

Shedding Light on the Structure of a Photoinduced Transient Excimer by Time-Resolved Diffraction

Ivan I. Vorontsov,¹ Andrey Yu. Kovalevsky,¹ Yu-Sheng Chen,² Tim Graber,³ Milan Gembicky,¹ Irina V. Novozhilova,¹ Mohammad A. Omary,⁴ and Philip Coppens^{1,*}

¹*Department of Chemistry, SUNY at Buffalo, Buffalo, New York 14260-3000, USA*

²*University of Toledo, Toledo, Ohio 43606, USA*

³*University of Chicago, Chicago, Illinois 60637, USA*

⁴*University of North Texas, Denton, Texas 76203, USA*

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Time-resolved single-crystal diffraction performed with synchrotron radiation shows that the 53(1) μ s phosphorescent state, generated in the crystalline phase of trimeric $\{[3, 5-(CF_3)_2\text{Pyrazolate}]\text{Cu}\}_3$ molecules by exposure to 355 nm of light at 17 K, is due to the formation of an excimer rather than the shortening of the intramolecular Cu \cdots Cu distances within the trimeric units, or the formation of a continuous chain of interacting molecules. One of the intermolecular Cu \cdots Cu distances contracts by 0.56 Å from 4.018(1) to 3.46(1) Å, whereas the interplanar spacing of the trimers is reduced by 0.65 Å from 3.952(1) to 3.33(1) Å. Density-functional theory calculations support the formation of a Cu \cdots Cu bond through the intermetallic transfer of a Cu 3*d* electron to a molecular orbital with a large 4*p* contribution on the reacting Cu atoms.

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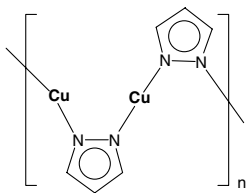
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Introduction.—The development of time-resolved (TR) diffraction methods now makes it possible to probe the geometry of transient species with lifetimes of microseconds and less. Thus geometry changes that occur upon photon absorption can be studied and information on the structure of highly reactive species that are intermediates in photochemical reactions can be obtained.

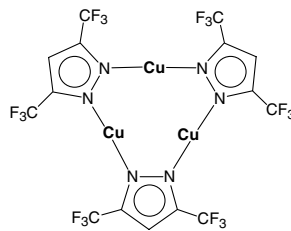
Among the dramatic photoinduced geometry changes that occur in the solid state are the metal-metal distance shortenings that occur in dinuclear d^8 - d^8 complexes of transition metals such as platinum and rhodium. Theoretical analysis shows that the shortening occurs as a result of the promotion of a *d* electron from the antibonding highest-occupied molecular orbital (HOMO) to a weakly bonding *p* σ orbital. In a recent communication, we described the first direct measurement of the Rh-Rh shortening in the solid state by time-resolved pump-probe diffraction of crystals of $\text{Rh}_2(\text{dimen})_4(\text{PF}_6)_2 \cdot \text{CH}_3\text{CN}$ (dimen = 1,8-diisocyanomethane), which show an excited triplet state lifetime of 11.7 μ s at 23 K. The intramolecular Rh-Rh distance in the complex contracts by as much as 0.85 Å [1]. A similar, but smaller, contraction on excitation of the d^8 - d^8 $[\text{Pt}_2(\text{pop})_4]^{4-}$ ion [pop = pyrophosphate, $(\text{H}_2\text{P}_2\text{O}_5)^{2-}$] was measured as 0.28(9) Å [2], 0.23(4) Å [3], and 0.23(4) and 0.28(5) Å [4] in independent experiments on different salts of the complex. The values are in excellent agreement with a solution value of \sim 0.21 Å estimated from analyses of the resonance Raman intensities [5] and of the vibrational fine structure of the absorption and emission spectra [6]. Other resonance Raman studies indicate that similar contractions also occur in binuclear complexes of monovalent coinage metals Au, Ag, and Cu [7].

