

HOARD, J. L. & SILVERTON, J. V. (1963). *Inorg. Chem.* **2**, 235–243.
International Tables for X-ray Crystallography (1965). Vol. III. Birmingham: Kynoch Press.
 LIPPARD, S. J. & RUSS, B. J. (1968). *Inorg. Chem.* **7**, 1686–1688.
 NIGAM, H. L., NYHOLM, R. S. & STIDDARD, M. H. B. (1960). *J. Chem. Soc.* pp. 1806–1812.

ORGEL, L. E. (1960). *J. Inorg. Nucl. Chem.* **14**, 136–138.
 PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
 RACAH, G. (1943). *J. Chem. Phys.* **11**, 214.
 SANDS, D. F. & ZALKIN, A. (1958). *Acta Cryst.* **11**, 615–619.
 STEWART, J. M. (1972). X-RAY system of programs, Univ. of Maryland Technical Report TR-192.

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The Crystal and Molecular Structure of Pseudoivalin Bromoacetate

BY R. GITANY, G. D. ANDERSON AND R. S. MCEWEN

Department of Chemistry, The Florida State University, Tallahassee, Florida 32306, U.S.A.

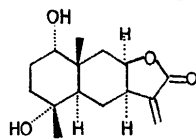
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The crystal structure at 25°C of the bromoacetate of the guaianolide pseudoivalin, $C_{17}H_{21}O_4Br$, has been determined from three-dimensional X-ray diffractometer data by heavy atom and Fourier methods. The crystal is orthorhombic, space group $P2_12_12_1$ with four molecules per unit cell. The cell dimensions are $a = 13.219$ (3), $b = 8.835$ (4), $c = 14.367$ (4) Å. All hydrogen atoms have been located and the structure refined by least-squares calculations to an R of 0.076. The absolute stereochemistry has been determined from the X-ray data, and this is in accord with the strong negative Cotton effect observed in the optical rotatory dispersion. The cyclopentane ring is highly puckered and the cycloheptene ring has a flattened twist-boat conformation.

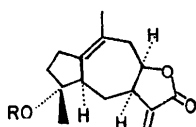
Introduction

The isolation from a chemical race of *Iva microcephala* Nutt. of microcephalin (I) (Herz, Högenauer & de Vivar, 1964) and pseudoivalin (IIa) (Herz, de Vivar & Lakshmikantham, 1964) has so far remained the only instance in which a guaianolide has been found to co-occur with a eudesmanolide. While the stereochemistry of microcephalin was established by chemical and physical means, the assignment of stereochemistry (IIa) to pseudoivalin was speculative and based primarily on the assumption that a common ten-membered ring precursor was involved. The nature of this precursor has been discussed (Parker, Roberts & Ramage, 1967).

To place speculations concerning the biogenetic origin of these and other sesquiterpene lactones (Herz, 1971) on a firmer footing, we undertook an X-ray crystallographic analysis of pseudoivalin bromoacetate (IIb), the results of which confirm formula (IIa) and support the hypothesis that (I) and (IIa) are formed by processes simulating Markownikow and anti-Markownikow oriented cyclization of the same (*cis*- $\Delta^{1,10}$?) germacradienoid precursor.



(I)



(II)

(a) R=H
 (b) R=CO.CH₂Br

Experimental

Crystallization was from methanol solution. A fairly equidimensional fragment (0.5mm diameter) was selected for study. Weissenberg and precession photography were used to determine the space group and approximate cell dimensions. The density was determined by flotation in aqueous potassium iodide. The crystal, mounted with the [010] direction approximately parallel to the goniometer axis, was then transferred to a Hilger and Watts four-circle automatic diffractometer and the cell constants refined by least-squares calculations on the observed angles for 11 reflections. Crystal data are given in Table 1.

