Synthesis and Crystal Structure of Rb_3AgO_2

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Received June 18th, 2002.

Dedicated to Professor Dieter Fenske on the Occasion of his 60th Birthday

Abstract. Rb_3AgO_2 was prepared via the azide/nitrate route. Stoichiometric mixtures of the precursors (Ag_2O, RbN_3 and $RbNO_3$) were heated in a special regime up to 450 °C and annealed at this temperature for 50 h in silver crucibles. Single crystals have been grown by subsequent annealing of the as prepared powder at 450 °C for 500 h in silver crucibles, which were sealed in glass ampoules under dried Ar. According to the X-ray analysis of the crystal structure ($P2_12_12_1$, $Z = 16$, $a = 12.800(1)$, $b = 12.848(1)$, $c = 14.329(1)$ Å, 6566 independent reflections, R(all) = 0.0795, R_w(all) = 0.0218), Rb_3AgO_2 is isostructural with K_3AgO_2. The structure can be derived from the fluorite structure type. Silver is linearly coordinated by oxygen atoms, while Rb has pseudo-tetrahedral coordination. The crystal under investigation was composed of four twin individuals.

Keywords: Silver; Rubidium silver oxide; Crystal structure; Twinning; Azide/nitrate route.

Synthese und Kristallstruktur von Rb_3AgO_2

Inhaltsübersicht. Rb_3AgO_2 wurde über die Azid/Nitrat-Route dargestellt. Stöchiometrische Gemenge der Edukte (Ag_2O, RbN_3 und $RbNO_3$) wurden unter besonderer Temperaturführung bis 450 °C aufgeheizt und bei dieser Temperatur 50 Stunden in Silbertiegeln getempert. Durch nachträgliches Tempern des erhaltenen Pulvers (450 °C, 500 h) in Silbertiegeln, die unter getrocknetem Ar in Glasampullen eingeschmolzen waren, wurden Einkristalle erhalten. Nach der Röntgenstrukturanalyse ($P2_12_12_1$, $Z = 16$, $a = 12{,}800(1)$, $b = 12{,}848(1)$, $c = 14{,}329(1)$ Å, 6566 unabhängige Reflexe, R(alle) = 0.0795, R_w(alle) = 0.0227) ist Rb_3AgO_2 isotyp zu K_3AgO_2. Die Struktur kann vom Fluorit-Typ abgeleitet werden. Silber ist linear von Sauerstoffatomen koordiniert, während das Rubidium eine pseudotetraedrische Umgebung aufweist. Der untersuchte Kristall war systematisch verzwillingt und wurde über vier Zwillingsindividuen beschrieben.

Introduction

Alkali metal oxoargenates(I) are known to form families of the compositions AAg_3O_2 (A = Li [1], Na [2]), AAgO (A = Li[3], Na[4], K [4, 5], Rb[4, 6, 7], Cs[4, 5, 7]), and A_3AgO_2 (A = Na [3], K [8, 9]). Within each family the constitution of the oxoargentate anion is uniformly determined by the Ag/O ratio, and the degree to which the basic linear unit AgO_2 is condensed varies from isolated (A_3AgO_2) through oligomeric $[Ag_4O_4]$ (AAgO) to infinite-crosslinked $^1_\infty[AgO_{2/3}]$ (AAg_3O_2). Na_3AgO_2 and K_3AgO_2 show particularly close relationships to the structures of the respective parent alkali metal oxides. However, the cation ordering is significantly different. Here we report on the synthesis and structure determination of the new homologue Rb_3AgO_2.

Results and Discussion

Rb_3AgO_2 can be readily prepared by the azide/nitrate route [10] as a micro-crystalline powder. The colourless products are extremely sensitive to air and moisture, and turn black, immediately, when exposed to humid air. The DTA/TG analysis has shown that Rb_3AgO_2 starts melting at ~620 °C.

