Symmetry Breaking in Ligand-Protected Gold Clusters

Probed by Nonlinear Optics

Electronic Supplementary Information

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1. Synthesis and Isolation

All materials used were purchased from standard suppliers and were used without further purification. Nanopure water was used.

Synthesis of $Au_{38}(SCH_2CH_2Ph)_{24}$ and $[Au_{25}(SCH_2CH_2Ph)_{18}]^{0.1}$ HAuCl₄*3H₂O (1.0 g) was dissolved in 200 mL methanol, L-glutathione (3.1 g) was dissolved in 100 mL water. The two solutions were combined at room temperature and stirred at 0 °C for 15 min. Next, sodium borohydride (1.3 g in 60 mL water) was added. The mixture immediately turned black. The reaction was stirred for 60 min and centrifuged. The precipitate was dissolved in 10 mL water. 15 mL neat 2-phenylethanethiol and 10 mL acetone were added. The mixture was stirred at 80 °C for 3 hours. After cooling to room temperature, the mixture was extracted with dichloromethane. The aqueous phase was discarded and the organic phase was washed with brine (three times) and concentrated to near dryness by rotary evaporation. Then, the clusters were precipitated by addition of ethanol. The clusters were filtered, re-dissolved in dichloromethane, concentrated to near dryness and washed with ethanol. This was repeated five times. Then, the clusters were dissolved in dichloromethane and passed over a syringe filter (PTFE, 0.2 µm) to remove insoluble material. Au₃₈(SCH₂CH₂Ph)₂₄ and [Au₂₅(SCH₂CH₂Ph)₁₈]⁰ clusters were isolated from the crude product by repeated size-exclusion chromatography (Biorad BioBeads S-X10, tetrahydrofuran). The pure clusters were washed with methanol (three times) prior to characterization.

 $[Au_{25}(capt)_{18}]^{-2}$ Tetrachloroauric acid (78 mg) and TOAB (127 mg) were dissolved in methanol (10 mL) under stirring. After 10 min, captopril (218 mg in 5 mL methanol) was added. After vigorous stirring for 30 min, a fresh solution of sodium borohydride (77 mg in 5 mL of ice-cold water) was added, and the reaction mixture turned deep brown immediately. The reaction was stirred for 16 hrs and then centrifuged to remove insoluble material. The supernatant was concentrated to near dryness by rotary evaporation and precipitated with ethanol. The precipitate was collected via centrifugation, dissolved in a minimum amount of methanol, and precipitated with ethanol. This was repeated five times. $Au_{25}(capt)_{18}$ clusters were separated by PAGE (Protean Tetra Mini, 20 % gel, TBE buffer), and the orange fraction was cut out off the gel, crushed and extracted with water. The extract was centrifuged and the supernatant containing the clusters was filtered over a syringe filter to remove remainders of the PAGE gel. The clusters were then concentrated by rotary evaporation, precipitated with ethanol and washed three times to remove remaining buffer. The purity of the $Au_{25}(capt)_{18}$ clusters was confirmed by running analytical PAGE against a sample of the crude reaction product.

Au₃₈(capt)₂₄.³ HAuCl₄*3H₂O (79 mg) and TOAB (127 mg) were dissolved in 15 mL methanol and stirred at 1200 rpm. After 15 min, captopril (130 mg) was added, and the solution was stirred for 30 min, turning into a white suspension. Next, the stirring speed was reduced to 600 rpm and sodium borohydride (38 mg in 5 mL cold water) was added. The mixture was allowed to stir for 24 h and was then concentrated to near dryness by rotary evaporation. The clusters were precipitated by addition of ethanol and centrifuged. The precipitate was dissolved in a minimum amount of methanol and precipitated again with ethanol. This was repeated three times. Au₃₈(capt)₂₄ clusters were separated by PAGE (Protean Tetra Mini, 20 % gel, TBE buffer), and the brown fraction was cut out off the gel, crushed and extracted with water. The extract was centrifuged and the supernatant containing the clusters was filtered over a syringe filter to remove remainders of the PAGE gel. The clusters were then concentrated by rotary evaporation, precipitated with ethanol and washed three times to remove remaining buffer. The purity of the Au₃₈(capt)₂₄ clusters was confirmed by running analytical PAGE against a sample of the crude reaction product.