Table 1. *Crystal data*

$C_{17}H_{21}O_4Br$	$M = 369.264$
Orthorhombic	Systematic absences:
$a = 13.219$ (3) Å	$h00, h = 2n + 1$
$b = 8.835$ (4)	$0k0, k = 2n + 1$
$c = 14.367$ (4)	$00l, l = 2n + 1$
$V = 1677.9$ Å ³	Space group:
$Z = 4$	$P2_12_12_1$
$F(000) = 760$	$D_{exp} = 1.47$ (2) g cm ⁻³
$\mu(\text{Mo } K\alpha) = 26$ cm ⁻¹	$D_{calc} = 1.462$

Intensity data were collected to a 2θ value of 60° by the $\omega/2\theta$ scan technique, with Zr-filtered Mo $K\alpha$ radiation, scintillation counter and pulse-height discrimination. Beyond a 2θ value of 39.0° a rapid sampling method was used to avoid measuring reflections for which $I < B + 3.5\sigma(B)$, where I is the intensity,

B the background and $\sigma(B)$ its standard deviation. Attenuators were inserted and reflections remeasured if the integrated intensity exceeded 250000 counts. (Counting time on a peak was 60 s for low orders.) Three standard reflections lying in widely separated regions of reciprocal space were monitored regularly throughout data collection towards the end of which some crystal decomposition was in evidence from discoloration and a fall in the standard intensities. In all, 2908 measurements were made. The intensities were adjusted to compensate for the small changes in the standard intensities. Standard corrections were applied and good approximate absorption corrections made by using factors appropriate to a spherical crystal. Initially Friedel pairs were averaged and 1130 positive independent F_o 's derived. Of these 69 had $F_o < 3\sigma(F)$.

Structure determination

All computations were performed on a CDC 6500 computer using local modifications of the X-RAY72 system of programs (Stewart, Kruger, Ammon, Dickenson & Hall, 1972), and a plotting program written by C.K. Johnson. Atomic form factors were taken from *International Tables for X-ray Crystallography* (1968).

The position of the bromine atom was obtained from a Patterson map, but attempts to locate the light atoms from bromine-phased F_o maps and a difference synthesis were unsuccessful. However, the F_o map showed the bromine peak to be extremely elongated along the y axis and the difference synthesis had large positive peaks at the same x and z coordinates as the bromine but with y coordinates above and below that of the bromine. When two bromine atoms, each having a population parameter of 0.5 were substituted for the original bromine, the carbon and oxygen atoms were readily found from a series of F_o maps. A structure-factor calculation with all 21 of these atoms assigned as carbons, the two half bromine atoms, and an overall temperature factor gave a conventional R value = $\sum|F_o| - K|F_c| / \sum|F_o|$ of 0.342.

When the maps obtained from the one bromine position model were re-examined, it was found that the light atom positions were represented, but were much less readily recognizable than from the two bromine model F_o maps. Presumably failure to recognise the extremely anisotropic character of the bromine thermal vibrations had obscured the solution initially.

Refinement

After four cycles of full-matrix, least-squares refinement with isotropic temperature factors and a further four cycles with anisotropic temperature factors, the conventional R value over all 1130 reflections was 0.100. The quantity minimized was $\sum(|F_o| - K|F_c|)^2$. 69 $F_o < 3\sigma$ were excluded from these cycles.

The data were now re-reduced without averaging Friedel pairs, giving 1774 reflections with $F_o > 3\sigma$. A further 135 had $F_o < 3\sigma$. The conventional R value over all 1909 reflections at this stage was 0.091. When the calculation was repeated with the enantiomer parameters, R was 0.106. In addition an examination of F_o and F_c for 25 Friedel pairs displaying particularly large anomalous scattering effects led to the same conclusion in every case that the originally chosen enantiomer was correct.

In further refinement the following weighting scheme was employed: $w = 1000/\sigma^2(I)$ when $F_o \geq 3\sigma(F)$, $w = 100/\sigma^2(I)$ when $F_o < 3\sigma(F)$. 33 reflections for which $F_o \ll F_c$ were assigned zero weight. After three cycles minimizing $\sum w(|F_o| - K|F_c|)^2$, all hydrogen atoms were located on a difference map. These were included at positions calculated on the basis of the heavy-atom positions. In the case of the methyl groups, of course, the difference map peaks were used. An overall temperature factor for hydrogen atoms was assigned and this was refined along with the heavy-atom parameters. The refinement converged at a conventional R of 0.076 and a weighted R , $\sum w||F_o| - K|F_c|| / \sum w|F_o|$ of 0.084. Refinement of all parameters including hydrogen coordinates and individual hydrogen isotropic temperature factors did not result in significantly better results.

