

科目：無機化學(1003)

校系所組：中央大學化學學系

交通大學應用化學系 (甲組)

清華大學化學系

清華大學材料科學工程學系 (丙組)

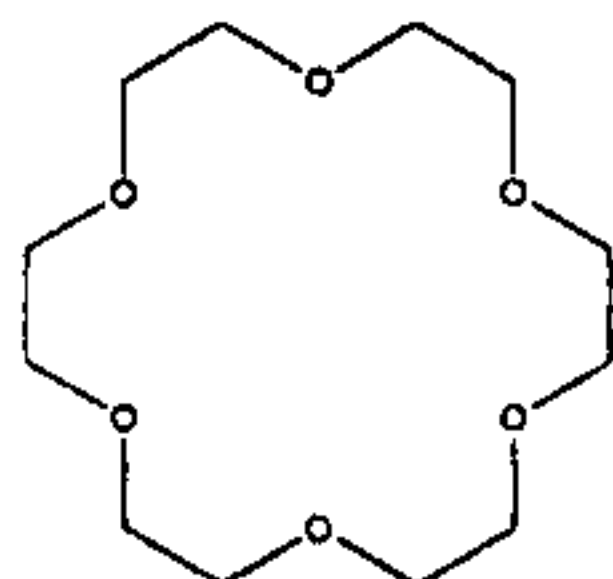
1. (10 pts) Write down the point groups and structures of the following compounds:

(A) XeF<sub>4</sub> (B) B<sub>3</sub>N<sub>3</sub>H<sub>6</sub> (C) B<sub>2</sub>H<sub>6</sub> (D) *cis*-CoCl<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub> (E) Mn<sub>2</sub>(CO)<sub>10</sub>.

2. (10 pts) Nitrogen monoxide (NO) is a radical and can bind to a low oxidation state metal atom. Terminally bound NO can adopt two different modes: linear or bent. (A) Write down the molecular orbital diagram of nitrogen monoxide (NO). (B) Predict the NO structure in the complexes [Fe(CO)<sub>2</sub>(NO)<sub>2</sub>].

3. (10 pts) The stability constants ( $\beta$ ) and rates ( $k_f$ ) of formation of complexes between alkali metal ions and 18-crown-6 (a macrocycle with six ether oxygen ligand atoms) are noted below. Identify, discuss, and explain the apparent conflicting trends shown by these two parameters.

M <sup>+</sup>	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>
Log $\beta$	1.5	4.6	6.0	5.2	4.6
$k_f \cdot 10^{-8}$	0.8	2.2	4.3	4.4	5.1



18-crown-6

4. (10 pts) The IR spectrum of the compound Mo(CO)<sub>3</sub>[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>3</sub> exhibits three bands at 1993, 1919, and 1890 cm<sup>-1</sup>. Please use character tables to determine which form (*mer* or *fac*) is assigned for the compound Mo(CO)<sub>3</sub>[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>3</sub>.

C <sub>2v</sub>	E	C <sub>2</sub> (z)	$\sigma_v(xz)$	$\sigma_v(yz)$		
A <sub>1</sub>	1	1	1	1	z	x <sup>2</sup> , y <sup>2</sup> , z <sup>2</sup>
A <sub>2</sub>	1	1	-1	-1	R <sub>z</sub>	xy
B <sub>1</sub>	1	-1	1	-1	x, R <sub>y</sub>	xz
B <sub>2</sub>	1	-1	-1	1	y, R <sub>x</sub>	yz

C <sub>3v</sub>	E	2C <sub>3</sub> (z)	3 $\sigma_v$		
A <sub>1</sub>	1	1	1	z	x <sup>2</sup> +y <sup>2</sup> , z <sup>2</sup>
A <sub>2</sub>	1	1	-1	R <sub>z</sub>	
E	2	-1	0	(x, y) (R <sub>x</sub> , R <sub>y</sub> )	(x <sup>2</sup> -y <sup>2</sup> , xy) (xz, yz)

5. (10 pts) The reduction potentials (E°) for some cobalt complexes are listed below. Please explain the trends.

Co <sup>3+/2+</sup> ,	1.92 V
[Co(bipy) <sub>3</sub> ] <sup>3+/2+</sup> ,	0.31 V
[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+/2+</sup> ,	0.11 V
[Co(CN) <sub>6</sub> ] <sup>3-</sup> /[Co(CN) <sub>5</sub> ] <sup>3-</sup> +CN <sup>-</sup>	-0.83 V

