UNIVERSITY OF ESWATINI

CHEMISTRY DEPARTMENT

RE-SIT EXAMINATION - JANUARY 2019

TITLE OF PAPER: PHYSICAL METHODS IN INORGANIC CHEMISTRY

COURSE NUMBER: CHE421

TIME ALLOWED: THREE (3) HOURS

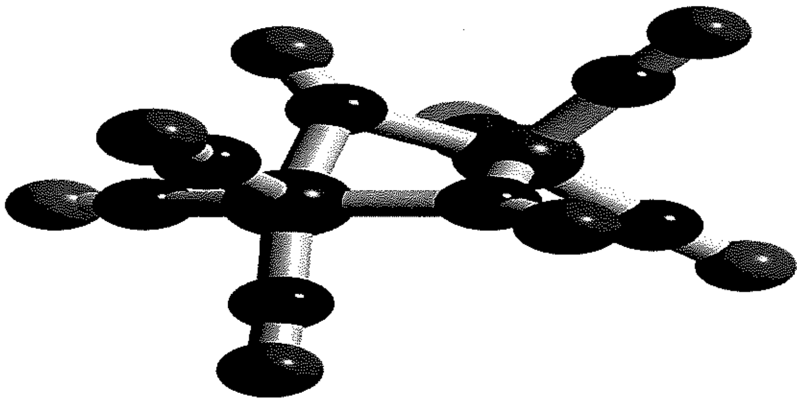
INSTRUCTIONS: THERE ARE SIX (6) QUESTIONS. ANSWER ANY FOUR (4) QUESTIONS. EACH QUESTION IS WORTH 25 MARKS.

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

Q. 1.

(a) Predict the form of the ^{19}F-NMR spectrum and the ^{77}Se spectrum of $^{77}SeF_4$. [For ^{77}Se: I = 1/2, 7.5% abundant; for ^{19}F: I = 1/2, 100% abundant] **[5]**

(b) Explain why the ^{13}C NMR spectrum of $[Co_2(CO)_9$ shows only a single peak at room temperature. The structural formula of the complex is given below. What do you think might happen if the ^{13}C NMR spectrum was obtained at very low temperature (without freezing the solution)? **[6]**



(c) You have prepared the complex $[Ru(py)_6][BF_4]_2$ (py = pyridine).

(i) What information can you obtain from the CHN elemental analysis including analysis for Ru? Which technique would you use to analyze for Ru? **[5]**

(ii) How would you confirm the presence of the $[BF_4]^-$ion? **[2]**

(iii) How would you confirm that all the pyridine ligands were in the same environment in solution? **[6]**

(iv) How would you confirm the presence of an octahedral $[Ru(py)_6]^{2+}$ ion in the solid state? **[2]**

(v) What would you expect to see in the ESI mass spectrum of $[Ru(py)_6][BF4]_2$? **[4]**

Q. 2.

a) For a paramagnetic compound of a d metal compound having one unpaired electron, outline the main difference you would expect between an EPR spectrum measured in aqueous solution at room temperature and one measured for a frozen solution. Take the complex $VO(acac)_2$ as an example. **[6]**

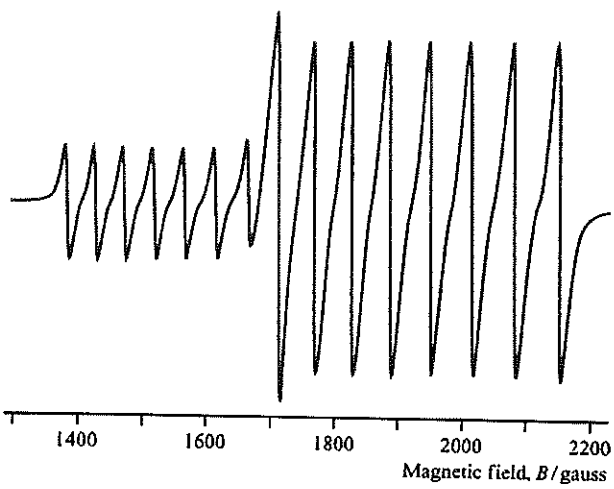
b) The figure below shows the 9.214 GHz EPR spectrum arising from the two sites of a low-spin dinuclear Co^{2+} complex (^{59}Co, 100% abundant, I=7/2) doped into magnesium acetate. The two sites do not couple with each other (i.e., electron on one site does not couple with the nucleus of the other site). Consequently, the sites differ slightly in their effective hyperfine coupling constants, and more significantly in their g-values.

