

Inorganic Chemistry Cumulative Exam

March 2nd, 2017

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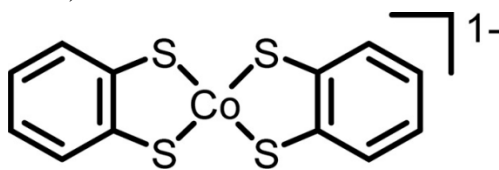
A few rules:

- There is no need for a calculator to complete this exam.
- Please read the questions carefully.
- One the critical aspects of a successful scientific article is conciseness. This is your opportunity to prepare. Please explain your answers *adequately, but concisely*.
- Last but not least, please **print legibly!**

The questions amount to 140 points. The point value of each question can be found in brackets. The pass line is at 75 points.

Highlights from the latest issue of Inorganic Chemistry (<http://pubs.acs.org/toc/inocaj/current>, February 20, 2017, Volume 56, Issue 4, Pages 1771-2362)

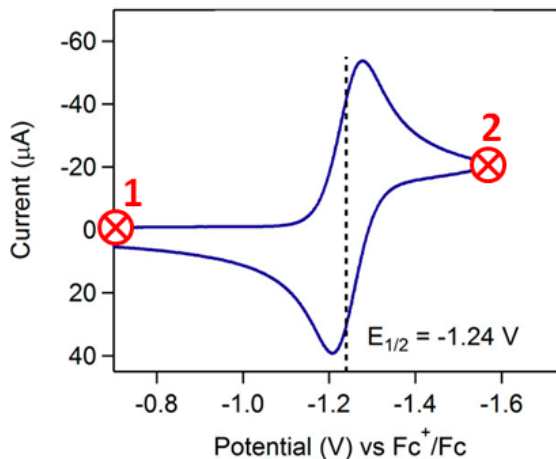
- 1) Lee *et al.* describe the electrochemical properties of the following complex (*Identification of an Electrode-Adsorbed Intermediate in the Catalytic Hydrogen Evolution Mechanism of a Cobalt Dithiolene Complex*, pp. 1988–1998):



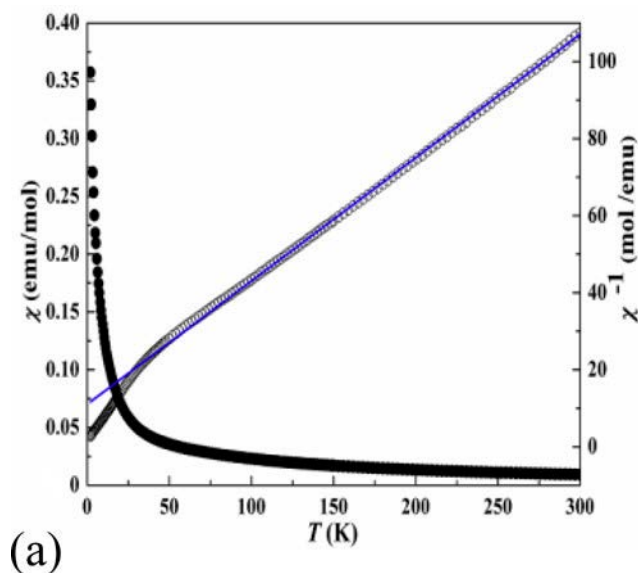
[Ligands are bdt = 1,2-benzenedithiolate]

- (5) **State** the oxidation state of Co.
- (5) **State** the *d* electron count of Co.
- (5) **State** the total valence electron count of the complex.

The paper also contains the following plot:



- d) (10) In the experiment depicted in the plot, $[\text{Co}(\text{bdt})]^-$ corresponds to point **1**. **Hypothesize** what product forms when the reaction reaches point **2**.
- 2) Moving on to solid systems, in a comprehensive paper combining experimental and computational approaches, Fernando Rodriguez (a fellow countryman) studies the effect of Jahn-Teller distortions of Cu^{2+} ions placed as impurities in solid fluorides. They replace Zn^{2+} in octahedral coordination sites (*Unveiling the Local Structure of Cu^{2+} Ions from d-Orbital Splitting. Application to $\text{K}_2\text{ZnF}_4:\text{Cu}^{2+}$ and $\text{KZnF}_3:\text{Cu}^{2+}$* , pp. 2029–2036).
- a) (10) **What** are the electronic configurations of Cu^{2+} and Zn^{2+} ?
- b) (10) **Draw** a schematic of an octahedral species presenting a Jahn-Teller distortion.
- Dr. Rodriguez states that “[a] salient feature concerning the [Jahn-Teller] distortion in MnF_6^{3-} and CuF_6^{4-} is the additional splitting shown by the parent octahedral [...] d orbitals of the M ion. The splitting of e_g into a_{1g} and b_{1g} can be measured by optical spectroscopy”.
- c) (15) Use crystal field theory to **depict** and **rationalize** the splitting of the d orbitals in an octahedral site subject to a Jahn-Teller distortion.
- d) (10) The labels e_g , a_{1g} and b_{1g} refer to symmetry treatments based on group theory. **Assign symmetry** labels to the diagrams in c).
- e) (10) **Why** is there a change in symmetry labels going from an undistorted to a distorted coordination?
- f) (10) **Explain** why the “splitting of e_g into a_{1g} and b_{1g} can be measured by optical spectroscopy”.
- g) (5) **Calculate** the number of unpaired electrons when Cu^{2+} is in this distorted coordination.
- 3) Continuing with Cu^{2+} , Guo *et al.* study an interesting family of complex solids showing geometrically frustrated magnetism (*Layered $\text{Cu}_7(\text{TeO}_3)_2(\text{SO}_4)_2(\text{OH})_6$ with Diluted Kagomé Net Containing Frustrated Corner-Sharing Triangles*, pp. 1830–1834). In it, the following plot is found:



It shows the change in magnetic susceptibility (χ , filled circles), and its inverse (χ^{-1} , empty circles) undergone by this compound with varying temperature.