 $[(AuAg)_{25}(SCH_2CH_2Ph)_{18}]^{0.4}$ Tetrachloroauric acid and silver nitrate were dissolved in tetrahydrofuran (10 mL) to give a total metal concentration of 0.45 mM. The molar ratio between Au and Ag was 1:0.01. To this, a solution of tetraoctylammonium bromide (600 mg in 10 mL THF) was added, and the mixture was stirred for 15 min. 2-Phenylethanethiol was added (0.335 mL) and the reaction was stirred at 0 °C for 30 min. A fresh solution of sodium borohydride (375 mL) in water (10 mL) was added all at once. Stirring was continued for 24 h, during which the reaction was allowed to warm up to room temperature. The phases were separated and the organic phase was concentrated to near dryness. The clusters were precipitated with ethanol and thoroughly washed. The clusters were then re-dissolved in dichloromethane and dried by rotary evaporation. This was repeated several times. Then, the clusters were dissolved in dichloromethane and filtered over a syringe filter (0.2 µm, PTFE), and dried. The crude clusters were extracted with acetonitrile, and purified via sizeexclusion chromatography (Biorad BioBeads S-X1, THF). $Au_{38-x}Ag_x(SCH_2CH_2Ph)_{24}$. Tetrachloroauric acid trihydrate (176 mg) and silver nitrate (38 mg) were dissolved in THF (20 mL) and stirred for 10 min. 2-Phenylethanethiol (0.362 mL) was added and stirred for another 20 min. After that, sodium borohydride (170 mg in 4 mL ice cold water) was added and the mixture was stirred for another 5 min. The solvent was removed by rotary evaporation and the residue was washed with methanol several times to remove excess thiol and other byproducts. Eventually, the product was extracted with acetonitrile to remove smaller byproducts such as $Au_{25-x}Ag_x(SR)_{18}$. The insoluble fraction was dissolved in toluene (0.50 mL) and etched in excess thiol for 3 days (80 °C). Then the final product was washed with methanol several times to remove excess thiol and extracted with toluene. The clusters were then extracted with acetonitrile for further removal of $Au_{25-x}Ag_x(SR)_{18}$ impurities and finally subjected to size-exclusion chromatography (BioRad Biobeads S-X1, THF) to separate pure $Au_{38-x}Ag_x(SR)_{24}$. It should be note that both SEC and solvent fractionation are necessary to remove the trace amount of $Au_{25-x}Ag_x(SR)_{18}$ present in the sample.

2. Characterization

UV-Vis-NIR spectra. UV-Vis-NIR spectra were measured on a Perkin-Elmer Lambda 900 spectrophotometer. The solvents were tetrahydrofuran or water, depending on the solubility of the clusters. The pathlength of the cuvette was 10 mm, unless noted otherwise. Prior to HRS measurements, the clusters were dissolved at a defined concentration in tetrahydrofuran (or water in the case of captopril-protected clusters) and the absorption at 650 nm was determined in a cuvette with 2 mm pathlength.

Mass spectrometry. Matrix-assisted laser desorption time-of-flight (MALDI-TOF) mass spectra were acquired using a Voyager DE PRO mass spectrometer with DCTB as a matrix.⁵ MS signal were processed to suppress the background noise under optimal laser fluence. Further, mass peak calibration was performed using $Au_{25}(SCH_2CH_2C_6H_5)_{18}$ as an external standard. Electrospray ionization mass spectra (ESI-MS) were acquired using a Waters SYNAPT Q-TOF HDMS instrument. ESI calibration was performed with 50:50 isopropanol:water solution of NaI. The clusters were mixed with 50:50 THF/CH₃CN or 50:50 DCM/CH₃CN solvent for analysis. MS signals were processed to suppress the background noise.

Hyper-Rayleigh Scattering. All Hyper-Rayleigh Scattering measurements to determine the orientionally averaged first hyperpolarizabilities β_{HRS} were carried out in THF or water, depending on the solubility of the sample. Before measurement, all solvents and samples were filtered (Millipore, 0.45 µm). Owing to the high absorbance of the compounds at the second-harmonic wavelength, even when using dilute concentrations (µmol/L), re-absorbance of the second-harmonic light could not be neglected. Therefore, Lambert-Beer correction terms were included (pathlength 1 mm) in the analysis.