Results and discussion

Final atomic positions for the non-hydrogen atoms are given in Table 2, and their temperature factors in Table 3. The overall temperature factor for the hydrogen atoms was $U = 0.120 \text{ \AA}^2$. Bond lengths and

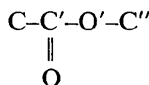
Table 2. Fractional coordinates ($\times 10^4$)

The estimated standard deviation of the least significant digits are given in parentheses.

	x	y	z
Br	6246.3 (8)	1774.7 (3)	8039.8 (1)
O(1)	-725 (4)	1170 (8)	5492 (4)
O(2)	-603 (5)	2400 (9)	4146 (4)
O(3)	3381 (3)	1062 (7)	7967 (3)
O(4)	4338 (4)	1308 (11)	9246 (4)
C(1)	669 (6)	1306 (9)	8333 (5)
C(2)	991 (6)	1005 (11)	9321 (5)
C(3)	2154 (6)	742 (12)	9261 (5)
C(4)	2444 (5)	1617 (11)	8424 (5)
C(5)	1608 (5)	1214 (10)	7701 (5)
C(6)	1585 (5)	2171 (9)	6828 (4)
C(7)	980 (5)	1316 (9)	6058 (5)
C(8)	-129 (5)	938 (10)	6332 (5)
C(9)	-606 (5)	1949 (10)	7057 (5)
C(10)	-273 (5)	1620 (9)	8074 (5)
C(11)	837 (6)	2253 (10)	5199 (5)
C(12)	-215 (6)	1983 (12)	4857 (6)
C(13)	1470 (7)	3169 (13)	4763 (5)
C(14)	-1135 (6)	1714 (13)	8761 (5)
C(15)	2537 (6)	3302 (12)	8571 (5)
C(16)	4244 (6)	1031 (11)	8437 (6)
C(17)	5087 (6)	564 (14)	7803 (5)

angles are listed in Tables 4 and 5.* The closest intermolecular contact is 3.61 Å between Br of the reference molecule and C(14) of the adjacent molecule related by $1+x, y, z$. The thermal ellipsoid plot produced by the plotting program *ORTEP*, given in Fig. 1, shows the stereochemistry of the molecule which corresponds to (IIb), thus confirming the proposed stereochemistry and in accord with the strong negative Cotton effect (Anderson, Gitany, McEwen & Herz, 1973). Fig. 2 shows the arrangement of four molecules with respect to the unit cell.

All but one of the $C(sp^3)-C(sp^3)$ bond distances fall within 3σ of the expected value of 1.537(5) Å (Sutton, 1965). The bond C(3)-C(4) of 1.48(1) seems significantly shorter. Also all but one of the $C(sp^3)-C(sp^2)$ lengths are within 3σ of the expected value of 1.510(5) Å. C(9)-C(10) is 1.55 (1) Å. In the side chain, C(16)-O(3) [1.325(9) Å] is short and C(4)-O(3) [1.485(9) Å] long. Similar results in acetate side chains have been found before (Pollard & Ahmed, 1971; Braun, Hornstra & Leenhouts, 1970). While neglect of thermal vibration corrections and underestimation of e.s.d.s may in part explain these figures, it seems that the side-chain bond lengths do fall into a pattern for the grouping



in general. Merlino (1971) notes that increasing con-

* A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30418 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

tribution of the resonance form

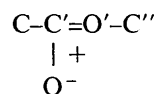


Table 4. Bond distances (Å)

