AUSTRALIAN SCIENCE OLYMPIADS

CHEMISTRY

2000 NATIONAL QUALIFYING EXAMINATION

SOLUTIONS GUIDE

Answers are a guide only and do not represent a preferred method of solving problems.

Section A

1B, 2A, 3C, 4C, 5D, 6D, 7A, 8B, 9E, 10B, 11A, 12D, 13E, 14C, 15E

Section B

Q16

(a) $2PbS(s) + 3O_2(g) \longrightarrow 2PbO(s) + 2SO_2(g)$

(b) It is important to limit the supply of air to avoid further oxidation of PbO to PbO_2 and SO_2 to SO_3.

(c) The elemental lead must also be oxidised under these conditions, and so will react to form PbO as well:

$$2Pb(s) + O_2(g) \longrightarrow 2PbO(s)$$

(d)

$$\begin{aligned} PV_{SO_2} &= n_{SO_2}RT \\ n_{SO_2} &= \frac{PV_{SO_2}}{RT} \\ but\ \ n_{PbS} &= n_{SO_2} \\ so\ \ n_{PbS} &= \frac{PV_{SO_2}}{RT} \\ &= \frac{101.3kPa.V_{SO_2}}{8.314JK^{-1}mol^{-1}.298K} \\ &= 0.0409molL^{-1} \times V_{SO_2} \end{aligned}$$

(e) $2PbO(s) + PbS(s) \longrightarrow 3Pb(s) + SO_2(g)$

(f) Pb^{2+} oxidises S(-II) to S(IV) and so is the oxidising agent in this reaction

(g) From the equation given in part (d) we have

$$\begin{aligned} n_{PbS} &= 0.0409molL^{-1} \times V_{SO_2} \\ so\ \ n_{PbS} &= 0.0409molL^{-1} \times 0.0662L \\ &= 2.71 \times 10^{-3}mol \\ &\ \ but\ this\ is\ only\ for\ two\ thirds\ of\ the\ sample \\ so\ total\ n_{PbS} &= \tfrac{3}{2} \times 2.71 \times 10^{-3}mol \\ &= 4.06 \times 10^{-3}mol \end{aligned}$$

(h)

$$\begin{aligned} Purity &= \frac{m_{PbS}}{m_{galena}} \\ &= \frac{4.06 \times 10^{-3}mol \times 239.266gmol^{-1}}{1.045g} \\ &= 0.929g/g\ of\ galena \quad or \quad 93.0\% \end{aligned}$$

(i)

$$\begin{aligned} m_{PbO} &= n_{PbS} \times FW_{PbO} \\ &= 2.71 \times 10^{-3}mol \times 223.2gmol^{-1} \\ &= 0.605g \end{aligned}$$

(j)

$$n_{Pb+PbS} = \frac{m_{Pb}}{FW_{Pb}}$$
$$= \frac{0.8663g}{207.2gmol^{-1}}$$
$$= 4.18 \times 10^{-3} mol$$

$$so\,\%Elemental\ Lead = \frac{n_{Pb}}{n_{Pb+PbS}}$$
$$= \frac{4.18 \times 10^{-3} mol - 4.06 \times 10^{-3} mol}{4.18 \times 10^{-3} mol}$$
$$= 2.9\%$$

(k) In the solution we have $4.18x10^{-3}$mol of Pb^{2+} to $1.67x10^{-2}$mol of OH^{-}, which is in the ratio 1:4. Hence we would suspect $[Pb(OH)_4]^{2-}$ to be present in solution. Note that the oxidation state of Pb is unchanged in this species.

Q17

(a) 9 Ser-Gly-Cys-Lys-Ile-Ile-Ser-Ala-Ser-Thr-Cys-Pro-Ser-Tyr-Pro-Asp-Lys

(b) 2 Lys-Ser-Cys-Cys-Pro-Asn-Thr-Thr-Gly-Arg

(c) 6 Asn-Thr-Cys-Arg-Phe

7 Gly-Gly-Gly-Ser-Arg-Glu-Val-Cys-Ala-Ser-Leu

(d) *Peptides from trypsin cleavage:*

1 Asn-Ile-Tyr-Asn-Thr-Cys-Arg

2 Lys-Ser-Cys-Cys-Pro-Asn-Thr-Thr-Gly-Arg

3 Ile-Ile-Ser-Ala-Ser-Thr-Cys-Pro-Ser-Tyr-Pro-Asp-Lys

4 Phe-Gly-Gly-Gly-Ser-Arg

5 Ser-Cys-Cys-Pro-Asn-Thr-Thr-Gly-Arg

Peptides from chymotrypsin cleavage:

6 Asn-Thr-Cys-Arg-Phe

7 Gly-Gly-Gly-Ser-Arg-Glu-Val-Cys-Ala-Ser-Leu

8 Lys-Ser-Cys-Cys-Pro-Asn-Thr-Thr-Gly-Arg-Asn-Ile-Tyr

9 Ser-Gly-Cys-Lys-Ile-Ile-Ser-Ala-Ser-Thr-Cys-Pro-Ser-Tyr-Pro-Asp-Lys

(e) 7 Gly-Gly-Gly-Ser-Arg-Glu-Val-Cys-Ala-Ser-Leu

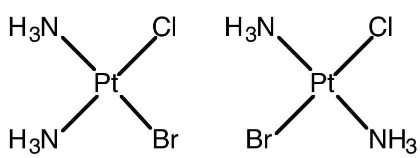
Leu is a C-terminus resulting from a chymotrypsin cleavage and this is unexpected as chymotrypsin normally cleaves an amide bond to leave a C-terminus of either Phe, Tyr or Trp.

(f)

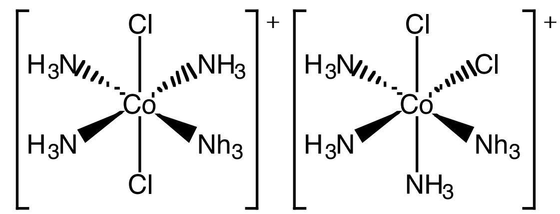
Lys – Ser – Cys – Cys – Pro – Ans – Thr – Thr – Gly – Arg –
Asn – Ile – Tyr – Asn – Thr – Cys – Arg – Phe – Gly – Gly –
Gly – Ser – Arg – Glu – Val – Cys – Ala – Ser – Leu – Ser –
Gly – Cys – Lys – Ile – Ile – Ser – Ala – Ser – Thr – Cys –
Pro – Ser – Tyr – Pro – Asp – Lys

Q18

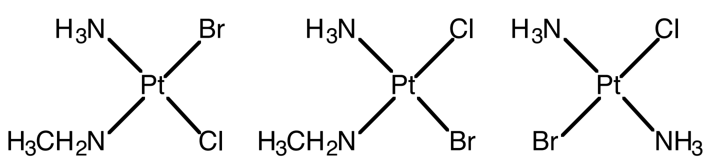
(a) (i) 2 geometrical isomers



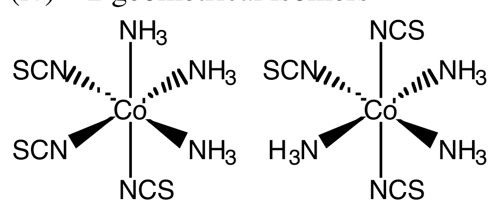
(ii) 2 geometrical isomers



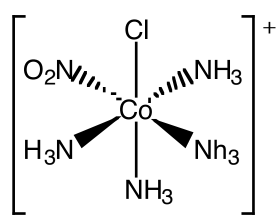
(iii) 3 geometrical isomers



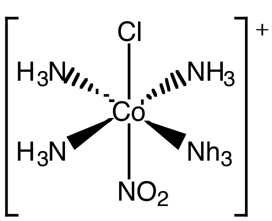
(iv) 2 geometrical isomers



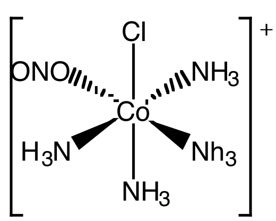
(b) (i) cis-$[CoCl(NO_2)(NH_3)_4]^+$ has the structure



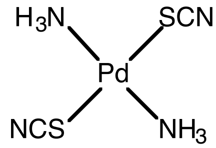
1 geometrical isomer



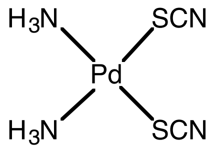
1 linkage isomer



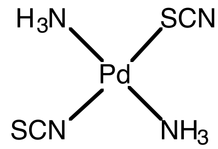
(ii) trans-[$Pd(SCN)_2(NH_3)_2$]. Has the structure