All measurements were performed using a SpectraPhysics Insight[®]DeepSee+ laser, at 1300 nm (80 MHz repetition rate, 100 fs pulses, 700 mW average power). In this setup, the collection optics are coupled to a spectrograph (model Bruker 500is/sm), together with an EMCCD camera (Andor Solis model iXon Ultra 897). Correction for multiphoton induced fluorescence was done by subtracting the broad MPF background signal from the narrow HRS peak (FWHM 14 nm). The higher sensitivity of this setup enables us to use the solvent as an internal reference. As a calibration standard, neat THF was used. Since this is also the solvent for the hyperpolarizability measurements of the clusters, this precludes the need for Lorentz-Lorenz correction factors. Following the procedure in ref. 6, the hyperpolarizability of THF was

measured to be $\beta_{\text{HRS},1300,\text{THF}} = 0.118 * 10^{-30}$ esu, using chloroform as reference. This value was subsequently used as a calibration standard for all measurements in THF. The measurement of the chiral Au₂₅ and Au₃₈ clusters in H₂O was calibrated against DR1, a standard reference at this wavelength ($\beta_{1300,\text{HRS},\text{THF}} = 54\pm5 * 10^{-30}$ esu).⁷ In this case standard Lorentz-Lorenz correction factors were included.

Extrapolation of the first hyperpolarizability measured at 1300 nm to zero frequency was done using the following formula⁸:

$$\beta_0 = \beta_{laser} \left(1 - \left(\frac{\lambda_{max}}{\lambda_{laser}} \right)^2 \right) \left(1 - \left(\frac{\lambda_{max}}{\lambda_{HRS}} \right)^2 \right)$$

where *laser* = 1300 nm, *HRS* = 650 nm and *max* = see Table 1.

3. Mass Spectrometry

a) $[Au_{25}(SCH_2CH_2Ph)_{18}]^0$ and $Au_{38}(SCH_2CH_2Ph)_{24}$



Figure S-1. Left: MALDI-TOF mass spectra of $[Au_{25}(SCH_2CH_2Ph)_{18}]^0$ (black) and $Au_{38}(SCH_2CH_2Ph)_{24}$ clusters (red). Right: ESI-TOF mass spectra of $[Au_{25}(SCH_2CH_2Ph)_{18}]^0$ (black) and $Au_{38}(SCH_2CH_2Ph)_{24}$ clusters (red). The inset shows the 2+ peak of the $Au_{38}(SCH_2CH_2Ph)_{24}$ cluster.

b) Au_{25-x}Ag_x(SCH₂CH₂Ph)₁₈



Figure S-2. Top: ESI mass spectra of $[Au_{25}(SCH_2CH_2Ph)_{18}]^0$ and $[Au_{25}_xAg_x(SCH_2CH_2Ph)_{18}]^0$ clusters. Bottom, left: Zoom into the 1+ peak region of $[Au_{25}_xAg_x(SCH_2CH_2Ph)_{18}]^0$. Bottom, right: Zoom into the 2+ peak region of $[Au_{25}_xAg_x(SCH_2CH_2Ph)_{18}]^0$.

| Table S-1. Relative peak intensities of the $[Au_{25-x}Ag_x(SCH_2CH_2Ph)_{18}]^0$ | clusters | in |
|--|----------|----|
| ESI-TOF mass spectra (positive mode) for the first and second ionization s | tates. | |

| X | 1+ | 2+ | |
|---------------------|--|--|--|
| 7 | 0.307 | 0.286 | |
| 8 | 0.955 | 0.912 | |
| 9 | 1 | 1 | |
| 10 | 0.391 | 0.588 | |
| 11 | - | 0.156 | |
| Average composition | Au _{16.5} Ag _{8.5} (SCH ₂ CH ₂ Ph) ₁₈ | Au _{16.2} Ag _{8.8} (SCH ₂ CH ₂ Ph) ₁₈ | |

c) Au_{38-x}Ag_x(SCH₂CH₂Ph)₂₄



Figure S-3. Left: ESI mass spectra of $Au_{38}(SCH_2CH_2Ph)_{24}$ and $Au_{38}_{x}Ag_{x}(SCH_2CH_2Ph)_{24}$ clusters. Right: Zoom into the 2+ peak region of $Au_{38}_{x}Ag_{x}(SCH_2CH_2Ph)_{24}$.

