

Results of this analysis, together with the previous work cited in the introduction, again illustrate the occurrence of unusual trigonal beryllium oxygen coordinations in oxides lacking clear thermodynamic stability.

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The Crystal Structure of Sparteine-N(16)-oxide Sesquiperchlorate

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Sparteine-N(16)-oxide sesquiperchlorate, $2C_{15}H_{26}N_2O \cdot 3HClO_4$, crystallizes in the space group $P2_12_12$. The unit-cell dimensions are $a=18.01$, $b=12.47$, $c=8.14$ Å and $Z=2$. The structure has been refined by block-diagonal least squares to the R value of 0.096 with use of photographic data for 1894 observed reflexions. All four rings of this compound are in the chair conformation and the oxygen atom is attached to the nitrogen atom of the *cis*-quinolizidine system. The crystallographically symmetrical hydrogen bond between the oxygen atoms of two neighbouring molecules of the alkaloid was found to be 2.479 ± 0.008 Å.

Introduction

The X-ray analysis of α -isosparteine monohydrate, (Przybylska & Barnes, 1953) confirmed the *cis-cis* configuration proposed for α -isosparteine by Marion & Leonard (1951), as the two hydrogen atoms, at C(6) and C(11), were found to be *cis* with respect to the methylene bridge. The molecule consists of two *trans*-quinolizidine systems (see Fig. 1). The results of the molecular and crystal structure determination of 7-hydroxy- β -isosparteine perchlorate, which is the *trans-trans* compound and has two *cis*-quinolizidine systems, were

published by Pinkerton & Steinrauf (1967) when this investigation was in its final stages. Sparteine-N(16)-oxide sesquiperchlorate is the first *cis-trans* C_{15} lupine alkaloid studied by X-ray analytical methods.

On the basis of chemical and physico-chemical evidence the oxygen atom was expected to be attached to N(16) of the *cis*-quinolizidine system; however, a confirmation of this fact by a structural determination was considered useful, as both types of evidence had weak points.

The conformation of the rings was also of interest because the inversion of N(16) can apparently readily take place in solution, transforming the ring C into a boat form (Bohlmann, Schumann & Arndt, 1965; Wiewiorowski, Edwards & Bratek-Wiewiorowska, 1967).

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Baranowski, Skolik & Wiewiorowski (1964) compared the infrared spectra of α -isosparteine-*N*-oxide diperchlorate monohydrate, $C_{15}H_{26}N_2O \cdot 2HClO_4 \cdot H_2O$ with those of sparteine-*N*(16)-oxide sesquiperchlorate, $2C_{15}H_{26}N_2O \cdot 3HClO_4$. They found that the hydrogen bond $N^+(1)-H \dots O$ in the latter is weaker, the N-H frequency occurring at $\sim 2900 \text{ cm}^{-1}$, whereas in the diperchlorate derivative it occurs at $\sim 2630 \text{ cm}^{-1}$. To explain these results and the chemical behaviour of these compounds, they postulated the formation of the dimeric cation in sesquiperchlorate with an intermolecular symmetrical hydrogen bonding between the oxygen atoms of neighbouring molecules of sparteine-*N*(16)-oxide. Since the above infrared study combined with that of the corresponding deuterated compounds did not establish the structure, a detailed X-ray analysis was suggested by Dr M. Wiewiorowski, who supplied authentic crystals suitable for this investigation.

Crystal data

Formula $2C_{15}H_{26}N_2O \cdot 3HClO_4$, $M = 802.1$.

Orthorhombic, space group $P2_12_12$ with $Z = 2$.

Unit-cell dimensions are: $a = 18.01 \pm 0.02$, $b = 12.47 \pm 0.02$ and $c = 8.14 \pm 0.01 \text{ \AA}$.

Systematic absences: $h00$ for h odd and $0k0$ for k odd. $D_m = 1.470 \text{ g.cm}^{-3}$ (by flotation in a mixture of carbon tetrachloride and toluene). $D_c = 1.457 \text{ g.cm}^{-3}$.

$F(000) = 852$. $\mu = 29.0 \text{ cm}^{-1}$ (Cu $K\alpha$).

The chemical analysis was carried out by Mr H. Séguin:

C, 45.49; H, 7.11; Cl, 13.28; N, 6.98%.

Calculated for $2C_{15}H_{26}N_2O \cdot 3HClO_4$: C, 44.92; H, 6.91; Cl, 13.26; N, 6.99%.

