azo derivatives of 3- and 5-pyrazolones have been noted before,[11b] and the cause is probably a steric one.

The ratio of log β_2 to log β_1 for the *para* and *meta* derivatives is less than 2. This is in agreement with expected behavior but differs from that found for other *para*- and *meta*-substituted benzeneazo-5-pyrazolones in which the ratio is greater than 2. The extra charge on the chelate ion for the sulfonic acid derivatives probably accounts for this difference. The extra charge on the chelate ion would also account for the lack of 3:1 (azo compound to metal ion) coordination found with the sulfonic acid derivatives.

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The Crystal Structure of Diiodobis(*o*-phenylenebis(dimethylarsine))gold(III) Iodide—a Discrete Six-Coordinate Cationic Complex of Gold(III)

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The crystal structure of diiodobis(*o*-phenylenebis(dimethylarsine))gold(III) iodide, abbreviated as $Au(diars)_2I_3$, has been determined from three-dimensional, photographically recorded X-ray data. The compound crystallizes in the monoclinic system with $a = 21.6 \pm 0.2$ Å, $b = 8.92 \pm 0.04$ Å, $c = 16.10 \pm 0.08$ Å, $\beta = 107 \pm 1°$, $Z = 4$, and space group C2/c. The structure, refined by least-squares methods to a final conventional R factor for nonzero data of 0.14, consists of layers of $Au(diars)_2I_2^+$ cations interspersed with iodide ions. The cations have $\bar{1}$-C_i symmetry and the gold(III) atom is coordinated to two diarsine ligands, approximately in a square plane, with iodine atoms in octahedral positions. The Au–As bond distances are shorter than normal, indicating a degree of π bonding. The Au–I distances are longer than normal but nevertheless are indicative of strong interactions between the gold and iodine atoms. The latter atoms are each cushioned on four methyl groups which prevent any closer approach.

Introduction

Tervalent gold compounds are invariably diamagnetic and early investigations[1-3] established the occurrence of four-coordinate square-planar structures in which the $5d6s6p^2$ hybrid orbitals of the gold atom were used for bonding.

Coordination numbers greater than 4 have been reported recently for gold(III) complexes. Charlton, Harris, Patil, and Stephenson[4] determined the crystal structure of trichlorobiquinolylgold(III) and found the metal atom to be five-coordinate. Solution studies have lead to postulated five-coordinate gold(III) species and in some cases[5-7] the coordination number is claimed to be 6.

The cationic complex $Au(diars)_2I_2^+$, where diars represents the bidentate ligand *o*-phenylenebis(dimethylarsine), has been investigated using conductometric and spectroscopic methods[5] and a six-coordinate species was postulated to exist in solution. In view of the high coordination numbers induced by this diarsine ligand[8-11] the crystal structure of diiodobis(*o*-phenylenebis(dimethylarsine))gold(III) iodide was undertaken to establish whether a six-coordinate cation of gold(III) exists in the solid state.

Experimental Section

The substance was provided by Professor C. M. Harris. It is obtained as a dark red solid by the addition of the *o*-phenylenebis(dimethylarsine) ligand and sodium iodide to a solution of sodium tetrachloroaurate (all in ethanol). Recrystallization was carried out by taking up the solid in nitromethane, near its boiling point, in a test tube and allowing the solution to cool very slowly by immersing the test tube in a large reservoir of boiling water. The irregularly shaped crystals which formed were invariable multiple crystals and the resulting X-ray data were of extremely poor quality. Nevertheless these data were considered suitable enough to aid in attempting the crystal structure determination. Efforts to find more suitable solvents for recrystallization resulted in a change in crystal structure. This will be discussed later. The unit cell dimensions were obtained from zero-level precession photographs taken with Mo Kα radiation.

