National Student Team Contest (first stage)
Solution of task 5. Porous metal from ionic cluster

2. The point No.2 should be solved as the 1st step to propose the composition for the complex anion of the unknown compound.

   Most likely, the given IR modes correspond to chemisorbed CO molecules or carbonyl ligands in the complex anion.

1. Molecular weight of metal is not obvious however that is possible to estimate the percentage of CO ligands in the unknown substance A. Weight of all gaseous products is as follows:

$$m_{gases} = 1 - 0.574 = 0.426 \text{ g.}$$

   The molar ratios of CO : H_2O : N_2 is 34 : 20 : 1. So, if the anion X^{3-} does not contain nitrogen and is just a carbonyl compound (no other kinds of ligands) the unknown substance A is $[NEt_4][Rh_{15}(CO)_{27}]^{3-}$ compound. Check the charge balance to confirm the accuracy of your solution.

$$\frac{2}{3}[N(C_2H_5)_4]_3[Rh_{15}(CO)_{27}] + 18\,O_2 \rightarrow 10\,Rh + 34\,CO + 20\,H_2O + N_2$$

3. Simple electron-counting schemes such as the effective atomic number (EAN) and the skeletal electron pair (SEP) rules, which result from these systematic studies, are extremely useful in correlating the structures of a vast number of clusters to their electron counts.

   According to the Nevil V. Sidgwick theory and EAN rule. The electron configuration of rhodium is [Kr]$4d^8 5s^1$ and so the number of electrons for the neutral Rh^0 is 45. The EAN number for the $[RH\ (CO)_{1.8}]^{0.2-}$ cluster is 45 + 2·1.8 + 0.2 = 48.8 that is much below the atomic number of Xenon. So the complex could be stable if Rh-Rh bonding takes part.

   The fifteen metal atoms could be distributed uniformly forming a Rh-centered $[Rh_{15}(CO)_{27}]^{3-}$ cluster. In such a case, most likely, the 1st coordination sphere could be cubic (body-centered cube) and the 2nd coordination sphere forms a hexa-capped cube of pentadecavertex metal cluster as shown in Figure 1a.

   Structure of $[NEt_4][Rh_{15}(CO)_{27}]^{3-}$ has the structure as the following given in Figure 1b. The structure is similar to that of previously reported $[Rh_{15}(CO)_{30}]^{3-}$ and only differs in the number and stereochemistry of the carbonyl groups. Two kinds of CO groups are presented – bridging and terminal.

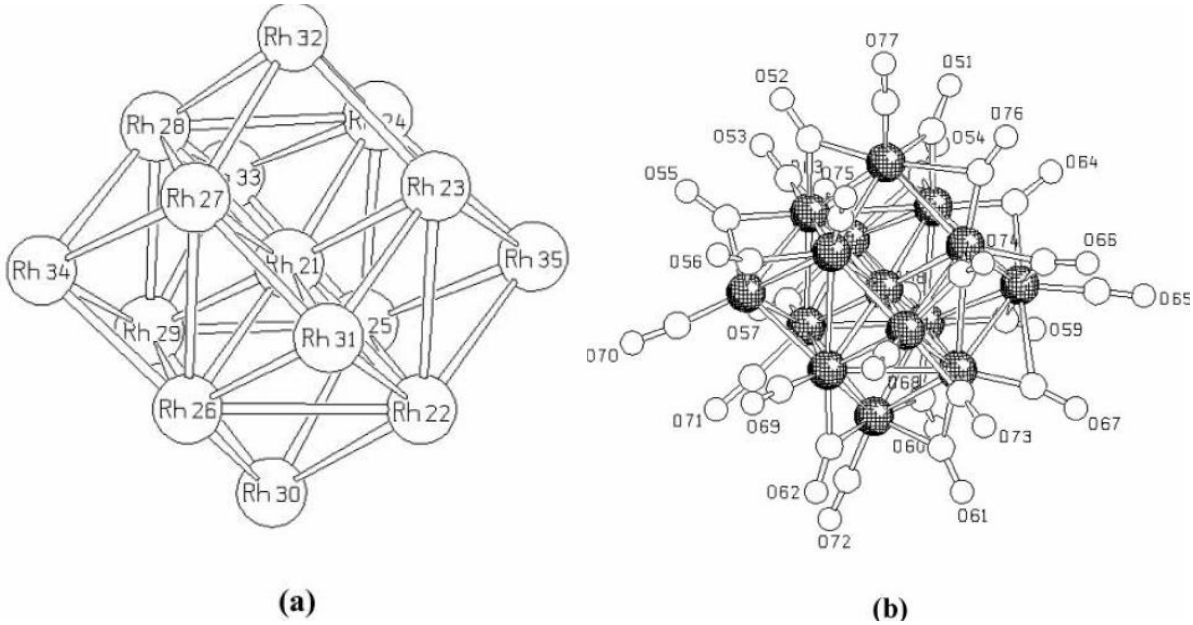

Figure 1. Structure of the ordered $[Rh_{15}(CO)_{27}]^{3-}$ *trianion (only one of the two independent anions are present in the unit cell is represented):*
(a) rhodium framework with a numbering scheme;
(b) whole structure with numbering of O atoms
(C atoms are numbered as the corresponding O atoms).

The unit cell of the $[NEt_4][Rh_{15}(CO)_{27}]^{3-}$ salts contains two pairs of independent $[Rh_{15}(CO)_{27}]^{3-}$ cluster anions and 12 $[NEt_4]^+$ cations separated by normal van der Waals contacts.

4. Synthesis of the substance A could be performed in laboratory using simpler rhodium carbonyls as reagents and hydrated cadmium chloride $CaCl_2 \cdot xH_2O$, $InCl_3 \cdot xH_2O$ or $ZnCl_2 \cdot xH_2O$ as catalysts for controlled protonation of the complex. The following equations are:

$$2[Rh_7(CO)_{16}]^{3-} + 2\,H^+ \rightarrow 2\{[HRh_7(CO)_{16}]^{2-}\} \rightarrow [Rh_{14}(CO)_{25}]^{4-} + H_2 + 7\,CO$$

$$[Rh_{14}(CO)_{25}]^{4-} + H^+ \rightarrow [HRh_{14}(CO)_{25}]^{3-}$$

$$[HRh_{14}(CO)_{25}]^{3-} + [Rh_1(CO)_2]^+ \rightarrow [Rh_{15}(CO)_{27}]^{3-} + H^+$$

All $[NEt_4]^+$ salts could be separated successfully by differential solubility.

5. The specific surface area could be estimated roughly using corresponding TEM data. The round shaped metal particle of 5 nm diameter has its surface area of 314.12 nm^2 and volume of 523.533 nm^3. The density is of 12.41 g/cm^3. So the unit weight should be $6.497 \cdot 10^{-21}$ kg or $6.497 \cdot 10^{-18}$ g. So the metal sponge weight is 0.5742 g that corresponds roughly to $0.884 \cdot 10^{18}$ or $8.84 \cdot 10^{16}$ particles. Each separate particle has its theoretical surface area of 314.12 nm^2 while all independent rhodium nanoparticles results in maximal surface of 27.76 m^2. The resulting maximum of BET area could be 48.3 m^2/g.

   To be more accurate we can take into consideration that the accessible surface area is lower than the theoretical.