary X-ray diffraction data indicate that all lanthanide(III) nitrate-biuret complexes, obtained under the same conditions, are isostructural with [Sm(NH₂CONHCONH₂)₄](NO₃)₃ and all belong to space group C2/c. It will be of interest, among other things, to note the disposition of the twelve nitrate moieties per unit cell in the eight asymmetric units of C2/c.

Experimental. Reagent-grade biuret (NH₂-CONHCONH₂) and samarium(III) nitrate hydrate in the molar ratio 6:1 (10⁻³ mol Sm³⁺) were refluxed in 95% ethanolic solution for several hours. Needle-like, clear, pale yellow crystals suitable for X-ray diffraction were separated upon slow evaporation. Air dried. M.p. 503 K. Analysis calculated for Sm(C₂H₅N₃O₂)₄(NO₃)₃: C 12.88, N 28.06, H 2.69, Sm 20.08%; found: C 12.96, N 28.11, H 2.73, Sm 19.82%.

Density measured by flotation in 1,2-dibromoethane and ethanol. Crystal used for data collection cut from a larger crystal to the following dimensions, centre to face, mm (face), 0.075 (100), 0.075 ($\bar{1}00$), 0.130 (010), 0.130 (0 $\bar{1}0$), 0.065 (001), 0.065 (00 $\bar{1}$). Crystal volume 0.00538 mm³. Enraf-Nonius CAD-4 diffractometer, Mo K α radiation, graphite monochromator. Attenuation factor of 18.19. Scan rate 4.0–32.0° min⁻¹. ω -2 θ scan. Lattice parameters and crystal orientation by a least-squares fit of the setting angles of 25 reflections with $\theta = 25$ –30°. One fourth of the reciprocal lattice up to $h, k, \pm l$ of 18, 7, ± 22 , 1601 reflections within $5 < \theta < 22.5^\circ$ at ambient temperature. 1526 reflections with $I_o > 3.0\sigma(I_o)$. 1467 reflections included in least-squares refinement. The three standard reflections showed no significant change during data collection. Transmission factors min. = 52.25, max. = 75.02 with a mesh size of 0.02 mm for absorption corrections. Data reduction and structure solution and refinement were performed using the computer programs of

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$B_{eq} = \frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ac(\cos\beta)\beta_{13}]$$

	x	y	z	B _{eq} (Å ²)
Sm*	0.0000 (0)	0.22904 (3)	0.2500 (0)	1.98 (1)
O(1A)	-0.0769 (1)	0.4933 (3)	0.26277 (10)	2.71 (8)
O(2A)	-0.1481 (1)	0.1612 (3)	0.20608 (11)	2.85 (8)
C(1A)	-0.1392 (2)	0.5630 (4)	0.2206 (2)	2.6 (1)
C(2A)	-0.2093 (2)	0.2626 (4)	0.1815 (2)	2.8 (1)
N(1A)	-0.1466 (2)	0.7455 (4)	0.2103 (2)	4.6 (2)
N(2A)	-0.2063 (2)	0.4578 (4)	0.1834 (1)	3.2 (1)
N(3A)	-0.2843 (2)	0.1953 (4)	0.1499 (2)	3.9 (1)
O(1B)	0.0104 (1)	-0.0414 (3)	0.18492 (9)	2.65 (8)
O(2B)	-0.0476 (1)	0.3012 (3)	0.13004 (11)	2.86 (8)
C(1B)	-0.0151 (2)	-0.0940 (4)	0.1234 (1)	2.4 (1)
C(2B)	-0.0817 (2)	0.2052 (4)	0.0774 (2)	2.6 (1)
N(1B)	0.0005 (2)	-2.2658 (3)	0.1053 (2)	3.2 (1)
N(2B)	-0.0610 (1)	0.0195 (3)	0.0708 (1)	2.6 (1)
N(3B)	-0.1394 (2)	0.2753 (4)	0.0234 (2)	4.1 (1)
N(1)	0.1258 (2)	0.2347 (3)	0.0898 (1)	2.9 (1)
O(1)	0.1721 (2)	0.2911 (4)	0.14686 (13)	4.2 (1)
O(2)	0.1279 (1)	0.0622 (3)	0.07538 (12)	4.0 (1)
O(3)	0.0794 (1)	0.3430 (4)	0.04747 (12)	4.4 (1)
N(2)†	0.2500 (0)	0.2500 (0)	0.0000 (0)	5.3 (2)
O(4)‡	0.3038 (4)	0.170 (1)	0.0471 (4)	7.5 (2)¶
O(5)‡	0.2679 (4)	0.382 (1)	0.0546 (3)	7.0 (2)¶
O(6)§	0.2276 (6)	0.385 (2)	-0.0368 (6)	5.2 (2)¶
O(7)§	0.2581 (6)	0.095 (2)	-0.0047 (5)	5.3 (3)¶

* Located at crystallographic symmetry site 2, Wyckoff position 4(e).

