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The Crystal Structure of M-$LiTa_3O_8$ and Its Relationship to the Mineral Wodginite

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M–$LiTa_3O_8$ crystallizes in the monoclinic system with unit-cell dimensions (from single crystal data) $a = 9.413$, $b = 11.522$, $c = 5.050$ Å, $\beta = 91.05°$, and space group $C2/c$, $Z = 4$. The structure was solved using three-dimensional Patterson and Fourier techniques. Of the 754 reflections measured by counter techniques, 714 with $I \geqslant 3\sigma\ (I)$ were used in the least-squares refinement of the model to a convention R of 0.043 ($wR = 0.055$). M–$LiTa_3O_8$ has the α–PbO_2 type of structure with hexagonally close-packed oxygen ions with lithium and tantalum occupying octahedral sites in an ordered way. This structure can be regarded as a simple analogue of the complex mineral wodginite.

Introduction

During an investigation of the $LiTaO_3$–Ta_2O_5 system (*1*, *2*) the compound $LiTa_3O_8$ was synthesized and found to exist in three crystallographic modifications. Crystals of the intermediate temperature form (M) were grown (*1*) by the flux evaporation technique from a composition of $30Li_2O$, $12Ta_2O_5$, $58MoO_3$ (mole%). X-ray precession studies revealed that the phase is monoclinic, space group $C2/c$ or Cc, least squares refinement of cell dimensions based on X-ray powder data yield $a = 9.414(1)$, $b = 11.531(1)$, $c = 5.052(1)$ Å, and $\beta = 91°3.12'(1)$. Subsequently, it became apparent that the crystallographic properties of M–$LiTa_3O_8$ were similar to those of the mineral wodginite.

Wodginite, an accessory mineral in pegmatites, has been described from many localities (*3*–*8*). Typically, the mineral contains high concentrations of Ta, Nb, Mn, Fe, and, often, Sn. Synthetic wodginite was prepared in the $MnTa_2O_6$–$FeTaO_4$ system by Turnock (*9*). Single phase material was found to exist within the region $Mn^{2+}_{2-2w}Fe^{3+}_{3w}Ta_{4-w}O_{12}$, $0.08 < w < 0.29$, at 1200°C. Nickel *et al.* (*4*) reported the space group of wodginite (Bernic Lake, Manitoba) to be $C2/c$ or Cc. The unit cell parameters, $a = 9.52$, $b = 11.47$, $c = 5.10$ Å, and $\beta = 91°18'$ were shown to be related to those of ixiolite and columbite (*10*). A structural similarity, therefore, was inferred. Ixiolite (*10*), ideally A_4O_8 (A = Ta, Fe, Sn, Nb, Mn), has the α–PbO_2 structure type (*11*) but the metal atoms, octahedrally coordinated by oxygen ions, are disordered. Columbite (*12*), ideally $Fe_4Nb_8O_{24}$, is also a variant of the α–PbO_2 structure type but the metals are ordered, resulting in a larger unit cell. The following correlations exist among ixiolite (i), columbite (c), and wodginite (w).

$$a_i \approx a_c \approx b_{w/2},$$
$$b_i \approx b_{c/3} \approx a_{w/2},$$
$$c_i \approx c_c \approx c_w,$$
$$Z = (X_4O_8)_i = (X_{12}O_{24})_c/2 = (X_{16}O_{32})_w/4;$$
$$X = \text{octahedral cation}.$$

The structure of wodginite has not been previously solved unambiguously. The data above suggest, however, that it is another

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variant of the α–PbO_2 structure type in which the metals are ordered, probably in response to stoichiometry imposed requirements. As M–$LiTa_3O_8$ is of simple stoichiometry, the determination of the wodginite structure type is facilitated. A preliminary structure was deduced based on the α–PbO_2 type and an ordering scheme generated by three sets of nonequivalent octahedral cations as suggested by the formulations $Li_4Ta_4Ta_8O_{32}$. Preliminary powder pattern intensity calculations using the program of Smith (*13*) indicated that this structure hypothesis was nearly correct. This paper presents the quantitative determination of the structure.