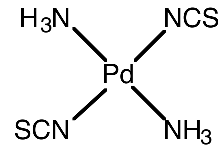


1 geometric isomer

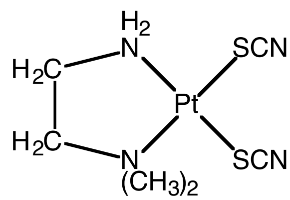


2 linkage isomers



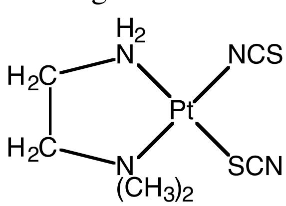


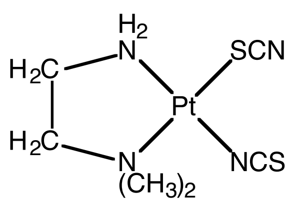
(c) (i) square planar [$Pt(SCN)_2$(dmen)] has the structure

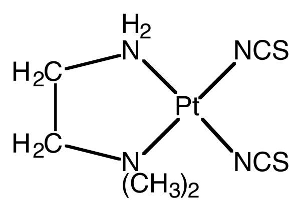


As there is only one structure possible there is therefore no geometrical isomer.

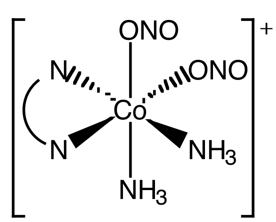
3 linkage isomers



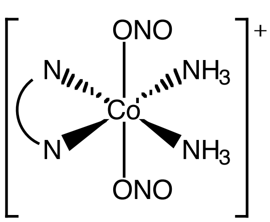


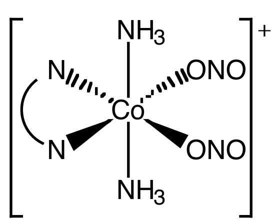


(ii) cis-[$Co(ONO)_2(NH_3)_2$(en)]$^+$.has the structure

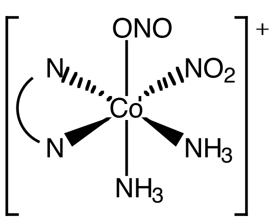


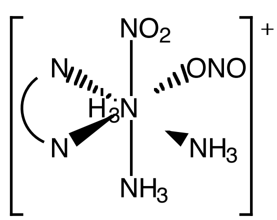
2 geometrical isomers

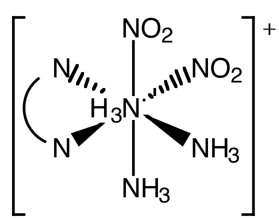




3 linkage isomers





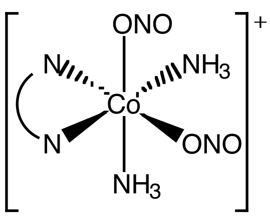
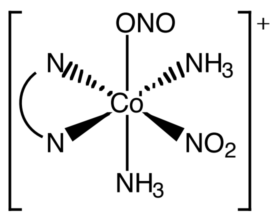
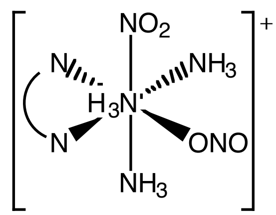
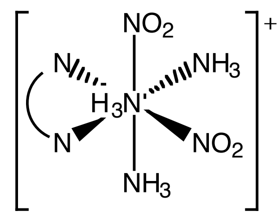


If you have been alert and careful you will have seen that there is another structure for the cis isomer and each of the three linkage isomers, these are shown and explained in (d).

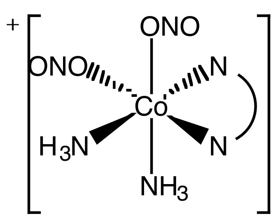
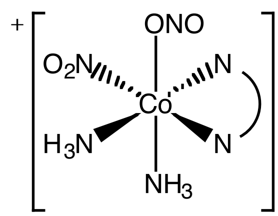
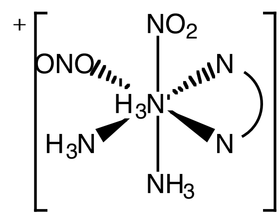
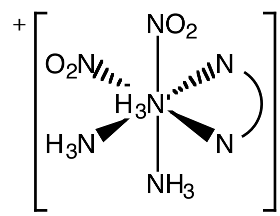
(d) The complex ion cis-$[Co(ONO)_2(NH_3)_2(en)]^+$ (c) (ii) and its three linkage isomers all have non-superimposable mirror images and hence exhibit optical isomerism. All the rest have superimposable mirror images and hence do not exhibit optical isomerism.