Table S-2. Relative peak intensities of the $Au_{38-x}Ag_x(SCH_2CH_2Ph)_{24}$ clusters in ESI-TOF mass spectra (positive mode) for the second ionization state.

| X | 2+ |
|---------------------|--|
| 2 | 0.073 |
| 3 | 0.319 |
| 4 | 0.753 |
| 5 | 1.0 |
| 6 | 0.770 |
| 7 | 0.303 |
| 8 | 0.078 |
| Average composition | Au _{33.0} Ag _{5.0} (SCH ₂ CH ₂ Ph) ₂₄ |

4. Gel Electrophoresis and Linear Absorption Spectra

Au₂₅(SR)₁₈ clusters are stable both in the anionic and charge-neutral form.^{9,10} The two charge states can be identified by the absorption spectra of the clusters and the colors of the solutions. Size-exclusion chromatography typically yields the charge-neutral species due to oxidation on the column.¹¹ PAGE separation of water-soluble clusters yields the anionic species. This is evidenced by the absorption spectra shown below. In the case of silver-doped [(AuAg)₂₅(SCH₂CH₂Ph)₁₈]⁰, the assignment of the charge state cannot be made without doubt. The crystal structure and optical spectra were recorded for the anionic cluster.¹² The Ag-content in the clusters, however, alters the absorption spectra.¹³ The spectra for the neutral clusters were not reported so far. Since we isolated the clusters via SEC, we assume that they underwent oxidation similar to the all-gold cluster.



Figure S-4. Left: Developed PAGE gel of as prepared $[Au_{25}(capt)_{18}]^-$ clusters (left trace) and pure $Au_{25}(capt)_{18}$ after isolation (right trace). Right: Absorption spectrum of the pure $[Au_{25}(capt)_{18}]^-$ cluster (in water).



Figure S-5. Left: Developed PAGE gel of pure $Au_{38}(capt)_{24}$ after isolation. All traces are the same sample at different concentrations. Right: Absorption spectrum of the pure $Au_{38}(capt)_{24}$ cluster (in water).



Figure S-6. Linear absorption spectra of $[Au_{25}(SCH_2CH_2Ph)_{18}]^0$ (in THF, black trace), $[Au_{25}(capt)_{18}]^-$ (in water, red trace) and $[(AuAg)_{25}(SCH_2CH_2Ph)_{18}]^0$ (in THF, blue trace. The spectra were normalized at 300 nm and are off-set for clarity. The dashed lines indicate the offset. The spectrum of $[Au_{25}(capt)_{18}]^-$ was measured up to 900 nm only.



Figure S-7. Left: Linear absorption spectra of $Au_{38}(SCH_2CH_2Ph)_{24}$ (in THF, black trace), $Au_{38}(capt)_{24}$ (in water, red trace) and $(AuAg)_{38}(SCH_2CH_2Ph)_{24}$ (in THF, blue trace. The spectra were normalized at 300 nm and are off-set for clarity. The dashed lines indicate the offset. Right: Zoom into the NIR region of the spectra. The curves were normalized at 600 nm.

5. Hyper-Rayleigh Scattering – Spectral Dispersion



Figure S-8. Spectral dispersion of the photon intensity generated from $[Au_{25}(SCH_2CH_2Ph)_{18}]^0$ (left) and $Au_{38}(SCH_2CH_2Ph)_{24}$ (right) clusters (fundamental wavelength 1300 nm, tetrahydrofuran). The arrows indicate increasing concentrations. The pure solvent is shown in black. Not all measured spectra are shown for clarity. The peak at 650 nm in $[Au_{25}(SCH_2CH_2Ph)_{18}]^0$ does not increase with increasing concentration, but does in $Au_{38}(SCH_2CH_2Ph)_{24}$. Both clusters also show significant fluorescence generated from multiphoton absorption.



Figure S-9. Spectral dispersion of the photon intensity generated from $[Au_{25}(capt)_{18}]^-$ (left) and $Au_{38}(capt)_{24}$ (right) clusters (fundamental wavelength 1300 nm, water). The arrows indicate increasing concentrations. The pure solvent is shown in black. Not all measured spectra are shown for clarity. Both clusters also show significant fluorescence generated from multiphoton absorption.



