1450 *Inorg. Chem.* **1980**, *19*, 1450-1452

Contribution from Department of Chemistry,
Texas A&M University, College Station, Texas 77843

A Mixed-Ligand Complex of Quadruply Bonded Ditungsten(II): Bis(2,4-dimethyl-6-oxopyrimidine)bis(1,3-diphenyltriazino)ditungsten

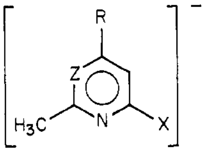
F. ALBERT COTTON,* WILLIAM H. ILSLEY, and WOLFGANG KAIM

Received November 19, 1979

The reaction of $W_2(dmhp)_4$ (dmhp = the anion of 2,4-dimethyl-6-hydroxypyrimidine) with the lithium salt of 1,3-diphenyltriazine, $Li[(PhN)_2N]$, gives only the product in which two dmhp ligands have been replaced, in a transoid fashion, by two $[(PhN)_2N]^-$ ligands. The orange crystalline compound $W_2(dmhp)_2[(PhN)_2N]_2 \cdot 2THF$ is thermally stable but somewhat air sensitive and only slightly soluble in THF. The compound crystallizes in the space group $C2/c$ with $Z = 4$, with the molecules lying on a crystallographic inversion center. The W–W distance of 2.169 (1) Å is very similar to that in $W_2(dmhp)_4$ and $W_2(dmhp)_2[(PhN)_2CCH_3]_2 \cdot 2THF$. The unit cell dimensions are $a = 21.680$ (3) Å, $b = 10.177$ (3) Å, $c = 23.089$ (1) Å, $\beta = 115.19$ (1)°, and $V = 4610$ (3) Å^3. The structure has been refined to final discrepancy factors of $R_1 = 0.040$ and $R_2 = 0.055$.

Introduction

In view of the large number and varied types of quadruply bonded dimetal compounds with bridging ligands formed by rhenium(III),[1] chromium(II)[1] and especially molybdenum(II),[1,2] the existence of only a very few such species for ditungsten(II) has for some time been considered as surprising and, perhaps, even anomalous. Those few that are known have two common features. (1) They have all been of the type $W_2(L\text{-}L)_4$, where the bidentate bridging ligand, L-L, has been of the general type **1**. (2) All such compounds have been made in the same way, namely, by reaction of $W(CO)_6$ with the protonated ligand, i.e., with the compound corresponding to **1** in which X = O or NH is replaced by XH. Compounds characterized by X-ray crystallography include $W_2(mhp)_4$[3] (Hmhp = 6-methyl-2-hydroxypyridine), $W_2(map)_4$[4] (Hmap = 6-methyl-2-aminopyridine), $W_2(dmhp)_4$[5] (Hdmhp = 2,4-dimethyl-6-hydroxypyrimidine), and, most recently, $W_2(chp)_4$ (Hchp = 6-chloro-2-hydroxypyridine).[6]



1, $R = CH_3$, H
$Z = HC$, N
$X = O$, NH

Efforts to obtain other ditungsten compounds with different types of bridging bidentate anionic ligands by direct reaction of the ligand parent acids with $W(CO)_6$ have been unsuccessful. We have therefore explored the possibility of using ligand replacement reactions, in which one of the compounds that can be readily obtained from $W(CO)_6$ serves as the starting material. For example, the reaction of $W_2(dmhp)_4$ with an amidine anion, $[PhNC(CH_3)NPh]^-$, was examined, but it was found that even under conditions as drastic as boiling diglyme (162 °C), only *two* dmhp ligands could be replaced.[7] Our goal, of course, was to replace all four and thus obtain a compound, $W_2(RNCR'NR)_4$, that would be stereoelectronically similar to the as yet unknown $W_2(O_2CR)_4$ compounds.