The unit-cell dimensions were determined from precession photographs with copper radiation and were refined by the measurement of over-exposed Weissenberg photographs which were corrected for film shrinkage (Srivastava, 1959). Equi-inclination, multiple-film, Weissenberg photographs were taken for $k = 0 \dots 10$ and for $l = 0 \dots 6$ and intensities of 1894 independent reflexions were measured by visual comparison with a calibrated scale. The intensities were corrected for Lorentz and polarization factors and then correlated. The absolute scale and overall temperature factors were evaluated by Wilson's (1942) method. The absorption corrections were considered negligible and were not applied because the crystals were cut so that they were cylindrical in shape and of diameters between 0.2 and 0.3 mm. They deteriorated on prolonged exposure to the X-ray beam and were therefore changed several times to ensure data as accurate as possible.

Structure determination and its refinement

The unit cell contains two molecules of $2(C_{15}H_{26}N_2O) \cdot 3HClO_4$, therefore there are four molecules of sparteine and six perchlorate anions, four of which are in general positions and two were found to be situated on

twofold axes. The coordinates of the chlorine atoms were determined from a three-dimensional Patterson synthesis, sharpened by the zero level $1/L_p$ function, and they were: (0.126, 0.086, 0.168) and (0, 0.5, 0.287). From the first Fourier synthesis based on the contributions of the heavy atoms alone, the locations of ten atoms of the sparteine skeleton were derived. The next Fourier cycle revealed unambiguously the remaining atoms of the cation and the R index decreased from 0.37 to 0.29. After one least-squares refinement, a three-dimensional $\rho_o - \rho_c$ synthesis was computed. The positions of four oxygen atoms attached to the chlorine atom in the general position could thus be determined with much greater accuracy than was previously possible. Four least-squares cycles had brought R to 0.17, the anisotropic refinement of the chlorine and the four oxygen atoms having been undertaken.

An additional difference synthesis, which was carried out at this stage, gave information concerning the remaining oxygen atoms. Four peaks, of roughly half the weight of the other oxygen atom peaks, were located, and by applying the required symmetry operation of the twofold axis, a total of eight oxygen atoms surrounding the chlorine atom Cl(2) was therefore obtained. Stereochemical examination gave two acceptable tetrahedral ClO_4^- groups. The subsequent five refinement cycles decreased the R value to 0.13.

To be more consistent with the presence of disorder, the refinement of the chlorine atom on the twofold axis, Cl(2), was changed by placing it in a general position, slightly displaced from the twofold axis and assigned half occupancy. As expected, the thermal parameters of the chlorine atom had decreased considerably, but the refinement was not affected, the R value remaining the same. The final coordinates and their estimated standard deviations are given in Table 1.

Table 1. Final fractional coordinates and their estimated standard deviations

	x/a	y/b	z/c
Cl(1)	0.1258 (1)	0.0857 (2)	0.1737 (3)
Cl(2)	0.0054 (3)	0.4946 (6)	0.2892 (3)
N(1)	0.1715 (3)	0.8470 (5)	0.8346 (8)
C(2)	0.2393 (4)	0.8997 (7)	0.9001 (13)
C(3)	0.2634 (4)	0.9914 (7)	0.7910 (14)
C(4)	0.2757 (4)	0.9562 (8)	0.6189 (15)
C(5)	0.2083 (4)	0.8935 (7)	0.5536 (12)
C(6)	0.1878 (4)	0.8031 (6)	0.6637 (10)
C(7)	0.1257 (4)	0.7295 (6)	0.6004 (10)
C(8)	0.1124 (5)	0.6399 (6)	0.7263 (12)
C(9)	0.0789 (5)	0.6957 (6)	0.8790 (10)
C(10)	0.1389 (5)	0.7683 (8)	0.9531 (11)
C(11)	0.0038 (5)	0.7458 (5)	0.8423 (8)
C(12)	-0.0530 (5)	0.6560 (7)	0.8166 (12)
C(13)	-0.1303 (5)	0.6958 (7)	0.7634 (13)
C(14)	-0.1218 (4)	0.7599 (6)	0.6081 (11)
C(15)	-0.0702 (4)	0.8540 (6)	0.6396 (10)
N(16)	0.0062 (3)	0.8214 (4)	0.6970 (6)
C(17)	0.0518 (4)	0.7800 (5)	0.5530 (8)
O(18)	0.0398 (3)	0.9189 (3)	0.7506 (6)
O(19)	0.1981 (7)	0.0992 (15)	0.2001 (34)
O(20)	0.1095 (4)	0.0483 (7)	0.0160 (8)