Figure S-10. Spectral dispersion of the photon intensity generated from $[Au_{25.} Ag_x(SCH_2CH_2Ph)_{18}]^0$ (left) and $Au_{38-x}Ag_x(SCH_2CH_2Ph)_{24}$ (right) clusters (fundamental wavelength 1300 nm, tetrahydrofuran). The arrows indicate increasing concentrations. The pure solvent is shown in black. Not all measured spectra are shown for clarity. Both clusters also show significant fluorescence generated from multiphoton absorption (although relatively weak in $[Au_{25-x}Ag_x(SCH_2CH_2Ph)_{18}]^0$ when compared to the other clusters).



Figure S-11. Data fitting of the measured HRS and multiphoton excited fluorescence (MPEF) response. The Au₃₈(SCH₂CH₂Ph)₂₄ cluster was chosen as example. The peaks were fitted using a multi-Gaussian approach to discriminate the HRS signal (black line) from MPEF. Two Gaussians were used for MPEF (red and cyan line) The residual (blue line) between the cumulative peak fit (the sum of fitted HRS and MPEF peaks, green line) is shown as well. This approach was used for each measured spectrum. The residual HRS peak was integrated and used in Figures 2 – 4 in the manuscript.

6. Power Dependence of the HRS Signal

For a true HRS signal, a quadratic dependence of the HRS intensity with the laser power is expected. Another way to express this dependence is to plot the intensity of the HRS signal against $(P/P_{max})^2$; in this case, a linear correlation is expected.

We measured such a dependence for $Au_{38}(SCH_2CH_2Ph)_{24}$ in THF (excitation wavelength 1300 nm). This supports our assumption that thermal effects, or more general, an intensity dependence of the refractive index does not occur in our measurements. Otherwise, a deviation from the observed correlation would be found. We chose the $Au_{38}(SCH_2CH_2Ph)_{24}$ cluster to probe this, since it is the only cluster studied here (together with $Au_{38}(capt)_{24}$, which shows virtually the same absorption spectrum) that absorbs close to the excitation wavelength. We attempted to measure HRS at shorter wavelengths, but this was not possible due to thermal effects that alter the beam shape. Therefore, the excitation wavelength was moved into a region where none of the clusters absorbs.



Figure S-12. Power dependence of the HRS intensity of $Au_{38}(SCH_2CH_2Ph)_{24}$. The signal scales linearly with the square of the (normalized) laser intensity $(P/P_{max})^2$.

7. DFT Calculations

All DFT calculations were carried out using the Amsterdam Density Functional software suite (ADF2014.01).¹⁴ The structures were generated from the crystal structure of $[Au_{25}(SCH_2CH_2Ph)_{18}]^{-,15}$ and model ligands –SH were used. The isomers of $[Au_{25-x}Ag_x(SH)_{18}]^{-}$ were generated and labeled as described in ref. 16. The structure of $Au_{38}(SCH_3)_{24}$ was generated from the crystal structure coordinates of $Au_{38}(SCH_2CH_2Ph)_{24}$.¹⁷ The structures were optimized using the X α functional and the TZP basis set. The static first hyperpolarizabilities were calculated at the LB94/TZP level. Scalar-relativistic ZORA and medium frozen cores were used. The tensor components of the hyperpolarizabilities were orientationally averaged using the Kleinman formula.¹⁸ General details on the computations can be found in ref. ¹⁹. The convention for hyperpolarizabilities is T = AB.²⁰ The isomers of the silver-doped Au_{25} clusters were weighted using a Boltzmann population taking into account their relative energies and degeneracies.



Figure S-13. Au-Au distances in $Au_{38}(SR)_{24}$ clusters (R = -CH₂CH₂Ph, black; -H, red; -SCH3, blue). The distances of the model clusters were calculated after optimization at the X α /TZP level, and compared to those from the crystal structure. The values for the –SCH₃ protected clusters are more realistic than those for the –SH protected ones, indicating that a more realistic ligand yields more realistic atomic distances.