† Located at crystallographic symmetry site $\bar{1}$, Wyckoff position 4(c).

‡ Occupancy $\frac{1}{2}$.

§ Occupancy $\frac{1}{3}$.

¶ Isotropic refinement.

Enraf-Nonius SDP (Frenz & Okaya, 1980). Atomic scattering factors were those supplied internally by SDP. Corrections for anomalous-dispersion effects for Sm were made using f' and f'' . Phases determined by Patterson and Fourier methods and the magnitudes of ΔF minimized in diagonal-matrix least-squares refinement of 190 parameters. All H atoms were observed in the final electron density map; however, H atoms were treated as fixed atoms. $R = 0.0185$, $wR = 0.0252$, $w = 1/\sigma(F_o)^2$; fudge factor ($p = 0.02$) introduced to prevent overweighting strong reflections (Eigenbrot & Raymond, 1982). $(\Delta/\sigma)_{\max} = 0.03$ (0.06 for disordered O atoms). $(\Delta\rho)_{\max} = 0.19 \text{ e } \text{Å}^{-3}$. $S = 1.866$. Extinction coefficient not refined. Final positional and equivalent isotropic thermal parameters with their standard deviations are listed in Table 1.* Bond distances, bond angles and hydrogen-bond details are in Table 2.

* Lists of structure factors, anisotropic thermal parameters, least-squares planes, shape parameters of the coordination polyhedron and a schematic representation of the eight-coordinate dodecahedron (D_{2d}) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44072 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å), bond angles (°) and hydrogen-bond lengths (Å) with *e.s.d.*'s in parentheses

Sm—O(1A)	2.361 (1)	O(1A)—Sm—O(2A)	69.02 (5)
Sm—O(2A)	2.456 (2)	Sm—O(1A)—C(1A)	129.0 (2)
O(1A)—C(1A)	1.236 (3)	O(1A)—C(1A)—N(1A)	121.5 (2)
C(1A)—N(1A)	1.310 (3)	O(1A)—C(1A)—N(2A)	123.1 (2)
C(1A)—N(2A)	1.373 (3)	N(1A)—C(1A)—N(2A)	115.4 (2)
N(2A)—C(2A)	1.385 (3)	C(1A)—N(2A)—C(2A)	125.1 (2)
C(2A)—N(3A)	1.327 (4)	N(2A)—C(2A)—N(3A)	113.2 (2)
C(2A)—O(2A)	1.236 (3)	N(2A)—C(2A)—O(2A)	123.4 (3)
		N(3A)—C(2A)—O(2A)	123.4 (2)
		C(2A)—O(2A)—Sm	132.6 (2)
Sm—O(1B)	2.380 (1)	O(1B)—Sm—O(2B)	69.82 (5)
Sm—O(2B)	2.377 (2)	Sm—O(1B)—C(1B)	138.0 (2)
O(1B)—C(1B)	1.246 (3)	O(1B)—C(1B)—N(1B)	121.6 (2)
C(1B)—N(1B)	1.327 (3)	O(1B)—C(1B)—N(2B)	122.6 (2)
C(1B)—N(2B)	1.367 (3)	N(1B)—C(1B)—N(2B)	115.9 (2)
N(2B)—C(2B)	1.383 (3)	C(1B)—N(2B)—C(2B)	125.6 (2)
C(2B)—N(3B)	1.314 (4)	N(2B)—C(2B)—N(3B)	115.1 (2)
C(2B)—O(2B)	1.245 (3)	N(2B)—C(2B)—O(2B)	122.9 (2)
		N(3B)—C(2B)—O(2B)	122.0 (2)
		C(2B)—O(2B)—Sm	132.9 (2)
N(1)—O(1)	1.243 (3)	O(1)—N(1)—O(2)	118.2 (2)
N(1)—O(2)	1.262 (2)	O(1)—N(1)—O(3)	121.7 (2)
N(1)—O(3)	1.232 (3)	O(2)—N(1)—O(3)	120.1 (2)
N(2)—O(4)	1.230 (7)	O(4)—N(2)—O(5)	76.9 (4)
N(2)—O(5)	1.414 (6)	O(5)—N(2)—O(6)	84.8 (7)
N(2)—O(6)	1.203 (11)	O(6)—N(2)—O(7)	139.0 (6)
N(2)—O(7)	1.114 (13)	O(7)—N(2)—O(4)	62.2 (6)
N(1A)...O(1)	2.975 (4)	N(1B)...O(3)	3.023 (3)
N(1A)...O(5)	3.189 (7)	N(2B)...O(2)	2.891 (3)
N(2A)...O(1)	3.081 (3)	N(3B)...O(4)	3.060 (8)
N(2A)...O(2)	3.066 (3)	N(3B)...O(6)	2.91 (1)
N(3A)...O(1)	2.958 (3)	N(3B)...O(7)	2.82 (1)
N(3A)...O(2)	3.138 (3)	N(3B)...O(2)	3.187 (3)