The crystal structure of the novel rubidium argenate, which crystallises orthorhombic ($P2_12_12_1$), was determined from a crystal which showed systematic twinning as is already suggested by the observed pseudotetragonal metrics. Four individuals have to be taken into account (see Table 1). The second individual results from the first through a rotation by 90° around the crystallographic c-axis; the third one is connected via a centre of symmetry, and the fourth is the resulting rotoinversion by 90°. Of the four individuals only the first three have significant volume fractions. Although the sum of individual I and III already account for 90 % of the complete volume of the crystal the introduction of individuals II and IV in the refinement process led to a considerable improvement of the agreement factors (about 3 %) and thus confirmed the correctness of the description.

For further details of the measurement, structure determination and additional crystallographic data see Tables 1−3. Interatomic distances, coordination numbers (CN), effective coordination numbers (ECoN) and mean fictive ionic radii (MEFIR) [11] for Rb_3AgO_2 are given in Table 4. The difference between the Madelung part of lattice energy

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Table 1 X-ray and crystallographic data for Rb_3AgO_2 (293 K)

Crystal data	
Crystal system	Orthorhombic
Space group, Z	$P2_12_12_1$ (no 19), 16
Lattice constants (from powder), Å	a = 12.800(1) b = 12.848(1) c = 14.329(1)
Molar volume, cm^3/mol	88.86
Calculated density, g/cm^3	4.47
Crystal shape, color	irregular, colourless
Crystal size, mm	0.2 x 0.1 x 0.1
Data collection	
Diffractometer	STOE IPDS II
Monochromator	Graphite
Wavelength, Å	MoK_α, 0.71073
2Θ range for data collection	$2.0 < 2\Theta < 59.1$
$h.k.l$-range	$-17 < h < 17$, $-17 < k < 17$, $-19 < l < 19$
Absorption correction	Gauss [14]
T_{min}, T_{max}	0.2497, 0.6504
Total no. reflection	24749
Unique reflections	6566
Absorption coefficient. μ (mm^{-1})	27.9
F(000)	2784.0
Structure refinement	
Structure solution	SHELXS97 [15]
Structure refinement	Jana2000 [16]
Parameters refined	221
R(obs) (> 3σ)	0.0398
R_w(obs)	0.0218
R(all)	0.0795
R_w(all)	0.0227
Twin matrix II	$010 / \bar{1}00 / 001$
Twin matrix III	$\bar{1}00 / 0\bar{1}0 / 00\bar{1}$
Twin matrix IV	$0\bar{1}0 / 100 / 00\bar{1}$
Twin volume I	0.39(2)
Twin volume II	0.10(1)
Twin volume III	0.48(1)
Twin volume IV	0.02(1)
Extinction coefficient	0.0393(6)

Table 2 Atomic coordinates and isotropic displacement parameters for Rb_3AgO_2

atom	x	y	z	U_{iso}
Ag1	0.9997(2)	0.9977(2)	0.17544(7)	0.0192(3)
Ag2	0.2342(1)	0.2557(1)	0.9195(1)	0.0198(4)
Ag3	0.9993(2)	0.9906(2)	0.85054(8)	0.0205(3)
Ag4	0.2288(1)	0.2341(1)	0.5929(1)	0.0189(4)
Rb1	0.2021(2)	0.3038(2)	0.1452(2)	0.0333(7)
Rb2	0.9895(2)	0.0045(2)	0.4249(1)	0.0325(5)
Rb3	0.1959(2)	0.1971(2)	0.3607(2)	0.0321(7)
Rb4	0.0685(2)	0.9168(2)	0.6281(1)	0.0386(6)
Rb5	0.0057(2)	0.2127(1)	0.7272(1)	0.0498(7)
Rb6	0.9805(2)	0.2846(2)	0.4944(1)	0.0287(6)
Rb7	0.9874(2)	0.1997(2)	0.0075(1)	0.0235(6)
Rb8	0.9474(1)	0.2497(2)	0.2443(1)	0.0219(4)
Rb9	0.2055(2)	0.0100(2)	0.0088(1)	0.0230(6)
Rb10	0.7826(2)	0.9790(2)	0.0092(1)	0.0239(6)
Rb11	0.2471(2)	0.9554(2)	0.2612(1)	0.0237(6)
Rb12	0.7346(2)	0.0440(2)	0.2441(1)	0.0251(6)
O1	0.610(1)	0.390(1)	0.823(1)	0.028(5)
O2	0.390(1)	0.616(1)	0.822(1)	0.036(6)
O3	0.349(1)	0.146(1)	0.917(1)	0.028(4)
O4	0.124(1)	0.366(1)	0.939(1)	0.031(5)
O5	0.387(1)	0.401(1)	0.143(1)	0.023(4)
O6	0.115(1)	0.884(1)	0.839(1)	0.029(5)
O7	0.339(1)	0.347(1)	0.607(1)	0.023(4)
O8	0.123(1)	0.120(1)	0.569(1)	0.032(5)