Table S-3. Calculated static first hyperpolarizabilities β_0 (in 10⁻³⁰ esu) of Au₃₈(SH)₂₄ and Au₃₈(SCH₃)₂₄ in the gas phase and with inclusion of solvent models. Included is the experimental value (in THF) for Au₃₈(SCH₂CH₂Ph)₂₄ for comparison.

| | ε _r | SH | SCH ₃ | SCH ₂ CH ₂ Ph |
|-----------------|----------------|------|------------------|-------------------------------------|
| Gas phase | 1 | 5.7ª | 0.8 | - |
| Toluene | 2.38 | 16.8 | 2.5 | - |
| THF | 7.58 | 42.4 | 6.7 | 8±1 |
| dichloromethane | 8.9 | 45.7 | 7.3 | - |

a: as reported in ref. 19.



Figure S-14. Averaged static first hyperpolarizabilities of $[Au_{25-x}Ag_x(SH)_{18}]^-$ clusters as a function of Ag atoms. The hyperpolarizabilities of the individual isomers were scaled with the Boltzmann population factor of the isomer. A peak in the distribution at x = 6 is observed, while for x = 0 (homo-metallic) and x = 12 (Ag_{12} icosahedron filled with a single Au atom), virtually no hyperpolarizability is calculated. This corresponds with the centrosymmetry of the x = 0 and x = 12 clusters. Overall, the symmetry-breaking by Ag-alloying of the Au₂₅(SR)₁₈ cluster is clearly reflected in the first hyperpolarizabilities.

Table S-4. Relative energies, HL-gaps, relative degeneracies, Boltzmann factors, and hyperpolarizabilities of $[Au_{25-x}Ag_x(SH)_{18}]^-$ clusters (X α /TZP structures, followed by LB94/TZP single point calculations). The relative energies and HL gaps refer to the single point calculations in the gas phase.

| X | Isomer | E _{rel} /kJ*mol ⁻¹ | Degeneracy | Boltzmann factor | $\beta_{\theta}/10^{-30}$ esu | β_{θ} , scaled/10 ⁻³⁰ esu |
|---|--------|--|------------|------------------|-------------------------------|---|
| 0 | a | 0.00 | 1 | 1 | 0.016 | 0.016 |
| 1 | a | 0.00 | 1 | 1 | 1.91 | 1.91 |
| | a | 4.77 | 5 | 0.454094094 | 1.85 | |
| 2 | b | 0.00 | 5 | 0.454969277 | 3.09 | 2.25 |
| | с | 1.56 | 1 | 0.090936628 | 0.015 | |
| | a | 6.72 | 1 | 0.090747488 | 2.25 | |
| | b | 2.235 | 3 | 0.272735963 | 3.30 | |
| 3 | с | 2.50 | 3 | 0.272705634 | 1.72 | 2.59 |
| | d | 1.49 | 3 | 0.272817144 | 2.58 | |
| | e | 0.00 | 1 | 0.090993771 | 3.47 | |
| | а | 8.32 | 2 | 0.060547886 | 2.45 | |
| | b | 7.70 | 4 | 0.12112643 | 3.80 | |
| | с | 7.91 | 4 | 0.121116039 | 1.66 | |
| | d | 0.00 | 2 | 0.06075151 | 4.11 | |
| 4 | е | 7.47 | 4 | 0.121137591 | 3.02 | 2 62 |
| | f | 3.89 | 4 | 0.121312459 | 1.91 | 2.02 |
| | g | 6.56 | 4 | 0.121181862 | 3.3 | |
| | h | 3.30 | 1 | 0.030335375 | 0.122 | |
| | i | 4.03 | 4 | 0.121305521 | 2.55 | |
| | j | 6.49 | 4 | 0.121185327 | 2.08 | |
| | а | 8.55 | 5 | 0.075626466 | 3.56 | |
| | b | 6.95 | 5 | 0.075675181 | 1.68 | |
| | с | 4.80 | 5 | 0.075741011 | 2.31 | |
| | d | 0.25 | 5 | 0.075879916 | 2.65 | |
| | е | 4.20 | 10 | 0.151518286 | 2.75 | |
| 5 | f | 7.98 | 5 | 0.075643769 | 2.55 | 2.47 |
| | g | 0.00 | 5 | 0.075887712 | 1.87 | |
| | h | 0.76 | 5 | 0.075864407 | 4.41 | |
| | i | 1.93 | 5 | 0.075828821 | 3.16 | |
| | j | 9.42 | 1 | 0.015119976 | 3.90 | |
| | k | 4.56 | 10 | 0.151496623 | 2.98 | |
| | 1 | 5.56 | 5 | 0.075717832 | 1.75 | |
| 6 | a | 17.35 | 6 | 0.012926103 | 3.23 | 3.11 |

