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Dynamic Crystals: Visually Detected Mechanochemical Changes in the Luminescence of Gold and Other Transition-Metal Complexes**

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One usually thinks of the crystalline state as a static, highly ordered array of atoms, molecules, or ions. That feature has allowed X-ray crystallography to become one of the most used and useful methods for determining the molecular and ionic structure of a wide array of substances. Of course, the atoms within crystals move, but that movement is severely constrained. However, the application of a mechanical force to crystals can produce some remarkable changes. This is particularly apparent in some new observations made on a number of transition-metal complexes. Remarkably, each case appears to be unique. In many cases a fully satisfactory explanation for the changes, which are readily observed visually, has been difficult to obtain.

In a recent report, Ito, Sawamura, and co-workers described the reversible changes in the luminescence brought about by simply grinding the colorless, blue-luminescent complex $[(F_5C_6Au)_2(\mu\text{-}1,4\text{-}CN_2C_6H_4)]$.[1] Figure 1 shows photographs of $[(F_5C_6Au)_2(\mu\text{-}1,4\text{-}CN_2C_6H_4)]$ crystals under various conditions. Figure 1 a shows the emission of a sample before (on the left) and after (on the right) grinding. A reversible transformation of the colorless crystals (Figure 1 b) from a blue-emitting form ($\lambda_{max} = 415$ nm) to a yellow/green-emitting form ($\lambda_{max} = 533$ nm) is evident from the photographs shown in Figure 1 c–f. Treating the sample with dichloromethane after thorough grinding to give the yellow/green-emitting form shown in Figure 1 c produces the blue-emitting form shown in Figure 1 d,e. Further grinding of this blue-emitting material again forms the yellow/green-emitting form as seen in Figure 1 f. In their original publication,[1] the authors have provided an informative video that nicely demonstrates their observations.

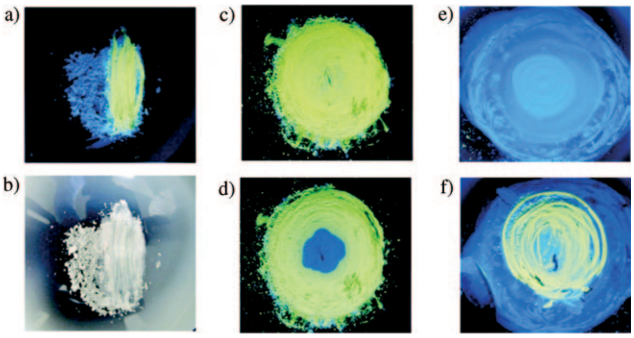

Figure 1. Photographs showing crystals of $[(F_5C_6Au)_2(\mu\text{-}1,4\text{-}CN_2C_6H_4)]$ on an agate mortar under UV irradiation with black light (365 nm), unless otherwise noted: a) $[(F_5C_6Au)_2(\mu\text{-}1,4\text{-}CN_2C_6H_4)]$ powder after grinding the right-half with a pestle, b) the same sample under ambient light, c) entirely ground powder, d) partial reversion to the blue luminescence by dropwise addition of dichloromethane onto the center of the ground powder, e) powder after treatment with dichloromethane, and f) regeneration of the yellow emission by scratching the powder with a pestle. Reprinted from reference [1] with permission.

The crystal structure of the blue-emitting form reveals that the individual molecules are widely spaced, with the closest contact between adjacent gold centers being 5.19 Å (Scheme 1). The authors have ascribed the blue luminescence from this form to phosphorescence resulting from an intraligand-localized π–π* excited state. The X-ray powder diffraction (XRD) pattern of the complex prior to grinding is consistent with the single-crystal diffraction data. Grinding the sample results in a broadening and lowering of the intensity of the reflections in the XRD spectrum, which is consistent with the formation of an amorphous material. The authors propose that in this amorphous material the gold(I) ions are positioned sufficiently close to one another that aurophilic interactions are present.[2] Such aurophilic interactions are weakly attractive bonds that are caused by a combination of relativistic and correlation effects.[3] The resulting emission was thus suggested to arise from proximate gold(I) ions in the amorphous phase. There are ample precedents for the variation of aurophilic interactions causing alterations in luminescence.[4,5] Individual polymorphs of two-coordinate gold(I) complexes (for example, $[Au(CNC_6H_{11})_2](PF_6)$,[6] solvoluminescent $[Au_3(MeOC{=}NMe)_3]$,[7,8] and $Zn[\{Au(CN)_2\}_2]$[9]) display distinctive emission properties that result from the self-association of the gold ions, and exhibit Au···Au distances in the range of 2.9 to 3.5 Å.