i) Calculate the g-values for the two sites. **[6]**

ii) Explain why the central peak is more intense than the other peaks. **[3]**

iii) What would happen if the difference in g-values of the two sites is smaller than is observed in this case. **[2]**

iv) Consider a situation where the two sites are equivalent. Give a sketch of the splitting pattern for the resulting electron spin system in a magnetic field. How many peaks are expected in the EPR spectrum of the sample? Explain. **[8]**



Q. 3.

a) How is single crystal neutron diffraction of use in inorganic Chemistry **[4]**

b) Describe three methods that are commonly used for growing single crystals to be used in single-crystal X-ray diffraction. **[6]**

c) Calculate the wavelength associated with a neutron moving at 2.20 km s^{-1}. Is this wavelength suitable for diffraction studies? (mass of proton = 1.675 x 10^{-27} kg). **[5]**

d) Discuss the information available from the following techniques in the analysis of pigments of used in antique oil paintings. (i) powder X-ray diffraction, (ii) Infrared and Raman spectroscopies, (iii) UV-Visible spectroscopy, (iv) X-ray fluorescence **[4]**

e) Sodium carbonate, boron oxide, and silicon dioxide when heated together and quickly cooled produce a borosilicate glass. Explain why the powder diffraction of this product shows no diffraction maxima. Heating the borosilicate glass in a DTA instrument shows an exothermic event at 500°C and the powder X-ray diffraction pattern observed from the product shows diffraction maxima. Explain these observations. **[5]**

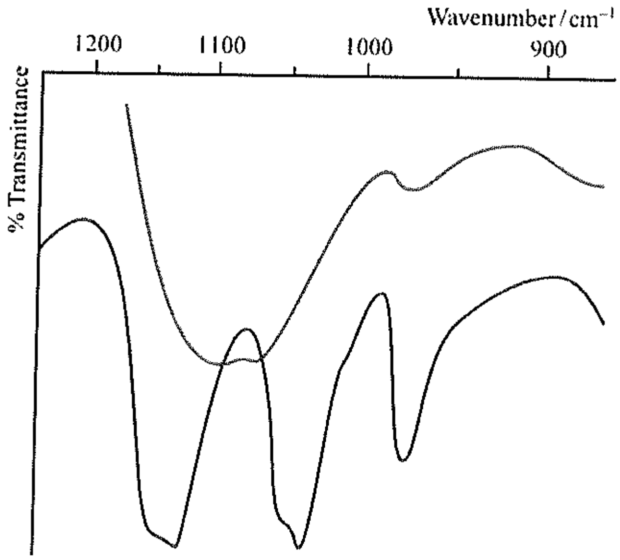
Q. 4.

a) The fundamental stretching vibration for O_2 is at 1580 cm^{-1}. Why would you use Raman, and not IR, spectroscopy to observe this absorption? [2]

b) Each of the Raman and IR spectra of O_3 exhibits three bands at 1135, 1089 and 716 cm^{-1}. Explain why this provides evidence that O_3 is a non-linear molecule. [8]

c) Why is the fundamental stretching vibration of NO both Raman and IR active? [2]

d) Portions IR spectra of $[Co(NH_3)_6]_2[SO_4]_3.5H_2O$ (with broad peak) and $[Co(NH_3)_5(OSO_3)]Br$ (peak split into three) due to the stretching modes of the sulphate ion are shown in the figure below. In each case, use group theory to rationalize the spectra in terms of the coordination modes of the sulphate ion. [13]