Experimental

A small single crystal of dimensions 0.04 × 0.05 × 0.06 mm was mounted on a quartz capillary using "araldite" and the following data were determined using a Philips PW 1100 computer controlled diffractometer. Unit-cell parameters were determined with a standard diffractometer computer program which investigates rows in the reciprocal lattice through the origin and scans the highest weighted reflexions and their antireflexions (weighted by intensity and $\sin\theta$). The centres of gravity of these eight profiles are then used in a least-squares refinement of the d spacing for that row.

Crystal data. M–$LiTa_3O_8$, $M = 677.8$, $a = 9.413(5)$, $b = 11.522(6)$, $c = 5.050$ (3) Å, $\beta = 91.05°(10)$. $U = 547.6 A^3$. $D_c = 8.22$ g cm^{-3} for $Z = 4$. The amount of material was insufficient to measure an experimental density. $F(000) = 336$, $\mu = 628$ cm^{-1} for Mo$K\alpha$ radiation ($\lambda = 0.7107$Å). Systematic absences observed were hkl, $h + k = 2n + 1$; $h0l$, h and $l = 2n + 1$, suggesting space group Cc or $C2/c$. As the refinement using $C2/c$[1] progressed normally to a low conventional R and recognizing the potential limitations (extinction, absorption, dispersion) inherent in the data, refinement using Cc was considered unproductive.

Intensity measurements. Intensity measurements were made with the crystal described above using the diffractometer and Mo$K\alpha$ radiation monochromated with a flat graphite monochromator crystal. A unique data set was collected out to 2θ (Mo$K\alpha$) $= 60°$ using the θ–2θ scan technique with a symmetric scan range of $\pm 0.5°$ in 2θ from the calculated Bragg angle, at a scan rate of $0.0168°$ sec^{-1}. No reflection was sufficiently intense to require the insertion of an attenuation filter. Of the 754 independent reflexions measured, 714 were considered to be significantly above the background [$I \geqslant 3\sigma I$] and only these were used in subsequent calculations. Three standard reflexions measured at 2-hr intervals showed no significant variations in intensity.

The data were processed using a program written specifically for the PW 1100 diffractometer (*14*). The background-corrected intensities were assigned standard deviations according to $\sigma(I) = [CT + (t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$ where CT is the total integrated peak count obtained in a scan time t_c; B_1 and B_2 are background counts each obtained in time $\frac{1}{2}t_b$, and $I = CT - (t_c/t_b)(B_1 + B_2)$; p was 0.04. The inclusion of this last term is to allow for "machine errors". Values of I and $\sigma(I)$ were then corrected for Lorentz and polarization effects. Since the plane of reflection of the graphite monochromator was perpendicular to that of the specimen crystal, the Lorentz-polarization correction was:

$$(Lp)^{-1} = \sin 2\theta(1 + \cos^2 2\theta_m)/(\cos^2 2\theta + \cos^2 2\theta_m)$$

where θ_m is the Bragg angle of the monochromator.

A spherical absorption correction was applied to the data based upon a crystal radius of 0.0025 cm ($\mu R = 1.57$). Three reflections were considered to be affected by extinction and were omitted in the final stages of refinement. The atomic scattering factors used were for Ta°, O°, and Li° from Ref. (*15*). All calculations dealing with the structure solution and refinement were per-

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[1] After this investigation powdered M–$LiTa_3O_8$ was examined at NBS using the method of Kurtz and Perry (*24*) for evidence of asymmetry. The test yielded positive results which strongly indicate the true space group as being Cc. This is in accord with recent results of Graham and Thornber (*25*) who investigated the crystal structure of the mineral wodginite.

formed on the Monash University CDC 3200 computer, the major programs used being MONLS, a modified version of the full-matrix program of Busing, Martin, and Levy (*16*), MONDLS, a block-diagonal least-squares program adapted from the 'SF series' of Shiono (*17*), and the Fourier summation program, MONFR (*18*).