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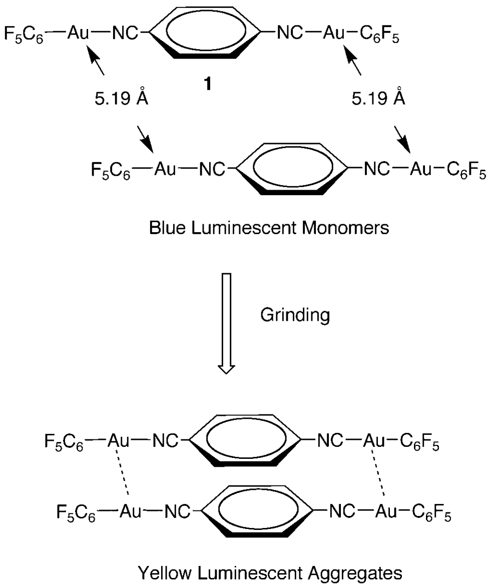


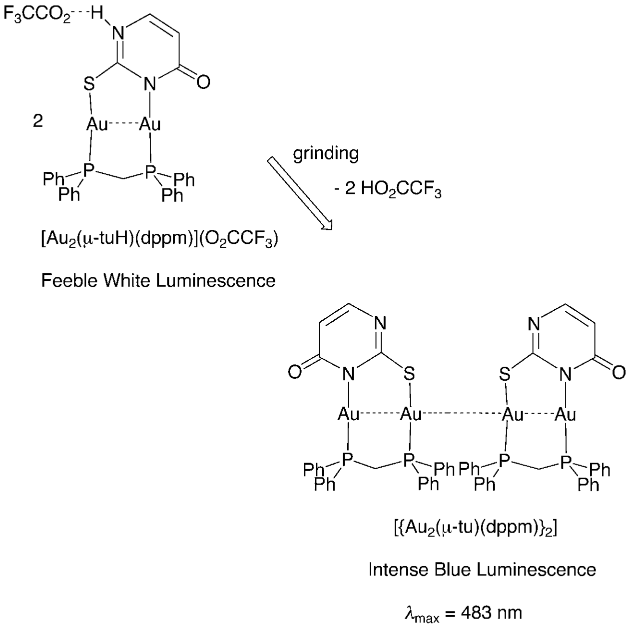
Scheme 1. Structural changes accompanying the luminescence changes of $[(F_5C_6Au)_2(\mu\text{-}1,4\text{-}CN_2C_6H_4)]$.

Other cases of related, but nevertheless distinctive, mechanically induced alterations in luminescence have been reported. Lee and Eisenberg have found that the thiouracil (tuH) complex $[Au_2(\mu\text{-tuH})(dppm)](O_2CCF_3)$ (dppm = bis(diphenylphosphanyl)methane) also undergoes a dramatic pressure-induced change in its luminescence (Scheme 2).[10] This thiouracil complex contains a doubly bridged Au_2 unit with a short Au···Au distance of 2.8797(4) Å. The binuclear units are arranged in a head-to-tail fashion and form helical chains through additional Au···Au interactions, with an Au···Au separation of 3.3321(5) Å between dimers. In the crystalline form this colorless complex displays a weak white luminescence, but an intense blue luminescence is observed upon grinding. This transformation is accompanied by the liberation of acid vapor. The intensely blue-emissive complex $[\{Au_2(\mu\text{-tu})(dppm)\}_2]$ has been prepared by treatment of $[Au_2(\mu\text{-tuH})(dppm)](O_2CCF_3)$ with a suitable base. In this form, a pair of binuclear complexes are arranged in a head-to-head fashion and are connected by a short (2.9235(4) Å) Au···Au interaction. Heating also causes acid loss from $[Au_2(\mu\text{-tuH})(dppm)](O_2CCF_3)$ to generate the blue-emissive form. Thus, it may be that grinding also causes local heating that results in the extrusion of acid. It should also be noted that there are several relevant cases where the reversible uptake and loss of gaseous hydrogen chloride occurs in crystalline copper complexes and results in marked color changes in the solids.[11,12]