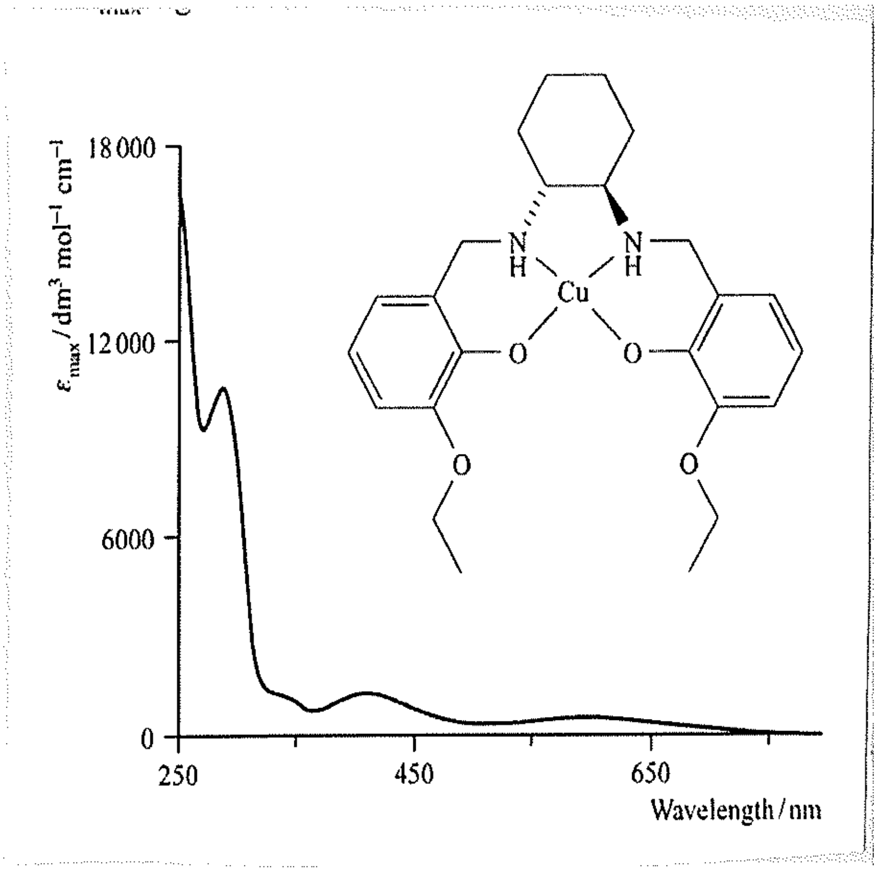
Q. 5.

a) The figure below shows the UV-VIS spectrum of a CH_2Cl_2 solution of a copper(II) complex. A 1-cm cuvette was used for the measurement. Solutions of the complex are brown. The intense bands in the spectrum arise from ligand-based transitions.

(i) Suggest how the ligand-based transitions arise **[4]**

(ii) Which absorption or absorptions give rise to the observed colour of the complex in solution? Explain. **[3]**

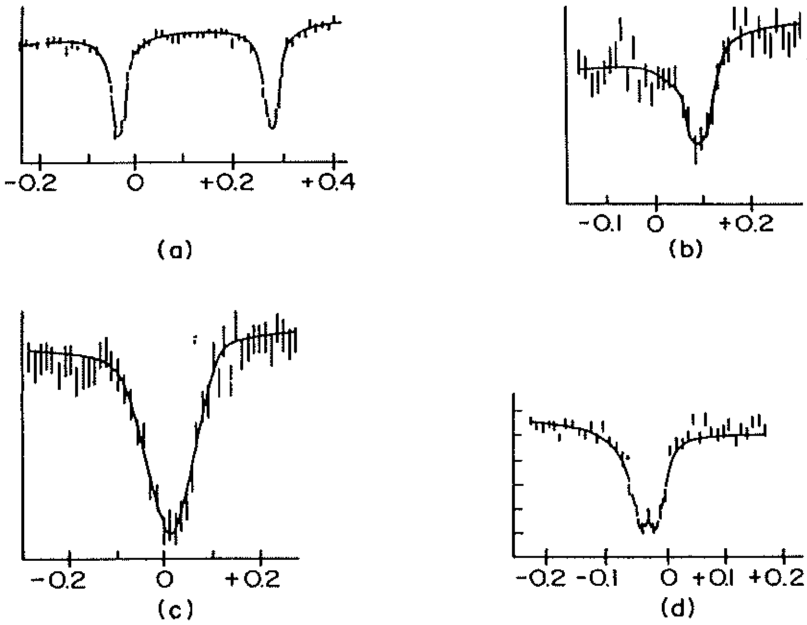
(iii) Calculate the absorbance that corresponds to the absorption around 292 nm. **[2]**



Q. 5.

b) The Mossbauer spectra for the complexes $[Fe(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3-}$, $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ are shown below. Rationalize each of the spectra. [Note: H_2O is a weak field ligand whereas CN- is a strong-field ligand]

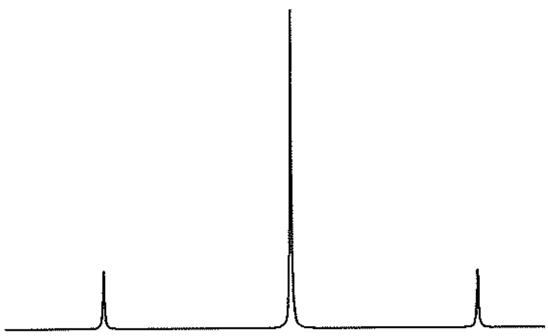
[12]



