2024/25. õa keemiaolümpiaadi lõppvoor
11.–12. klass
Lahendused

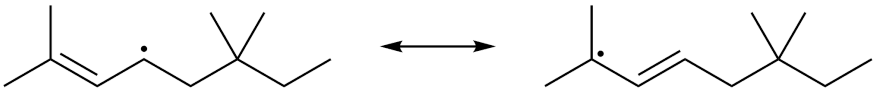
1. Kui lahe atmosfäär… Autor: Lisette-Liis Loorits (10 p)

Allikas:

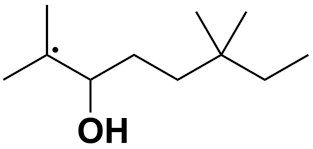
- K. Riedel; K, Lasse. (2008). Detergent of the atmosphere. *Water and Atmosphere*, 16(1), 22–23. https://niwa.co.nz/sites/default/files/import/attachments/detergent.pdf

a) *Hindamine: 0,5 p iga korrektse osakese eest, kokku 4p.* (8×0,5)
A = $HO^{\bullet}$, **B** = O_3, **C** = O_2, **D** = $O^{\bullet}$, **E** = $HO_2^{\bullet}$, **F** = NO, **G** = NO_2, **H** = $NO_3^{\bullet}$

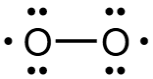
b) *Hindamine: 1 p korrektselt joonistatud radikaali struktuurivalemi eest.* (1)



c) *Hindamine: 1 p korrektselt joonistatud radikaali struktuurivalemi eest.* (1)



d) *Hindamine: 1 p korrektselt joonistatud radikaali Lewis'i struktuurivalemi eest.* (1)



e) Fluororadikaal on klororadikaalist ebastabiilsem, mistõttu fluorosüsivesinikud ei fotodissotseeru ega moodusta atmosfääris vabu radikaale. (1)

f) **i)** $Cl^{\bullet} + O_3 \rightarrow ClO^{\bullet} + O_2$ (1)
ii) $ClO^{\bullet} + O^{\bullet} \rightarrow Cl^{\bullet} + O_2$ või $ClO^{\bullet} + O_3 \rightarrow Cl^{\bullet} + 2O_2$ (1)

2. Keemiline vulkaan. Autor: Vladislav Ivaništšev (10 p)

Allikad:

- B. Mahieu; D.J. Apers; P.C. Capron. (1971). Thermal decomposition of ammonium dichromate. 33(9), 2857–2866. https://doi.org/10.1016/0022-1902(71)80047-7
- Z. Ying, et al. (2023). A study on the preparation of Cr_2O_3 from $(NH_4)_2Cr_2O_7$ based on thermal decomposition including the thermal decomposition temperature effect, mechanism and kinetics. *Materials Science and Engineering: B*, 298, 116824. https://doi.org/10.1016/j.mseb.2023.116824

a) **A** = Cr_2O_3 (1)

b) $(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4H_2O$ (1)

c) Gaasiliste produktidena võivad tekkida ainult NH_3, N_2 ja H_2O.
Kolonnis olev KOH on hügroskoopne aine, mis seob veeauru:
$n(H_2O) = 2{,}66/18{,}02 = 0{,}145$ mol (1)
Hape absorbeerib ainult pool ülejäänud gaasisegust, seega on tegu 1 : 1 NH_3 ja N_2 seguga.
$n(NH_3) = n(N_2) = (18{,}61 - 14{,}83 - 2{,}66)/(28 + 17{,}03) = 0{,}0249$ mol (1)
Gaaside moolisuhe on $n(H_2O) : n(N_2) : n(NH_3) = 6 : 1 : 1$, mis tähendab, et **B** sisaldab NH_3.
$M(\mathbf{B}) = 14{,}83/18{,}61 \cdot 252{,}07 = 200{,}87$ g·mol^{-1}
B = $Cr_2O_5 \cdot NH_3$ ehk tegu on CrO_3, CrO_2 ja NH_3 koosneva ühendiga. (1)

