## 86 學年度 國立成功大學 化学研究所 無機 1七岁試題 共 2 頁 第 / 頁

(1) (6%) The resonance structures of thiocyante ion, SCN-, are shown below. Assign formal charges for each of the structures. Which one is the most important structure of the ion? Explain.

$$:S \longrightarrow C \longrightarrow N:$$
  $:S \longrightarrow C \longrightarrow N:$   $:S \longrightarrow C \longrightarrow N:$ 

(2) (6%) The energy required to break a particular bond is not always constant. Compare the N-Cl bond energies in NOCl and NCl3:

NOCI 
$$\longrightarrow$$
 NO + CI  $\Delta$ H° = 158 kj/mol NCI<sub>3</sub>  $\longrightarrow$  NCI<sub>2</sub> + CI  $\Delta$ H° = 375 kj/mol

Why is there such a great discrepancy in the apparent N-Cl bond energies?

(3) Answer the following: (30%)

(a) The order of reducing abilities in aqueous solution is Li > K > Na, which is not the order expected from the relative ionization energies of these metals. Explain your answer.

(b) Predict the most likely structure of PCl<sub>2</sub>F<sub>3</sub> and explain your reasoning.

(c) Square planar d<sup>8</sup> paramagnetic complexes are extremely rare. Account for this observation with a crystal field argument.

(d) Many complexes exhibiting charge transfer bands in the visible region are unstable in sunlight. Explain.

(e) The high-spin  $d^4$  complex cation  $[Cr(H_2O)_6]^{2+}$  is labile, but the low-spin  $d^4$  complex anion  $[Cr(CN)_6]^{4-}$  is inert. Explain.

(4) (8%) Determine the number of IR active CO stretching modes for *trans*-[Fe(CO)4Cl<sub>2</sub>].

D44	E	2C4	$C_1$	2C1'	2C,"	i	254	$\sigma_{k}$	20,	204		
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B.,	1	-!	:	!	-!	-!	•	!	-!	!	1	
B,. E.	2	0	- 2	- 0	0	-1 -2	0	- 1 2	ò	0	(x, y)	

- (5) (a) Sketch all the Schlenk glassware required on a laboratory bench for a simple filtration to obtain the solid precipitate from a reaction solution. The solid is airsensitive. (6%) (b) Sketch a glove box and a glove bag, which can help synthesis and reactions of various air-sensitive compounds (4%).
- (6) Give the electron count for each ruthenium atom in the following complex (4%), having recently been prepared in one laboratory at the department of chemistry, national Cheng Kung University, and explain why this complex is diamagnetic.(2%) Is it a chiral (or optically active) compound (2%)? How many IR active CO stretching bands should be observed in this complex (1%)? Give one reason to your prediction without referring to Group theory or using a Character Table (1%).

- (7) (a) The anion [Ni<sub>2</sub>Cl<sub>8</sub>]<sup>2</sup>- belongs to the C<sub>2h</sub> point group. Each nickel has a square pyramidal arrangement of ligands, and there are no Ni-Ni bonds. Sketch the structure (3%). (b) Describe and sketch simple structures for (i) tetragonal (Jahn-Teller) distortion, (ii) Trigonal distortion, and (iii) Twist distortion of an idealized octahedral complex [ML<sub>6</sub>] (9%).
- (8) (a) Write the electron configuration of the  $N_2$  and  $O_2$  molecules (2%) and calculate the bond order for each molecule (2%). Compare the N-N or O-O bond lengths: which one is shorter (2%). (b) Why is  $O_2$  more chemically reactive than  $N_2$ ? (2%)
- (9) It is not the *trans*-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] but *cis*-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] as the active antitumor reagent. Both chloride anions, rather than the NH<sub>3</sub> ligands, of this complex are known to be displaced during the antitumor process. When the NH<sub>3</sub> is replaced by a phosphorus compound, the activity is sharply dropped down. It is also found that the activity is cis-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] < cis-[PtCl<sub>2</sub>(RNH<sub>2</sub>)<sub>2</sub>] < cis-[PtCl<sub>2</sub>(NR<sub>3</sub>)<sub>2</sub>]. Explain why the active isomer is cis-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] but not trans-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] (4%) and explain the reduced activity in other substituted complexes such as cis-[PtCl<sub>2</sub>(NR<sub>3</sub>)<sub>2</sub>] (6%).