Structure Solution and Refinement

The structure was solved for the tantalum atom positions by conventional Patterson techniques and calculation of structure factors, for the two tantalum atoms only, resulted in $R = \sum||F_0| - |F_c||/\sum|F_0| = 0.238$. The four independent oxygen atoms were located in a difference Fourier synthesis and full-matrix least-squares refinement of positional parameters in the succeeding structure factor calculation gave $R = 0.10$. Several further cycles of refinement varying isotropic thermal parameters in addition to weighting reflexions according to the inverse of the variance of the observed structure amplitudes resulted in $R = 0.061$. At this stage it was evident from a difference Fourier synthesis that the tantalum atoms were vibrating somewhat anisotropically and further refinement was carried out using block-diagonal least-squares techniques, which enabled both anisotropic and isotropic thermal parameters (for oxygen) to be varied simultaneously, resulting in $R = 0.043$ and $wR = [\sum w(|F_0| - |F_c|)^2/\sum wF^2]^{1/2} = 0.055$.

In spite of the difference in scattering power between tantalum and lithium efforts were made to locate the latter in the final difference Fourier synthesis, which showed minor variations in the vicinity of the tantalum atoms in particular, with no success.

The final parameters with their estimated standard deviations are presented in Table I.[2]

TABLE I

FINAL ATOMIC PARAMETERS WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) Atoms with anisotropic temperature factors

Atom	x/a	y/b	z/c	U_{11}^{a}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta(1)	0.2415(1)	0.0864(1)	0.2466(2)	0.0023(4)	0.0038(5)	0.0036(4)	0.0008(3)	−0.0007(3)	−0.0002(5)
Ta(2)	0.0	0.3299(1)	0.25	0.0018(6)	0.0029(6)	0.0045(6)	0.0	0.0001(4)	0.0

(b) Atoms with isotropic temperature factors

Atom	x/a	y/b	z/c	B
O(1)	0.3541(20)	0.4516(17)	0.4413(37)	0.62(28)
O(2)	0.3846(22)	0.1788(17)	0.4270(39)	0.61(27)
O(3)	0.1332(20)	0.4375(18)	0.0792(36)	0.48(26)
O(4)	0.1185(22)	0.1967(18)	0.1069(38)	0.64(28)
Li	0.0000	0.8034	0.2500	—

[a] The anisotropic temperature factor is of the form:

$$\exp[-\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

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[2] A table of observed and calculated structure factors has been deposited as Document No. NAPS-02747 with the ASIS National Auxiliary Publications Service C/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016. A copy may be secured by citing the document number and by remitting $5.00 for photocopies or $3.00 for microfiche. Advance payment is required. Make check or money order payable to "Microfiche Publications".

Description of the Structure

The M-$LiTa_3O_8$ structure consists of a slightly distorted hexagonal close-packed array of oxygen anions with Ta^{5+} ions occupying octahedral sites in an ordered arrangement. As indicated earlier it was not possible to locate the Li^+ ions in the presence of the dominant scattering due to the Ta^{5+} ions. However, by comparison with L-$LiNb_3O_8$ (*19*, *20*) with which L-$LiTa_3O_8$ was shown to be isostructural (*20*), and bearing in mind the suggested weak tendency of Ta^{5+} to share octahedral edges (see later) and the unlikely possibility of face-sharing with tantalum, the lithium ions were placed in octahedral sites as shown in Fig. 1. This figure has been drawn to emphasize the relationship of the structure of this compound to that of α-PbO_2 (*11*) and is an [001] projection, the c axis being characteristically ~5.0 Å long. For comparison the structure of L-$LiTa_3O_8$ is illustrated in Fig. 2 as an [0$\bar{1}$0] projection and shows clearly the difference in ordering of the Li^+ and Ta^{5+} ions between the L- and M-forms of this compound.

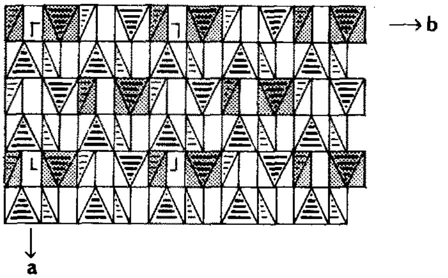


FIG. 1. An [001] projection (idealized) of the structure of M-$LiTa_3O_8$. Li atom octahedra are shaded, and the unit-cell outline shown.