(MAPLE) [12] of Rb_3AgO_2 and that calculated for the sum of the binary oxides (see Table 5) is satisfactorily low (0.98 %).

Table 3 Anisotropic thermal displacement parameters (in $Å^2$) for Rb_3AgO_2

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ag1	0.0196(5)	0.0173(5)	0.0206(4)	−0.0003(5)	−0.0003(9)	−0.0004(7)
Ag2	0.0176(7)	0.0197(7)	0.0222(6)	0.0010(6)	0.0015(6)	0.0012(6)
Ag3	0.0187(5)	0.0211(7)	0.0217(5)	0.0006(5)	−0.0011(8)	−0.0002(7)
Ag4	0.0199(8)	0.0162(7)	0.0207(6)	0.0007(6)	0.0008(6)	0.0002(6)
Rb1	0.039(1)	0.035(1)	0.027(1)	−0.018(1)	0.006(1)	−0.0043(9)
Rb2	0.028(1)	0.0286(8)	0.0406(7)	0.0060(8)	0.001(1)	0.004(1)
Rb3	0.031(1)	0.033(1)	0.032(1)	0.013(1)	−0.002(1)	−0.001(1)
Rb4	0.038(1)	0.045(1)	0.0320(9)	−0.0170(9)	−0.0076(9)	0.0006(8)
Rb5	0.055(1)	0.040(1)	0.054(1)	0.021(1)	0.029(1)	0.0219(9)
Rb6	0.025(1)	0.031(1)	0.031(1)	0.0025(9)	−0.004(1)	−0.008(1)
Rb7	0.026(1)	0.0209(8)	0.0242(9)	−0.0007(9)	0.0002(9)	−0.0003(8)
Rb8	0.0215(6)	0.0223(8)	0.0218(7)	0.001(1)	−0.0002(9)	−0.0002(6)
Rb9	0.024(1)	0.023(1)	0.0228(9)	0.0001(8)	0.0018(8)	0.0017(9)
Rb10	0.025(1)	0.0211(8)	0.026(1)	−0.0003(8)	0.0005(9)	−0.0002(8)
Rb11	0.024(1)	0.024(1)	0.0226(8)	−0.0030(8)	0.0007(8)	0.0006(8)
Rb12	0.0232(9)	0.027(1)	0.025(1)	0.0001(8)	0.0029(8)	0.0024(8)
O1	0.041(8)	0.013(8)	0.031(8)	−0.006(6)	−0.002(7)	−0.004(7)
O2	0.012(10)	0.044(9)	0.050(10)	0.020(7)	−0.008(8)	0.005(7)
O3	0.045(9)	0.022(7)	0.017(7)	−0.002(6)	0.005(6)	−0.003(6)
O4	0.025(10)	0.020(7)	0.048(9)	0.010(7)	−0.005(8)	0.003(7)
O5	0.016(7)	0.029(7)	0.024(6)	−0.006(5)	0.001(6)	−0.003(6)
O6	0.017(7)	0.029(8)	0.040(8)	0.013(6)	0.011(6)	−0.008(7)
O7	0.031(8)	0.019(6)	0.019(6)	0.004(6)	−0.001(6)	0.001(5)
O8	0.037(8)	0.009(7)	0.048(9)	−0.016(6)	0.005(7)	−0.006(7)

