UNIVERSITY OF ESWATINI

RESIT EXAMINATION 2020/2021

TITLE OF PAPER: PHYSICAL METHODS OF INORGANIC CHEMISTRY

COURSE NUMBER: CHE421

TIME ALLOWED: TWO (2) HOURS

INSTRUCTIONS: THIS PAPER CONTAINS TWO (2) SECTIONS. **ANSWER ALL QUESTIONS FROM SECTION A AND ANY OTHER TWO (2) QUESTIONS FROM SECTION B**. SECTION A IS WORTH 30 MARKS AND EACH QUESTION IN SECTION B IS WORTH 20 MARKS.

A PERIODIC TABLE AND OTHER USEFUL DATA HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER

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SECTION A: ANSWER ALL QUESTIONS

QUESTION 1 COMPULSORY [30 MARKS]

(a) What experimental characterization techniques could be used to:

1. Determining whether O-H or O-D bonds vibrate at higher frequencies (wavenumbers)? [3]
2. Determine whether a sample is dimethylsilane ($(CH_3)_2SiH_2$) or ethylsilane ($C_2H_5SiH_3$)? [2]
3. Determine the composition of the solid product from the reaction of CH_3NH_3Cl with $PdCl_2$ in aqueous 2 M HCl? [4]

(b) Calculate the:

1. Wavelength of an electron moving with a speed of 5.97 $\times 10^6$ ms^{-1} ? ($m_e = 9.11 \times 10^{-31}$ kg). [2]
2. The energy of one photon when a laser emits light with a frequency of 4.12 $\times 10^{14}$ s^{-1}. [2]

(c) Explain why

1. Even though d-d transitions are Laporte forbidden, spectra of much lower absorbance are still observed in a UV-Visible spectrum? [2]
2. Transition metal complexes are coloured? [2]
3. X-ray crystallography is important to the inorganic chemist. [4]

(d) Considering the bonding in metal carbonyls, what factors would affect the C–O stretching vibrations? [3]

(e) Predict the sign of g for Mo^{5+}. [2]

(f) Discuss 2 factors which can affect the chemical shift in NMR spectroscopy. [4]

SECTION B

ANSWER ANY 2 QUESTIONS FROM THIS SECTION

QUESTION 2 [20 MARKS]

(a) Sketch the first derivative spectrum of a radical containing one $I = {}^{1}/_{2}$ nuclei with a hyperfine coupling constant A of 100 G, and one $I = {}^{3}/_{2}$ nuclei with a hyperfine coupling constant of 20 G. Assume that $g = 2.0023$ and the operating frequency is 9.25 GHz. Sketch the spectrum with the hyperfine coupling constants reversed. [4]

(b) Explain why many complexes of Ln^{2+} and Ln^{4+} are intensely coloured. [4]

(c) In the broadband decoupled ($^{13}C\{^{1}H\}$) spectrum of the *cis* and *trans* forms of $W(CH_3)_2(CO)_4$, how many ^{13}C resonance peaks would you expect? Justify your answer. (NB: Take W as NMR inactive). [4]

(d) Explain why the proton decoupled ^{31}P NMR spectrum of ***trans***-$Pt[PMe_3]_2Cl_2$ consists of three resonances with intensity ratios 1:4:1. Predict the expected features in the ^{31}P NMR spectrum of ***cis***-$Pt[PMe_3]_2Cl_2$. (^{195}Pt, $I = 1/2$, 33.8% abundant). [4]

(e) The ^{19}F NMR spectrum of a sample containing the $[BF_4]^-$ anion consisted of a quartet of equal intensity peaks (total relative intensity 80%) and a septet of equal intensity resonances (total relative intensity 20%). Explain this observation. [4]

QUESTION 3 [20 MARKS]

A student has prepared a sample of $[Zn(en)_3]Cl_2$ (en = $H_2NCH_2CH_2NH_2$) but is worried that the complex appears blue when $[Zn(en)_3]Cl_2$ should be colourless. The student wonders if she picked up a bottle of nickel(II) chloride instead of zinc(II) chloride. The experimental CHN analysis for the complex is C 23.00%, H 7.71% and N 26.92%.