Diiodobis(*o*-phenylenebis(dimethylarsine))gold(III) Iodide, $AuI_3As_4C_{20}H_{32}$.—The formula weight of this compound is 1149.8. It crystallizes in a monoclinic system with $a = 21.6 \pm 0.2$ Å, $b = 8.92 \pm 0.04$ Å, $c = 16.10 \pm 0.08$ Å, $\beta = 107 \pm 1°$, $V = 296.8$ Å^3, $D_m = 2.63$ g cm^{-1} (by flotation), $D_o = 2.57$ g cm^{-1}, $Z = 4$, $F(000) = 2088$, and space group Cc or C2/c from systematic absences (visually absent).

The intensity data $h0l$–$k7l$ were collected on multiple-film packs of five. Equiinclination Weissenberg geometry was used together with Cu Kα radiation.

Correlation data were obtained from zero-level precession photographs and were adequate during the initial stages of the structure determination. Interlayer scale factors were introduced as variables during the final refinement stages.

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(1) R. F. Phillips and H. M. Powell, *Proc. Roy. Soc.* (London), **A173**, 147 (1939).

(2) M. F. Perutz and O. Weisz, *J. Chem. Soc.*, 438 (1946).

(3) E. S. Clark, D. H. Templeton, and C. H. MacGillavry, *Acta Cryst.*, **11**, 284 (1958).

(4) R. J. Charlton, C. M. Harris, H. Patil, and N. C. Stephenson, *Inorg. Nucl. Chem. Letters*, **2**, 409 (1966).

(5) C. M. Harris and R. S. Nyholm, *J. Chem. Soc.*, 63 (1957).

(6) C. M. Harris and S. E. Livingstone, *Rev. Pure Appl. Chem.*, **12**, 16 (1962).

(7) R. E. Rundle, *J. Am. Chem. Soc.*, **76**, 3101 (1954).

(8) N. C. Stephenson, *J. Inorg. Nucl. Chem.*, **24**, 791 (1962).

(9) N. C. Stephenson, *Acta Cryst.*, **17**, 592 (1964).

(10) N. C. Stephenson, *ibid.*, **17**, 1517 (1964).

(11) N. C. Stephenson and G. A. Jeffrey, *Proc. Chem. Soc.*, 173 (1963).

Table I

Observed and Calculated Structure Factors for Diiodobis(*o*-phenylenebis(dimethylarsine))gold(III) Iodide[a]

[a] The columns from left to right read *h*, *l*, F_o, and F_c The asterisk denotes reflections with badly distorted spots on Weissenberg photographs. These reflections were excluded from the least-squares refinement but were included in the calculation of the final residual (*R*).

The intesnsities of 1114 observed reflections were estimated visually with the aid of a calibrated strip and the Lorentz and polarization corrections were applied on an IBM 360/50 computer using the programs of Craig.[12] Neither extinction nor absorption corrections were applied to these data, since the data were of such poor quality. The final scaling of structure amplitudes (Table I) is based upon the calculated structure amplitudes.

Determination and Refinement of the Structure

The intensities of reflections for which $k + l = 2n$ were observed to be stronger than those with $k + l = 2n + 1$. The four gold atoms were therefore considered most likely to be found in position 4(d)[13] of the space group C2/c. Confirmation of this placement was obtained from a three-dimensional Patterson function. The resulting electron density map, based upon data reliably phased by the gold atoms, contained false symmetry but nevertheless it was possible to locate the positions of the heavy atoms. The carbon atoms were located using successive cycles of structure factors and difference Fourier syntheses.

The atomic parameters were refined by full-matrix least-squares methods in which the values of $\Sigma w(|F_o| - |F_c|)^2$ were minimized. Isotropic thermal parameters and interlayer scale factors were refined in addition to the positional parameters. Unit weights were used initially but this scheme was replaced after two cycles with Cruickshank's weighting scheme[14] in which $w = 1/(a + |F_o| + c|F_c|^2)$, $a = 2F_{\min}$, and $c = 2/F_{\max}$. Unobserved data were not used in these least-squares calculations, which converged to give a final reliability index (*R*) of 0.14 ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$).

