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The insert has a periodic table. Enter all work to be graded on the exam pages

1) (37 points) The tetrafluoronickelate(II) complex anion is paramagnetic.

a) Propose a three-dimensional structure for the anion. Provide an argument to support your structure.

Reasonable arguments suggest two possible structures.

Nickel(II) has a d^8 configuration which suggests a square planar structure with 4 mostly non-bonding orbitals and one anti-bonding MO. The 8 electrons fill the non-bonding orbitals so the material would be expected to be diamagnetic.

However, all the ligands are fluoride anions. The identity of the ligands suggests tetrahedral complexation with 2 non-bonding MO's and 3 anti-bonding MO's. The 4 of the 8 electrons would fill the non-bonding MO's and the remaining 4 would partially fill the anti-bonding MO's. Paramagnetism results.

A comparison of the two predictions with the experimental observation of paramagnetism demonstrates a tetrahedral structure for the complex anion.

b) What is the color of the complex?

Blue. Fluoride is a weak field ligand so the gap between the non-bonding and anti-bonding orbitals is small. The wavelength of the absorbed photon will lie at the red end of the spectrum so the transmitted light will lie at the blue end.

c) Use the correlation diagram for the complex and provide

i) the number of electrons in bonding MO's: 8

In either case, there are four bonding MO's that are completely filled by the 8 electrons from the four ligands.

ii) the number of electrons in non-bonding MO's: 4

iii) the number of electrons in anti-bonding MO's: 4

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2) (28 points) The compound $\text{Na}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$ was once a member of the inorganic synthesis repertoire. The NCS^- ligands bind to the chromium ion at the N end.

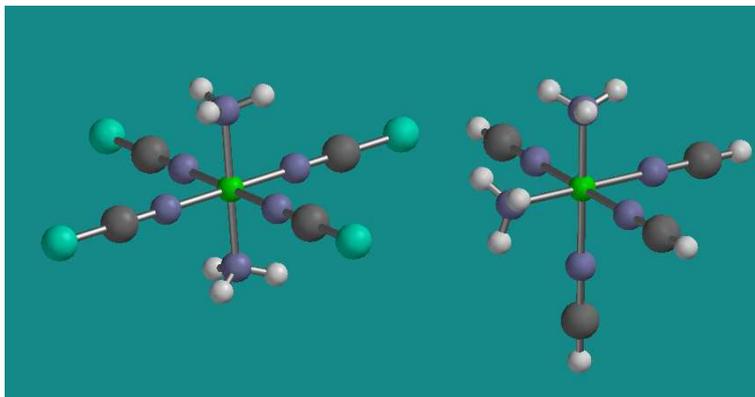
a) Provide the IUPAC name for the compound.

Sodium diäminetetraäsothiocyanatochromate(III)

The name of the SCN^- ion is thiocyanate. As a ligand it becomes thiocyanato. The prefix iso indicates that the nitrogen end of the ligand binds to the metal. Most Americans would use chromate. Think of the compound potassium dichromate. However, a classicist would prefer chromiate. Chromium would be recognized as a second declension neuter noun and the “i” would be retained in its declension, e.g. chromium, chromii, chromio, chromium, chromio, *et cetera*. This classical preference is used in naming compounds in which deuterium is substituted for hydrogen. One refers to deuteriated compounds and not deuterated compounds. Latin wins in complexes of iron, copper, silver, mercury, tin, and gold. The complex anion AgF_4^{4-} would tetrafluoroärgentate(I).

b) Provide the three-dimensional structure of the complex portion of the compound. If isomers are possible, give the structures of all isomers.

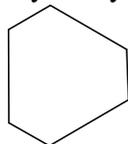
Six monodentate ligands are attached to the d^3 chromium(III) so octahedral complexation is expected. Trans (E) [structure on the left] and cis (Z) [structure on the right] isomers are possible. Both species have planes of symmetry so there are no optical isomers (enantiomers).



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3) (20 points) Single crystals of alpha quartz, the stablest form of silicon dioxide, have six sides and rotate the plane of polarized light. A cross section of a quartz crystal is shown below.

a) Which element(s) of symmetry does crystalline quartz possess? To which crystal system does it belong?



A three-fold rotational axis of symmetry. Six sides suggests a six-fold axis of symmetry. However, the cross section shows that quartz is a distorted hexagon and lacks a six-fold axis of symmetry. The mineral beryl has both. The six sides and the three-fold axis of symmetry show that quartz belongs to the Trigonal/Hexagonal Crystal System.

b) Which element(s) of symmetry does crystalline quartz lack? Briefly explain.