Table 1 (cont.)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
O(21)	0.1048 (11)	0.0028 (14)	0.2780 (16)
O(22)	0.0817 (8)	0.1724 (10)	0.2117 (14)
O(23)	-0.0277 (8)	0.5229 (18)	0.4429 (14)
O(24)	0.0585 (8)	0.5898 (13)	0.2607 (19)
O(25)	-0.0522 (8)	0.5140 (22)	0.1720 (19)
O(26)	0.0408 (15)	0.4066 (13)	0.2867 (44)

One more $\rho_o - \rho_c$ synthesis was calculated for the sake of locating the hydrogen atoms and it indicated the positions of most of them. On closer examination, however, a number of them were found to be too displaced from theoretically expected locations to be acceptable for the least-squares refinement. Their coordinates were therefore computed assuming the distances 1.07 and 1.03 Å for the C-H and N-H bonds respectively. The temperature factor $B = 5.0 \text{ \AA}^2$ was used in the calculation of their contribution. Their coordinates, given in Table 2, were not refined, with the exception of the hydrogen atom H(18), situated on the twofold axis, midway between the oxygen atoms of two neighbouring molecules of the alkaloid.

Table 2. Fractional coordinates of the hydrogen atoms

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
H(1)	0.129	0.902	0.828
H(2)	0.227	0.930	1.021
H(2')	0.283	0.842	0.909
H(3)	0.221	1.052	0.790
H(3')	0.314	1.024	0.836
H(4)	0.284	1.024	0.542
H(4')	0.323	0.905	0.614

Table 2 (cont.)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
H(5)	0.222	0.862	0.434
H(5')	0.162	0.947	0.543
H(6)	0.236	0.755	0.682
H(7)	0.142	0.695	0.485
H(8)	0.076	0.581	0.677
H(8')	0.165	0.603	0.756
H(9)	0.072	0.637	0.974
H(10)	0.117	0.812	1.054
H(10')	0.184	0.718	0.997
H(11)	-0.013	0.795	0.943
H(12)	-0.032	0.603	0.723
H(12')	-0.058	0.612	0.929
H(13)	-0.154	0.745	0.859
H(13')	-0.167	0.629	0.742
H(14)	-0.100	0.711	0.514
H(14')	-0.176	0.791	0.571
H(15)	-0.064	0.898	0.528
H(15')	-0.094	0.904	0.731
H(17)	0.062	0.846	0.473
H(17')	0.019	0.721	0.490
H(18)	0	0	0.727 ($\sigma = 0.015$)

The introduction of the hydrogen atoms and of the anisotropic refinement for all other atoms of the molecule has brought the final value of the reliability index to 0.096, excluding the unobserved reflexions. The final vibrational parameters and their standard deviations derived from the least-squares residuals, are presented in Table 3. The final atomic shifts were less than 1/10th of their corresponding standard deviations, except the shifts of the atoms of the 'twofold axis' perchlorate anion, where some values were as high as one fourth of their e.s.d.'s.

Table 3. Vibration tensor components (\AA^2) and their e.s.d.'s ($\times 10^3$), for the expression

