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: $Ca_3Al_2Si_3O_{12}$,[1] 11.851 Å; $Mg_3Al_2Si_3O_{12}$, 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]

[1] S. Geller, *Z. Krist.*, **125**, 1 (1967), and pertinent references therein.

[2] A. E. Ringwood and M. J. Seabrook, *J. Geophys. Res.*, **68**, 4601 (1963).

[3] Based on wavelengths 1.54050 and 1.54434 Å of Cu $K\alpha_1$ and $K\alpha_2$, respectively.

[4] S. Geller, C. E. Miller, and R. G. Treuting, *Acta Cryst.*, **13**, 179 (1960).

When the new garnet is fired on platinum, a reaction must take place which distributes platinum cations through it; the specimen then has a dense blue color throughout. When fired on rhodium, the specimen is pink, indicating a reaction with rhodium. The specimen is colorless when fired on $CaZrO_3$, touching it only on a limited area. The Pt and Rh impurities have no measurable effect on the lattice constants, and it is probable that only very small amounts cause the coloration.

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