We show here that an instantaneous and reversible bond formation can occur intermolecularly between molecules in a solid and describe the first diffraction analysis of the geometry of a transient intermolecular excimer. Polynuclear aromatic organic molecules provide classical examples for intermolecular excimers, which are usually characterized by photophysical data showing unstructured emissions that are much lower in energy than the monomer absorption energy [8]. For excimer formation to occur in the solid state, the organic molecules must be stacked in columns or arranged in pairs with interplanar distances of \sim 3.5 Å [9]. The metalloorganic Cu(I) pyrazolates are a series of compounds of current interest which show strong emission with microsecond lifetimes and which frequently stack in columns of cyclic trimers [10]. They provide examples of large Stokes shifts of the phosphorescence, strong temperature dependence of the emission wavelength (luminescence thermochromism), strong dependence of the luminescence on the rigidity of the medium in dilute environments (luminescence rigidochromism), and a pronounced dependence of the emission wavelength on concentration in solutions (concentration luminochromism). Copper (I) pyrazolates exhibit structures ranging from polymers to tetramers and trimers. $[\text{Cu}(\text{Pz})]_n$ (Pz = pyrazolate) is polymeric (Scheme 1) [11]. Structurally characterized trinuclear copper (I) pyrazolates containing nine-membered Cu_3N_6 metallacycles include $\{[3, 5-(\text{Me})_2\text{Pz}]\text{Cu}\}_3$ [12], $\{[3, 4, 5-(\text{Me})_3\text{Pz}]\text{Cu}\}_3$ [13], $\{[3, 5-(i\text{-Pr})_2\text{Pz}]\text{Cu}\}_3$ (*i*-Pr = isopropyl) [14], and $\{[3, 5-(\text{CF}_3)_2\text{Pz}]\text{Cu}\}_3$ [15] (Me = methyl). The current study involves the last, fluorinated, compound (Scheme 2). It crystallizes in a column-type arrangement with intermolecular Cu \cdots Cu distances of 3.787(1) and

4.018(1) Å (17 K) between the essentially planar trimeric molecules (Fig. 1). Such separations have been argued to represent “*cuprophilic bonding*” [10,16,17]. It belongs to the general “*metallophilic bonding*” type in closed-shell transition metals and their complexes, which has been attributed primarily to correlation [18] or hybridization [19] effects. The crystallographic arrangement of the $\{[3, 5-(\text{CF}_3)_2\text{Pz}]\text{Cu}\}_3$ trimers is comparable to that of planar aromatic organic molecules which exhibit intermolecular excimer emissions. The emission maximum of the crystals at 17 K occurs at 590 nm with 366 nm excitation, and at 660 nm with 337 nm excitation. The phosphorescence lifetime is 53(1) μs in both cases.



Scheme 1



Scheme 2

Experimental and data analysis.—The complex was synthesized as described in the literature [15] and characterized by ground-state structure analysis at both 90 and 15 K [20]. To elucidate the nature of the phosphorescent excited state of the complex, single-crystal TR diffraction experiments were performed at the 15-ID beam line at the Advanced Photon Source at Argonne National Laboratory with monochromatic ($\lambda = 0.49594$ Å) radiation at a temperature of 17 K. A pulsed Nd vanadate laser at a repeat rate of 12 kHz, synchronized with the x-ray pulses, was employed for excitation. The fundamental frequency was tripled to 355 nm. The x-ray probe beam was pulsed with a 64-slot chopper wheel with 0.7 mm slot width, rotating at 6400 rpm, producing an 18 μs x-ray pulse at a frequency of 6.8 kHz. The pulse width is selected such as to be less than the excited-state lifetime of 53 μs , which maximizes the effective population. Measurement of each “laser-on” frame of data was immediately followed by a “laser-off” frame [21] to eliminate the effect of long-range variations in intensity and thus allow more precise measurement of intensity changes on light exposure. The first step of the analysis involved the calculation of photodifference maps, defined as the difference between the electron densities in the light-exposed and dark crystals. The subsequent structure refinement is based on the response ratios, defined as the relative change in each of the reflection intensities on excitation, as described elsewhere [22]. Two different scattering formalisms were tested. The first is based on a random distribution of excited molecules and is identical to the one applied in our previous studies of light-induced metastable [23] and of transient species in crystals [1,2]. In

the course of the analysis, it became evident that the excitation involves an intermolecular rearrangement; a second formalism was tested, which assumes formation of domains of excited molecules in the parent crystal [24]. As the two models lead to quite different intensity expressions, a distinction is generally possible. In the current case, the refinement was successful only with the random distribution formalism.