Mossbauer spectra of some iron(II) and iron(III) complexes.
(a) Spin-free iron(II)-$FeS0_4$ $7H_2O$.
(b) Spin-free iron(III)-$FeCI_3$).
(c) Spin-paired iron (II)- $K_4Fe(CN)_6 \cdot 3H_20$.
(d) Spin-paired iron(III)-$K_3Fe(CN)_6$.
[From P. R. Brady, P. P. F. Wigley, and J. F. Duncan, Rev. Pure Appl. Chem., 12, 181 (1962).]

c) Explain how the ^{19}F NMR spectrum (shown below) of the pentagonal planar $[XeF_5]^-$ ion, arises. The isotopic abundances are: ^{19}F, I = 1/2, 100% abundance; ^{129}Xe, I = 1/2, 26.4% abundance. Assume that the other isotopes of xenone are not NMR-sensitive.

[4]



Q. 6.

a) The EI mass spectrum of lead(II) acetate shows four peak envelopes, each with an isotope pattern characteristic of Pb. The most intense peak in each envelope appears at m/z 326.0, 267.0, 224.0 and 208.0 respectively. (i) By using information provided, sketch the pattern that is exhibited by each envelope. (ii) Assign the peaks. **[8]**

b) CHN analysis for a complex $[TiCl_n(py)_{6-n}]$ gives C 46.03, H 3.85, N 10.72%. What is the value of n? **[6]**

c) The reaction of $NbCl_4(THF)_2$ with pyridine in the presence of a reducing agent gives $NbCl_x(py)_y$ which contains 50.02% C, 4.20% H and 11.67% N. Determine the values of x and y. **[6]**

d) Thermogravimetric analysis of a zeolite of composition $CaAl_2Si_6O_{16}.nH_2O$ shows a mass loss of 25% on heating to dryness. Determine n. **[5]**

Commonly Used Physical Constants

Constant	Symbol	Value
acceleration due to gravity	g	9.8 m s^{-2}
atomic mass unit	amu, m_u or u	1.66 $x10^{-27}$ kg
Avogadro's Number	**N**	**6.022 x 10^{23} mol^{-1}**
Bohr radius	a_o	0.529 x 10^{-10} m
Boltzmann constant	k	1.38 x 10^{-23} J K^{-1}
electron charge to mass ratio	$-e/m_e$	-1.7588 x 10^{11} C kg^{-1}
electron classical radius	r_e	2.818 x 10^{-15} m
electron mass energy (J)	m_ec^2	8.187 x 10^{-14} J
electron mass energy (MeV)	m_ec^2	0.511 MeV
electron rest mass	m_e	9.109 x 10^{-31} kg
Faraday constant	F	9.649 x 10^4 C mol^{-1}
fine-structure constant	α	7.297 x 10^{-3}
gas constant	R	8.314 J mol^{-1} K^{-1}
gravitational constant	G	6.67 x 10^{-11} Nm^2kg^{-2}
neutron mass energy (J)	m_nc^2	1.505 x 10^{-10} J
neutron mass energy (MeV)	m_nc^2	939.565 MeV
neutron rest mass	m_n	1.675 x 10^{-27} kg
neutron-electron mass ratio	m_n/m_e	1838.68
neutron-proton mass ratio	m_n/m_p	1.0014
permeability of a vacuum	μ_o	4π x 10^{-7} N A^{-2}
permittivity of a vacuum	ε_o	8.854 x 10^{-12} F m^{-1}
Planck constant	h	6.626 x 10^{-34} J s
proton mass energy (J)	m_pc^2	1.503 x 10^{-10} J
proton mass energy (MeV)	m_pc^2	938.272 MeV
proton rest mass	m_p	1.6726 x 10^{-27} kg
proton-electron mass ratio	m_p/m_e	1836.15
Rydberg constant	R_H	1.0974 x 10^7 m^{-1}
speed of light in vacuum	C	2.9979 x 10^8 m/s
Electronic Charge	e	1.602 x 10^{-19} C

Main isotopes of lead ($_{82}Pb$)

	abundance
^{204}Pb	1.4%
^{206}Pb	24.1%
^{207}Pb	22.1%
^{208}Pb	52.4%

Isotopic abundances vary greatly by sample

Stable isotopes of silver ($_{47}Ag$)

Isotope	
	abundance
^{107}Ag	51.839%
^{109}Ag	48.161%

Standard atomic weight **107.868**

4. The C_{nv} Groups

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
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	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	−1	−1	R_z	
B_1	1	−1	1	1	−1		$x^2 - y^2$
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_2	3	0	−1	−1	1	(x, y, z)	(xy, xz, yz)