Quartz's ability to rotate the plane of polarized light means that it is chiral and therefore a quartz crystal lacks a center of symmetry and planes of symmetry. Also, improper rotational axes of all order are also excluded.

4) (20 points) If an simple amide such as formamide, HCONH_2 , is dissolved in D_2O , the amide protons rapidly exchange with the heavy water yielding a deuteriated species, e.g. HCOND_2 in the case of formamide. When structured proteins are dissolved in heavy water, some of the amide protons exchange very slowly. Provide an explanation for this striking difference in the rate of the exchange reaction.

Hydrogen bonding is a prominent feature in structured proteins and is a dominant factor leading to structure such as alpha helices and beta sheets. Amide protons involved in hydrogen bonds are stabilized by this interaction and therefore are less available for exchange with the water.

5) (25 points) If one examines the catalogues of chemical vendors, one is struck by two facts. Salts of transition metals are commonly sold in the form of a hexahydrate, i.e. six moles of water per mole of metal. Completely anhydrous salts, if available at all, are quite expensive. Provide an explanation for these peculiar facts.

These salts are prepared from aqueous solutions and the counterion is usually not a ligand. Water is present at a high concentration of ca. 55 M and forms an octahedral complex. Because of the coordinate covalent bond between the metal ion and the water molecules, their removal is difficult. This difficulty translates to a high price.

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6) (25 points) Suppose that you are provided a sample of a black powder which could be either graphite, an inexpensive substance, or buckminsterfullerene (C_{60}), a very expensive material. Propose a simple solubility test that would allow you to determine the identity of the powder. Briefly provide the basis for your test.

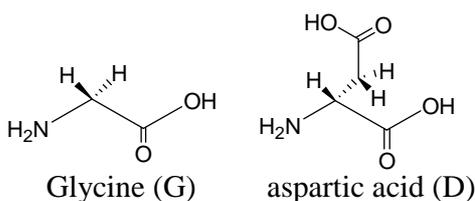
Graphite is a prominent example of a network covalent solid and will be insoluble in all solvents. Buckminsterfullerene is a molecular solid and will be soluble in organic solvents but not water. Buckminsterfullerene is constructed from benzene rings so benzene would be a good choice of solvent. Water would not as the hydrogen bonding between water molecules would exclude dissolving a highly non-polar substance such as an allotrope of carbon.

7) (25 points) Predict the crystal structure of hematite, iron(III) oxide. The ionic radii of the iron(III) and oxide ions are 0.62 \AA and 1.40 \AA , respectively. The critical ratios are given below:

0.732	0.414	0.225	0.155
cubic	octahedral	tetrahedral	triangular
=====	=====	=====	=====
			linear

The oxide anion is the larger of the two so arrange the oxide anions in a closest packing (cp) arrangement. In the case of hematite, nature prefers hexagonal closest packing but a polymorph with cubic closest packing should be possible. The ratio of ionic radii is 0.44 which is greater than 0.414 so the iron(III) cations will be packed into the octahedral holes of the cp lattice of oxide anions. Two-thirds of the octahedral sites will be filled. The iron cations will have a coordination number of 6. It follows from this and the stoichiometry Fe_2O_3 that the coordination number of oxygen is $(6)(2/3) = 4$.

8) (20 points) Glycine and aspartic acid are two of the 20 essential amino acids. Their covalent structures are given below. A chemist wishing to prepare a dipeptide mixes one mole of each amino acid and induces a reaction by heating. Explain why this procedure will generate a mixture of several substances rather than a single product.



Peptides are prepared by the condensation reaction whereby the amino end of one amino acid reacts with the COOH (carboxy) end of a second amino acid. Removal of water leads to the formation of the peptide bond. With a mixture of unmodified glycine and aspartic acid, several permutations are possible: $G + G = GG$, $D + D = DD$, $G + D = GD$ (the carboxyl group of glycine reacts with the amino group of aspartic acid), and $D + G = DG$ (the amino group of aspartic acid reacts with the carboxyl group of glycine). In addition, aspartic acid has a side chain with a carboxyl group so the glycine could react with it instead of the carboxyl group on the backbone. In short, a mess results. One prevents this by adding protective groups to block the undesired reactions. Students have pointed other factors that will contribute to a mixture. The reaction might not go to completion. Also, the reaction might not stop at the first step. That is a dimer might react with a monomer and produce a trimer.