| | b | 10 79 | 10 | 0.021600578 | 4 57 | |
|---|---|-------|----|-------------|-------|------|
| | с | 5.01 | 30 | 0.064952969 | 3.80 | |
| | d | 14.54 | 30 | 0.064703801 | 3.19 | |
| | e | 5.59 | 60 | 0.129875673 | 3.60 | |
| | f | 4.02 | 15 | 0.03248942 | 1.63 | |
| | g | 3.90 | 60 | 0.12996415 | 2.39 | |
| | h | 2.62 | 15 | 0.032507869 | 2.87 | |
| | i | 1.86 | 60 | 0.130071283 | 3.10 | |
| | j | 4.23 | 60 | 0.129946945 | 3.50 | |
| | k | 10.03 | 30 | 0.064821709 | 2.88 | |
| | 1 | 6.99 | 15 | 0.032450629 | 2.44 | |
| | m | 10.27 | 10 | 0.021605154 | 3.03 | |
| | n | 0.00 | 5 | 0.010847404 | 0.114 | |
| | 0 | 5.50 | 6 | 0.012988049 | 4.57 | |
| | р | 3.57 | 30 | 0.064990678 | 3.92 | |
| | q | 7.69 | 15 | 0.032441454 | 2.63 | |
| | r | 7.16 | 5 | 0.010816132 | 0.112 | |
| | а | 14.08 | 5 | 0.075626499 | 4.18 | |
| | b | 15.86 | 5 | 0.075572213 | 2.42 | |
| | с | 11.65 | 5 | 0.075700545 | 3.17 | |
| | d | 10.03 | 5 | 0.075750189 | 3.56 | |
| | е | 12.84 | 10 | 0.151328628 | 3.20 | |
| 7 | f | 7.80 | 5 | 0.075818414 | 4.08 | 3.07 |
| | g | 8.43 | 5 | 0.075799064 | 2.07 | |
| | h | 0.00 | 5 | 0.0760572 | 4.00 | |
| | i | 3.16 | 5 | 0.075960356 | 3.41 | |
| | j | 9.80 | 1 | 0.01515161 | 3.25 | |
| | k | 11.20 | 10 | 0.151428512 | 2.57 | |
| | 1 | 8.18 | 5 | 0.075806771 | 1.45 | |
| | а | 14.03 | 2 | 0.060443865 | 3.53 | |
| 8 | b | 10.61 | 4 | 0.1210548 | 3.47 | |
| | с | 8.28 | 4 | 0.121168576 | 2.42 | |
| | d | 0.00 | 2 | 0.06078694 | 3.31 | |
| | e | 9.76 | 4 | 0.121096347 | 2.56 | 2.43 |
| | f | 4.28 | 4 | 0.121363925 | 2.51 | |
| | g | 6.46 | 4 | 0.121257542 | 2.36 | |
| | h | 4.56 | 1 | 0.030337639 | 0.015 | |
| | i | 4.88 | 4 | 0.121334879 | 1.77 | |
| | j | 8.55 | 4 | 0.121155487 | 1.49 | |

| | а | 7.96 | 1 | 0.090759914 | 2.98 | |
|----|---|-------|---|-------------|-------|-------|
| | b | 3.26 | 3 | 0.272796712 | 2.25 | |
| 9 | с | 3.27 | 3 | 0.272795845 | 1.82 | 2.06 |
| | d | 5.09 | 3 | 0.272595696 | 1.54 | |
| | e | 0.00 | 1 | 0.091051833 | 2.90 | |
| | а | 3.94 | 5 | 0.45420924 | 2.06 | |
| 10 | b | 0.00 | 5 | 0.454931881 | 1.71 | 1.72 |
| | с | 3.48 | 1 | 0.090858879 | 0.12 | |
| 11 | а | 0.00 | 1 | 1 | 1.71 | 1.71 |
| 12 | a | 0.000 | 1 | 1 | 0.057 | 0.057 |

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