Correspondence

Comments on the Effects of Axial Ligation on the Electronic Spectra of Copper(II) β-Diketonates

Sir:

The use of the effects of axial ligation in assigning the Gaussian components in the electronic spectra of copper(II) β-diketonates has been made for many years in terms of a model which assumes that the structure of the copper(II) β-diketonate remains constant upon five-coordinate adduct formation.[1-4] The principal results of this model are that upon addition of the fifth ligand along the z axis: (1) the d_{xy} and $d_{x^2-y^2}$ orbital levels are equally perturbed, and, thus, the $d_{xy} \rightarrow d_{x^2-y^2}$ transition energy is virtually unaffected by axial ligation; (2) the largest effect is on the d_{z^2} level which is raised in energy, so that the $d_{xy} \rightarrow d_{z^2}$ transition energy is decreased. Much smaller shifts to lower energy are expected for the $d_{xy} \rightarrow d_{xz}$, d_{yz} transitions.

An X-ray structure analysis of the copper bisacetylacetonate–quinoline adduct by Fernando[5] has shown that axial coordination to form the five-coordinate adduct is accompanied by a structural rearrangement in the parent copper β-diketonate in which the copper atom is moved above the plane of the four oxygens and the chelate rings are bent down and away from the axial coordination site. The purpose of this report is to examine the effects of axial ligation on the d energy levels in light of this known structural rearrangement and to use these results as an aid in understanding the electronic spectra of copper(II) β-diketonates.

By taking into consideration the rearrangement of the copper β-diketonate in the adduct and the increased electron density along the z axis, the following effects for axial ligation are expected: (1) the d_{xy} level being most involved in the copper–oxygen bonding will be significantly lowered in energy by the copper atom moving above the chelate oxygen plane and by the lengthening of the copper–oxygen bond distance, resulting in shifts to lower energy for all of the d–d transitions, $d_{xy} \rightarrow d_{z^2}$, d_{xz}, $d_{x^2-y^2}$, d_{yz}; (2) the d_{z^2} will be raised in energy by the axial perturbation and so the $d_{xy} \rightarrow d_{z^2}$ transition will undergo a relatively large shift to lower energy; (3) the $d_{x^2-y^2}$ level will be only slightly affected by disruption of the in-plane π bonding and the shift in the $d_{xy} \rightarrow d_{x^2-y^2}$ transition energy will primarily reflect the lower energy of the d_{xy} level; (4) the movement of the chelates out of the xy plane toward the yz plane will disrupt the out-of-plane π-bonding and will raise the d_{yz} level and lower the d_{xz} level.

Extended Hückel molecular orbital calculations were carried out in order to formulate these predicted d energy level changes in a semiquantitative fashion. The mo calculations reported here on the model system copper bis(diformylmethanido) [Cu(DFM)$_2$] are essentially identical with those of Cotton, Harris, and Wise.[6] These calculations have been extended to a model system for a five-coordinate adduct Cu(DFM)$_2\cdot$B having a pseudo-donor atom on the z axis and having coordinates in accordance with the known structural changes.[5] As can be seen from Table I, the calculated changes in energy of the d levels in going from the copper β-diketonate Cu(DFM)$_2$ to the adduct Cu(DFM)$_2\cdot$B support the above qualitative predictions made from considering the structural changes upon adduct formation. As shown by the differences in the calculated energies listed in Table I, the d_{xy} level is considerably lowered in energy, while d_{z^2} and d_{yz} are raised and $d_{x^2-y^2}$ and d_{xz} are only slightly affected. The calculated energy level order is the same for both Cu(DFM)$_2$ and Cu(DFM)$_2\cdot$B. The primary result is that all of the d–d transitions are significantly shifted to lower energy.