(a) Do the elemental analytical data distinguish between $[Zn(en)_3]Cl_2$ and $[Ni(en)_3]Cl_2$? Comment on your answer. [8]

(b) How would mass spectrometry help you to distinguish between the two compounds? [4]

(c) Suggest why ^1H NMR spectroscopy might be useful in distinguishing between $[Zn(en)_3]Cl_2$ and $[Ni(en)_3]Cl_2$. [2]

(d) Suggest why UV-VIS spectroscopy might be useful in distinguishing between $[Zn(en)_3]Cl_2$ and $[Ni(en)_3]Cl_2$ [2]

(e) A single crystal X-ray diffraction study was carried out and confirmed the presence of $[M(en)_3]Cl_2$. Can this technique unambiguously assign M to Zn or Ni? [2]

(f) How would you confirm the presence of the chloride ion? [2]

QUESTION 4 [20 MARKS]

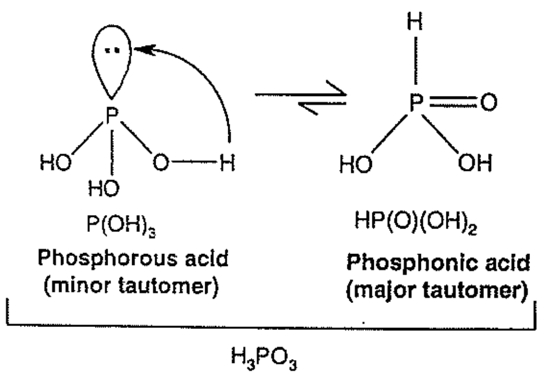
a) 12.915 g of a biochemical substance containing only carbon, hydrogen, and oxygen was burned in an atmosphere of excess oxygen. Subsequent analysis of the gaseous result yielded 18.942 g carbon dioxide and 7.749 g of water. Determine the empirical formula of the substance. [8]

b) Consider the two structures given below. Briefly explain how you can distinguish the two structures from each other based on:

1. ^{1}H NMR and;

2. $^{31}P\{^{1}H\}$ NMR.

Use suitable diagrams to illustrate your answer. [4]



c) An ESI MS spectra of a $[Co(en)_3]Cl_3$ complex is shown. Assign the peaks marked with m/z values and state the molecular ion peak. Show your calculations clearly. [8]

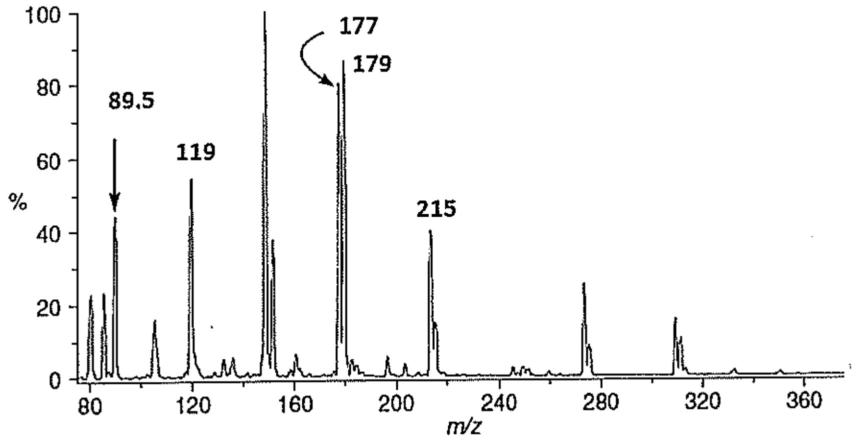


Fig 1: Positive-ion ESI MS spectra of the complex $[Co(NH_2CH_2CH_2NH_2)_3]Cl_3$ in methanol solvent

General data and fundamental constants

Quantity	Symbol	Value
Speed of light	c	$2.997\,924\,58 \times 10^{8}$ m s^{-1}
Elementary charge	e	$1.602\,177 \times 10^{-19}$ C
Faraday constant	$F = N_A e$	9.6485×10^{4} C mol^{-1}
Boltzmann constant	k	$1.380\,66 \times 10^{23}$ J K^{-1}
Gas constant	$R = N_A k$	$8.314\,51$ J K^{-1} mol^{-1}
		$8.205\,78 \times 10^{-2}$ dm^3 atm K^{-1} mol^{-1}
		6.2364×10 L Torr K^{-1} mol^{-1}
Planck constant	h	$6.626\,08 \times 10^{-34}$ J s
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34}$ J s
Avogadro constant	N_A	$6.022\,14 \times 10^{23}$ mol^{-1}
Atomic mass unit	u	$1.660\,54 \times 10^{-27}$ Kg
Mass		
electron	m_e	$9.109\,39 \times 10^{-31}$ Kg
proton	m_p	$1.672\,62 \times 10^{-27}$ Kg
neutron	m_n	$1.674\,93 \times 10^{-27}$ Kg
Vacuum permittivity	$\varepsilon_o = 1/c^2\mu_o$	$8.854\,19 \times 10^{-12}$ J^{-1} C^2 m^{-1}
	$4\pi\varepsilon_o$	$1.112\,65 \times 10^{-10}$ J^{-1} C^2 m^{-1}
Vacuum permeability	μ_o	$4\pi \times 10^{-7}$ J s^2 C^{-2} m^{-1}
		$4\pi \times 10^{-7}$ T^2 J^{-1} C^{-2} m^3
Magneton		
Bohr	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24}$ J T^{-1}
nuclear	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27}$ J T^{-1}
g value	g_e	2.002 32
Bohr radius	$a_o = 4\pi\varepsilon_o\hbar/m_e e^2$	$5.291\,77 \times 10^{-11}$ m
Fine-structure constant	$\alpha = \mu_o e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_o^2$	$1.097\,37 \times 10^{7}$ m^{-1}
Standard acceleration of free fall	g	$9.806\,65$ m s^{-2}
Gravitational constant	G	$6.672\,59 \times 10^{-11}$ N.m^2 Kg^{-2}