Discussion. Fig. 1 shows the structure and the atom numbering in the cationic complex tetrakis(biuret)samarium(III). The two ligands in the asymmetric unit are labelled *A* and *B*. The unit cell contains four monomeric complex cations $[\text{Sm}(\text{NH}_2\text{CONHCONH}_2)_4]^{3+}$ with Sm on 2 at 4(*e*), and twelve ionic nitrates, eight of which are at general positions 8(*f*), and four centred on $\bar{1}$ with N atoms, N(2), at 4(*c*). Since the nitrate ion itself is noncentrosymmetric these four nitrate ions are bound to exhibit disordered O atoms. Fig. 2 shows the molecular unit $[\text{Sm}(\text{NH}_2\text{CONHCONH}_2)_4](\text{NO}_3)_3$ projected down 2.

As in the case of the biuret complex with Sr^{II} , tetrakis(biuret)strontium(II) perchlorate (Haddad & Gentile, 1975), the two biuret ligands per asymmetric unit, *A* and *B*, assume a rather planar *trans-trans* configuration as they chelate to the metal cation *via* carbonyl O atoms, and along opposite square edges of an approximate square antiprism. The twist along the O...O line, the chelate bite line, is 15.1 and 15.7° for ligands *A* and *B* in the Sm^{III} case compared with 10.9 and 12.0° in the Sr^{II} case above, and 5.2° in the Zn^{II} case (Nardelli, Fava & Giraldi, 1963). Apparently, there is no simple relationship between the magnitude of twist along the bite line and the cation size or charge.

The hexagonal rings which the ligands *A* and *B* form with Sm^{III} are not planar (Fig. 2) as the sums of the internal angles are 702 and 712° respectively. The *A* and *B* hexagonal rings are folded about the O...O line by 27.5 and 17.9°, respectively. The difference in magnitude of folding is attributed to the disposition of the nitrate ions and to hydrogen bonding between the primary and secondary amines and the nitrate O atoms. There is no apparent correlation between the internal dimensions of the two biuret ligands, *A* and *B*, and the Sm—O bond lengths, or the magnitude of twist or fold along the O...O lines. The mean C—O bond lengths for ligands *A* and *B* [1.236 (0) and 1.245 (5) Å] $\{\sigma(\bar{x}) = [\sum(x-\bar{x})^2/(n-1)]^{1/2}\}$ show insignificant variance in spite of larger variance in the mean Sm—O bond lengths [2.409 (68) and 2.378 (2) Å], and in spite of a significantly higher degree of folding present along the O...O line in ligand *A* [27.5 vs 17.9°]. The same could be said about

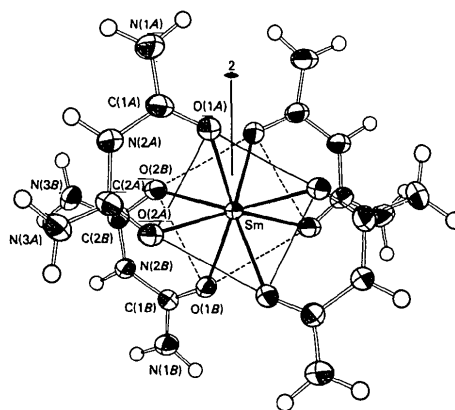


Fig. 1. ORTEP (Johnson, 1965) drawing of the complex cation tetrakis(biuret)samarium(III). The thermal ellipsoids are drawn at 50% probability.