In this report we describe the attempt to substitute the dmhp ligands in $W_2(dmhp)_4$ by the 1,3-diphenyltriazine anion, $[(PhN)_2N]^-$. Since fully substituted complexes of dichromium(II) and dimolybdenum(II) with 1,3-diphenyltriazine have been reported recently,[8] it seemed reasonable that the analogous tungsten derivative could be prepared. Again, however, we have been able to isolate only a partially substituted species, $W_2(dmhp)_2[(PhN)_2N]_2 \cdot 2THF$, in which the crystals contain THF of solvation, not coordinated to the tungsten atoms. The molecular and crystal structure of this compound have been determined by X-ray diffraction and are reported here.

Experimental Section

Preparation. 1,3-Diphenyltriazine[8] and $W_2(dmhp)_4 \cdot 0.5$diglyme[5] were prepared by methods described earlier. In these and subsequent preparative procedures an atmosphere of dry argon was maintained.

1,3-Diphenyltriazene (0.40 g, 2 mM) was dissolved in 25 mL of THF, and 1 equiv of *n*-BuLi was added to obtain the red anion $[C_6H_5NNNC_6H_5]^-$. Addition of $W_2(dmhp)_4 \cdot 0.5$diglyme (0.46 g, 0.5 mM) resulted in the slow precipitation of an orange solid, which was isolated after 2 days and redissolved in THF, in which it is slightly soluble. A hexane layer was allowed to diffuse slowly into the saturated THF solution, whereupon orange plate-shaped crystals were deposited at the glass wall.

X-ray Data Collection. A crystal of dimensions 0.20 × 0.15 × 0.40 mm was coated with epoxy cement and with the same cement attached to the end of a thin glass fiber, which was then mounted on an Enraf-Nonius CAD-4F automatic diffractometer. Intensity data were collected by using Mo Kα radiation ($\lambda_\alpha = 0.71073$ Å) monochromatized by a graphite crystal in the incident beam. The takeoff angle of the X-ray tube was 2.80° and the temperature during data collection was 26 ± 2 °C. Twenty-five reflections in the range $12.6 < \theta < 15.8°$ were located by using the standard CAD-4 automatic random searching routine. These reflections were subsequently centered and used as the basis for the indexing, carried out by using the standard CAD-4 indexing routine. Indexing yielded a cell of the monoclinic crystal system having dimensions $a = 21.680$ (3) Å, $b = 10.177$ (3) Å, $c = 23.089$ (3) Å, $\beta = 115.19$ (1)°, and $V = 4610$ (3) Å^3. With $Z = 2$ the calculated density is 1.613 g cm^{-3}. Systematic absences of hkl, $h + k = 2n$, and $h0l$, $l = 2n$, are consistent with the space groups $C2/c$ or Cc. The former was chosen and confirmed by successful solution of the structure.

The data were collected in the range $0 < 2\theta \leq 45°$ with all reflections measured by using an ω–2θ motion. The scan width for each

---

[1] Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 225.

[2] Bino, A.; Cotton, F. A. Proceedings of the Third International Conference on the Chemistry and Uses of Molybdenum, Ann Arbor, MI, Aug 1979; submitted for publication in *J. Less-Common Met.*

[3] Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4725.

[4] Cotton, F. A.; Niswander, R. H.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3541.

[5] Cotton, F. A.; Niswander, R. H.; Sekutowski, J. C. *Inorg. Chem.* **1979**, *18*, 1152.

[6] Cotton, F. A.; Ilsley, W. H.; Kaim, W., following paper in this issue.

[7] Cotton, F. A.; Ilsley, W. H.; Kaim, W. *Inorg. Chem.*, **1979**, *18*, 3569.

[8] Cotton, F. A.; Rice, G. W.; Sekutowski, J. C. *Inorg. Chem.* **1979**, *18*, 1143.