- a) (5) **Name** the kind of magnetic interaction that leads to this χ -T behavior.
- b) (10) We know that the magnetic response in this compound can be ascribed solely to the Cu^{2+} ions. **Qualitatively explain** how you can extract the value of effective magnetic moment, μ_{eff} , for Cu^{2+} using the plot provided.
- c) (10) The authors state that “[t]he effective magnetic moment was calculated to be close to the theoretical value”. **Calculate** the theoretical value of μ_{eff} for Cu^{2+} .

Bonus Questions

- 4) (5) Without asking anyone, how would you know what hazards you could be exposed to when entering a lab in the Department that does not belong to your group?
- 5) (5) How should chemicals be stored in a lab, when not in use?
- 6) (5) What acronym defines the steps you need to take to use a fire extinguisher?
- 7) (5) Who is the Safety Officer of the Department of Chemistry?

Additional Materials:

B = Solids **Hg = Liquids** **Kr = Gases** **Pm = Not found in nature**

1 1.00794 H	2 4.002602 He	3 6.941 Li	4 9.012182 Be	5 22.989770 Na	6 24.3050 Mg	7 20 B	8 10.811 C	9 12.0107 N	10 14.00674 O	11 15.9994 F	12 18.9984032 Ne	13 26.981538 Al	14 28.0855 Si	15 30.973761 P	16 32.066 S	17 35.4527 Cl	18 39.948 Ar
19 39.0983 K	20 40.078 Ca	21 44.955910 Sc	22 47.867 Ti	23 50.9415 V	24 51.9961 Cr	25 54.938049 Mn	26 55.845 Fe	27 58.933200 Co	28 58.6534 Ni	29 63.545 Cu	30 65.39 Zn	31 69.723 Ga	32 72.61 Ge	33 74.92160 As	34 78.96 Se	35 79.504 Br	36 83.80 Kr
37 85.4678 Rb	38 87.62 Sr	39 88.90585 Y	40 91.224 Zr	41 92.90638 Nb	42 95.94 Mo	43 98 Tc	44 101.07 Ru	45 102.90550 Rh	46 106.42 Pd	47 107.8682 Ag	48 112.411 Cd	49 114.818 In	50 118.710 Sn	51 121.760 Sb	52 127.60 Te	53 126.90447 I	54 131.29 Xe
55 132.90545 Cs	56 137.327 Ba	57 138.9055 La	58 140.116 Ce	59 140.50765 Pr	60 144.24 Nd	61 145 Pm	62 150.36 Sm	63 151.964 Eu	64 157.25 Gd	65 158.92534 Tb	66 162.50 Dy	67 164.93032 Ho	68 167.26 Er	69 168.93421 Tm	70 173.04 Yb	71 175.053 Lu	72 175.053 Y
87 223 Fr	88 226 Ra	89 232.0381 Ac	90 232.0381 Th	91 231.03888 Pa	92 238.0289 U	93 237 Np	94 244 Pu	95 243 Am	96 247 Cm	97 247 Bk	98 251 Cf	99 252 Es	100 257 Fm	101 258 Md	102 259 No	103 261 Lr	104 261 La
113 208.9804 Bh	114 208.9804 Hs	115 208.9804 Mt	116 208.9804 Ds	117 208.9804 Rg	118 208.9804 Cn	119 208.9804 Uut	120 208.9804 Uuq	121 208.9804 Uup	122 208.9804 Uuh	123 208.9804 Uuq	124 208.9804 Uup	125 208.9804 Uuh	126 208.9804 Uuq	127 208.9804 Uup	128 208.9804 Uuh	129 208.9804 Uuq	130 208.9804 Uuh
151 262 Nh	152 262 Fl	153 262 Mc	154 262 Lv	155 262 Ts	156 262 Ug	157 262 Uuq	158 262 Uup	159 262 Uuh	160 262 Uuq	161 262 Uup	162 262 Uuh	163 262 Uuq	164 262 Uup	165 262 Uuh	166 262 Uuq	167 262 Uuh	168 262 Uuq

Character table for D_{4h} point group

	E	2C ₄ (z)	C ₂	2C' ₂	2C'' ₂	i	2S ₄	σ _h	2σ _v	2σ _d	linears, rotations	quadratic
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	R _z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x ² -y ²
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R _x , R _y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

Character table for O_h point group

	E	8C ₃	6C ₂	6C ₄	3C ₂ =(C ₄) ²	i	6S ₄	8S ₆	3σ _h	6σ _d	linear, rotations	quadratic
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		

\mathbf{T}_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
\mathbf{T}_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		