The most characteristic feature of the structure is the linear AgO_2^{3-} anion, with d(Ag-O) ranging from 2.00 to 2.04 Å and O-Ag-O angles from 173.1° for Ag2 to 178.0° for Ag1. These data, related to the silver(I) anion, are basically in agreement for Rb_3AgO_2, K_3AgO_2 [8] and Na_3AgO_2 [3]. Yet the Ag-O distances in K_3AgO_2 as reported in [8] show a surprisingly wide spread from 1.91 to 2.10 Å (distances reported in the paper range from 1.95 to 2.12 Å but do not correspond to the given coordinates and lattice parameters). These distances do not appear very convincing and in particular a Ag-O bond length as short as 1.91 Å is without precedence. Furthermore, the displacement parameters of some of the potassium atoms are non positive definite and the oxygen atoms were refined only isotropically. One might imagine that the crystals of K_3AgO_2 were also twinned, but that the twinning was not taken into account during the structure refinement. In this context it is interesting that a refinement of Rb_3AgO_2 without taking into consideration the systematic twinning leads to a model in which the Ag-O bond lengths also show a stronger variation (from 1.98 to 2.09 Å).

All AgO_2 dumb-bells in Rb_3AgO_2 are oriented parallel (001), one half directing along $[\bar{1}10]$ and one half along the [110] direction (Fig. 1). This is different to Na_3AgO_2, where the AgO_2 dumb-bells are arranged along the [001] axis and point alternatively along the [120] and $[1\bar{2}0]$ direction.

The Rb atoms are coordinated pseudotetrahedrally by oxygen. An exception is Rb5 which has only three nearest neighbours, for this atom the fourth neighbour is shifted and is located at a considerably large distance of 3.92(2) Å. Some of the Rb-O distances are rather small with values below 2.7 Å. These, however, are comparable to other short Rb-O distances as observed in literature e.g. in Rb_2PbO_2 [17] or Rb_2TeO_3 [18]. The cation cation distances are in the range of 3.3-3.8 Å, which is quite common to that of other

Table 4 Interatomic distances (in Å). coordination numbers (CN). effective coordination numbers (EcoN) and mean fictive ionic radii (MEFIR) [11] for Rb_3AgO_2

atom	O1	O2	O3	O4	O5	O6	O7	O8	C.N.	ECoN	MEFIR
Ag1	2.02(2)	2.03(2)							2	2.0	0.62
Ag2			2.04(2)	2.01(2)					2	2.0	0.63
Ag3					2.00(1)	2.03(2)			2	2.0	0.61
Ag4							2.04(2)	2.03(2)	2	2.0	0.63
Rb1	2.79(2)	2.98(2)		3.22(2)	2.68(1)				4	3.4	1.34
Rb2			2.83(2)	3.02(2)			2.75(2)	3.07(2)	4	3.8	1.42
Rb3	3.06(2)	2.69(2)				2.65(2)		3.28(2)	4	3.0	1.30
Rb4			3.31(1)	2.73(2)		3.10(2)		2.83(2)	4	3.2	1.39
Rb5					2.81(1)	2.85(2)		2.97(2)	3	3.0	1.44
Rb6		3.23(2)				2.97(2)	2.87(1)	2.99(2)	4	3.7	1.52
Rb7	3.12(2)		2.87(2)	2.93(2)	2.83(1)				4	3.8	1.47
Rb8	2.91(2)	2.92(2)	2.95(2)				2.83(1)		4	4.0	1.46
Rb9	3.00(2)		2.86(2)			3.15(2)		2.89(2)	4	3.8	1.51
Rb10		3.04(2)		2.94(2)	2.99(1)		2.85(1)		4	3.9	1.50
Rb11	2.91(2)		2.86(2)			2.94(2)		3.36(2)	4	3.5	1.50
Rb12		3.02(2)		3.19(2)	2.90(1)		2.89(1)		4	3.8	1.53
C.N.	7	7	7	7	6	7	6	8			
ECoN	6.5	6.6	6.3	6.2	5.9	6.5	6.0	6.8			
MEFIR	1.46	1.47	1.43	1.46	1.41	1.45	1.40	1.47			