注意：背面有試題

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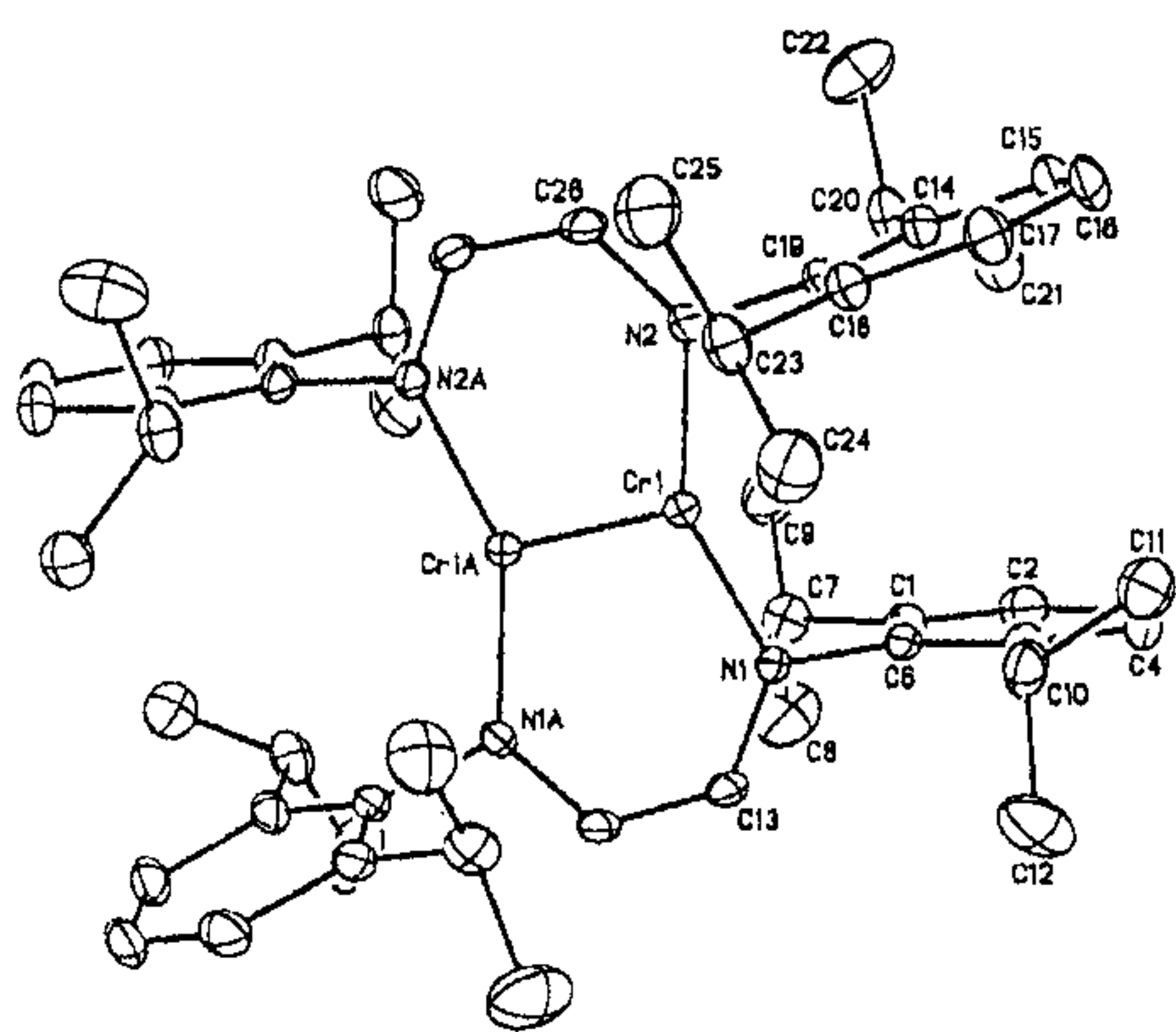
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6. (10 pts) The compound  $(\mu\text{-}\eta^2\text{-H}^i\text{L}^{i\text{Pr}})_2\text{Cr}_2$  (where  $\text{H}^i\text{L}^{i\text{Pr}} = \text{N,N}'\text{-bis(2,6-diisopropylphenyl)-1,4-diazadiene}$ ) contains a short Cr-Cr distance, which is considered the "quintuple bond".
- Use a bimetallic model, M-M, to construct a MO diagram based on the d orbital interactions. Fill in the essential electron(s) that will fulfill the bond order of five. Draw qualitative MO of each level.
  - How can you prove the molecule contain a Cr-Cr "quintuple bond"?



參考用

7. (10 pts) Calculate the electron counting for the following transition metal complexes.
- $\text{Mo}(\text{DME})\text{Cl}_2(\text{NMe})_2$  (DME =  $\text{MeOCH}_2\text{CH}_2\text{OMe}$ )
  - $[\text{CpOs}(\text{CO})_2(\text{C}\equiv\text{NMe})]$
  - $[\text{PtCl}_3(\text{CH}_2=\text{CH}_2)]$
  - $\text{V}(\text{CO})_6$
  - $\text{IrH}_2\text{Cl}(\text{CO})(\text{PPh}_3)_2$
8. (10 pts) Briefly describe the followings:
- Linear Combination of Atomic Orbitals
  - Shielding Effect
  - The Aufbau Principle
  - Olefin metathesis
  - Differences between metal, semiconductor and superconductor

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9. (20 pts) Match scientists who made contributions of the following milestone achievements.

- |                                 |       |
|---------------------------------|-------|
| (1) Ryoji Noyori:               | _____ |
| (2) Richard R. Schrock          | _____ |
| (3) Andre Geim                  | _____ |
| (4) Roald Hoffmann :            | _____ |
| (5) Wilkinson G.:               | _____ |
| (6) Ziegler K. and Natta G.:    | _____ |
| (7) Fisher E.O. :               | _____ |
| (8) Dan Shechtman               | _____ |
| (9) Pauson P. and Miller S. A.: | _____ |
| (10) Richard F. Heck:           | _____ |

- For their discovery and groundbreaking experiments regarding the two-dimensional material graphene
- For palladium-catalyzed cross couplings in organic synthesis
- First synthesized the carbene complexes contain metal-carbon double bonds.
- For the discovery of quasicrystals
- Developed a synthetic procedures to mass produce menthol using a homogeneous catalyst
- For the development of the metathesis method in organic synthesis
- Using Rh-based catalyst to selective hydrogenation of C=C bond
- Synthesized the sandwich compound ferrocene ( $C_5H_5$ )<sub>2</sub>Fe.
- Developed a heterogeneous catalyst containing  $TiCl_4$  and  $Al(C_2H_5)_3$  in hydrocarbon solvents for polymerizing alkenes.
- Developed the concept of isolobal analogy to correlate the organometallic fragment with main group element

參考用