

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)

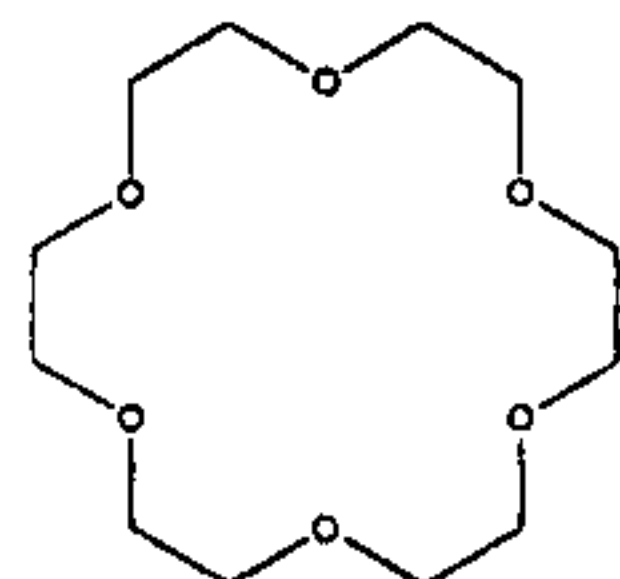
1. (10 pts) Write down the point groups and structures of the following compounds:

(A) XeF₄ (B) B₃N₃H₆ (C) B₂H₆ (D) *cis*-CoCl₂(NH₃)₄ (E) Mn₂(CO)₁₀.

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)₂(NO)₂].

3. (10 pts) The stability constants (β) 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 ⁺	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
Log β	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)₃[P(OCH₃)₃]₃ exhibits three bands at 1993, 1919, and 1890 cm⁻¹. Please use character tables to determine which form (*mer* or *fac*) is assigned for the compound Mo(CO)₃[P(OCH₃)₃]₃.

C _{2v}	E	C ₂ (z)	$\sigma_v(xz)$	$\sigma_v(yz)$		
A ₁	1	1	1	1	z	x ² , y ² , z ²
A ₂	1	1	-1	-1	R _z	xy
B ₁	1	-1	1	-1	x, R _y	xz
B ₂	1	-1	-1	1	y, R _x	yz

C _{3v}	E	2C ₃ (z)	3 σ_v		
A ₁	1	1	1	z	x ² +y ² , z ²
A ₂	1	1	-1	R _z	
E	2	-1	0	(x, y) (R _x , R _y)	(x ² -y ² , xy) (xz, yz)

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

Co ^{3+/2+} ,	1.92 V
[Co(bipy) ₃] ^{3+/2+} ,	0.31 V
[Co(NH ₃) ₆] ^{3+/2+} ,	0.11 V
[Co(CN) ₆] ³⁻ /[Co(CN) ₅] ³⁻ +CN ⁻	-0.83 V

注意：背面有試題

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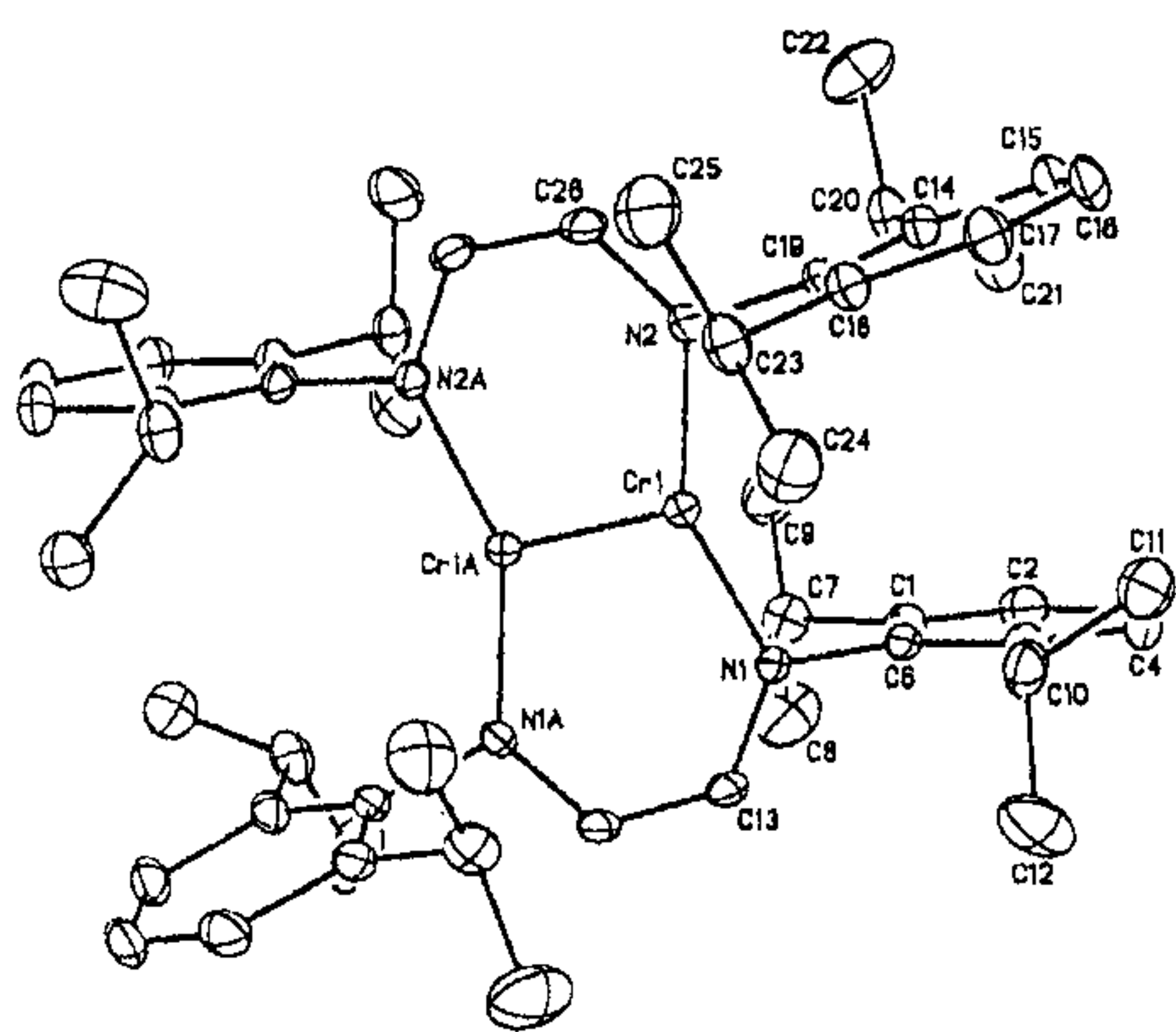
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6. (10 pts) The compound $(\mu\text{-}\eta^2\text{-H}^i\text{L}^{i\text{Pr}})_2\text{Cr}_2$ (where $\text{H}^i\text{L}^{i\text{Pr}} = \text{N,N}'\text{-bis(2,6-diisopropylphenyl)-1,4-diazadiene}$) contains a short Cr-Cr distance, which is considered 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: | _____ |

參考用

- 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)₂Fe.
- 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