0020-1669/80/1319-1450$01.00/0

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	0.01036 (2)	−0.00542 (4)	0.05021 (2)	2.73 (1)	3.51 (2)	2.27 (1)	−0.16 (2)	1.09 (1)	0.01 (2)
O(1)	−0.0205 (3)	0.1866 (7)	0.0544 (3)	4.2 (3)	3.8 (3)	2.3 (3)	0.3 (3)	1.5 (2)	−0.3 (2)
atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O(2)	0.230 (1)	0.360 (3)	0.485 (1)	28 (1)	O(3)	0.500 (0)	0.001 (4)	0.750 (0)	40 (3)
atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(1)	−0.0887 (4)	0.4048 (9)	−0.1062 (4)	3.6 (4)	3.9 (4)	5.2 (5)	0.6 (4)	0.9 (3)	1.1 (4)
N(2)	−0.0431 (4)	0.2055 (8)	−0.0517 (4)	2.9 (3)	2.9 (4)	3.0 (3)	0.2 (3)	1.2 (2)	0.7 (3)
N(3)	0.0905 (4)	0.0669 (9)	−0.0258 (4)	2.8 (3)	4.5 (4)	3.5 (3)	−0.7 (3)	2.1 (2)	−0.0 (3)
N(4)	0.1361 (4)	0.0851 (8)	0.0345 (4)	2.7 (3)	3.6 (4)	3.2 (4)	−0.6 (3)	0.9 (2)	0.3 (3)
N(5)	0.1105 (4)	0.0585 (9)	0.0757 (3)	1.9 (3)	4.5 (4)	2.1 (3)	−0.7 (3)	0.4 (2)	0.1 (3)
atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(1)	−0.0425 (5)	0.257 (1)	0.0050 (5)	3.7 (2)	C(12)	0.0882 (6)	0.032 (1)	−0.1295 (6)	5.0 (3)
C(2)	−0.0653 (5)	0.387 (1)	0.0040 (5)	4.4 (3)	C(13)	0.1591 (5)	0.074 (1)	0.1397 (5)	3.7 (2)
C(3)	−0.0903 (6)	0.456 (1)	−0.0522 (6)	5.2 (3)	C(14)	0.1385 (6)	0.141 (1)	0.1814 (5)	4.6 (3)
C(4)	−0.1183 (7)	0.595 (1)	−0.0558 (7)	6.5 (4)	C(15)	0.1835 (7)	0.154 (1)	0.2470 (6)	6.4 (4)
C(5)	−0.0682 (5)	0.281 (1)	−0.1058 (5)	4.2 (3)	C(16)	0.2464 (6)	0.099 (1)	0.2673 (6)	6.3 (3)
C(6)	−0.0695 (6)	0.228 (1)	−0.1654 (5)	4.7 (3)	C(17)	0.2685 (7)	0.032 (1)	0.2288 (7)	6.8 (4)
C(7)	0.1161 (5)	0.097 (1)	−0.0707 (5)	3.7 (2)	C(18)	0.2233 (6)	0.018 (1)	0.1619 (6)	5.2 (3)
C(8)	0.1663 (6)	0.196 (1)	−0.0573 (5)	4.7 (3)	C(19)	0.2592 (11)	0.298 (3)	0.5550 (10)	18.1 (11)
C(9)	0.1917 (6)	0.223 (1)	−0.1054 (6)	6.0 (3)	C(20)	0.2894 (21)	0.211 (5)	0.5697 (18)	14.3 (16)
C(10)	0.1616 (7)	0.160 (2)	−0.1629 (6)	6.9 (4)	C(21)	0.4823 (18)	0.106 (5)	0.6952 (14)	30.3 (21)
C(11)	0.1124 (6)	0.067 (1)	−0.1745 (6)	6.0 (3)	C(22)	0.4677 (21)	0.201 (4)	0.7278 (22)	29.8 (17)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

reflection was determined as 0.8 + 0.347 (tan θ and each reflection was measured with a preliminary scan rate of 20.12°/min. The scan rate for the final scan was calculated from the preliminary scan such that the ratio $I/\sigma(I)$ would be at least 20 and the maximum scan time would not exceed 30 s. If in the preliminary scan it was found that $I/\sigma(I) \geq 20$, this measurement was used as the datum. The scan rates used varied from 20.12 to 2.51°/min. The width of the adjustable vertical aperture at the detector was given by (1.5 + tan θ) mm. The horizontal slit was 4 mm. Of the 96 steps in the profile scan, the first and last 16 steps were considered to be background. Intensities and standard deviations of the intensities were assigned as