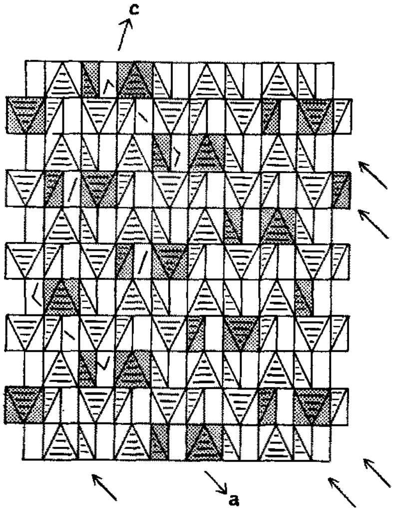
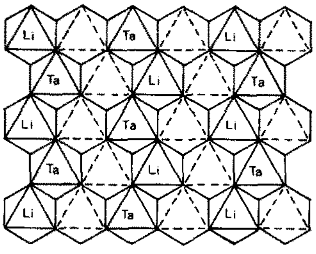
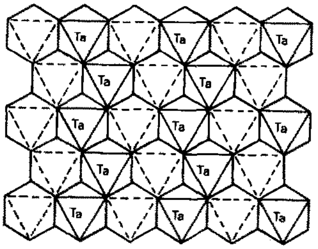


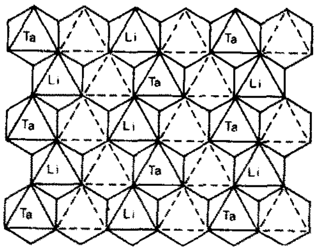
FIG. 2. An [0$\bar{1}$0] projection (idealized) of the structure of L-$LiTa_3O_8$. Li atom octahedra are shaded and the unit-cell outline shown. Arrows point along the 'strips' of structure, discussed in the text, that are parallel to the a axis. This direction corresponds to the [110] direction in M-$LiTa_3O_8$.



Layer 1



Layer 2



Layer 3

FIG. 3. Three of the four layers of octahedra that make up the M-$LiTa_3O_8$ structure. These are stacked in the order 1, 2, 3, 2, 1, . . ., layer 4 being a repeat of layer 2.

In Fig. 2 (L-$LiTa_3O_8$) "strips" of the structure parallel to the a axis are indicated by pairs of arrows indicating Li atom sites.

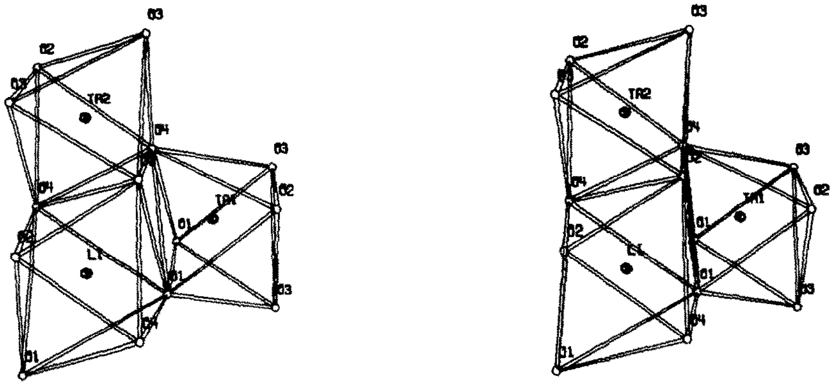


FIG. 4. A stereoscopic diagram of the Li and Ta octahedra that comprise the asymmetric unit of the structure of M-$LiTa_3O_8$.

The M-form structure is generated if the Li atoms in these strips are moved one octahedron in the direction of the arrows (or in the reverse direction), thus resulting in a more ordered arrangement of Li and Ta atoms. The four layers of metal–oxygen octahedra which make up the structure are shown in Fig. 3. Layer 1 contains staggered 'ribbons' of Li and Ta octahedra interspersed by vacant octahedra; layer 2 consists of Ta octahedra + vacant octahedra, and layer 3 has Li and Ta interchanged with respect to layer 1. Layer 4 is a repeat of layer 2. The nonidealized octahedra of oxygen atoms surrounding Li, Ta(1) and Ta(2) are shown in Fig. 4, a stereoscopic drawing (*21*), which also gives the numbering scheme used in Tables I and II.