$$T = \exp[-2\pi^2(U_{11}a^*2h^2 + \dots 2U_{23}b^*c^*kl + \dots)]$$

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
Cl(1)	0.081 (1)	0.074 (1)	0.047 (1)	-0.020 (2)	-0.026 (2)	0.013 (2)
Cl(2)	0.044 (1)	0.056 (1)	0.038 (1)	0.000 (7)	-0.011 (5)	0.038 (2)
N(1)	0.043 (3)	0.053 (3)	0.053 (4)	0.004 (6)	-0.014 (6)	0.013 (5)
C(2)	0.048 (4)	0.075 (5)	0.076 (6)	-0.022 (10)	-0.041 (8)	0.024 (8)
C(3)	0.042 (4)	0.060 (4)	0.104 (7)	-0.037 (12)	0.002 (9)	-0.011 (7)
C(4)	0.040 (3)	0.071 (5)	0.107 (8)	-0.015 (11)	0.036 (9)	-0.011 (7)
C(5)	0.040 (3)	0.072 (5)	0.080 (6)	0.024 (10)	0.022 (8)	0.004 (7)
C(6)	0.041 (3)	0.052 (4)	0.053 (4)	-0.022 (7)	0.000 (6)	0.019 (6)
C(7)	0.049 (3)	0.042 (3)	0.054 (4)	-0.015 (7)	-0.018 (7)	0.020 (6)
C(8)	0.064 (4)	0.036 (3)	0.076 (5)	0.002 (8)	-0.023 (9)	0.027 (7)
C(9)	0.074 (5)	0.045 (4)	0.048 (4)	0.015 (7)	-0.021 (8)	0.010 (8)
C(10)	0.068 (5)	0.074 (5)	0.051 (5)	0.036 (8)	-0.045 (8)	0.000 (9)
C(11)	0.060 (4)	0.040 (3)	0.039 (3)	0.004 (6)	0.013 (8)	-0.012 (6)
C(12)	0.075 (5)	0.054 (4)	0.062 (5)	0.023 (9)	0.019 (9)	-0.036 (8)
C(13)	0.062 (5)	0.064 (5)	0.076 (6)	-0.017 (10)	0.025 (10)	-0.042 (8)
C(14)	0.045 (3)	0.057 (4)	0.066 (5)	0.001 (8)	-0.021 (8)	-0.029 (7)
C(15)	0.035 (3)	0.042 (3)	0.054 (4)	-0.005 (7)	-0.017 (6)	-0.007 (5)
N(16)	0.040 (2)	0.031 (2)	0.039 (3)	-0.012 (4)	0.001 (5)	0.000 (4)
C(17)	0.045 (3)	0.039 (3)	0.038 (3)	-0.004 (6)	0.014 (6)	0.003 (5)
O(18)	0.036 (2)	0.028 (2)	0.063 (3)	-0.024 (5)	-0.019 (4)	0.002 (3)
O(19)	0.109 (8)	0.299 (19)	0.520 (38)	-0.454 (48)	-0.128 (31)	-0.118 (21)
O(20)	0.109 (5)	0.131 (6)	0.051 (4)	-0.064 (8)	-0.033 (8)	0.068 (10)
O(21)	0.393 (24)	0.025 (13)	0.115 (9)	0.139 (23)	0.038 (27)	-0.107 (37)
O(22)	0.273 (14)	0.176 (10)	0.107 (7)	-0.113 (15)	-0.149 (18)	0.300 (22)
O(23)	0.133 (16)	0.170 (19)	0.041 (6)	-0.071 (20)	0.090 (14)	-0.137 (32)
O(24)	0.083 (8)	0.105 (11)	0.091 (10)	0.010 (19)	0.073 (17)	-0.072 (17)
O(25)	0.070 (8)	0.238 (23)	0.074 (9)	0.055 (28)	-0.103 (15)	0.022 (25)
O(26)	0.247 (29)	0.068 (10)	0.274 (33)	0.083 (35)	0.193 (54)	0.157 (29)

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Table 4. Observed and calculated structure factors (x 10)

Table with multiple columns for observed and calculated structure factors, including labels like H, K, L and numerical values. The table is organized in a grid-like fashion with some data points highlighted in bold.

Table 7 (cont.)

	Angle	E.s.d.
C(6)–C(7)–C(17)	118.3	0.6
C(8)–C(7)–C(17)	109.5	0.6
C(7)–C(8)–C(9)	105.7	0.6
C(8)–C(9)–C(10)	107.9	0.7
C(8)–C(9)–C(11)	112.0	0.7
C(10)–C(9)–C(11)	117.5	0.7
N(1)–C(10)–C(9)	114.2	0.7
C(9)–C(11)–C(12)	108.7	0.6
C(9)–C(11)–N(16)	112.6	0.6
C(12)–C(11)–N(16)	111.6	0.6
C(11)–C(12)–C(13)	114.0	0.7
C(12)–C(13)–C(14)	108.5	0.7
C(13)–C(14)–C(15)	109.4	0.7
C(14)–C(15)–N(16)	113.7	0.6
C(11)–N(16)–C(15)	112.6	0.5
C(15)–N(16)–C(17)	110.2	0.5
C(11)–N(16)–O(18)	107.7	0.5
C(15)–N(16)–O(18)	104.6	0.5
C(17)–N(16)–O(18)	107.2	0.4
C(7)–C(17)–N(16)	114.7	0.5
O(19)–Cl(1)–O(20)	113.4	1.0
O(19)–Cl(1)–O(21)	105.2	1.1
O(19)–Cl(1)–O(22)	115.5	1.0
O(20)–Cl(1)–O(21)	104.7	0.8
O(20)–Cl(1)–O(22)	110.3	0.6
O(21)–Cl(1)–O(22)	106.8	0.9
O(23)–Cl(2)–O(24)	101.5	0.9
O(23)–Cl(2)–O(25)	103.8	1.1
O(23)–Cl(2)–O(26)	115.9	1.5
O(24)–Cl(2)–O(25)	102.6	1.0
O(24)–Cl(2)–O(26)	110.7	1.4
O(25)–Cl(2)–O(26)	120.0	1.5

