**Photochemical oxidation of copper (II) carboxylates in artwork**

Please read the provided paper, “Photochemical Origin of Darkening of Copper Acetate and Resinate Pigments in Historical Paintings,” Marion Alter, Laurent Binet, Nadia Touati, Nadeg̀e Lubin-Germain, Anne-Solenn Le Hô, Franco̧is Mirambet, and Didier Gourier, *Inorg. Chem.* **2019**, *58*, 11315-11328.

You will not have to read all sections of this paper in equal detail (particularly some of the more mathematical parts of the EPR section!). Use the questions below to help focus your efforts! Be sure to refer to your textbook or other resources to answer any questions that arise as you read.

1. Where are the scientists who carried out this study located?
2. What can you find out about the organization that supported this research?

1. Pick one of the authors and try to find out what their current position is. Using SciFinder Scholar, how many journal articles has that person published?
2. In your own words, describe the purpose of this study.

1. How do the authors support the hypothesis that light and O2 are the cause of the darkening in the pigments?

1. Examine **Figure 1**. Write the molecular formula for the copper(II) acetate complex shown in the figure (Hint: hydrogen atoms are not shown in the figure!).

1. How would you characterize each of the ligands (monodentate, chelating, bridging, etc.) in the copper (II) acetate complex shown in Figure 1?
2. For copper (II) resinate, where does the carboxylate represented by the green ellipse come from?
3. The caption for Fig. 1 states that the molecular structure of copper acetate was determined by X-ray and neutron diffraction. What are the fundamental differences between these two techniques? When might you need to use neutron diffraction instead of X-ray diffraction?
4. In Figure 2B and 2C, explain what the images represent in your own words.
5. Why is figure 2F shown in black and white and 2E is not?
6. The authors cite previous work using XANES and EXAFS that argues against a change in oxidation state of the copper (II) pigments. Explain what they mean in their argument in the middle of the first column on page 13116.
7. The authors made a series of samples to systematically investigate the effect of the binding medium and the pigment on the lightfastness of the verdigris pigments. What do you think of their choices of samples for investigation? Is there anything important that you would need to know if we wanted to replicate their study in our lab?
   1. The authors make the argument that their study using LED light simulates the amount of light the painting would receive from ambient light over 2800 years (this is discussed on the bottom of page 11317). Show this is the case using the calculations hinted at in the paper, starting with the fact that the LED exposes the sample to 320 mW of energy.

* 1. Research papers sometimes present values or data without explicitly stating how the authors calculated these values (or what assumptions they made). Imagine you are a researcher trying to reproduce or check the experimental results above. What information or calculations are lacking that would help you reproduce or verify their results?

1. The authors state that the unpaired electrons in the copper (II) dimers are in the dx2-y2 orbital. Assuming the other Cu (II) in the dimer occupies a “coordination site”, what geometry does the Cu (II) have? Draw and populate the crystal field splitting for this geometry and then draw and/or describe the correct position of the dx2-y2 orbital in the dimer.
2. The copper (II) dimers have two electron spin states that are populated, S=0 and S=1. Draw a cartoon of electron spins (using arrows) that represent these two states and their relative energy values. Which of these two states is EPR active? How would you expect the signal to change as the temperature of the system is increased? Explain briefly.
3. In EPR spectroscopy, signals from unpaired electrons can be split by nuclear spins of the atom where the unpaired spin is actually located (similar to how NMR peaks can be split by other nuclei). The authors state that “each transition splits into 2nI + 1 = 7 transitions by the hyperfine interaction A with the n = 2 nuclear spins I = 3/2 of copper.” Which diagram shows this hyperfine splitting? Explain what the n is in this equation.
4. Given the formula in equation 6 for complex C and descriptions of it in the paper. Draw a 3D diagram of this proposed decomposition product.

1. How do the authors rationalize the mechanism for the decomposition that they propose in equation 7 as opposed to the pathway represented by equations 4-6?
2. The band at 22,000 cm-1 is proposed to arise from complex C. What transition do they attribute the band at this frequency? Be as specific as you can.

1. The EPR section of the paper is pretty complicated (and you can ignore most of it!), but one of the important details to come out of it is the fact that the signals from the monomeric and dimeric complexes are different. In what ways are they different?
2. How specifically did the authors collect the data for Figure 9? What is the significance of the fact that the two bars added together are significantly less than 100% after illumination for the acetate version of the pigment after irradiation?
3. The trends in the chemical stability and photochemical stability of the copper (II) pigments are different in the different binding media discussed in the paper. Explain what is going on here!
4. Propose a possible additional study that this work suggests.