d) $3(NH_4)_2Cr_2O_7 \rightarrow 3Cr_2O_5 \cdot NH_3 + N_2 + NH_3 + 6H_2O$ (1)

e) Gaasisegu sisaldab NH_3 ja N_2 moolisuhtes 1 : 1. Oletades, et **B** : **C** suhe on 1 : 1, järeldub:
$M(\mathbf{C}) = 12{,}40/18{,}61 \cdot 252{,}07 = 167{,}96$ g·mol^{-1}, mille põhjal **C** = Cr_2O_4.
Järelikult, **B** : **C** moolisuhe on 1 : 2 ja $M(\mathbf{C}) = ½ \cdot 12{,}40/18{,}61 \cdot 252{,}07 = 83{,}98$ g·mol^{-1}

C = CrO_2 – ebastabiilne oksiid. (1)

f) $3Cr_2O_5{\cdot}NH_3 \rightarrow 6CrO_2 + NH_3 + N_2 + 3H_2O$ (1)

või $3Cr_2O_5{\cdot}NH_3 \rightarrow 3Cr_2O_4 + NH_3 + N_2 + 3H_2O$

g) $6(NH_4)_2Cr_2O_7 \rightarrow 6Cr_2O_3 + 4N_2 + 4NH_3 + 18H_2O + 3O_2$ (2)

3. pHenomenaalne neeldumine. Autor: Sofja Tšepelevitš (10 p)

Allikas:

- https://cran.r-project.org/web/packages/colorSpec/vignettes/phenolred.html

a) Neutraalse vormi XH neeldumismaksimum on λ_{max1} = **432 nm**. (1)

Hindamine: Õigeks lugeda väärtused vahemikus 427…437 nm.

Aniooni X^- neeldumismaksimum on λ_{max2} = **558 nm**. (1)

Hindamine: Õigeks lugeda väärtused vahemikus 555…560 nm.

b) i) Graafikul on **2 isosbestilist punkti**. (1)

ii) Nendele vastavad lainepikkused on $\lambda_1 \sim$ **370 nm** (õigeks lugeda 365…370 nm) ja $\lambda_2 \sim$ **477 nm** (õigeks lugeda 475…480 nm). (2×0,5)

c) i) $A_\lambda(\text{pH} = \text{M}) = A_\lambda(\text{M}) = \varepsilon_\lambda{\cdot}c{\cdot}l$

pH = 4 juures on aine täielikult protoneeritud ehk [XH] = c(XH), mis tähendab, et kogu neelduvus tuleneb neutraalsest vormist. Järelikult:

$A_{432}(4) = \varepsilon_{432}(\text{XH}){\cdot}c(\text{XH}){\cdot}l = 0{,}70$

$\varepsilon_{432}(\text{XH}) = A_{432}(4)/(c(\text{XH}){\cdot}l) = 0{,}70/(0{,}2025\ \text{M}{\cdot}1{,}\underline{0}0\ \text{cm}) = 3{,}456\ \text{M}^{-1}{\cdot}\text{cm}^{-1} \approx \mathbf{3{,}5\ M^{-1}{\cdot}cm^{-1}}$ (1)

Analoogiliselt on pH = 10 juures aine täielikult deprotoneeritud ehk $[X^-] = c$(XH). Seega:

$A_{558}(10) = \varepsilon_{558}(X^-){\cdot}c(\text{XH}){\cdot}l = 2{,}24 \Rightarrow \varepsilon_{558}(X^-) = A_{558}(10)/(c(\text{XH}){\cdot}l)$