The e.s.d. values are low, as on calculating the e.s.d. of a C–C bond from the scatter of the fourteen C–C bonds a value of 0.019 Å was obtained. The main reason for the disparity between these estimates lies in the fact that the e.s.d.'s obtained from the refinement were not increased to allow for the omission of the unobserved reflexions. Considering further the presence of disorder and the absence of thermal motion corrections, the differences between the C–C bonds do not seem to be real. The mean value of the C–C bonds

is 1.522 Å, which agrees well with 1.537 given by Sutton (1965).

The individual variations in the C–N bonds also cannot be considered as significant; it is of interest, however, that the average of N⁺(1)–C bonds was lower (1.502 Å) than for the N⁺(16)–C bonds (1.515 Å). The former is in good agreement with the weighted mean of 1.499 ($\sigma=0.002$) Å calculated by Birnbaum (1967) for thirty N⁺–C bonds with a protonated nitrogen atom attached to three C(sp³) atoms. In the case of N⁺(16)–C bonds, however, the nitrogen, instead of being protonated, is attached to an oxygen atom, and similar examples of such lengthening are found in anhydro-*N*-hydroxymethyldeoxyangustifoline perchlorate (Birnbaum, Cheung, Wiewiorowski & Bratek-Wiewiorowska, 1967) and 1,5-*endo*-methylenequinolizidium toluene-*p*-sulphonate (Huber, 1969).

The Cl(2)–O bonds in Table 6 were obtained with the coordinates listed in Table 1, *i.e.* with the chlorine atom displaced from the twofold axis. These bonds were recalculated with the chlorine on the twofold axis. Although the short Cl(2)–O(26) bond increased to 1.377 Å, the other three bonds became worse. This comparison therefore, did not yield any conclusive evidence as to which of these two possibilities should be accepted.

To eliminate the possibility that the large Cl(2)–O bond length variations may be a result of the fact that the oxygen coordinates may represent a false minimum in least-squares analysis (Donohue & Goodman, 1967), the atoms O(24) and O(26) were shifted to give more acceptable bond lengths. The subsequent refinement cycle brought them back close to their original positions.

The U_{ij} values of the perchlorate oxygen atoms are considerably higher than those of the other atoms. The principle radii of the vibration ellipsoids were also calculated and values above 30 Å² were obtained for the maxima for O(22) and O(26) atoms and 52 Å² for O(19) indicating an unusually high thermal motion or the presence of disorder in both ClO₄ groups. Marked

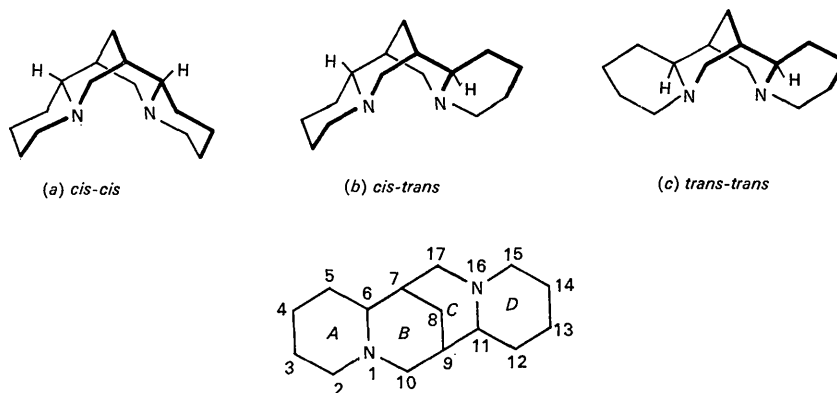


Fig. 1. The structural formulae of (a) α -isosparteine, (b) sparteine and (c) β -isosparteine.

thermal vibration was observed in the perchlorate ion by Birnbaum *et al.* (1967) and cases of disorder (Trefonas, Flurry, Majeste, Meyers & Copeland, 1966) and free rotation (Prosen & Trueblood, 1956) were also reported.