TABLE I

MOLECULAR ORBITAL 3d ENERGY LEVELS[a] FOR MODEL SYSTEMS Cu(DFM)$_2$ AND Cu(DFM)$_2\cdot$B

	Cu(DFM)$_2$[b] eV[g] (kK)[h]	[Cu(DFM)$_2$][c] eV (kK)	Cu(DFM)$_2\cdot$B[c,d] eV (kK)	ΔE,[e] eV (kK)	$\Delta\bar{\nu}_{\text{calcd}}$[f] ($d_{xy} \rightarrow$ d), kK
d_{xy}	−9.14	−9.38	−9.38	−0.24	
d_{z^2}	−11.27	−11.28	−11.14	+0.13	3.0
	(17.2)	(15.3)	(14.2)		
d_{xz}	−11.30	−11.30	−11.30	0.00	1.9
	(17.2)	(15.5)	(15.5)		
$d_{x^2-y^2}$	−11.35	−11.36	−11.36	−0.01	2.0
	(17.8)	(16.0)	(16.0)		
d_{yz}	−11.52	−11.39	−11.39	+0.13	3.0
	(19.2)	(16.2)	(16.2)		

[a] Molecular orbital of primarily 3d orbital character. [b] All input parameters identical with those of ref 8 except the Wolfsberg–Helmholtz K factor = 1.75. [c] Rearranged Cu(DFM)$_2$ without donor atom. Copper atom is 0.21 Å above the chelate oxygen plane. Copper–oxygen distance is 1.95 Å. Angle between acetylacetonate plane and plane through four oxygen atoms is 161°. All chelate bond angles and distances are unchanged from ref 8. [d] Rearranged Cu(DFM)$_2$ with donor atom. Pseudo-donor atom is Ne with VSIP(2s) = −25.00 eV, VSIP(2p) = −13.00 eV, and Slater orbital exponents (2s) = (2p) = 1.925; K = 1.75. [e] ΔE is the difference between the calculated energy for a 3d level in Cu(DFM)$_2$ and in Cu(DFM)$_2\cdot$B. [f] $\Delta\bar{\nu}$ is the calculated shift in transition energy upon axial coordination. [g] Orbital energies are given in electron volts. [h] The transition energies for $d_{xy} \rightarrow$ d as estimated from the difference of orbital energies is given in parentheses in units of kilokaisers.

A recent interpretation of the four components resulting from Gaussian analysis led to two "possible"

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sets of assignments of the electronic spectra for copper bis(acetylacetonate) [Cu(acac)$_2$] and copper bis(acetylacetonate)–pyridine [Cu(acac)$_2\cdot$py]:[4] (1) for Cu(acac)$_2$, $d_{xy} \gg d_{xz} > d_{x^2-y^2} > d_{yz} > d_{z^2}$ and, for Cu(acac)$_2\cdot$py, $d_{xy} \gg d_{z^2} > d_{xz} > d_{x^2-y^2} > d_{yz}$; (2) for Cu(acac)$_2$, $d_{xy} \gg d_{z^2} > d_{x^2-y^2} > d_{xz} > d_{yz}$, and for Cu(acac)$_2\cdot$py, $d_{xy} \gg d_{z^2} > d_{xz} > d_{x^2-y^2} > d_{yz}$. Both sets of assignments are probably incorrect for they were based on the unjustified assumption that the $d_{xy} \rightarrow d_{x^2-y^2}$ transition energy is unaffected by axial ligation. We find that by considering the structural changes on adduct formation all d–d transitions are shifted to lower energy and the d energy level ordering should be unchanged by axial ligation. On the assumption that the previously reported four-band Gaussian analysis approximates the positions and intensities of the four d–d bands in Cu(acac)$_2$ and Cu(acac)$_2\cdot$py,[4] two sets of spectral assignments are given in Table II, consistent with the analysis of axial ligation effects reported here, the intensity changes, and the most recent detailed studies of copper(II) β-diketonates.[7–9] The suggested order for both the acid and the adduct is $d_{xy} \gg d_{z^2} > d_{xz} > d_{x^2-y^2} > d_{yz}$ or $d_{xy} \gg d_{z^2} > d_{x^2-y^2} > d_{xz} > d_{yz}$. These results point out the need for considering structural changes when using the effects of axial ligation to aid in the assignment of electronic spectra.