$\varepsilon_{558}(X^-) = 2{,}24/(0{,}2025\ \text{M}{\cdot}1{,}\underline{0}0\ \text{cm}) = 11{,}06\ \text{M}^{-1}{\cdot}\text{cm}^{-1} \approx \mathbf{11\ M^{-1}{\cdot}cm^{-1}}$ (1)

ii) Jooniselt on näha, et lainepikkusel λ_{max2} = 558 nm aine neutraalne vorm ei neela üldse, mis tähendab, et pH = 7,8 juures tuleneb lahuse neelduvus ainult anioonist:

$A_{558}(7{,}8) = \varepsilon_{558}(X^-){\cdot}[X^-]{\cdot}l = 1{,}00 \Rightarrow [X^-] = A_{558}(7{,}8)/(\varepsilon_{558}(X^-){\cdot}l)$

$[X^-] = 1{,}00/(11{,}06\ \text{M}^{-1}\ \text{cm}^{-1}{\cdot}1{,}00\ \text{cm}) = \mathbf{0{,}0904\ M}$ (1)

Massibilansist tuleneb, et $[\text{XH}] = c(\text{XH}) - [X^-] = 0{,}2025\ \text{M} - 0{,}0904\ \text{M} = \mathbf{0{,}1121\ M}$ (1)

** On võimalik lahendada kasutades suvalist lainepikkust λ, mis ei ole isosbestiline punkt:*

$\alpha = [X^-]/([X^-]+[\text{XH}]) = (A_\lambda(7.8)-A_\lambda(4)) / (A_\lambda(10)-A_\lambda(4))$

d) i) *Hindamine: matemaatiliselt korrektse valemi variandi eest 1 p.*

Alustades happe dissotsiatsiooni tasakaalukonstandist $K_a = [X^-][H^+]/[\text{XH}]$ saame järgmise võrrandi:

$-\log(K_a) = -\log([X^-][H^+]/[\text{XH}]) = -\log[H^+] - \log([X^-]/[\text{XH}])$

$\mathbf{pK_a = pH - \log([X^-]/[XH])}$ (1)

ii) Vee pH on 7,8, mille jaoks $[X^-]$ ja [XH] on meil juba arvutatud.

$pK_a = \text{pH} - \log([X^-]/[\text{XH}]) = 7{,}8 - \log(0{,}0904/0{,}1121) = \mathbf{7{,}9}$ (1)

4. Keemiline kalibreerimine. Autor: Karl Johann Külv (10 p)

Allikad:

- Vogel's Textbook of Quantitative Chemical Analysis 5th ed., https://www.fondriest.com/environmental-measurements/parameters/water-quality/dissolved-oxygen/
- https://tsapps.nist.gov/srmext/certificates/archives/83b.pdf

a) Kui [HA] = $[A^-]$, siis pH = $pK_a - \log(1) = pK_a$. Tabelist on näha, et pH = 7,2 juures on $H_2PO_4^-$ osakaal 50,04% ehk umbes 50%. Kuna samal ajal on H_3PO_4 ja PO_4^{3-} osakaal 0%, peab ülejäänud 50% moodustama HPO_4^{2-}. Kuna $[H_2PO_4^-] = [HPO_4^{2-}]$, siis pK_a = pH = 7,2. Teades, et NaH_2PO_4 kontsentratsioon on 2 korda rohkem kui Na_2HPO_4 puhul ehk $[NaH_2PO_4] = 2[Na_2HPO_4]$, järeldub Henderson-Hasselbalchi võrrandist pH = 7,2 − log(2) = **6,9**. (1)

b) **i)** Pärast tärkliselahuse lisamist lahus on **must/sinine**. (0,5)

ii) Tiitrimine lõpetatakse, kui lahus muutub **värvituks**. (0,5)

c) **i)** $As_2O_3 + 2I_2 + 2H_2O \rightarrow As_2O_5 + 4HI$ (1)

ii) I_2 ja As(III) reageerivad vahekorras 2 : 1 ning moodustuvad I^- ja As(V), seega:

$c(I_2) = 2\cdot(0{,}77\ g/197{,}84\ g\cdot mol^{-1})\cdot(15{,}03\ cm^3/500\ cm^3)\cdot(1/30\ cm^3)\cdot(1000\ cm^3/1\ dm^3) = 7{,}799\cdot10^{-3}\ M \approx$ **$7{,}8\cdot10^{-3}$ M** (1)

d) **i)** $S_2O_3^{2-} + 4Br_2 + 5H_2O \rightarrow 2SO_4^{2-} + 8Br^- + 10H^+$ (1)

ii) $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4\downarrow$

Reaktsioonivõrrandist järeldub, et 1 mol $S_2O_3^{2-} \Leftrightarrow$ 2 mol Ba^{2+}. EDTA reageerib esmalt Ba^{2+}-ga, kuid kuna EDTA on liias, saab liia ja Ba^{2+} hulka määrata Mg^{2+} abil.

$n(Ba^{2+}) = 20\ cm^3\cdot(1\ dm^3/1000\ cm^3)\cdot0{,}05\ M - 29{,}18\ cm^3\cdot(1\ dm^3/1000\ cm^3)\cdot0{,}015\ M = 5{,}623\cdot10^{-4}$ mol

$c(S_2O_3^{2-}) = (5{,}623\cdot10^{-4}\ mol/55\ cm^3)\cdot(1000\ cm^3/\ 1\ dm^3)/2 =$ **$5{,}11\cdot10^{-3}$ M** (1)

e) Aluselises keskkonnas:

$4Mn^{2+} + O_2 + 2H_2O \rightarrow 4Mn^{3+} + 4OH^-$

$2Mn^{3+} + 2I^- \rightarrow 2Mn^{2+} + I_2$

Tekkinud joodi kogus tehakse kindlaks tiosulfaadi abil:

$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$

Järeldub, et 1 mol $O_2 \Leftrightarrow$ 4 mol $S_2O_3^{2-}$. (1)

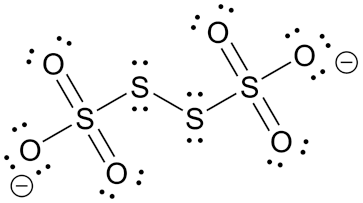
Kasutades $c(S_2O_3^{2-}) = 5{,}11\cdot10^{-3}$ M alapunktist **d)**:

$c(O_2) = 26{,}71\ cm^3\cdot5{,}11\cdot10^{-3}\ M\cdot1/4\cdot(1/120\ cm^3)\cdot32\ g\cdot mol^{-1}\cdot(1000\ mg/1\ g) =$ **$9{,}1\ mg\cdot dm^{-3}$** (1)

Kasutades $c(S_2O_3^{2-}) = 0{,}02025$ M:

$c(O_2) = 26{,}71\ cm^3\cdot0{,}02025\ M\cdot1/4\cdot(1/120\ cm^3)\cdot32\ g\cdot mol^{-1}\cdot(1000\ mg/1\ g) =$ **$36\ mg\cdot dm^{-3}$**

f) *Hindamine: keemiliselt korrektne Lewis'i struktuurivalemi eest 1 p.* (1)



g) $N_3^- + NO_2^- + 2H^+ \rightarrow N_2 + H_2O + N_2O$ (1)

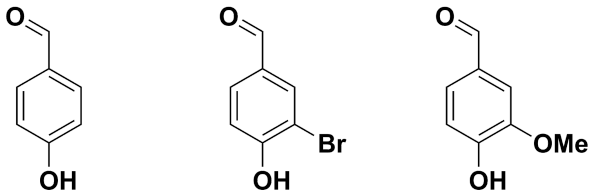
5. Mis aine see on? Autor: Ivo Leito (10 p)

Allikad:

- D.F. Taber; S. Patel; T.M. Hambleton and E.E. Winkel. (2007). Vanillin Synthesis from 4-Hydroxybenzaldehyde. *Journal of Chemical Education*, 84(7), 1158. https://doi.org/10.1021/ed084p1158
- https://webbook.nist.gov/cgi/cbook.cgi?ID=C121335&Mask=200#Mass-Spec

a) **X** = $C_8H_8O_3$ (0,5)

b) *Hindamine: iga korrektselt joonistatud struktuurivalem annab 1 p, kokku 3 p.* (3×1)



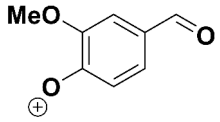
1 **2** **X**

c) Molekulaarioon (0,5)

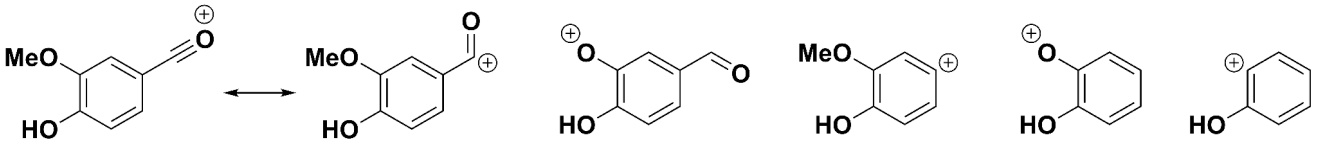
d) Fragmentioon (0,5)

e) Signaal m/z väärtusega 153 on eeskätt põhjustatud molekulaarioonist, milles üks süsinikuaatom on süsinik-13 ehk ^{13}C. (0,5)

f) *Hindamine: iga korrektselt joonistatud struktuurivalem annab 1 p, kokku 5 p.* (5×1)



või



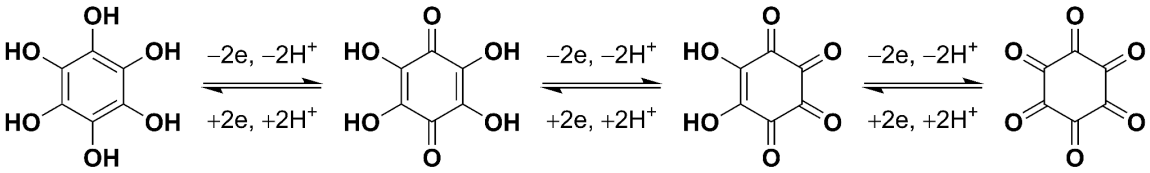
m/z = 151 *m/z* = 137 *m/z* = 123 *m/z* = 109 *m/z* = 93

6. Isomeerid ja raamistikud. Autor: Nikita Žoglo (18 p)

Allikad:

- L. Wang; R. Papoular; N. Horwitz; J. Xie; A. Sarkar; D. Campisi, et al. (2022). Linker Redox Mediated Control of Morphology and Properties in Semiconducting Iron-Semiquinoid Coordination Polymers. *ChemRxiv*. https://doi.org/10.26434/chemrxiv-2021-1v37x-v2
- C.W. Ong; S.-C. Liao; T.H. Chang; H.-F. Hsu. (2004). In Situ Synthesis of Hexakis(alkoxy)diquinoxalino[2,3-*a*:2‘,3‘-*c*]phenazines: Mesogenic Phase Transition of the Electron-Deficient Discotic Compounds. *The Journal of Organic Chemistry*, 69(9), 3181-3185. https://doi.org/10.1021/jo035840l
- Y. Liu; S. Li; L. Dai; J. Li; J. Lv; Z. Zhu; A. Yin; P. Li; B. Wang. (2021).The Synthesis of Hexaazatrinaphthylene-Based 2D Conjugated Copper Metal-Organic Framework for Highly Selective and Stable Electroreduction of CO2 to Methane. *Angew. Chem. Int. Ed.*, 60, 16409.https://doi.org/10.1002/anie.202105966
- J. Park; A.C. Hinckley; Z. Huang; D. Feng; A.A. Yakovenko; M. Lee; S. Chen; X. Zou; Z. Bao. (2018). Synthetic Routes for a 2D Semiconductive Copper Hexahydroxybenzene Metal–Organic Framework. *Journal of the American Chemical Society*, *140* (44), 14533-14537. https://doi.org/10.1021/jacs.8b06666