For the calculation of structure factors the atomic scattering curves of Berghuis, *et al.*,[15] and Thomas and Umeda[16] were used. A correction for the real component of the anomalous dispersion of each heavy-metal atom for Cu Kα radiation was applied.[17] An IBM 360/50 computer was used for all calculations, together with local versions of well-established programs.[18]

The final atomic parameters for the crystallographically independent atoms, together with estimated standard deviations, are listed in Table II. The effects of absorption are evident in these parameters, *e.g.*, a negative temperature factor for atom C(10). In view of the findings of Srivastava and Lingafelter,[19] the standard deviations in positional parameters would normally be considered to be reliable whereas the standard deviations in temperature factors would tend to underestimate the real errors in these parameters.

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(12) D. C. Craig, private communication.

(13) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p 101.

(14) D. W. J. Cruickshank in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press Inc., New York, N. Y., 1965, p 114.

(15) J. Berghuis, I. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenindaal, *Acta Cryst.*, **8**, 478 (1955).

(16) L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

(17) C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 841 (1955).

(18) The Fourier syntheses were calculated using "ERFR-2, a Fourier Summation Program," by W. G. Sly, D. P. Shoemaker, and J. H. van der Hende, Report CBRL-22M-52, Esso Research, June 1962. Structure factor calculations and least-squares refinements were performed with "ORFLS—Oak Ridge FORTRAN Least Squares," by W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., Aug 1962. Bond distances and angles were calculated using "ORFFE—Oak Ridge FORTRAN Function and Error Program," by W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(19) R. C. Srivastava and E. C. Lingafelter, *Acta Cryst.*, **20**, 918 (1966).

TABLE II

FRACTIONAL ATOMIC COORDINATES AND TEMPERATURE FACTORS FOR DIIODOBIS(o-PHENYLENEBIS(DIMETHYLARSINE))GOLD(III) IODIDE

Atom	x/a	y/b	z/c	Temp factor (B), Å$_2$	Esd of B, Å^2
Au(1)	0.2500	0.2500	0.5000	0.21	0.07
I(2)	0.5000	0.1416 (12)[a]	0.2500	3.84	0.18
I(3)	0.2830 (2)	0.5472 (07)	0.3933 (2)	2.11	0.10
As(4)	0.1677 (3)	0.1393 (9)	0.3790 (3)	0.69	0.12
As(5)	0.1568 (3)	0.3586 (10)	0.5370 (3)	1.06	0.13
C(6)	0.1476 (4)	0.269 (11)	0.2700 (42)	2.4	1.4
C(7)	0.1852 (32)	−0.0750 (88)	0.3512 (35)	1.5	1.1
C(8)	0.1641 (27)	0.3583 (82)	0.6617 (30)	0.7	0.9
C(9)	0.1393 (46)	0.579 (13)	0.4927 (57)	4.2	2.0
C(10)	0.0928 (22)	0.1380 (68)	0.4091 (24)	−0.42	0.74
C(11)	0.0361 (35)	0.038 (11)	0.3619 (42)	2.5	1.3
C(12)	−0.0300 (43)	0.050 (13)	0.3859 (53)	4.0	1.8
C(13)	−0.0286 (29)	0.1625 (89)	0.4515 (32)	1.0	1.0
C(14)	0.0217 (39)	0.248 (12)	0.4955 (44)	2.9	1.5
C(15)	0.0859 (28)	0.2510 (90)	0.4700 (33)	1.2	1.0

[a] Figures in parentheses are the standard deviations of the fractional coordinates and refer to the last decimal places in the value of the coordinates.

In this structure, however, other systematic errors probably caused standard deviations in positions as well to be underestimated.

Description of the Structure

The crystal structure of Au(diars)$_2$I$_3$ consists of positively charged diiodobis(o-phenylenebis(dimethylarsine))gold(III) ions and negatively charged iodide ions. The complex cations are arranged in layers parallel to (002) while the anions lie in channels running between these layers and parallel to [010]. The bond distances and angles in the cation are listed in Tables III and IV, respectively, and the structure of this ion is depicted in Figure 1.

