Inorganic Chemistry Cumulative Exam

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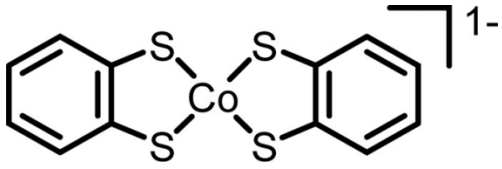
A few rules:

- 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):



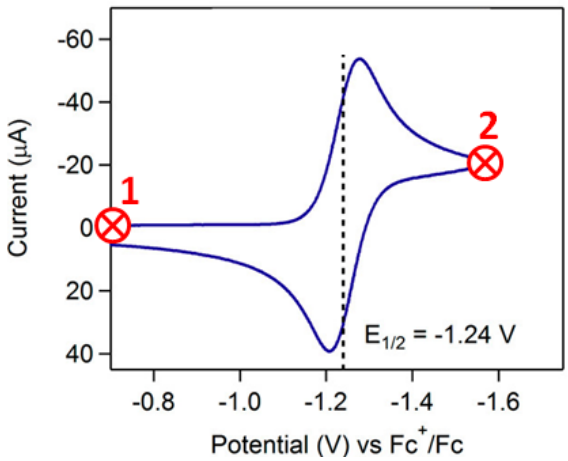
[Ligands are bdt = 1,2-benzenedithiolate]

a) (5) **State** the oxidation state of Co.

b) (5) **State** the *d* electron count of Co.

c) (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, $[Co(bdt)]^-$ 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 $K_2ZnF_4:Cu^{2+}$ and $KZnF_3:Cu^{2+}$*, 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.

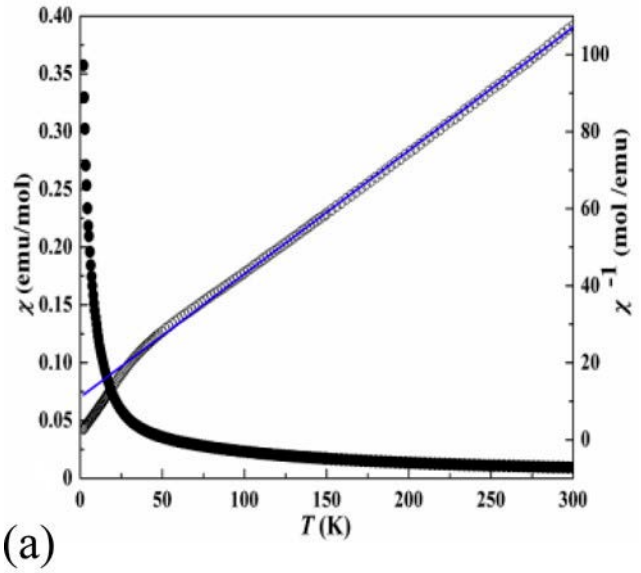
d) (10) The labels e_g, a_{1g} and b_{1g} refer to symmetry treatments based on group theory. **Assign <u>symmetry</u>** labels to the diagrams in c).

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 $Cu_7(TeO_3)_2(SO_4)_2(OH)_6$ 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.

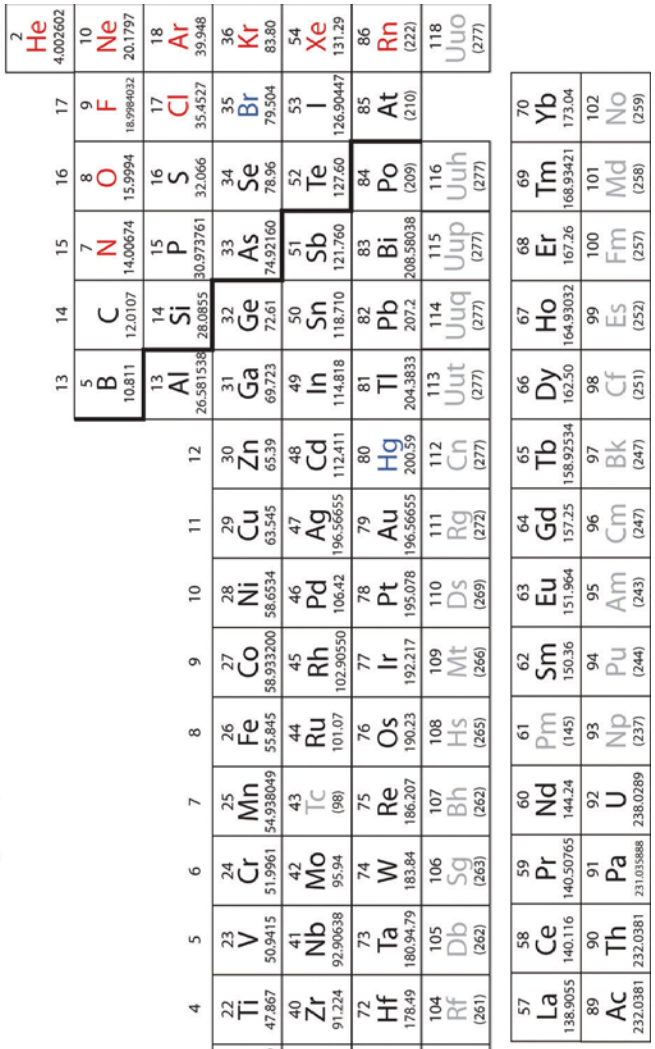
b) (10) We know that the magnetic response in this compound can be ascribed solely to the Cu^{2+} ions. **Qualitatively explain** how you can extract the value of effective magnetic moment, μ_{eff}, for Cu^{2+} using the plot provided.

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:



Character table for D_{4h} point group

	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	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	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	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		

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		