Results.—Refinement was started based on light-induced peaks observed in the photodifference maps. Variables included the excited-state population, the positional coordinates of the Cu atoms, the orientation of the excited-state pyrazolate ligands, each considered as a rigid body fragment, and the position and orientation of the ground-state molecules in the excited crystal. In a final refinement, the CF_3 groups were allowed to rotate around the exocyclic C-C bond, but only small rotations of 6° – 8° were observed. The most striking result of the refinement is the reduction of the intermolecular $\text{Cu}\cdots\text{Cu}$ distance from 4.018(1) to 3.46(1) Å (Fig. 1), which is more than 0.3 Å less than the shortest $\text{Cu}\cdots\text{Cu}$ distance in the ground-state crystal. The Cu_3 triangles tilt only slightly (by 0.9°) on photoexcitation. The interplanar spacing of two center-of-symmetry related $\{[3, 5-(\text{CF}_3)_2\text{Pz}]\text{Cu}\}_3$ trimers in the stack is reduced by 0.65 Å, from 3.952(1) to 3.33(1) Å (Fig. 1). The light effect is a dimerization and not a chain compression, as the second interplanar distance is *increased* from 3.610(1) to 3.91(1) Å. Thus, somewhat unexpectedly, the shorter interplanar distance increases while the longer spacing decreases.

Discussion.—The main conclusion of this work is the assignment of the phosphorescent state, generated in the crystalline phase by exposure to 355 nm of light at 17 K, to the formation of an intermolecular excimer rather than shortening of the intramolecular $\text{Cu}\cdots\text{Cu}$ distances within the trimer units, or the formation of a continuous

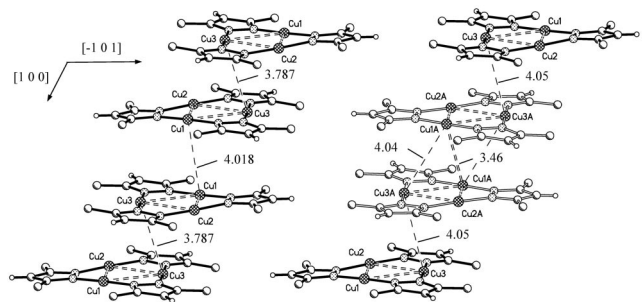


FIG. 1. Left: A column of the ground-state $\{[3, 5-(\text{CF}_3)_2\text{Pz}]\text{Cu}\}_3$ trimers (black bonds) before exposure. Right: Excimer formation within the same column. Fluorine atoms are omitted for clarity. The dashed single lines indicate intermolecular $\text{Cu}\cdots\text{Cu}$ distances in the range 3.78–4.05 Å, while the dashed double lines indicate intramolecular $\text{Cu}\cdots\text{Cu}$ distances in the range 3.20–3.26 Å and the $\text{Cu}\cdots\text{Cu}$ distance of 3.46(1) Å within the excimer.

chain of interacting molecules. In analogy to the light-induced metal-metal bond formation in binuclear complexes of monovalent coinage metals, investigated by resonance Raman techniques by Phillips *et al.* [7], and in the binuclear Pt and Rh complexes by both spectroscopic and TR diffraction techniques [1–5], the weak Cu-Cu bond formation is assigned to a $3d$ to $4p\sigma$ transition, with the important differences being that in the current case (i) the excited-state interaction is intermolecular rather than intramolecular, hence the M - M bonding here is unassisted by a bridging ligand, and (ii) the interactions here are much less easily predicted, as six metal atoms are involved compared to only two in the case of intramolecular bond formation in the binuclear complexes. It is remarkable that the light-induced compression of $\text{Cu} \cdots \text{Cu}$ distances does not occur between adjacent Cu atoms that have the shortest ground-state distances (i.e., the intramolecular separations) or even the next shortest separations [i.e., the $\text{Cu} \cdots \text{Cu}$ intermolecular separation], but involves the longer intermolecular $\text{Cu} \cdots \text{Cu}$ distance. This demonstrates that TR diffraction is an indispensable method to examine the excited-state structure for compounds such as trinuclear metal pyrazolates. In such a complex situation, the overall stabilization resulting from absorption of one photon seems to affect the weakest cuprophilic bonds but the contraction affects more than merely two metal atoms. Figure 1 shows that two additional $\text{Cu} \cdots \text{Cu}$ pairs of metal atoms within the excimer have become involved in weak cuprophilic bonding, while they were unbound in the ground state. While the primary enhancement is clearly for the $\text{Cu} \cdots \text{Cu}$ bonding, theoretical arguments have suggested that a genuine unassisted cuprophilic bonding at long distances, such as the two ~ 4.0 Å $\text{Cu} \cdots \text{Cu}$ distances in the excimer, may also play a role [25]. The bonding between metal atoms in crystals of compounds such as $\{[3, 5-(\text{CF}_3)_2\text{Pz}]\text{Cu}\}_3$ discussed here is delicate and quite flexible in both the ground state and even in the one-photon excimeric phosphorescent excited state in which the bonding may be cooperative, as suggested by a recent theoretical study of clusters of closed-shell transition metals [26]. This is in contrast to the situation in the intramolecular dimers in which only one M - M bond is affected such that it becomes a rather short single bond upon one-photon absorption. Because even the shortest compressed distance of 3.46 Å is still much longer than the ~ 2.5 – 2.6 Å distance in a Cu-Cu single bond, we expect a greater stabilization and compression for crystals of $\{[3, 5-(\text{CF}_3)_2\text{Pz}]\text{Cu}\}_3$ and similar compounds upon absorption of a second photon, a premise that we plan to pursue in future studies.