The riding motion corrections (Busing & Levy, 1964) of the perchlorate oxygen atoms were calculated but they were not considered meaningful. A correction of 0.27 Å was obtained for the Cl(1)–O(19) bond giving a corrected length of 1.60 Å, which was unacceptable on comparison with the value of 1.46 ± 0.01 Å ob-

tained by Truter, Cruickshank & Jeffrey (1960) for Cl–O bonds in nitronium perchlorate.

A perspective view of the molecule of sparteine-*N*(16)-oxide along the *b* axis is shown in Fig. 2. The projection of the structure along the *c* axis, given in Fig. 3, shows alkaloid molecules forming dimers joined by hydrogen bonding as predicted by Baranowski, Skolik & Wiewiorowski (1964).

The X-ray analysis confirms the attachment of the oxygen atom to the nitrogen atom of the *cis*-quinolizidine system.

All the piperidine rings have the chair conformation. This is in agreement with the postulate of Krueger & Skolik (1967), who studied the nuclear magnetic resonance and infrared spectra of perchlorate salts of sparteine-*N*-oxide.

The smallest angle of 105.7° was found at the C(8) carbon atom. This result was not unexpected because of the shorter C–N bonds on the opposite sides of the two central rings.

The distance between the nitrogen atoms was found to be 3.198 Å ($\sigma = 0.008$). It is longer than in the other lupine alkaloids studied so far by X-rays and this is probably due to the accommodation of the hydrogen bonded oxygen, O(18). The angles C(6)–C(7)–C(17) and C(10)–C(9)–C(11) give an average of 117.9° and this large value seems to be related to the N...N

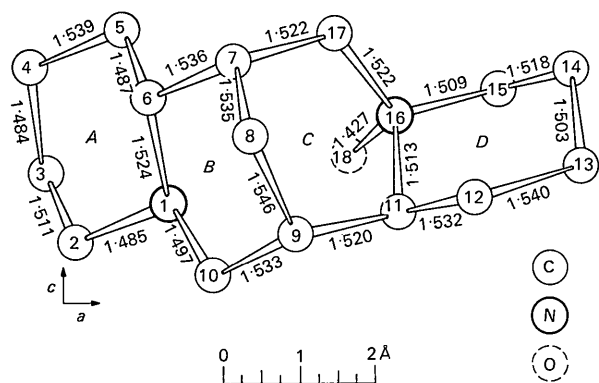


Fig. 2. The molecule viewed along the *b* axis.