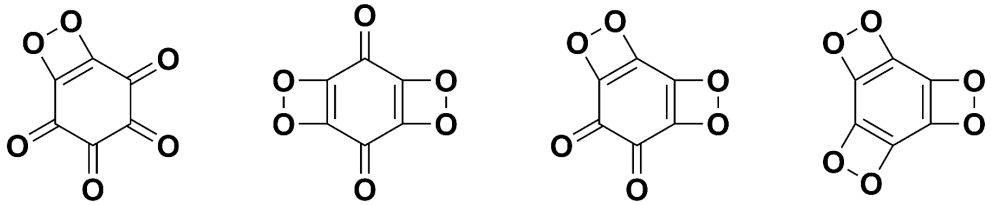
a) *Hindamine: iga korrektselt joonistatud struktuurivalem annab 0,5 p, kokku 1,5 p.* (3×0,5)



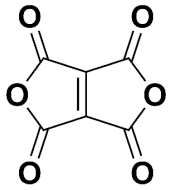
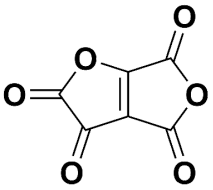
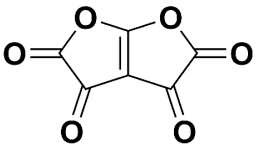
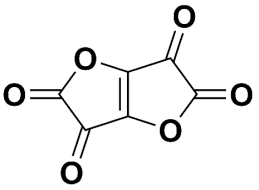
X1 **X2** **X3** **X4**

b) *Hindamine: iga korrektselt joonistatud struktuurivalem annab 0,5 p, kokku maksimaalselt 3 p.*

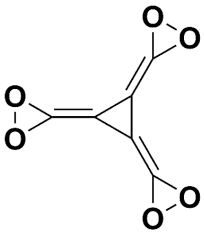
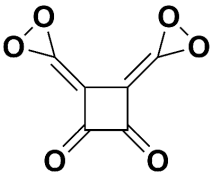
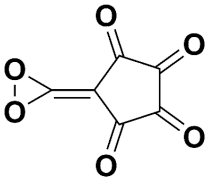
i) Sobivad ***kaks*** järgmistest või sarnastest variantidest: (2×0,5)



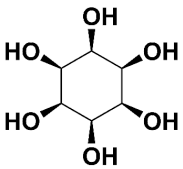
ii) Sobivad ***kaks*** järgmistest või sarnastest variantidest: (2×0,5)

iii) Sobivad ***kaks*** järgmistest või sarnastest variantidest: (2×0,5)

c) *Hindamine: iga korrektselt joonistatud stereoisomeer annab 0,5 p, iga korrektselt märgitud kiiralne stereoisomeer (**7** ja **8**) annab 0,5 p, kokku 5,5 p.* (11×0,5)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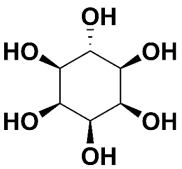
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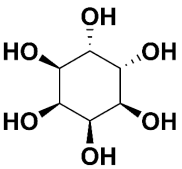
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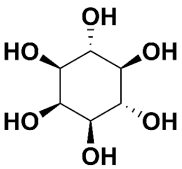
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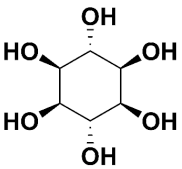
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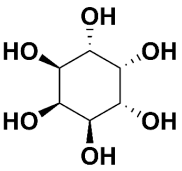
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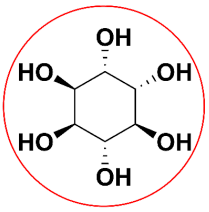
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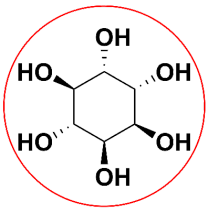
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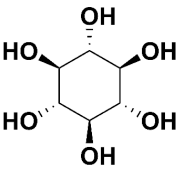
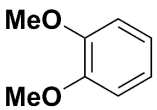
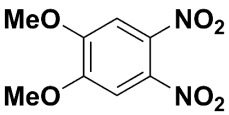