Selected bond lengths and angles are listed in Table II and are within the ranges observed for other similar compounds.

Relationship between M-$LiTa_3O_8$ and the Mineral Wodginite

Published chemical analyses for the mineral (*4*, *5*) and phase equilibria data for synthetic products (*9*) reveal that wodginite is a chemically complex species. This complexity can be rationalized by considering the crystal structure of M-$LiTa_3O_8$ which represents the ideal, fully ordered prototype of wodginite-type phases. If the unit cell content of wodginite is expressed as $A_4B_4C_8O_{32}$, where A, B, and C are nonequivalent octahedrally coordinated cations, several chemical features become apparent. A minimum of eight Ta^{5+} cations are essential and these fill the C site. The structure tolerates very little, if any, Nb^{5+} at this site judging from chemical analyses of natural material. This point will be discussed later with respect to $LiNb_3O_8$. Given a $[Ta_8O_{32}]^{24-}$ configuration, the A and B sites are filled by appropriate cations which can easily order and which provide for charge compensation. The simplest stoichiometry M-$LiTa_3O_8$ ($Li_4Ta_4Ta_8O_{32}$) has the greatest disparity between positive charges at the A and B sites, thus facilitating the ordering process. In natural and synthetic wodginite-type phases, excess Ta^{5+} and any available Nb^{5+} partially fill the B site. The remainder consists of other highly charged cations, Sn^{4+}, Fe^{3+}, and possibly Ti^{4+}. The A site is occupied by a total of four cations of low charge, Li^+, Mn^{2+} and probably Fe^{2+}. Normally, the dominant constituent of the A site is manganese.

The considerations above permit structural formulations of chemically analyzed wodginite from Wodgina, Australia and from Bernic Lake, Manitoba to be approximated by,[3]

$$Mn_{3.98}[Fe_{0.48}Sn_{1.54}Nb_{1.49}Ta_{0.29}]Ta_8O_{32}$$

[3] The structure of natural wodginite proposed by Graham and Thornber (*25*) is essentially identical to that herein. The octahedral sites occupied by Mn are in this case occupied by Li and the remaining octahedral sites are occupied by Ta.

and

$$[Mn_{3.38}Fe_{0.62}][Ti_{0.79}Fe_{0.07}Sn_{2.32}Nb_{0.27}Ta_{0.40}]Ta_8O_{32},$$

respectively. Some error is inherent in the analyses as the iron and manganese oxidation states could not be determined and hence were calculated on the basis of FeO and MnO (*4*). Turnock (*9*), however, has shown that wodginite in the $MnTa_2O_6$–$FeTaO_4$ system contains Fe^{3+} and Mn^{2+}. Typical end-member compositions in the wodginite homogeneity range can be formulated as

$$Mn_4[Mn_{0.91}Fe_{0.64}Ta_{2.45}]Ta_8O_{32}$$

and

$$[Mn_{3.78}Fe_{0.22}][Fe_{2.10}Ta_{1.90}]Ta_8O_{32}.$$

Within this series, synthetic wodginite remains stoichiometric as a potential A or B site deficiency is compensated by either a small excess of Fe^{3+} or Mn^{2+}.