Table 5 Madelung part of lattice energy (MAPLE) for Rb_3AgO_2 (in kcal/mol)

atom	binary	ternary	ΣΔ[a]
Ag1	132.5[b]	137.6	+5.0
Ag2	132.5	135.9	+3.2
Ag3	132.5	132.0	−0.7
Ag4	132.5	132.5	−0.1
Rb1	100.2[c]	118.0	+17.8
Rb2	100.2	120.1	+19.8
Rb3	100.2	113.8	+13.6
Rb4	100.2	106.4	+6.2
Rb5	100.2	91.3	−8.9
Rb6	100.2	89.2	−11.1
Rb7	100.2	95.7	−4.5
Rb8	100.2	98.9	−1.3
Rb9	100.2	88.1	−12.1
Rb10	100.2	100.8	+0.6
Rb11	100.2	86.1	−14.1
Rb12	100.2	96.9	−3.2
O1	453.8[b]	384.8	−69.0
O2	453.8	378.9	−74.9
O3	372.5[c]	385.7	+13.1
O4	372.5	373.9	+1.3
O5	372.5	389.3	+16.7
O6	372.5	396.7	+24.2
O7	372.5	387.2	+14.6
O8	372.5	387.4	+14.9
Σ	4875.0	4827.3	Δ = −47.7 (−0.98 %)

[a] ternary-binary: MAPLE(Rb_3AgO_2) − 1.5 MAPLE(Rb_2O) − 0.5 MAPLE-(Ag_2O)
[b] from Ag_2O
[c] from Rb_2O

complex alkali transition metal oxides like Na_2RbAuO_2 [19] or Cs_3AuO_2 [20].

The Rb_3AgO_2 structure can be derived from that of Rb_2O (*anti* CaF_2 type) by substituting silver for one fourth of the rubidium atoms which are located at the tetrahedral sites of the *fcc* packing of oxygen atoms: $Rb_3AgO_2 \triangleq Rb_4O_2$.

Viewing along [001] one can distinguish two different types of chains of edge sharing tetrahedra. One type is occupied exclusively by rubidium (Rb5-Rb12, Fig. 1 top), the second one contains rubidium and silver in equal amounts (Rb1-Rb4 and Ag1-Ag4, Fig. 1 bottom). The ordering sequence along [001] in the mixed rows is -Ag-Ag-Rb-Rb- (Fig. 2; right).

Because of the strong preference for a linear twofold coordination silver is shifted from the centre to the edge of the tetrahedra. The rubidium atoms are necessarily influenced by these shifts and move in directions of neighbouring octahedral sites. As a consequence, the tetrahedral sites of the fluorite parent structure are now empty (Fig. 2, right) in the partial structure discussed.

A similar mode of substitution can also be applied to derive the structures of K_3CuO_2 and Na_3AgO_2 from the respective alkali metal oxides.

Experimental

Starting materials for the preparation of Rb_3AgO_2 were rubidium nitrate (Johnson Matthey, 99 %), rubidium azide and silver oxide Ag_2O (Johnson Matthey, 99 %). Rubidium azide was synthesised [13] from aqueous HN_3 and rubidium carbonate (Johnson Matthey, 99 %). The starting materials (RbN_3, $RbNO_3$ and Ag_2O) were mixed in the required ratio according to the equation

$$5\ RbN_3 + RbNO_3 + Ag_2O = 2\ Rb_3AgO_2 + 8\ N_2,$$

ground in a planet ball mill, pressed in pellets under 10^5 N, dried under vacuum (10^{-3} mbar) at 150 °C for 12 h, and placed under argon in a tightly closed steel container provided with a silver inlay. In a flow of dry argon the following temperature treatment was applied: 25→260 °C (100 K/h); 260→380 °C (5 K/h); 380→450 °C (50 K/h) followed by subsequent annealing for 50 h at 450 °C.