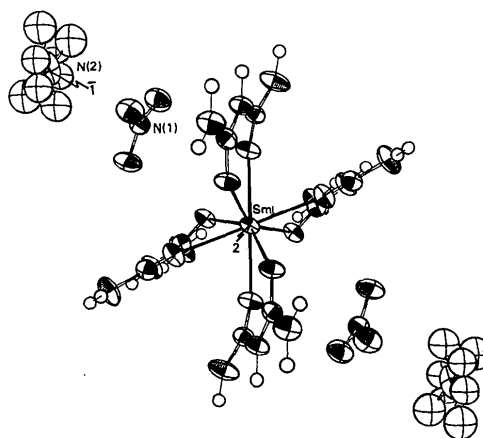


Fig. 2. ORTEP drawing of the molecular unit $[\text{Sm}(\text{NH}_2\text{CONHCONH}_2)_4](\text{NO}_3)_3$ showing ordered and disordered nitrates: Sm on 2, N(2) on $\bar{1}$. The thermal ellipsoids are drawn at 50% probability. O atoms of disordered nitrate are refined isotropically.

the mean C—NH₂ bond lengths for ligands *A* and *B* [1.318 (12) and 1.320 (9) Å].

Two of the nitrate ions per molecular unit are in general positions and are planar ($\chi^2 = 2$), while the third is centred on $\bar{1}$ and is disordered. There are eight regions of high electron density around N(2) of the disordered nitrate. Four regions correspond to O(4), O(4)', O(5), O(5)' (primed at \bar{x} , \bar{y} , \bar{z}) each with occupancy $\frac{1}{2}$, and another four correspond to O(6), O(6)', O(7), O(7)' each with occupancy $\frac{1}{4}$. The disordered nitrate is not planar ($\chi^2 = 1445$) with O(4) and O(4)' 0.218 (8) Å from the mean plane. O(5), O(5)', O(6), O(6)', O(7), O(7)' are on the other hand coplanar with N(2) ($\chi^2 = 1$) and with O(4) and O(4)' 0.27 (1) Å from this mean plane. The vibrations of the disordered O atoms were relatively high and their parameters did not converge when refined anisotropically. Isotropic thermal parameters, however, converged to rather high values (5.2–7.5 Å²).

The coordination polyhedron is closer to a perfect square antiprism (D_{4d}) than to a trigonal-faced dodecahedron (D_{2d}) or a cube (O_h). This conclusion is based on the shape-parameter considerations (Muetterties & Guggenberger, 1974) reported in Table 5 (deposited). The bidentate ligands span *m* edges of the idealized eight-coordination polyhedron with O(1A) and O(1B) at the *A* site and O(2A) and O(2B) at the *B* site of the *BAAB* trapezoids. The twist angles in the two *BAAB* trapezoids, ϕ , defined to be the dihedral angle between the planes *A*, *A*, and the centroid of the two *B* positions, and *B*, *B*, and the centroid of the two *A* positions, are 30.6 and 26.3°, much closer to the D_{4d} (24.5°) than the D_{2d} (0.0°) case. The dihedral angles along the dodecahedral *b* edges, δ_b , are 4.4° and 60.9° compared with the theoretical D_{4d} angles (0.0 and

52.4°), and the theoretical D_{2d} angles (29.5 and 29.5°). The coordination polyhedron is strikingly different from the one found in tetrakis(tironato)cerate(IV) (Haddad & Raymond, 1986), where the bidentate ligands span the *m* edges of an almost regular trigonal-faced dodecahedron (D_{2d}).

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Structure of the Mixed-Valence Compound Poly{[*N,N*-bis(3,5-dimethyl-1-pyrazolylmethyl)aminobenzene]-tris(μ -thiocyanato-*S,N*)-dicopper(I,II)}

BY WILLEM L. DRIESSEN,* HENK L. BLONK, WINFRIED HINRICHS† AND JAN REEDIJK

Department of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands

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Abstract. [Cu₂(C₁₈H₂₃N₅)(NCS)₃]_n, $M_r = 610.74$, monoclinic, $P2_1/n$, $a = 13.473$ (1), $b = 21.975$ (2),

$c = 8.666$ (1) Å, $\beta = 92.93$ (1)°, $V = 2562.4$ Å³, $Z = 4$, $D_x = 1.58$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 19.25$ cm⁻¹, $F(000) = 1244$, $T = 293$ K, final $R = 0.028$ for 1624 significant reflections. Each Cu^{II} ion is surrounded by five N atoms in a geometry which is very close to square pyramidal. The deviation from a square pyramid is largely due to the constraint of the ligand

* To whom correspondence should be addressed.

† Present address: Institute of Crystallography, Department of Chemistry, Free University of Berlin, 1000 Berlin 33, Federal Republic of Germany.