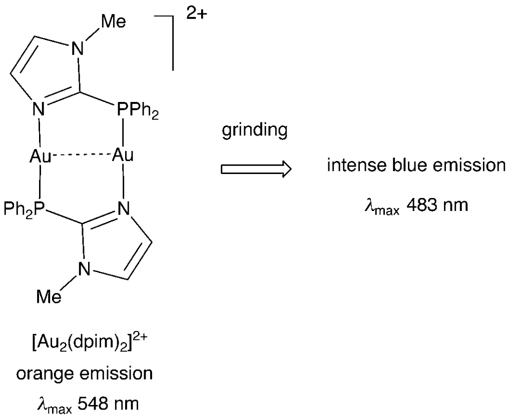
Eisenberg and co-workers have also examined the luminescent properties of some analogues of $[Au_2(\mu\text{-tuH})(dppm)](O_2CCF_3)$ where variously substituted benzimidazolethiolate ligands replaced the tuH ligand.[13] These complexes did not release acid vapors upon crushing, but did show a shift of the emission maxima to higher energies (for example, from 484 to 459 nm) when ground. The origin of these spectral changes remains to be determined.

Catalano and Horner reported that the colorless, binuclear gold(I) complex $[Au_2(dpim)_2](ClO_4)_2{\cdot}2\,MeCN$ (dpim = 2-(diphenylphosphanyl)-1-methylimidazole) exhibited an orange emission (λ_{max} 548 nm, λ_{ex} 336 nm) when it was initially prepared.[14] However, after grinding, the material showed a blue emission (λ_{max} 483 nm, λ_{ex} 368 nm) that was much more intense than the former orange emission (Scheme 3). Recrystallization of the orange-emitting crystals produced only blue-emitting crystals. Consequently, the authors concluded that an impurity in the initial preparation was responsible for the formation of the orange-emitting crystals, but the mechanism by which the grinding produces the change in the luminescence remains an intriguing mystery.

In a slightly different vein, Fackler and co-workers noted that colorless crystals of $[(tpa)_2Au][Au(CN)_2]$ (where tpa is the monodentate phosphine 1,3,5-triaza-7-phosphaadamantane) were not luminescent until they were crushed.[15] Crushing produced a sample with blue emission (λ_{max} 420 nm,



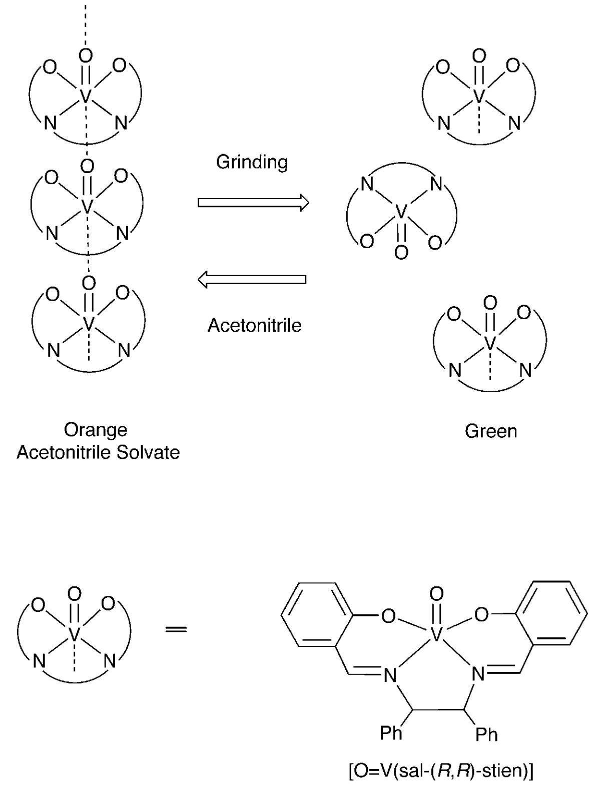
Scheme 2. Structural changes accompanying the luminescence changes of $[Au_2(\mu\text{-tuH})(dppm)](O_2CCF_3)$.



Scheme 3. Luminescence changes of $[Au_2(dpim)_2](ClO_4)_2{\cdot}2\,MeCN$.

λ_{ex} 320 nm) or green emission (λ_{max} 500 nm, λ_{ex} 380 nm) when irradiated with light of different wavelengths. This salt contains linear chains of alternating cations and anions that are connected by aurophilic interactions, with an Au···Au distance of 3.457(1) Å. The powder X-ray diffraction data for the crushed sample showed no difference from that of the initial crystals. The authors attributed the luminescence to the formation of either surface charges or defect sites in the crushed powder.