TABLE III

INTERATOMIC DISTANCES (Å) IN THE DIIODOBIS(o-PHENYLENEBIS(DIMETHYLARSINE))GOLD(III) ION[a]

Au(1)–I(3)	3.35 (02)	As(5)–C(15)	1.86 (07)
Au(1)–As(4)	2.43 (03)	C(10)–C(11)	1.53 (09)
Au(1)–As(5)	2.46 (02)	C(11)–C(12)	1.60 (12)
As(4)–C(6)	2.04 (08)	C(12)–C(13)	1.45 (12)
As(4)–C(7)	2.02 (08)	C(13)–C(14)	1.35 (10)
As(4)–C(10)	1.82 (05)	C(14)–C(15)	1.56 (10)
As(5)–C(8)	1.97 (05)	C(15)–C(10)	1.44 (09)
As(5)–C(9)	2.10 (11)		

[a] Standard deviations are given in parentheses and refer to the last two decimal places. They are estimated by the least-squares analysis and are probably somewhat underestimated. See text.

Some of the closer contacts between the cations and also between the cations and anions are listed in Table V. Each iodide ion I(2) lies on a twofold axis and makes close contact with benzene carbon atoms C(11) and C(12) and methyl groups C(6) and C(7). Each iodine atom I(3) of the cation is surrounded by a cage of methyl groups and the interatomic distances (all 3.9 Å) indicate close intraionic approaches. In the other reported diarsine structures[20] these iodine atoms make close contacts with carbon atoms of the benzene rings on adjacent molecules.

Coordination about the Gold(III) Atom

The octahedral environment of the gold atom is evident in Figure 1. The point group symmetry of the cation is $\bar{1}$-C$_i$ so that each gold atom and the four coordinated arsenic atoms are coplanar. The equation of this plane, with respect to the crystallographic axes, is $0.209X + 0.802Y - 0.597Z + 1.889 = 0$.

There is no significant difference between the two Au–As bond lengths (2.43, 2.46 Å (each ±0.03 Å)) but both are less than the sum of the square covalent radius[21] for gold(III) and the tetrahedral covalent radius for arsenic ($1.40 + 1.18 = 2.58$ Å, $\Delta/\sigma = 5$ and 6 for Au–As(4) and Au–As(5), respectively). Similar shortenings of metal–arsenic bond lengths were found in the octahedral complexes Ni(diars)$_2$I$_2$[9] and Pt(diars)$_2$X$_2$.[8,10] The Au–As bonding in the Au(diars)$_2$I$_2^+$ cation can be similarly explained in terms of the formation of π bonds, in addition to σ bonds, by donation of electrons from metal to ligand through overlap of suitably oriented 5d orbitals on the metal and 4d orbitals on the arsenic atoms. The resulting decrease in charge on the metal increases its ability to attract the additional ligands in the axial sites to complete the octahedral coordination.

The Au–I distance (3.35 Å) is significantly greater than the covalent sum for these atoms ($1.40 + 1.33 = 2.73$ Å) but is less than the nonbonded distance ($2.2 + 2.2 = 4.4$ Å). These radii are those given by Pauling,[21] with the exception of the van der Waals radius for the gold atom, which was estimated to be 2.2 Å following an observation made by Pauling that this radius, for many elements, exceeds the corresponding single-bond radius by 0.75–0.83 Å. Long metal–iodine bonds are also observed in the structures of Ni(diars)$_2$I$_2$ and Pt(diars)$_2$I$_2$ where these bond lengths are 3.21 and 3.50 Å, respectively. In these compounds the iodine atom is de-

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(20) We have prepared another crystalline form of Au(diars)$_2$I$_3$ by recrystallization from nitrobenzene. The unit cell is monoclinic with $a = 16.57$, $b = 18.26$, $c = 9.20$ Å (all to 0.5%), and $\beta = 97.7 \pm 0.5°$. There are four molecules of Au(diars)$_2$I$_3$ per unit cell and the space group is P2$_1$. We are currently determining the crystal structure.

(21) L. E. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 246, 249.