Br—C(17)	1.900 (9)	C(4)—C(15)	1.509 (14)
O(1)—C(8)	1.456 (8)	C(5)—C(6)	1.512 (10)
O(1)—C(12)	1.342 (10)	C(6)—C(7)	1.560 (10)
O(3)—C(4)	1.485 (9)	C(7)—C(8)	1.555 (10)
O(3)—C(16)	1.325 (9)	C(7)—C(11)	1.499 (10)
O(2)—C(12)	1.201 (10)	C(8)—C(9)	1.510 (11)
O(4)—C(16)	1.195 (10)	C(9)—C(10)	1.554 (10)
C(1)—C(2)	1.506 (10)	C(10)—C(14)	1.510 (10)
C(1)—C(5)	1.540 (10)	C(11)—C(12)	1.495 (11)
C(2)—C(3)	1.558 (11)	C(16)—C(17)	1.497 (12)
C(3)—C(4)	1.481 (11)	C(1)—C(10)	1.330 (10)
C(4)—C(5)	1.556 (10)	C(11)—C(13)	1.322 (12)

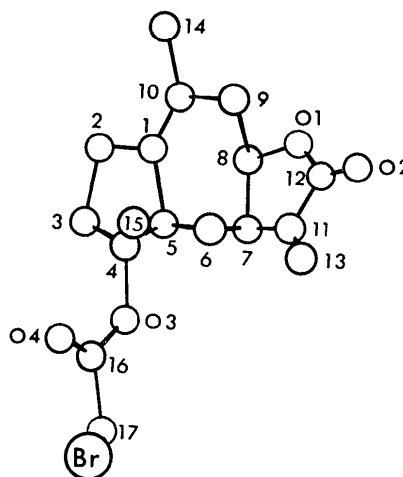


Fig. 1. *ORTEP* plot of the molecular structure.

Table 3. Thermal parameters ($\times 10^2$), Å²

The form of the temperature factor expression is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* \cos \gamma^* + 2U_{13}hla^*c^* \cos \beta^* + 2U_{33}klb^*c^* \cos \alpha^*)]$.