Theoretical calculations performed with the ADF suite of programs [27] show that the HOMO and the HOMO-1 of the ground-state complex have large d -orbital contributions from the two Cu atoms that do not participate in the excimer bonding, whereas the lowest unoccupied molecu-

lar orbital (LUMO) shows a $p\sigma$ bonding orbital linking the interacting Cu atoms, with additional contributions from the $p\pi$ orbitals on the adjacent nitrogen atoms (Fig. 2), thus indicating an intermetallic rather than a ligand field transition prior to excimer formation.

Several important issues concerning the complex photo-physical behavior of the trinuclear Cu(I) pyrazolate class of coordination compounds remain to be resolved. Our spectroscopic measurements indicate that the lifetime of $\{[3, 5-(\text{CF}_3)_2\text{Pz}]\text{Cu}\}_3$ increases from 53(1) to 77(1) μs on heating to 77 K, and then decreases to 41(1) μs on further warming to room temperature, an unusual trend. Even more intriguing is the behavior of $\{[3, 5-(i\text{-Pr})_2\text{Pz}]\text{Cu}\}_3$ [10]. On cooling of the crystal from room temperature to 77 K, the emission color changes from orange through yellow to green. At both 77 K and at 4 K, the green emission is composed of two bands with a green (~ 515 nm) and a lime-green (~ 570 nm) color, respectively [10]. The lime-green and the orange bands appear coupled, and may thus be in thermal equilibrium, while the green band has a different thermal behavior. $\{[3, 5-(i\text{-Pr})_2\text{Pz}]\text{Cu}\}_3$ has a dimer-of-trimer structure in its ground state, with short intertrimer Cu-Cu distances of 2.989 Å [10]. The nature of the phosphorescent state of this complex, and its variation with temperature and emitting wavelength, is not known, but will be the subject of further investigations. Other pyrazolates show a large variation in photophysical properties with substitution, temperature, and excitation wavelength, which remain to be explored. TR diffraction studies can shed light on the structural changes underlying their complex behavior and can point the way to rational design of light-emitting materials.

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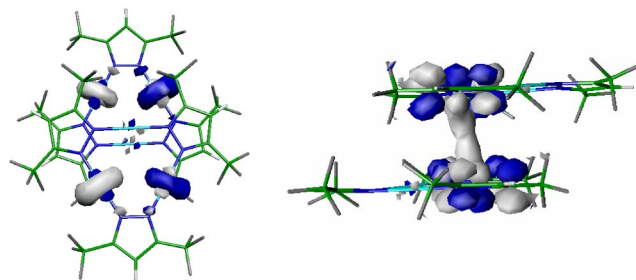


FIG. 2 (color online). The HOMO seen from above (left) with the bond forming Cu atoms [Cu(1)] in the center, and the LUMO, seen sideways, of the $\{[3, 5-(\text{CF}_3)_2\text{Pz}]\text{Cu}\}_3$ trimer. Surfaces are at an isodensity value of ± 0.03 a.u.

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*Electronic address: coppens@buffalo.edu

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