TABLE II

SELECTED INTERATOMIC DISTANCES WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Ta(1)–O(4)	1.85(2)	Ta(2)–O(2)^{Va}	1.95(2)
O(1)^{Va}	1.88(2)	O(2)^{VIId}	1.95(2)
O(2)	1.93(2)	O(3)	1.97(2)
O(1)^{VIb}	2.02(2)	O(3)^{II}	1.97(2)
O(3)^{V}	2.06(2)	O(4)	2.04(2)
O(3)^{VIb}	2.25(2)	O(4)^{II}	2.04(2)
Li–O(2)^{IVg}	2.02(2)	O(1)–O(3)^{IIIf}	2.55(3)
O(2)^{VI}	2.02(2)	O(3)	2.75(3)
O(4)^{If}	2.10(2)	O(1)^{IIIf}	2.76(3)
O(4)^{IIIf}	2.10(2)	O(1)^{IIIh}	2.76(3)
O(1)^{IVg}	2.41(2)	O(2)^{Va}	2.79(3)
O(1)^{VI}	2.41(2)	O(4)^{VI}	2.85(3)
		O(4)^{Va}	2.86(3)
		O(1)^{II}	3.01(3)
Ta(1)–Ta(1)^{III}	3.215(1)		
Ta(1)^{IIIc}	3.215(1)		
Ta(2)	3.611(2)		
Ta(1)–Li	3.489(1)		
Ta(2)–Li	2.955(1)		

The numbering of the atoms is in accordance with that shown in Table I, with Roman numerals indicating the symmetry transformation involved and letters indicating that the atom is in an adjacent cell, the relationship of which to the primary unit cell is given by:

a	0, 0, +.	*c*	0, 0, −.	*e*	0, +, +.
b	0, −, 0.	*d*	−, 0, −.	*f*	0, +, 0.
g	−, 0, 0.	*i*	+, +, +.		
h	0, +, −.				

Symmetry transformation.

I $\bar{x}, \bar{y}, \bar{z}$; II $\bar{x}, y, \frac{1}{2} - z$; III $x, \bar{y}, \frac{1}{2} + z$;
IV $\frac{1}{2} + x, \frac{1}{2} + y, z$; V $\frac{1}{2} - x, \frac{1}{2} - y, \bar{z}$;
VI $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$;
VII $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

The complex stoichiometries noted above also lead to the conclusion that wodginites can deviate in varying degrees from nearly perfect order. Within the A and B sites, a disordering of cation appears necessary. It, therefore, follows that A versus B site ordering, enhanced by a large difference between average positive charges at these sites, is the dominant driving force for phase stabilization. This phenomenon is supported by the phases $A_4^{3+}B_4^{3+}Ta_8O_{32}$ (i.e., $FeTaO_4$ and $MnTaO_4$) and $A_4^{2+}[B_{1\frac{1}{3}}^{2+}Ta_{2\frac{2}{3}}]Ta_8O_{32}$ (i.e. $MnTa_2O_6$ and $FeTa_2O_6$) which adopt rutile, trirutile, or columbite structures rather than that of wodginite.

$LiNb_3O_8$ does not have the wodginite structure but is a monoclinic variant of the α-PbO_2 type wherein Li^+ and Nb^{5+} cations are ordered in a different arrangement (*19*, *20*). Blasse (*21*) has suggested that the structural differences among oxides containing M^{5+} can be understood qualitatively by considering possible metal–metal bonding (pairing) between M^{5+} cations. He concluded that this bonding is very effective for Nb^{5+}, not effective for Sb^{5+}, and only weakly effective for Ta^{5+}. Structural and thermal stability data for $LiNb_3O_8$ and $LiTa_3O_8$ lend further support to this hypothesis. In $LiNb_3O_8$, Li^+ ions are ordered in a complex manner such that the edge-sharing of octahedra containing Nb^{5+} is maximized. The phase does not transform to other polymorphs and remains stable to its incongruent melting point (*1*). $LiTa_3O_8$, however, is trimorphic (*1*). Below 800°C, the compound is isostructural with $LiNb_3O_8$ (*20*). Above 800°C, this form transforms irreversibly to M-$LiTa_3O_8$ which is characterized by less edge-sharing of octahedra containing Ta^{5+} as a result of the simpler ordering configuration of Li^+ atoms. The fact that the phase has monoclinic rather than orthorhombic symmetry may suggest that a slight distortion ($\beta < 92°$) is necessary to favor the existing pairing of Ta^{5+}. M–$LiTa_3O_8$ irreversibly transforms above ~1150°C to another modification unrelated to the α–PbO_2 structure type (*23*) in any simple way.

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