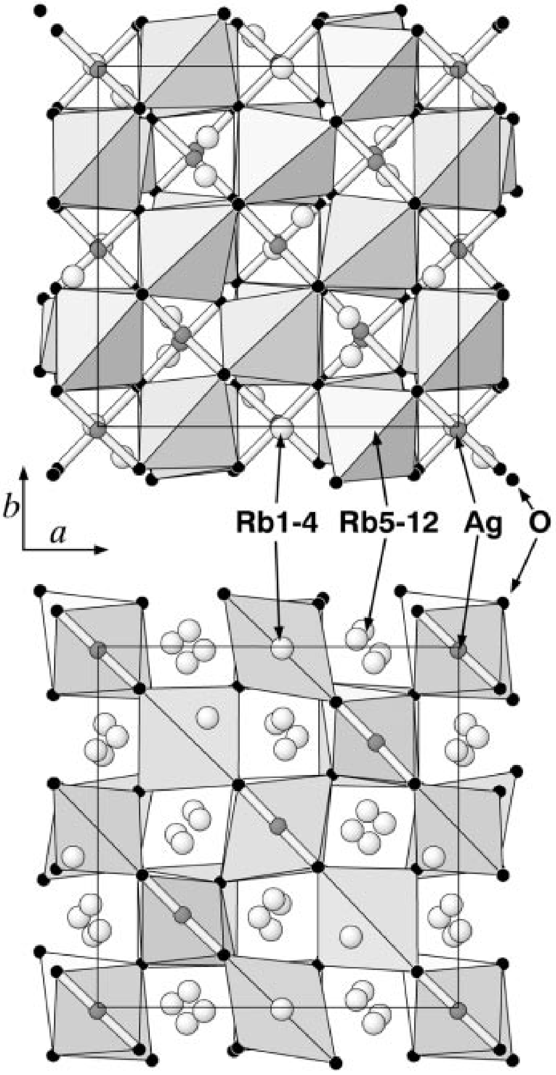

Fig. 1 Crystal structure of Rb_3AgO_2, emphasising the chains of edge sharing tetrahedra fully occupied by rubidium (**top**), and with rubidium and silver (**bottom**); see text.

The obtained colourless powder was sealed in glass ampoules under argon atmosphere and all following manipulations were performed in inert atmospheres of purified argon. Single crystals have been grown by subsequent annealing of the as prepared powder at 450 °C for 500 h in silver crucibles, which were sealed in glass ampoules under dried Ar. The X-ray investigation on a powder sample was performed on a STOE Stadi P diffractometer with Cu-Kα_1 radiation (λ=1.54178 Å) at room temperature using a position sensitive detector and a curved germanium monochromator. The powder diffraction experiment confirms he pureness of the sample (Table 6). Details on single crystal diffraction experiments are given in Table 1.

Thermal analyses were carried out using a DTA/TG device (STA 409, Netzsch) coupled with a quadrupole mass spectrometer (QMG 421, Balzers). The sample (m = 46.2 mg) was heated at a rate of 10 K/min in a corundum crucible under dry argon.

