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Mixed Acetylacetonato Complexes of Copper(II) .

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In a recent paper Nicholas and Walker[1] extended our published work[2] on the preparation and characterization of mixed acetylacetonato complexes of copper(II). In their work they found several discrepancies between their results and our published data. It is the purpose of this note to clarify these discrepancies.

The first is the difference in melting points for $Cu(hfac)_2$, for which we reported 95-98°C while Nicholas and Walker reported 135°C. Their explanation for the difference in the melting points was that "Farona *et al*.... may have recorded the melting point of the dihydrate". In fact, Nicholas and Walker have recorded the melting point of $Cu(hfac)_2 \cdot 2H_2O$; the problem of the anhydrous and hydrated forms of $Cu(hfac)_2$ was reported in 1966 by Bertrand and Kaplan,[3] who reported the melting points of $Cu(hfac)_2$ and $Cu(hfac)_2 \cdot 2H_2O$ as 95-98°C, and 134-136°C, respectively. Other workers have verified their values.[4,5] Furthermore, like $Cu(hfac)_2$, the mixed chelate Cu(hfac)(tfac) also forms a green hydrate, which upon dehydration over concentrated H_2SO_4, yields the purple anhydrous form with melting point 110-112°C.[6] Once again, Nicholas and Walker have observed the melting point of the hydrate of Cu(hfac)(tfac). For our Cu(acac)(tfac) complex, we have rechecked its melting point and still find one of 230-232°C. The only other melting point disagreement is for $Cu(acac)_2$, a very well-characterized compound. Our value is in agreement with the literature available to us, see, *e.g.*, Moshier and Sievers.[7]

The R_f value discrepancy is real, however. The values in our publication are incorrect, not because we observed those values, but because of an error on our part in transferring the numbers from research notebook to manuscript. We have actually observed R_f values for $Cu(acac)_2$, Cu(acac)(tfac) and $Cu(tfac)_2$ as 0.06, 0.12, and 0.29, respectively. These values are of the same trend as observed by Nicholas and Walker; the actual differences between our values and those reported by Nicholas and Walker for $Cu(acac)_2$ and $Cu(tfac)_2$ are probably due to differences in technique.** However, the most important difference is that for Cu(acac)(tfac), only one spot, albeit somewhat elongated like those of $Cu(acac)_2$ and $Cu(tfac)_2$, is observed. This contrasts the observation by Nicholas and Walker whereby two spots were reported for Cu(acac)(tfac).

Nicholas and Walker apparently are unconvinced that our methods of characterization warranted conclusion of mixed chelation. The mixed β-diketonate complexes were characterized in our publication primarily from solid-state infrared studies, and esr spectra of the compounds both in solution and in the frozen state. These studies, particularly those by esr in the frozen state, are irrefutable. The one question which remained concerning the esr spectra was that of the high field, low-intensity peaks. We now feel that they are due to small amounts of dimer formation. Of particular interest, however, is that we have been able to observe this phenomenon even in the spectra of some unmixed copper acetylacetonate samples.

We cannot agree that solid state visible spectra provide more conclusive evidence than solid state infrared data. Because of the very large difference in line widths in the two spectral regions, it would appear that infrared is clearly the superior of the two methods.

It is true that X-ray diffraction studies and comparison of respective powder patterns also provide strong evidence in support of the formulation of the compounds as mixed chelate complexes. Our *d* values are available in the Ph. D. Thesis of Dr. Perry.[6]

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(**) Thin-layer chromatograms were obtained on 6060 silica gel Eastman Chromagram sheets, using benzene as the eluting solvent.