TABLE II

REASSIGNMENT OF Cu(acac)$_2$ AND Cu(acac)$_2\cdot$py GAUSSIAN COMPONENTS

	Cu(acac)$_2$[a]		Cu(acac)$_2\cdot$py[a]		$\Delta\bar{\nu}$,[c] kK	Alternate assignments[d] (this work)
	$\bar{\nu}$, kK	$10^{-4}f$[b]	$\bar{\nu}$, kK	$10^{-4}f$[b]	($d_{xy} \rightarrow d$)	$d_{xy} \rightarrow$
I	14.1	2.2	10.2	2.2	3.9	d_{z^2}
II	14.9	3.5	12.7	4.7	2.2	d_{xz} ($d_{x^2-y^2}$)
III	17.4	2.8	14.9	3.6	2.5	$d_{x^2-y^2}$ (d_{xz})
IV	18.8	2.9	15.4	7.7	3.4	d_{yz}

[a] Data are taken from ref 4. [b] f is oscillator strength. [c] $\Delta\bar{\nu}$ is the shift in transition energy upon axial coordination. [d] The suggested d energy level ordering for Cu(acac)$_2$ is the same as that for Cu(acac)$_2\cdot$py.

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New Garnet with Ca^{2+} Ions in Octahedral Sites

Sir:

In this communication, we report a new garnet, prepared by solid-state reaction, at atmospheric pressure, containing Ca^{2+} ions in substantial amount in octahedral sites; its formula is $\{Ca_3\}[CaZr](Ge_3)O_{12}$.

There are many garnets which contain Ca^{2+} ions in *dodecahedral* or eight-coordination sites;[1] a typical one is $\{Ca_3\}[Al_2](Si_3)O_{12}$. However, no garnet has previously been made at atmospheric pressure with Ca^{2+} ions in octahedral coordination. Ringwood and Seabrook[2] have reported a pressure-induced CaGeO$_3$ with garnet structure, *i.e.*, $\{Ca_3\}[CaGe](Ge_3)O_{12}$. However, experiments carried out by us[1] on this material have always yielded specimens which are not cubic, although, nevertheless, their powder patterns indicate a close relation to the garnet structure.

The existence of the garnet $\{Ca_3\}[CaZr](Ge_3)O_{12}$ appears to confirm the close relationship of the CaGeO$_3$ pressure-induced phase to the garnet; in fact, the $\{Ca_3\}[CaGe](Ge_3)O_{12}$ phase would then be one of very few distorted garnet structures—unlike spinels and perovskites, in which cases there are many examples of reduced-symmetry structures. Apparently, replacement of one of the Ge^{4+} ions with the larger Zr^{4+} ion leads to the stabilization of the cubic structure at atmospheric pressure.

The new garnet was prepared by mixing appropriate amounts of CaCO$_3$, ZrO$_2$, and GeO$_2$, compacting, calcining at 900° for 0.5 hr and 1215° for 0.5 hr, regrinding, recompacting, and firing in air at 1340° for 17 hr followed by regrinding, recompacting, and refiring at 1375° for 4 hr.

The lattice constant[3] of the new garnet is 12.716 ± 0.003 Å, 0.202 Å greater than the lattice constant of $\{Ca_3\}[MgZr](Ge_3)O_{12}$,[4] 12.514 Å. To see that this is about as it should be, we note the following *a* values: Ca$_3$Al$_2$Si$_3$O$_{12}$,[1] 11.851 Å; Mg$_3$Al$_2$Si$_3$O$_{12}$, 11.459 Å—a difference of 0.392 Å. There are only two-thirds as many octahedral as dodecahedral sites in the garnet, and, *neglecting* the effect of coordination difference, this would predict a difference of 0.261 Å between the lattice constants of $\{Ca_3\}[CaZr](Ge_3)O_{12}$ and $\{Ca_3\}[MgZr](Ge_3)O_{12}$. The difference in coordination, could easily account for the extra 0.06 Å.

No change occurs in a specimen when it is subjected to a pressure of 45 kbars and temperature of 720° for 7 hr.

When the new garnet is heated in (1 atm) air to 1410° for 16 hr, it loses weight, presumably because of a loss of GeO$_2$; the loss is 1.7% of the amount of GeO$_2$ in the specimen. The lattice constant of the garnet increases to 12.729 ± 0.003 Å; it appears that the high-temperature firing produces Ge^{4+} and O^{2-} vacancies in the structure.[4]

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