Conversion factors

1 cal	4.184 joules (J)	1 erg	1×10^{-7} J
1 eV	$1.602\,2 \times 10^{-19}$ J	1 eV/molecule	96 485 kJ mol^{-1}
			23.061 kcal mol^{-1}

Prefixes

f	p	n	μ	m	c	d	k	M	G
femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

Spectrochemical Series

$I^- < Br^- < S^{2-} < Cl^- < NO_3^- < F^- < OH^- <$ EtOH $< C_2O_4^{2-} < H_2O <$ EDTA $< (NH_3$, py$) <$ en $<$ dipy $< NO_2^- < CN^- <$ CO

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIB	IVB	VB	VIB	VIIB		VIIIB		IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1.008 **H** 1																	4.003 **He** 2
2	6.941 **Li** 3	9.012 **Be** 4										Atomic mass **Symbol** Atomic No.	10.811 **B** 5	12.011 **C** 6	14.007 **N** 7	15.999 **O** 8	18.998 **F** 9	20.180 **Ne** 10
3	22.990 **Na** 11	24.305 **Mg** 12					**TRANSITION ELEMENTS**						26.982 **Al** 13	28.086 **Si** 14	30.974 **P** 15	32.06 **S** 16	35.453 **Cl** 17	39.948 **Ar** 18
4	39.098 **K** 19	40.078 **Ca** 20	44.956 **Sc** 21	47.88 **Ti** 22	50.942 **V** 23	51.996 **Cr** 24	54.938 **Mn** 25	55.847 **Fe** 26	58.933 **Co** 27	58.69 **Ni** 28	63.546 **Cu** 29	65.39 **Zn** 30	69.723 **Ga** 31	72.61 **Ge** 32	74.922 **As** 33	78.96 **Se** 34	79.904 **Br** 35	83.80 **Kr** 36
5	85.468 **Rb** 37	87.62 **Sr** 38	88.906 **Y** 39	91.224 **Zr** 40	92.906 **Nb** 41	95.94 **Mo** 42	98.907 **Tc** 43	101.07 **Ru** 44	102.91 **Rh** 45	106.42 **Pd** 46	107.87 **Ag** 47	112.41 **Cd** 48	114.82 **In** 49	118.71 **Sn** 50	121.75 **Sb** 51	127.60 **Te** 52	126.90 **I** 53	131.29 **Xe** 54
6	132.91 **Cs** 55	137.33 **Ba** 56	138.91 ***La** 57	178.49 **Hf** 72	180.95 **Ta** 73	183.85 **W** 74	186.21 **Re** 75	190.2 **Os** 76	192.22 **Ir** 77	195.08 **Pt** 78	196.97 **Au** 79	200.59 **Hg** 80	204.38 **Tl** 81	207.2 **Pb** 82	208.98 **Bi** 83	(209) **Po** 84	(210) **At** 85	(222) **Rn** 86
7	223 **Fr** 87	226.03 **Ra** 88	(227) ****Ac** 89	(261) **Rf** 104	(262) **Ha** 105	(263) **Unh** 106	(262) **Uns** 107	(265) **Uno** 108	(266) **Une** 109	(267) **Uun** 110								

***Lanthanide Series**	140.12 **Ce** 58	140.91 **Pr** 59	144.24 **Nd** 60	(145) **Pm** 61	150.36 **Sm** 62	151.96 **Eu** 63	157.25 **Gd** 64	158.93 **Tb** 65	162.50 **Dy** 66	164.93 **Ho** 67	167.26 **Er** 68	168.93 **Tm** 69	173.04 **Yb** 70	174.97 **Lu** 71
****Actinide Series**	232.04 **Th** 90	231.04 **Pa** 91	238.03 **U** 92	237.05 **Np** 93	(244) **Pu** 94	(243) **Am** 95	(247) **Cm** 96	(247) **Bk** 97	(251) **Cf** 98	(252) **Es** 99	(257) **Fm** 100	(258) **Md** 101	(259) **No** 102	(260) **Lr** 103

( ) indicates the mass number of the isotope with the longest half-life.