$$I = [P - 2(B_1 + B_2)]S$$

$$\sigma(I) = [P + 4(B_1 + B_2)]^{1/2}S$$

where P is the gross peak intensity, B_1 and B_2 are the background intensities, and S is the scan rate. During data collection, three orientation standards as well as three intensity standards were measured every 100 reflections. The intensity standards showed no significant decrease in intensity throughout data collection so no decay correction was applied. Lorentz and polarization corrections were applied[9] as well as an empirical absorption correction (μ = 53.39 cm^{-1}), based on ψ scans at χ = 90°. Eight scans were made, each from $0 \leq \psi \leq 360°$. The minimum, maximum, and average transmission factors were 69.3, 99.9, and 88.1%.

Solution and Refinement. The structure was solved[9] in the monoclinic space group $C2/c$. The position of the one crystallographically independent tungsten atom was found by solution of the three-dimensional Patterson function. Subsequent Fourier and difference syntheses gave the positions of the remaining nonhydrogen atoms. Full-matrix isotropic refinement of the carbon atoms as well as the two oxygen atoms of the THF molecules and anisotropic refinement of the tungsten, nitrogen, and ring oxygen atoms yielded final discrepancy factors of

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.040$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.055$$

and a goodness of fit parameter of 1.487. The function $\sum w(|F_o| - |F_c|)^2$ was minimized with the weighting factor, w, equal to $4F_o^2/\sigma(F_o^2)^2$. All structure factor calculations and least-squares refinements were executed by using only those 1916 reflections for which $F_o^2 > 3\sigma(F_o^2)$. Atomic scattering factors were those of Cromer and Waber.[10]

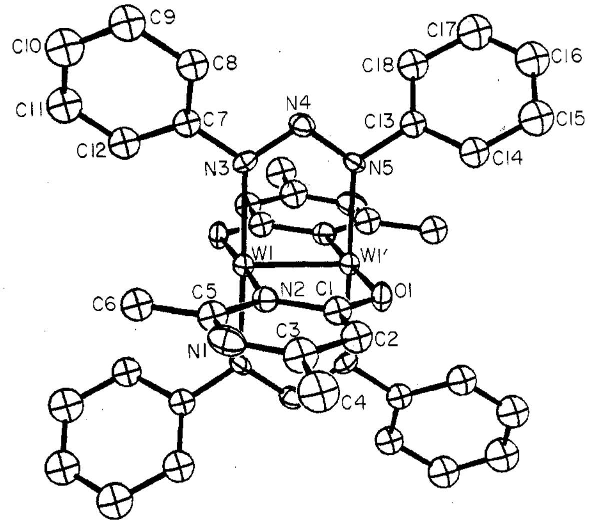


Figure 1. A computer-generated (ORTEP) drawing of the molecule, in which atoms are represented by their ellipsoids of thermal vibration scaled to enclose 50% of the electron density.

Table II. Bond Distances (Å)

W(1)–W(1)′	2.169 (1)	C(3)–C(4)	1.52 (2)
O(1)′	2.081 (6)	C(5)–C(6)	1.48 (1)
N(2)	2.153 (7)	C(7)–C(8)	1.42 (1)
N(3)	2.108 (7)	C(12)	1.39 (1)
N(5)′	2.097 (7)	C(8)–C(9)	1.46 (2)
O(1)–C(1)	1.26 (1)	C(9)–C(10)	1.36 (2)
N(1)–C(3)	1.37 (1)	C(10)–C(11)	1.37 (2)
C(5)	1.33 (1)	C(11)–C(12)	1.39 (2)
N(2)–C(1)	1.40 (1)	C(13)–C(14)	1.40 (1)
C(5)	1.37 (1)	C(18)	1.38 (1)
N(3)–N(4)	1.33 (1)	C(14)–C(15)	1.42 (2)
C(7)	1.40 (1)	C(15)–C(16)	1.36 (2)
N(4)–N(5)	1.32 (1)	C(16)–C(17)	1.36 (2)
N(5)–C(13)	1.41 (1)	C(17)–C(18)	1.44 (2)
C(1)–C(2)	1.41 (1)	O(3)–C(21)	1.58 (6)
C(2)–C(3)	1.37 (2)	C(21)–C(22)	1.34 (6)
		C(22)–C(22)′	1.34 (9)

---

(9) Calculations were performed using the Molecular Structure Corp. PDP-11/45 computer and the Enraf-Nonius structure determination package with programs written chiefly by Frenz and Okaya.