9

d) *Hindamine: iga korrektselt joonistatud struktuurivalem annab 1 p, kokku 4 p.* (4×1)


A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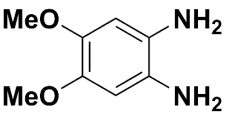
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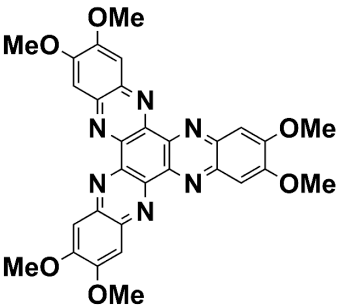
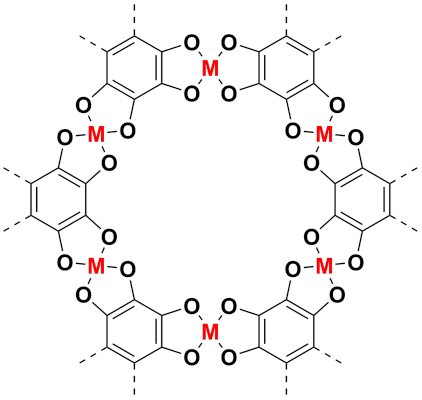
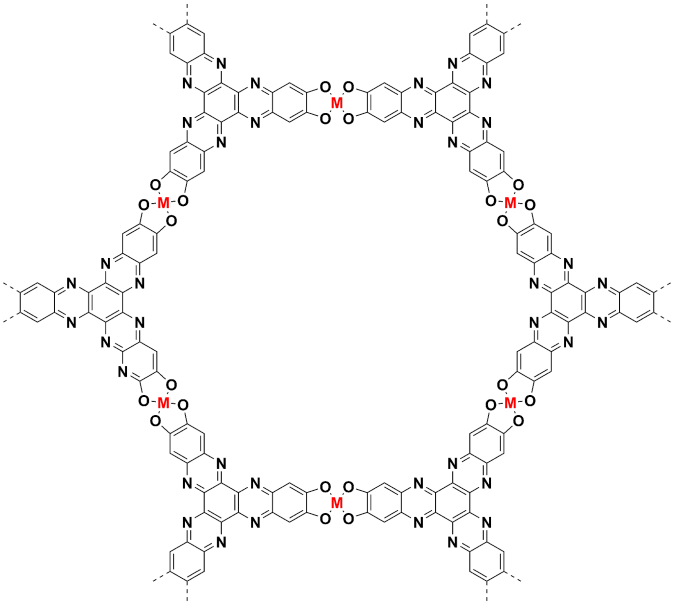

D

e) Heksagonaalsed (1)

f) *Hindamine: iga korrektselt joonistatud poori struktuur annab 1 p, kokku 2 p.* (2×1)





g) Igas pooris on 6 metalliaatomit ning iga aatom on võrdselt jagatud kahe poori vahel ehk 6/2 = 3 metalliaatomit ühe poori kohta.
Sarnaselt on igas pooris 6 ligandi L molekuli, mis on võrdselt jagatud kolme poori vahel ehk 6/3 = 2 ligandi ühe poori kohta.
Niisiis vastab MOF-ide molekulivalemile $\mathbf{M_3L_2}$. (1)