TABLE IV

BOND ANGLES (DEG) IN THE DIIODOBIS(*o*-PHENYLENEBIS(DIMETHYLARSINE))GOLD(III) CATION, WHERE THE CENTRAL ATOM IS AT THE VERTEX[a]

I(3)–Au(1)–As(4)	97.2 (6)	Au(1)–As(5)–C(9)	112 (2.7)
I(3)–Au(1)–As(5)	97.2 (6)	C(8)–As(5)–C(9)	108 (3.3)
As(4)–Au(1)–As(5)	84.0 (8)	C(8)–As(5)–C(15)	113 (2.7)
As(4)–Au(1)–As(5)[b]	96.0 (8)	C(9)–As(5)–C(15)	105 (2.5)
I(3)–Au(1)–As(4)[b]	82.8 (6)	As(4)–C(Z0)–C(15)	117 (4.1)
I(3)–Au(1)–As(5)[b]	82.8 (6)	As(5)–C(15)–C(10)	121 (4.3)
Au(1)–As(4)–C(10)	107 (1.6)	As(4)–C(10)–C(11)	121 (4.1)
Au(1)–As(4)–C(6)	112 (2.4)	As(5)–C(15)–C(14)	120 (4.6)
Au(1)–As(4)–C(7)	115 (1.7)	C(10)–C(11)–C(12)	119 (6.4)
C(6)–As(4)–C(7)	111 (3.0)	C(11)–C(12)–C(13)	113 (7.1)
C(6)–As(4)–C(10)	105 (2.7)	C(12)–C(13)–C(14)	128 (6.9)
C(7)–As(4)–C(10)	107 (2.7)	C(13)–C(14)–C(15)	121 (6.6)
Au(1)–As(5)–C(15)	105 (2.2)	C(14)–C(15)–C(10)	117 (5.6)
Au(1)–As(5)–C(8)	115 (1.9)	C(15)–C(10)–C(11)	121 (5.0)

[a] Standard deviations are those estimated by the least-squares analysis and are probably somewhat underestimated. See text.
[b] Atom at $^1/_2 - x$, $^1/_2 - y$, $1 - z$.

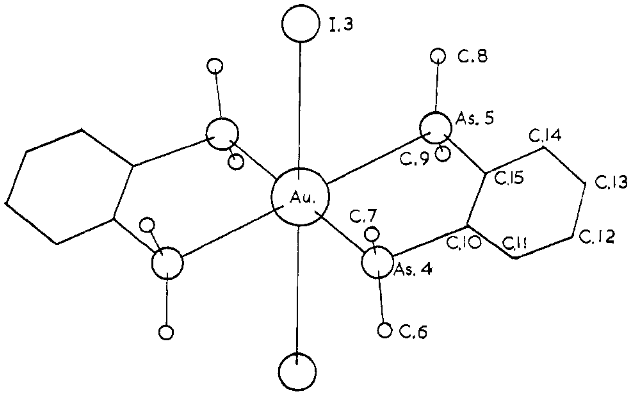

Figure 1.—A diagram illustrating the configuration of the diiodobis(*o*-phenylenebis(dimethylarsine))gold(III) cation.

TABLE V

SELECTED INTERIONIC APPROACH DISTANCES (Å) IN THE COMPOUND DIIODOBIS(*o*-PHENYLENEBIS(DIMETHYLARSINE))GOLD(III) IODIDE[a]

I(2)–C(7)^1	4.61 (08)	C(7)–C(12)^9	4.40 (12)
I(2)–C(11)^1	3.94 (09)	C(9)–C(7)^7	4.10 (13)
I(2)–C(12)^2	4.33 (07)	C(9)–C(13)^8	3.60 (13)
I(2)–C(6)^3	4.55 (09)	C(9)–C(14)^8	3.90 (14)
I(2)–C(9)^4	4.20 (11)	C(10)–C(13)^{10}	4.00 (09)
I(3)–C(8)$_5$	3.95 (07)	C(11)–C(11)^9	3.50 (14)
I(3)–C(6)^1	3.92 (08)	C(11)–C(11)^9	4.00 (11)
I(3)–C(7)^1	4.40 (11)	C(11)–C(13)^{10}	3.50 (10)
I(3)–C(9)^6	3.90 (11)	C(11)–C(14)^{10}	3.90 (12)
I(3)–C(7)^7	3.93 (08)	C(12)–C(12)^{10}	3.60 (17)
C(6)–C(8)^5	3.80 (11)	C(12)–C(13)^{10}	3.20 (12)
C(6)–C(9)^5	4.60 (12)	C(12)–C(14)^{10}	3.34 (14)
C(6)–C(12)^9	3.60 (13)	C(12)–C(15)^{10}	4.03 (13)
C(6)–C(11)^9	4.40 (12)	C(13)–C(13)^{10}	3.41 (15)
C(6)–C(13)^9	3.90 (10)	C(13)–C(14)^{10}	3.83 (14)