Table III. Bond Angles (Deg)

W(1)–W(1)′–O(1)	94.4 (2)	C(1)–C(2)–C(3)	120 (1)
N(2)′	89.0 (2)	C(2)–C(3)–C(4)	121 (1)
N(3)′	90.6 (2)	N(1)	121 (1)
N(5)	90.1 (2)	C(4)–C(3)–N(1)	118 (1)
O(1)–W(1)′–N(2)′	176.6 (2)	N(1)–C(5)–C(6)	118 (1)
N(3)′	88.5 (3)	N(2)	122 (1)
N(5)	90.6 (3)	N(2)–C(5)–C(6)	119 (1)
N(2)′–W(1)′–N(3)′	91.2 (3)	N(3)–C(7)–C(8)	120 (1)
N(5)	89.6 (3)	C(12)	118 (1)
N(3)′–W(1)′–N(5)	178.9 (3)	C(8)–C(7)–C(12)	121 (1)
W(1)′–O(1)–C(1)	120.0 (6)	C(7)–C(8)–C(9)	118 (1)
C(3)–N(1)–C(5)	120 (1)	C(8)–C(9)–C(10)	118 (1)
C(1)–N(2)–C(5)	118.9 (8)	C(9)–C(10)–C(11)	122 (1)
W(1)–N(2)–C(1)	117.8 (6)	C(10)–C(11)–C(12)	122 (1)
C(5)	123.2 (7)	C(11)–C(12)–C(7)	118 (1)
W(1)–N(3)–C(7)	124.0 (7)	N(5)–C(13)–C(14)	117 (1)
N(4)	122.9 (6)	C(18)	122 (1)
C(7)–N(3)–N(4)	113.0 (8)	C(14)–C(13)–C(18)	121 (1)
N(3)–N(4)–N(5)	111.9 (7)	C(13)–C(14)–C(15)	120 (1)
W(1)′–N(5)–N(4)	124.5 (6)	C(14)–C(15)–C(16)	117 (1)
C(13)	123.3 (6)	C(15)–C(16)–C(17)	124 (1)
N(4)–N(5)–C(13)	112.2 (7)	C(16)–C(17)–C(18)	119 (1)
O(1)–C(1)–N(2)	118.8 (8)	C(17)–C(18)–C(13)	118 (1)
C(2)	123 (1)	C(21)–O(3)–C(21)	94 (6)
C(2)–C(1)–N(2)	118.1 (9)	O(3)–C(21)–C(22)	94 (5)
		C(21)–C(22)–C(22)′	91 (4)

Anomalous dispersion effects were included in the scattering factors of tungsten. The observed and calculated structure factors are available as supplementary material.

Results and Discussion

The structure of the molecule is shown in Figure 1 which also defines the atomic numbering scheme. The atomic positional and thermal parameters are listed in Table I. Bond distances and angles are given in Tables II and III, respectively, and the equations for some planes and the dihedral angles between them are given in Table IV.

The molecule is located with the midpoint of the W–W bond upon a crystallographic inversion center. The overall symmetry of each molecule approximates to C_{2h} except for the twist angles of the phenyl groups. The molecules have like ligands trans to each other and the dmhp ligands are oriented in opposite directions so that on each tungsten atom O and N atoms are trans to each other as required by the crystallographic inversion center.