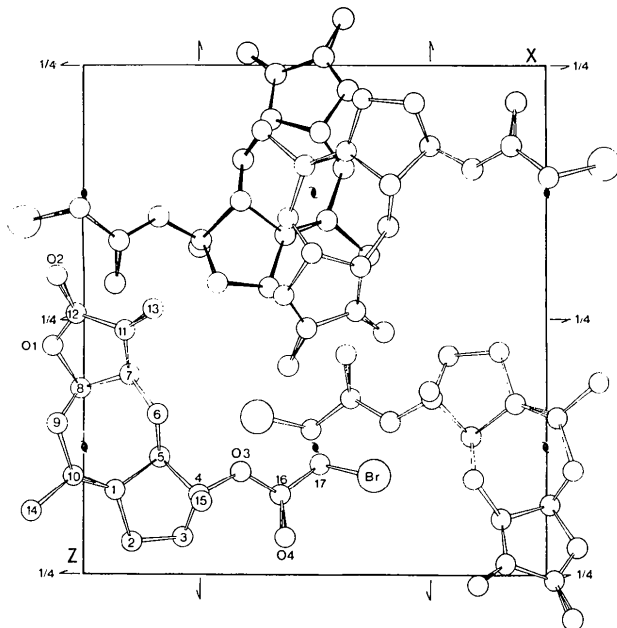
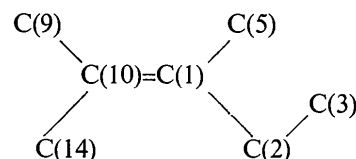
	U_{11}	U_{22}	U_{33}	U_{13}	U_{23}	U_{33}
Br	5.54 (6)	28.03 (24)	12.40 (10)	-3.38 (8)	1.58 (6)	-5.94 (12)
O(1)	5.00 (28)	12.17 (51)	4.67 (28)	-1.02 (35)	-1.05 (24)	-0.34 (32)
O(2)	8.17 (40)	14.15 (59)	4.76 (31)	1.28 (43)	-2.58 (28)	0.63 (36)
O(3)	3.27 (20)	10.40 (40)	5.13 (24)	0.68 (25)	-0.31 (22)	0.31 (29)
O(4)	5.76 (33)	18.34 (75)	5.44 (36)	1.03 (44)	-1.44 (27)	-1.36 (42)
C(1)	5.20 (40)	7.32 (50)	4.00 (35)	0.13 (40)	-0.01 (32)	0.31 (38)
C(2)	4.58 (39)	10.89 (62)	3.47 (34)	-0.30 (44)	0.03 (30)	0.16 (42)
C(3)	5.98 (43)	10.72 (68)	3.73 (38)	0.43 (49)	-0.84 (34)	1.28 (40)
C(4)	3.75 (34)	8.41 (64)	4.93 (37)	0.79 (39)	-1.00 (31)	0.19 (43)
C(5)	3.91 (32)	8.09 (56)	4.83 (39)	0.18 (38)	-0.16 (30)	1.72 (39)
C(6)	3.38 (27)	8.61 (55)	3.84 (36)	0.42 (33)	-0.75 (28)	-0.42 (36)
C(7)	4.86 (38)	6.84 (51)	4.51 (38)	0.37 (37)	-0.55 (30)	1.19 (38)
C(8)	4.09 (34)	9.28 (60)	3.83 (36)	0.43 (40)	-0.63 (31)	-0.53 (40)
C(9)	4.22 (33)	9.35 (56)	4.73 (39)	-0.66 (40)	-0.68 (34)	0.15 (43)
C(10)	3.84 (33)	7.66 (54)	4.63 (36)	0.48 (33)	1.75 (33)	0.22 (41)
C(11)	5.74 (39)	7.77 (58)	3.72 (38)	0.22 (43)	-0.26 (34)	-0.47 (39)
C(12)	6.28 (45)	9.78 (70)	4.93 (44)	1.57 (49)	-0.15 (43)	-0.03 (48)
C(13)	7.90 (54)	11.20 (78)	4.87 (39)	-2.67 (61)	-0.09 (42)	0.78 (49)
C(14)	4.92 (40)	13.12 (80)	4.75 (38)	0.03 (55)	0.74 (35)	-0.09 (49)
C(15)	4.53 (38)	10.57 (78)	6.68 (45)	-1.02 (46)	-0.50 (36)	-0.35 (51)
C(16)	5.04 (44)	11.92 (76)	5.01 (48)	1.53 (51)	-0.68 (37)	0.08 (49)
C(17)	4.58 (39)	13.63 (86)	5.70 (46)	1.13 (50)	0.27 (40)	0.61 (50)

Table 5. Bond angles (°)

C(2)—C(1)—C(5)	108.6 (6)	O(1)—C(8)—C(9)	105.2 (6)
C(2)—C(1)—C(10)	124.4 (6)	C(7)—C(8)—C(9)	116.2 (6)
C(5)—C(1)—C(10)	127.0 (6)	C(8)—C(9)—C(10)	114.8 (6)
C(1)—C(2)—C(3)	104.6 (6)	C(1)—C(10)—C(9)	124.6 (6)
C(2)—C(3)—C(4)	102.9 (6)	C(1)—C(10)—C(14)	122.4 (6)
O(3)—C(4)—C(3)	113.8 (7)	C(9)—C(10)—C(14)	113.0 (6)
O(3)—C(4)—C(5)	102.8 (5)	C(7)—C(11)—C(12)	107.4 (7)
O(3)—C(4)—C(15)	108.7 (6)	C(7)—C(11)—C(13)	130.5 (7)
C(3)—C(4)—C(5)	103.8 (6)	C(12)—C(11)—C(13)	122.1 (7)
C(3)—C(4)—C(15)	115.0 (7)	O(1)—C(12)—O(7)	121.8 (8)
C(5)—C(4)—C(15)	112.1 (7)	O(1)—C(12)—C(11)	109.2 (6)
C(1)—C(5)—C(4)	99.6 (5)	O(2)—C(12)—C(11)	128.9 (8)
C(1)—C(5)—C(6)	116.3 (6)	O(3)—C(16)—O(4)	125.6 (7)
C(4)—C(5)—C(6)	116.1 (6)	O(3)—C(16)—C(17)	109.7 (7)
C(5)—C(6)—C(7)	109.2 (6)	O(4)—C(16)—C(17)	124.8 (7)
C(6)—C(7)—C(8)	114.1 (5)	Br—C(17)—C(16)	109.7 (7)
C(6)—C(7)—C(11)	112.4 (6)	C(8)—O(1)—C(12)	111.5 (6)
C(8)—C(7)—C(11)	102.0 (6)	C(4)—O(3)—C(16)	119.9 (6)
O(1)—C(8)—C(7)	105.7 (5)		