O	E	$8C_3$	$3C_2(=C_4^2)$	$6C_4$	$6C_2$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	−1	1	−1	$(R_x, R_y, R_z); (x, y, z)$	
T_2	3	0	−1	−1	1		(xy, xz, yz)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

Periodic Table of the Elements

Main Group Representative Elements (groups 1–2) · Transition metals (groups 3–12) · Main Group Representative Elements (groups 13–18)

☐ Metals ☐ Metalloids ☐ Nonmetals

Period	1A[a] 1	2A 2	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8	8B 9	8B 10	1B 11	2B 12	3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
1	1 **H** 1.00794																	2 **He** 4.002602
2	3 **Li** 6.941	4 **Be** 9.012182											5 **B** 10.811	6 **C** 12.0107	7 **N** 14.0067	8 **O** 15.9994	9 **F** 18.998403	10 **Ne** 20.1797
3	11 **Na** 22.989770	12 **Mg** 24.3050											13 **Al** 26.981538	14 **Si** 28.0855	15 **P** 30.973761	16 **S** 32.065	17 **Cl** 35.453	18 **Ar** 39.948
4	19 **K** 39.0983	20 **Ca** 40.078	21 **Sc** 44.955910	22 **Ti** 47.867	23 **V** 50.9415	24 **Cr** 51.9961	25 **Mn** 54.938049	26 **Fe** 55.845	27 **Co** 58.933200	28 **Ni** 58.6934	29 **Cu** 63.546	30 **Zn** 65.39	31 **Ga** 69.723	32 **Ge** 72.64	33 **As** 74.92160	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
5	37 **Rb** 85.4678	38 **Sr** 87.62	39 **Y** 88.90585	40 **Zr** 91.224	41 **Nb** 92.90638	42 **Mo** 95.94	43 **Tc** [98]	44 **Ru** 101.07	45 **Rh** 102.90550	46 **Pd** 106.42	47 **Ag** 107.8682	48 **Cd** 112.411	49 **In** 114.818	50 **Sn** 118.710	51 **Sb** 121.760	52 **Te** 127.60	53 **I** 126.90447	54 **Xe** 131.293
6	55 **Cs** 132.90545	56 **Ba** 137.327	71 **Lu** 174.967	72 **Hf** 178.49	73 **Ta** 180.9479	74 **W** 183.84	75 **Re** 186.207	76 **Os** 190.23	77 **Ir** 192.217	78 **Pt** 195.078	79 **Au** 196.96655	80 **Hg** 200.59	81 **Tl** 204.3833	82 **Pb** 207.2	83 **Bi** 208.98038	84 **Po** [208.98]	85 **At** [209.99]	86 **Rn** [222.02]
7	87 **Fr** [223.02]	88 **Ra** [226.03]	103 **Lr** [262.11]	104 **Rf** [261.11]	105 **Db** [262.11]	106 **Sg** [266.12]	107 **Bh** [264.12]	108 **Hs** [269.13]	109 **Mt** [268.14]	110 **Ds** [281.15]	111 **Rg** [272.15]	112 **Cn** [285]	113 [284]	114 **Fl** [289.2]	115 [288]	116 **Lv** [293]	117 ** [294]	118 [294]

Lanthanide series	57 **La** 138.9055	58 **Ce** 140.116	59 **Pr** 140.90765	60 **Nd** 144.24	61 **Pm** [145]	62 **Sm** 150.36	63 **Eu** 151.964	64 **Gd** 157.25	65 **Tb** 158.92534	66 **Dy** 162.50	67 **Ho** 164.93032	68 **Er** 167.259	69 **Tm** 168.93421	70 **Yb** 173.04
Actinide series	89 **Ac** [227.03]	90 **Th** 232.0381	91 **Pa** 231.03588	92 **U** 238.02891	93 **Np** [237.05]	94 **Pu** [244.06]	95 **Am** [243.06]	96 **Cm** [247.07]	97 **Bk** [247.07]	98 **Cf** [251.08]	99 **Es** [252.08]	100 **Fm** [257.10]	101 **Md** [258.10]	102 **No** [259.10]

[a] The labels on top (1A, 2A, etc.) are common American usage. The labels below these (1, 2, etc.) are those recommended by the International Union of Pure and Applied Chemistry (IUPAC).
Except for elements 114 and 116, the names and symbols for elements above 113 have not yet been decided.
Atomic weights in brackets are the names of the longest-lived or most important isotope of radioactive elements.
Further information is available at http://www.webelements.com
** Discovered in 2010, element 117 is currently under review by IUPAC.