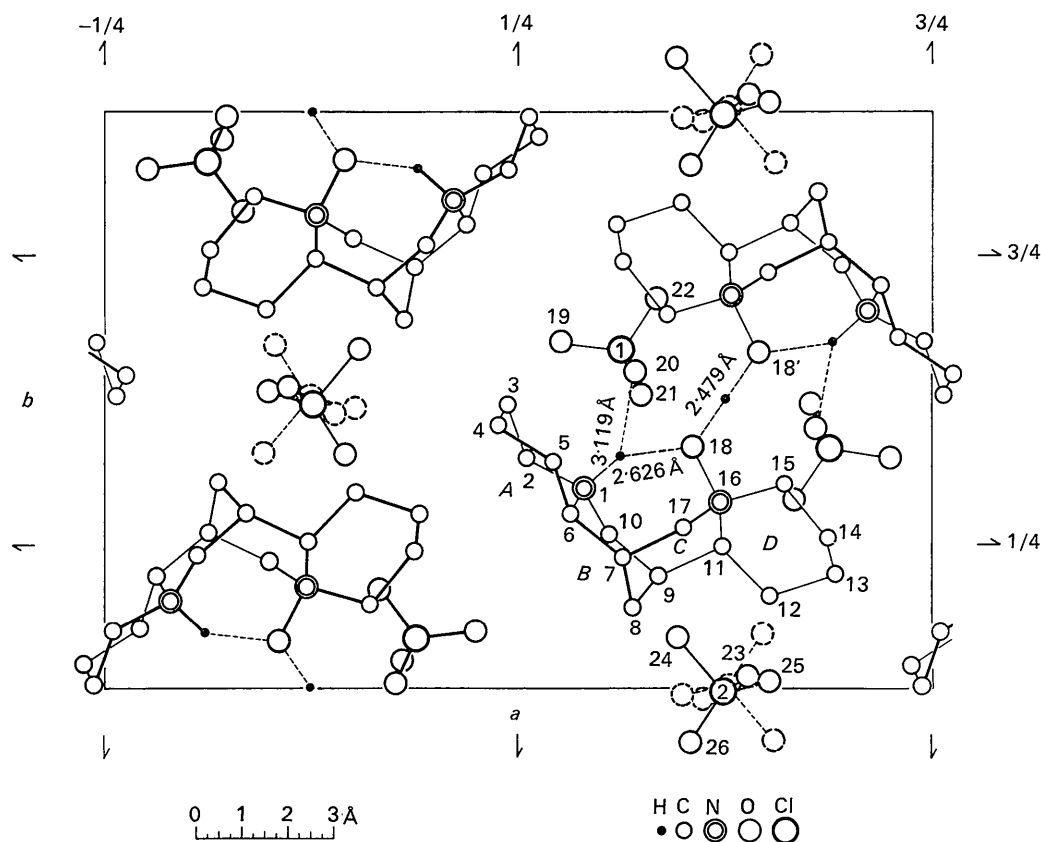


Fig. 3. The (001) projection of sparteine-*N*(16)-oxide sesquiperchlorate showing the hydrogen bonds.

separation. The H(5') to H(17) contact is 2.27 Å and it was pointed out by the referee that an intramolecular repulsion between these atoms may also be responsible for the increased angles at C(7) and C(9). Similar repulsion appears to be present in α -isosparteine (Przybylska & Barnes, 1953), where the distance between the nitrogen atoms is smaller (3.01 Å), but the angles at C(7) and C(9) are 119.9°. It is interesting that in angustifoline (Birnbaum *et al.* 1967) where the nitrogen atoms, being bonded to a methylene group between them, are separated by only 2.447 Å, these angles give an average of only 108.6°, and the repulsion between the corresponding hydrogen atoms leads to an appreciable increase (115.3°) in the angle C(5)–C(6)–C(7).

The angle C(15)–N(16)–O(18) is smaller by about 3°, than the angles C(17)–N(16)–O(18) and C(11)–N(16)–O(18). This difference would probably be more marked if the nitrogen N(1) and oxygen O(18) were not hydrogen bonded.

The distance between the oxygen atoms of the molecules of the dimer, O(18) and O(18') was found to be 2.479 Å (see Fig. 3). The e.s.d. value for this distance, multiplied by $\sqrt{2}$ because these atoms are related by a twofold axis, is 0.008 Å. The hydrogen atom between these oxygen atoms was located on the difference maps on the twofold axis, but displaced from the centre of the O(18)···O(18') line. This displacement refined to a value of 0.19 Å. In view of the large estimated standard deviation of its z coordinate (0.12 Å), it is not significant. It is of interest, however, that it leads to a value of 113.4° for the N(16)–O···H angle, which is closer to the tetrahedral value than that of the N(16)–O(18)···O(18') angle of 116.7°.

The B factor of the hydrogen atom refined to 2.66 Å². Any argument, however, for the existence of the truly symmetrical hydrogen bonding with the proton centrally situated, based on this low thermal vibration is not valid, since a considerably higher value would have been obtained if the scattering factors of Stewart, Davidson & Simpson (1965) had been used. We therefore wish to withdraw such an argument made in the preliminary account of this work (Srivastava & Przybylska, 1968).

The O···H···O bond shows a significant deviation from Speakman's (1967) weighted mean of 2.446 ± 0.003 Å obtained for seven crystallographically symmetrical bonds encountered in acid salts of the type MHX_2 , which are probably genuinely symmetrical. However the possibility of the existence of the truly symmetrical OH hydrogen bond in sparteine-N(16)-oxide sesquiperchlorate cannot be dismissed, as the O···O distance characteristic of the shift from an asymmetric to a symmetric hydrogen bond is not well defined (Hamilton & Ibers, 1968).