The alternative structures alluded to in (c) (ii) are

cis-$[Co(ONO)_2(NH_3)_2(en)]^+$ 3 linkage isomers

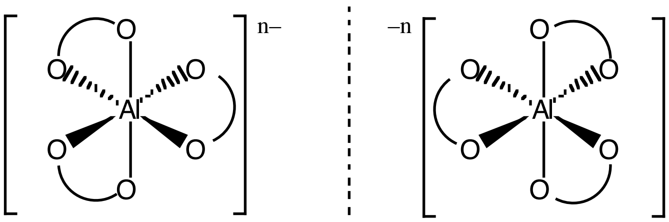





Rotating these four structures 180° around the vertical axis produces the structures drawn below and we can see that they are the mirror images of the cis isomer and its three linkage isomers in (c) (ii).

(e) (i) There are two stereoisomers.

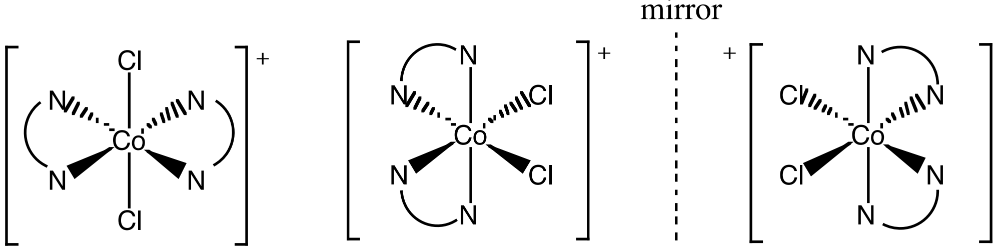
mirror



(where O O is $C_2O_4^{3-}$ and n = 3)

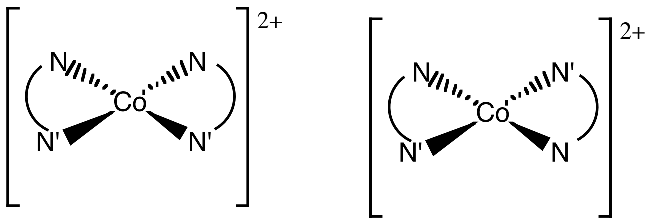
(ii) There are three stereoisomers.

mirror



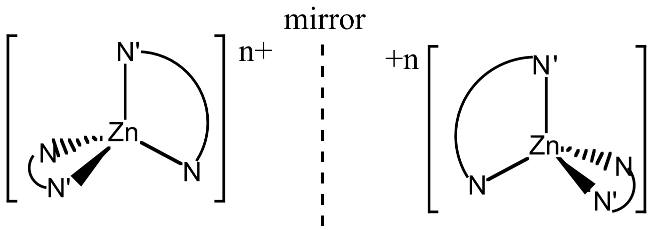
(where N N is **en**

(iii) There are two stereoisomers.



(where N⌒N' is **dmen**

(iv) There are two stereoisomers.



(where N⌒N' is **dmen**
and n is 2

Q19

(a) Person A has a dormant tumor in the left eye.
Person B has an active tumor in the right eye.

$$\text{Activity after 3 hours} = \frac{\begin{array}{ccc}\text{average count} & - & \text{Count rate for} \\ \text{around 3 hours} & & \text{normal eye}\end{array}}{30\ \text{photons / Bq}}$$

$$= \frac{470 - 190}{30}$$

$$= 9.3\ \text{Bq}$$

$$\text{Proportion of original injection in eye} = \frac{9.3}{3.7 \times 10^{-6}}$$

$$= 2.5 \times 10^{-4}\%$$

(b) The β particle is an electron emitted from the nucleus when a neutron transforms to a proton.

$$^{1}_{0}\text{n} \rightarrow {}^{1}_{+}\text{p} + {}^{0}_{-}\beta$$

The ^{32}P becomes ^{32}S

$$^{32}_{15}\text{P} \rightarrow {}^{32}_{16}\text{S} + \beta$$

(c)

$$t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

$$\text{so} \quad k = \frac{\ln 2}{t_{\frac{1}{2}}}$$

$$= \frac{6.9315 \times 10^{-1}}{14}$$

$$= 0.049511$$

If A is final activity, A_0 is initial activity and t is time

then $A = A_0 e^{-kt}$

$$= 3.7 \times 10^{6} \times e^{-(0.049511 \times 20)}$$

$$= 3.7 \times 10^{6} \times 3.7150 \times 10^{-1}$$

$$= 1.37 \times 10^{6}\,\text{Bq}$$