All of the examples considered so far involve gold(I) complexes where the low coordination number for gold allows the close approach of these complexes, which is a key factor in producing and altering their luminescence. However, related mechanical changes in color, rather than luminescence, have been observed by the research groups of Kojima, Tsuchimoto, and Ohba for a number of vanadyl complexes of Schiff bases.[16–19] Scheme 4 shows one of the complexes studied (H_2sal-(*R*,*R*)-stien = *N*,*N*′-disalicylidene-(*R*,*R*)-1,2-diphenyl-1,2-ethanediamine), while Figure 2 shows some relevant photographic data. Orange crystals of the solvate [O=V(sal-(*R*,*R*)-stien)]·CH_3CN (Figure 2B) contain chains of the vanadyl complex connected by weak interactions of the oxygen atom of one V=O group with the vanadium ion in an adjacent molecule (Scheme 4). Grinding of these orange crystals results in their conversion into a green form (Figure 2a,b). Green crystals of solvate [O = V(sal-(*R*,*R*)-stien)]·CH_3OH (Figure 2A) have been obtained by crystallization from methanol, and contain isolated complexes that lack the V=O···V=O··· interactions seen in the orange form. Thus, it appears that grinding results in the disruption of the linear chains of complexes that are characteristic of the orange form of the complex.



Scheme 4. Mechanochromism of vanadyl complexes.

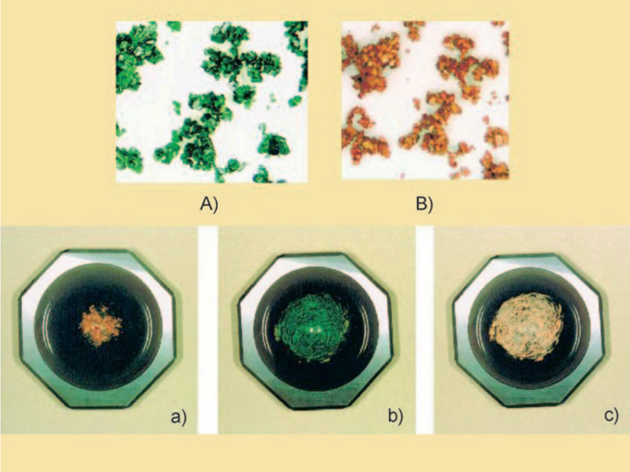


Figure 2. Top: A) green crystals of [O=V(sal-(*R*,*R*)-stien)]·CH_3OH; B) orange crystals of [O=V(sal-(*R*,*R*)-stien)]·CH_3CN. Bottom: A series of photographs showing the color change of [O=V(sal-(*R*,*R*)-stien)]: a) orange crystals of [O=V(sal-(*R*,*R*)-stien)]·CH_3CN; b) the green product obtained by grinding [O=V(sal-(*R*,*R*)-stien)]·CH_3CN in a mortar; and c) the regenerated orange form obtained by moistening the green product with acetonitrile. Reprinted from reference [16] with permission.

Recently two planar platinum(II) complexes were reported to undergo changes in their luminescence upon grinding.[20] For example, grinding yellow [Pt(5dpb)Cl] (5dpbH = 1,3-di(5-methylpyrid-2-yl)benzene) resulted in a change in its luminescence from yellow to a more intense orange, without any change in the X-ray powder diffraction pattern of the material, which retained its yellow color under ambient light.

As these results indicate, there are a number of cases where mechanical treatment of crystalline metal complexes results in some rather striking alterations in the luminescence or color of the sample. Generally, some sort of structural reorganization accompanies the spectral shifts. These changes have been designated mechanochromism or luminescence tribochromism and are one of a number of transformations that can be wrought on solids through the application of mechanical pressure. A recent review covers some other aspects where mechanical energy is utilized to modify covalent bonds.[21] While several gold(I) complexes have been shown to display luminescence tribochromism, no common mechanism has emerged as a cause, and in some cases a fully satisfactory explanation for the changes in luminescence has not been forthcoming. The studies of Ito, Sawamura, and co-workers[1] and of Lee and Eisenberg[10] provide the best-understood examples of luminescence tribochromism that we currently have. Mechanochromism and luminescence tribochromism are not necessarily confined to transition-metal complexes. Some organic chromophores have also been identified that undergo changes in absorption and/or emission upon grinding.[22,23] As yet, practical applications have not been developed from the materials that display mechanochromism. However, the utilization of mechanochromism for sensing motion and changes in mechanical force seems possible.

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