The W–W distance, 2.169 (1) Å, is in the same range as those of other bridged ditungsten(II) compounds: $W_2(mhp)_4$, 2.161 (2) Å;[3] $W_2(map)_4$, 2.164 (1) Å;[4] $W_2(dmhp)_4 \cdot 0.5$diglyme, 2.155 (2) Å;[5] $W_2(dmhp)_4 \cdot$diglyme, 2.163 (1) Å;[5] $W_2(dmhp)_2[(PhN)_2CCH_3]_2 \cdot 2$THF, 2.174 (1) Å.[7]

The W–O and W–N distances to the dmhp ligands are 2.081 (6) and 2.153 (7) Å, respectively. These distances are in good agreement with the analogous distances in $W_2(dmhp)_2[(PhN)_2CCH_3]_2 \cdot 2$THF[7] [W–O = 2.09 (1) Å, W–N = 2.17 (1) Å] and $W_2(dmhp)_4 \cdot$diglyme[5] [W–O = 2.064 (3) Å average; W–N = 2.143 (4) Å average]. The $(PhN)_2N$ ligands are symmetrically bonded to the tungsten atoms with W–N distances of 2.108 (7) and 2.097 (7) Å. The N–N distances within the ligands are 1.33 (1) and 1.33 (1) Å and are in reasonable agreement with the corresponding distances in $Cr_2[(PhN)_2N]_4$ and $Mo_2[(PhN)_2N]_4$.[8] The C–N distances within the $(PhN)_2N$ ligands are 1.40 (1) and 1.41 (1) Å and are also in good agreement with the corresponding distances in $Cr_2[(PhN)_2N]_4$ and $Mo_2[(PhN)_2N]_4$.

Table IV. Some Planes and Dihedral Angles (Deg)

Planes[a]

	atoms	displacements, Å
P_1: $A = -0.3050$	N(3)	−0.009
$B = 0.9517$	W(1)′	0.008
$C = -0.0354$	W(1)	−0.008
$D = 0.0000$	N(5)	−0.006
	N(4)	0.002
P_2: $A = 0.4858$	C(13)	0.004
$B = 0.8511$	C(14)	−0.004
$C = -0.1988$	C(15)	0.001
$D = 1.0627$	C(16)	0.001
	C(17)	0.000
	C(18)	−0.003
P_3: $A = -0.6022$	C(7)	−0.009
$B = 0.7086$	C(8)	0.024
$C = -0.3678$	C(9)	0.027
$D = -0.6826$	C(10)	0.013
	C(11)	0.004
	C(12)	−0.006
P_4: $A = -0.9137$	N(2)	−0.002
$B = -0.3181$	W(1)′	0.003
$C = -0.2529$	W(1)	−0.003
$D = 0.0005$	O(1)	0.003

Dihedral Angles

planes	angle, deg	planes	angle, deg
P_1/P_2	48.0	P_1/P_3	29.4
		P_1/P_4	90.9

[a] Each plane, P_n, is defined by $A_nX + B_nY + C_nZ = D_n$.

The two THF molecules are not coordinated to the tungsten atoms but are present simply as solvent of crystallization. Both THF molecules are located on crystallographic twofold axes. Unfortunately, as was the case for the $W_2(dmhp)_2[(PhN)_2CCH_3]_4 \cdot 2$THF structure, we were unable to refine either of the THF molecules satisfactorily despite repeated efforts to do so. In fact we were not able to find adequate atomic positions for one of the THF molecules at all. Probable atomic positions were found for the molecule containing O(3), but, as is evident in the bond distances, angles, and thermal parameters, these positions are poorly defined and inaccurate. For the other THF molecule, which contains O(2), refinable atomic positions could not be found at all; no physically reasonable way of disordering a THF molecule that would explain the observed peaks was found. The difficulties may arise from partial occupancy, large vibrational motions, disorder, or some combination of two or more of these factors. The most prominent peaks in the region of this THF molecule that appeared in the difference map were refined as carbon atoms.

Acknowledgment. We thank the National Science Foundation for financial support. W.K. thanks the Verband der Chemischen Industrie for a Liebig Stipend.

Registry No. $W_2(dmhp)_2[(PhN)_2N]_2 \cdot 2$THF, 73261-72-0; $W_2(dmhp)_4$, 69351-88-8.

Supplementary Material Available: A table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

---

(10) Cromer, D. T.; Waber, J. T. "International Tables of X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.