leads to values of C'—O' and O'—C'' in agreement with ours. It is possible that the anomalous cyclic C—C bond lengths are to some extent connected with the resonance in the side chain and to strain transmission effects.

The cyclopentane ring (*A*) is in a highly puckered envelope conformation, C(1), C(2), C(3) and C(5) defining a plane and C(4) being 0.69 Å distant. This distance is comparable with that found in a number of steroids (Altona, Geise & Romers, 1965). This conformation and the presence of the C(10)=C(1) double bond in the neighboring ring results in a high degree of planarity for the group:

Fig. 2. Projection of the structure down the *b* axis.

The equation of the plane referred to the unit cell axes is: $2.28X + 8.62Y + 1.89Z = 2.88$ with a χ^2 value of 10.63.

The cycloheptene ring (*B*) is in a somewhat flattened twist-boat conformation. However, C(6) is closer to the plane C(9)—C(10)=C(1)—C(5) than is C(8); C(7) lies on the same side as C(8). This is achieved by opening the C(8)—C(9)—C(10) angle to 115° while keeping the C(5)—C(6)—C(7) angle at the tetrahedral value. This conformation appears to stem from the requirement of near planarity for the lactone ring (*C*). If *B* were in a chair conformation, the torsional angles at the *B/C* ring junction would be 60° for C(6)—C(7)—C(8)—C(9) and an intolerable 60° for O(1)—C(8)—C(7)—C(11). In the observed structure these angles are 25° and 20° respectively. Some important torsional angles are listed in Table 6.

Table 6. Torsional angles

The torsional angle $\phi(1-2-3-4)$ denotes the angle between a plane defined by atoms 1, 2, 3 and a plane defined by 2, 3, 4. The angle is positive if the bond in front has to be turned clockwise in order to eclipse the rear bond.

O(1)—C(8)—C(7)—C(11)	+19.9°
C(9)—C(8)—C(7)—C(6)	+25.1
C(10)—C(1)—C(5)—C(6)	+28.5
C(2)—C(1)—C(5)—C(4)	-25.7
C(4)—C(3)—C(2)—C(1)	+26.9
C(5)—C(4)—C(3)—C(2)	-43.9
C(1)—C(5)—C(4)—C(3)	+43.0
C(3)—C(2)—C(1)—C(5)	-0.5

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References

- ALTONA, C., GEISE, H. J. & ROMERS, C. (1968). *Tetrahedron*, **24**, 13–32.
- ANDERSON, G. D., GITANY, R., MCEWEN, R. S. & HERZ, W. (1973). *Tetrahedron Lett.* pp. 2409–2412.
- BRAUN, P. B., HORNSTRA, J. & LEENHOUTS, J. I. (1970). *Acta Cryst.* **B26**, 352–356.
- HERZ, W. (1971). In *Pharmacognosy and Phytochemistry*, edited by M. WAGNER and L. HÖRHAMMER, pp. 64–92. Berlin, Heidelberg, New York: Springer Verlag.
- HERZ, W., HÖGENAUER & DE VIVAR, R. A. (1964). *J. Org. Chem.* **29**, 1700–1703.
- HERZ, W., DE VIVAR, A. R. & LAKSHMIKANTHAM, M. V. (1965). *J. Org. Chem.* **30**, 118–122.
- International Tables for X-ray Crystallography* (1968). Vol. III. Birmingham: Kynoch Press.