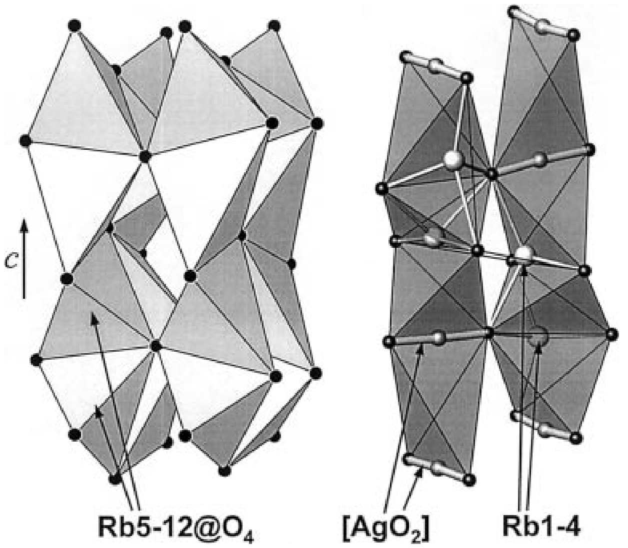

Fig. 2 Sections of the crystal structure of Rb_3AgO_2, showing edge sharing edge sharing tetrahedra, all centred by rubidium (**left**), with silver and rubidium shifted off-centre (**right**).

Table 6 Powder diffraction data of Rb_3AgO_2 (d > 2.25 Å). Results of a profile fit using the local parameters from the single crystal investigation.

h	*k*	*l*	*d*/Å	I/I_0 (%)	*h*	*k*	*l*	*d*/Å	I/I_0 (%)
1	1	1	7.6626	2.2	1	4	1	3.0443	9.8
0	1	2	6.2571	0.1	1	2	4	3.0391	2.2
1	0	2	6.2518	0.1	2	1	4	3.0372	8.7
0	2	1	5.8619	0.1	4	1	1	3.0347	1.3
2	0	1	5.8434	0.3	3	3	1	2.9575	16.6
1	2	0	5.7413	0.2	0	4	2	2.9309	0.1
2	1	0	5.7288	0.7	1	4	2	2.8570	0.5
1	2	1	5.3294	0.9	2	3	3	2.8540	0.2
2	1	1	5.3192	0.4	3	2	3	2.8513	3.4
0	2	2	4.7829	1.5	4	1	2	2.8490	0.8
2	0	2	4.7729	1.3	2	4	1	2.8148	1.6
2	2	0	4.5338	1.0	2	2	4	2.8107	100.0
1	1	3	4.2257	5.4	4	2	1	2.8087	0.5
3	0	1	4.0892	0.1	1	0	5	2.7965	1.0
3	1	1	3.8966	0.3	0	3	4	2.7476	1.0
0	2	3	3.8328	0.3	1	1	5	2.7325	22.0
2	0	3	3.8278	0.4	3	1	4	2.6829	0.3
1	2	3	3.6718	0.7	2	4	2	2.6648	5.2
2	1	3	3.6685	0.4	4	2	2	2.6596	4.0
3	0	2	3.6658	0.7	4	0	3	2.6585	0.3
2	3	0	3.5592	0.1	1	4	3	2.6093	0.4
1	3	2	3.5331	1.1	3	4	0	2.5661	0.4
2	3	1	3.4543	0.5	1	2	5	2.5640	2.1
0	1	4	3.4505	0.1	4	3	0	2.5634	1.4
3	2	1	3.4496	1.8	2	1	5	2.5629	1.2
1	1	4	3.3316	0.1	3	3	3	2.5541	24.2
2	2	3	3.2882	0.6	3	4	1	2.5259	1.0
0	4	0	3.2120	24.7	2	3	4	2.5248	6.1
4	0	0	3.2000	30.9	3	2	4	2.5230	1.3
0	3	3	3.1885	0.7	1	5	1	2.4813	10.4
2	3	2	3.1875	5.8	5	1	1	2.4730	7.9
3	2	2	3.1839	1.0	0	5	2	2.4187	1.2
3	0	3	3.1820	0.1	4	3	2	2.4136	0.5
0	4	1	3.1342	1.2	0	4	4	2.3914	1.6
0	2	4	3.1286	0.2	4	0	4	2.3865	2.3
2	0	4	3.1258	0.1	3	0	5	2.3789	3.6
4	0	1	3.1230	0.1	0	1	6	2.3479	0.8
1	4	0	3.1154	2.3	1	0	6	2.3476	0.7
4	1	0	3.1051	12.8	4	1	4	2.3463	1.0
1	3	3	3.0940	28.7	4	4	0	2.2670	24.5
3	1	3	3.0886	18.1	5	0	3	2.2563	3.8

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