The N⁺(1)–H···O(18) distance was found to be 2.626 Å ($\sigma=0.007$), which represents a strong hydrogen bond. The hydrogen atom, attached to N(1) was located on a three-dimensional synthesis, however, its coordinates were calculated assuming 1.03 Å for the

length of the N–H bond. The angle N⁺(1)–H···O(18) is 142.1°.

The N⁺(1)···O(20) distance of 3.119 Å ($\sigma=0.010$) is longer than the sum of the oxygen and nitrogen van der Waals radii (2.9 Å), however the distance between H(1) and O(20) was found to be 2.41 Å suggesting that a weak bifurcated hydrogen bonding may be present. This is indicated in Fig. 3. Its existence is supported by the fact that O(20) has considerably lower vibration parameters than the remaining oxygen atoms of that ClO₄⁻ group. The angle N(1)–H···O(20) is 125.5°.

The C···C intermolecular contacts are normal, the shortest being 3.75 Å. The smallest C···O distances were the following: C(15)···O(18'), 3.02 Å; C(2)···O(20), 3.13 Å; C(5)···O(21), 3.22 Å. All other C···O approaches are greater than 3.3 Å. The closest O···O contacts are between O(20) and the two hydrogen bonded oxygen atoms O(18) and O(18') of sparteine molecules and they are 2.97 and 3.47 Å respectively.

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The Structure of 2,2'-Dimercaptodiethylsulphidepalladium(II): A Trimeric Molecule Containing Bridging Sulphur Atoms

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2,2'-Dimercaptodiethylsulphidepalladium(II) crystallizes in the monoclinic system, space group $P2_1/c$; with lattice constants $a = 10.69 \pm 0.05$, $b = 24.40 \pm 0.13$ and $c = 9.44 \pm 0.05$ Å, $\beta = 111.5 \pm 0.5^\circ$. The intensities of the three-dimensional equi-inclination Weissenberg data were estimated visually and the structure was solved by Patterson and Fourier techniques. Refinement of atomic parameters was carried out by difference Fourier methods and full-matrix least-squares procedures. The molecules are trimeric with a formula unit $\text{Pd}_3\text{S}_9\text{C}_{12}\text{H}_{24}$. Each palladium atom is surrounded by four sulphur atoms in approximately square-planar arrangement. The three sulphur atoms of one ligand molecule form three corners of each square and the squares are completed by one thiol sulphur of each ligand molecule being shared by two palladium atoms, forming a sulphur bridge. The molecule is not flat but bent at the bridging atoms so that the three squares are inclined towards each other and the molecule may be regarded as basin-shaped. There is considerably less strain in this trimeric structure than in the corresponding dimeric 2,2'-dimercaptodiethylsulphidenickel(II).

Introduction

The ligand 2,2'-dimercaptodiethylsulphide has been shown to form complexes with a variety of metals including palladium(II) (Mathias, 1946). Apart from the nickel complex these compounds are extremely insoluble, which led Harley-Mason (1952) to suggest polymeric structures for these molecules involving bridging sulphur atoms.

Spectroscopic and magnetic studies of some of these complexes (Barclay, McPartlin & Stephenson, 1968) were consistent with sulphur-bridged molecules and a recent X-ray crystal structure analysis (Barclay, McPartlin & Stephenson, 1969) on the nickel(II) compound confirmed the existence of bridging sulphur atoms in a dimeric molecule of formula $\text{Ni}_2\text{S}_6\text{C}_8\text{H}_{16}$.

X-ray powder photographs showed that the palladium complex is not isomorphous with the dimeric nickel complex. This and the very low solubility of the

palladium compound suggested that there may be more than two palladium atoms in the polymeric molecule.

Experimental

Crystals of 2,2'-dimercaptodiethylsulphidepalladium(II) were very difficult to grow and the best results were obtained by taking a solution of potassium tetrachloropalladate in water and acetone (at 0°C) and slowly adding, with stirring, a solution of the ligand and sodium acetate in water and acetone (at 0°C). The precipitate which formed slowly during the next 10 hours was then alternately boiled with the solution for two hours followed by cooling at 0°C overnight. After some days the precipitate looked crystalline and yielded thin, fragile, orange plates of irregular shape. The unit-cell dimensions were obtained from zero level precession photographs taken with Mo $K\alpha$ radiation.

Density measurements indicated that there were twelve monomeric units of composition $\text{PdS}_3\text{C}_4\text{H}_8$ in the unit-cell. As there are four general equivalent positions in the space group $P2_1/c$ (determined uniquely

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