JOHNSON, C. K. (1970). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 MERLINO, S. (1971). *Acta Cryst.* B27, 2491–2492.
 PARKER, W., ROBERTS, J. S. & RAMAGE, R. (1967). *Quart. Rev.* 21, 331–363.
 POLLARD, D. R. & AHMED, F. R. (1971). *Acta Cryst.* B27, 1976–1982.

STEWART, J. M., KRUGER, G. J., AMMON, M. L., DICKINSON, C. & HALL, S. R. (1972). Technical Report TR-192 of the Computer Science Center, Univ. of Maryland.
 SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions*. Supplement 1956–1959. London: The Chemical Society.

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Electron-Density Distribution in Crystals of γ -Ni₂SiO₄

BY F. MARUMO[†] AND M. ISOBE

Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

AND Y. SAITO, T. YAGI AND S. AKIMOTO

The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

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The electron-density distribution in γ -Ni₂SiO₄ has been calculated on the basis of carefully measured intensity data collected by diffractometry with Mo K α radiation. There was an indication in the final difference Fourier maps that the charge densities of the nickel atom were deformed in an octahedral crystal field. Residual electron densities were observed between Si and O atoms.

Introduction

In the final difference synthesis of [Co(NH₃)₆][Co(CN)₆], eight peaks with heights of about 0.3 e Å⁻³ were arranged at the corners of a cube around the cobalt atom, the peaks being at 0.45 Å from the cobalt atom (Iwata & Saito, 1973). These peaks were suspected of being an indication of 3d electrons in the *t*_{2g} orbitals of the cobalt. This point must be examined in detail with reference to other transition-metal complexes. Crystals of γ -Ni₂SiO₄ have a strictly normal spinel structure with the cell dimension $a = 8.044$ (1) Å and the symmetry *Fd*3*m* (Yagi, Marumo & Akimoto, 1974). They were used for a close examination of the residual electron-density because the crystals are suitable for diffractometry and have only one positional parameter to be determined.

Experimental

A crystal specimen shaped into a sphere of about 0.08 mm diameter was used for X-ray work. The intensity data were collected on a Rigaku automated four-circle diffractometer. The experimental conditions were

broadly similar to those described in the previous paper (Iwata & Saito, 1973). The ω -2 θ scan technique was employed with a scanning speed of 2° min⁻¹ in ω , using Mo K α radiation monochromated by a graphite plate. Scanning range was calculated from the formula $1.5 + 0.8^\circ \times \tan \theta$. If the value of $\sigma(|F|)/|F|$ was greater than 0.0025, the measurement was automatically repeated until $\sigma(|F|)/|F|$ became less than 0.0025, where $\sigma(|F|)$ is the standard deviation of $|F|$ due to the counting statistics. The maximum number of repetitions was limited to eight. Reflexions with $h \geq k \geq 0$ and $l \geq 0$ were measured up to a 2 θ value of 135°. Three symmetry-related reflexions are contained in this range for reflexions with general indices, two for *hhl* and one for *hhh*. The *hhh* reflexions were also measured in order to check for accidental errors in *F(hhh)*. For the structure refinement and the electron-density calculation, reflexions in the range $l \geq h \geq k$ were used, excluding weak ones whose $|F|$ was smaller than $3\sigma(|F|)$. In total, 210 independent data were collected. The intensities were corrected for Lorentz, polarization and absorption effects. The structure was refined by the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970) by assuming isotropic extinction. The

Table 1. *Final atomic coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10^5$)

The temperature factors are in the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	6250	6250	6250	132 (1)	132 (1)	132 (1)	-9 (3)	-9 (3)	-9 (3)
Si	0	0	0	109 (4)	109 (4)	109 (4)	0	0	0
O	3689 (1)	3689 (1)	3689 (1)	152 (4)	152 (4)	152 (4)	-17 (11)	-17 (11)	-17 (11)