[a] The superscripts denote the following symmetry transformations of the parameters of Table II: (no superscript) x, y, z; (1) $^1/_2 - x, ^1/_2 + y, ^1/_2 - z$; (2) $^1/_2 + x, ^1/_2 + y, z$; (3) $^1/_2 - x, y - ^1/_2, ^1/_2 - z$; (4) $^1/_2 + x, y - ^1/_2, z$; (5) $x, 1 - y, z - ^1/_2$; (6) $^1/_2 - x, ^3/_2 - y, 1 - z$; (7) $x, 1 + y, z$; (8) $\bar{x}, 1 - y, 1 - z$; (9) $\bar{x}, y, ^1/_2 - z$; (10) $\bar{x}, \bar{y}, 1 - z$; (11) $^1/_2 - x, ^1/_2 - y, 1 - z$.

scribed as being "cushioned" on four of the methyl groups attached to the arsenic atoms, and such a description may also be used for the positions of the iodine atoms in this investigation. The close intraionic nonbonding contacts involving these methyl groups are listed in Table VI. The four I–CH_3 contacts (3.9–4.0 Å) are all close to the sum of the corresponding van der Waals radii (2.15 + 2.00 = 4.15 Å) and are probably responsible for the tilt of the Au–I bond away from the axis of the octahedron toward the methyl groups C(7) and C(8). The angles I(3)–Au(1)–As(4) and I(3)–Au(1)–As(5), both 97.2°, provide a measure of this tilt. Similar displacements of halogen atoms from the octahedral sites are also observed in the four metal–diarsine complexes studied by Stephenson.

TABLE VI

SOME NONBONDING APPROACH DISTANCES (Å) BETWEEN ATOMS WITHIN THE SAME DIIODOBIS(*o*-PHENYLENEBIS(DIMETHYLARSINE))GOLD(III) CATION[a]

I(3)–C(7)^{11}	3.98 (07)	C(6)–C(8)^{11}	4.12 (10)
I(3)–C(8)^{11}	3.97 (07)	C(7)–C(8)^{11}	3.82 (10)
I(3)–C(6)	3.91 (09)	C(7)–C(9)^{11}	3.93 (12)
I(3)–C(9)	3.90 (10)	C(8)–C(9)	3.32 (12)
C(6)–C(7)	3.36 (12)		

[a] Superscripts have the same significance as in Table V.

The methyl group C(7) makes close nonbonding contacts with methyl groups C(8) and C(9) of the other diarsine ligand in the same cation (3.8, 3.9 Å). These close approaches could be responsible for the distortion in the angles Au(1)–As(4)–C(7) and Au(1)–As(5)–C(8) which both have values of 115° and may be considered to be significantly larger than the normal tetrahedral angles (Δ/σ = 3.1, 2.8).

The other bond distances and angles in the chelate ring, as well as the benzene ring, do not deviate significantly from the expected values.

The plane of best fit through the benzene ring, referred to the crystallographic axes, is $-0.128X + 0.692Y - 0.642Z + 3.607 = 0$. Deviations from this plane (in Å) are: C(10), 0.03; C(11), 0.00; C(12), 0.01; C(13), 0.02; C(14), 0.04; C(15), 0.05; and none is significant. The dihedral angle between this plane and the gold–arsenic plane is 28°, which is considerably greater than those values found for the other diarsine complexes, where they vary between 9° 3′ and 12° 30′.