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A very large Rh–Rh bond shortening on excitation of the [Rh2(1,8-diisocyano-*p*-menthane)4]2+ ion by time-resolved synchrotron X-ray diffraction

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A very large Rh–Rh contraction of ~0.85 Å occurs on excitation of the [Rh2(1,8-diisocyano-*p*-menthane)4]2+ ion to its triplet state.

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

Among the dramatic changes that can occur in the solid state are the metal–metal distance shortenings on excitation of dinuclear d^8–d^8 complexes of transition metals such as platinum and rhodium.

As first pointed out by Miskowski *et al.* the ground-state Rh–Rh bond length in [Rh2(dimen)4]2+ (dimen = 1,8-diisocyano-menthane) (Fig. 1) salts shows an unusually large variation, the distance being equal to 4.48 Å in the PF_6^- and 3.861 Å in the [B(C6H5)4]2 salts,[1] attesting to the shallowness of the internuclear potential. In Rh–Rh complexes with the flexible 1,6-diisocyano-hexane ligand the bond length is even shorter at 3.0988(7) and 3.207(2) Å in the PF_6 and calix[4]arenate salts respectively.[2]

We have previously reported a bond-shortening of 0.28(9) Å in the [Pt2(pop)4]4– ion (pop = pyrophosphate, $(H_2P_2O_5)^{2-}$) in its (TEA)3H(Pt2(pop)4), (TEA = tetraethyl ammonium) salt,[3] a result supported by a subsequent study by Ozawa *et al.* (0.23(4) Å)[4] and recent results on a mixed (methylviologen)K2[Pt2(pop)4] salt (0.23(4) and 0.28(5) Å for the two independent molecules).[5]

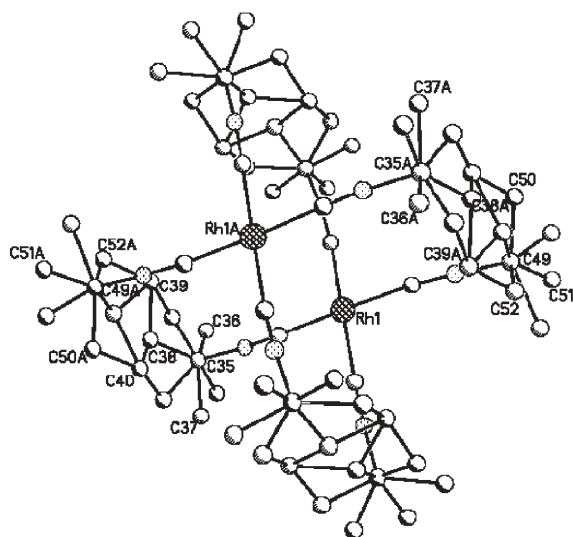For [Rh2(diprop)4]2+ (diprop = 1,3-diisocyanopropane) analysis of the band shape of the absorption system revealed an excited state contraction of ~0.3 Å in the ^3A_u excited state,[6] a value confirmed by our DFT calculations, which for the ground state give a contraction of 0.39 Å on excitation.[7] The shortening, due to $d\sigma^* \rightarrow p\sigma$ excitation, appears much larger for Rh2(dimen)4. Though no spectroscopic value is available, Miskowski *et al.* infer from semiquantitative calculations that the Rh–Rh bond shortens from a ground state value of about 4.2 Å to ~3.2 Å.

We describe here a first direct measurement of the Rh–Rh shortening in the solid state by time-resolved diffraction of crystals of Rh2(dimen)4(PF6)2·CH3CN.† In the crystals the triplet excited state lifetime increases with decreasing temperature (Fig. 2) to reach 11.7 μs at 23 K, with an emission maximum at 660 nm. The temperature dependence is indicative of a two level system with a shorter lifetime for the thermally accessible upper state. Both the lifetime and the position of the emission maximum are invariant in the 355–532 nm excitation range.

The experiments were performed at the 15-ID beamline at the Advanced Photon Source at Argonne National Laboratory with monochromatic ($\lambda = 0.49594$ Å) radiation. A Nd vanadate laser at a repeat rate of 12 kHz, synchronized with the X-ray pulses, was employed for excitation. The fundamental frequency was doubled to $\lambda = 532$ nm and tripled to 355 nm in two successive experiments. The X-ray probe beam was pulsed with a 180 slot chopper wheel rotating at 4000 rpm, giving a 9.5 μs opening time, which is less than the excited state lifetime, as required to maximize the effective population. Measurement of each 'laser-on' frame of data was immediately followed by a 'laser-off' frame.[3,8] This strategy eliminates the effect of long range variations in intensity and
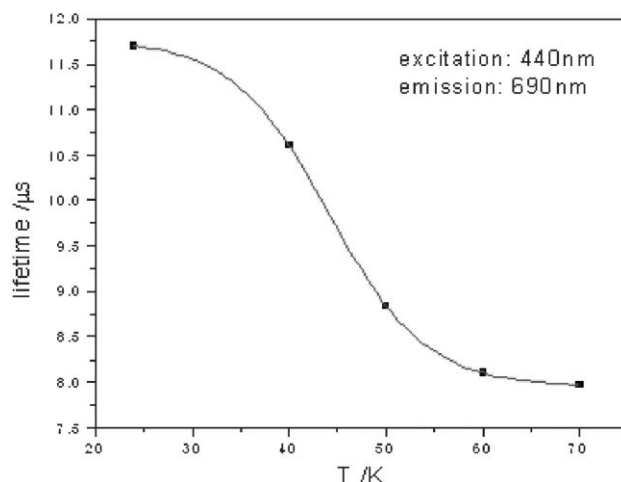

Fig. 1 Drawing of the [Rh2(dimen)4]2+ ion in the crystal. Note the disorder in the bridging ligands.

Fig. 2 Temperature dependence of the lifetime of the triplet excited state of [Rh2(dimen)4]2+ in crystals of Rh2(dimen)4(PF6)2·CH3CN.

thus allows more precise measurement of intensity changes on light exposure, which is crucial given the often small conversion percentages. The data analysis is performed on the *response ratios* defined as the relative change in each of the reflection intensities on excitation.[9] A total of 6717 (2871 + 3846) response ratios larger than $2\sigma(\eta)$ were measured at a nominal temperature of 17 K on two small crystals of size $90 \times 70 \times 70 \ \mu m^3$. 15877 unique reflections with $I > 2\sigma$ were collected without laser light at 17 K to provide a ground-state structure to be used as reference in the refinement.

Refinement of the response ratios was performed varying five parameters including the three positional parameters of Rh, the excited state population, and the temperature scale factor which account for the heating of the crystals during laser exposure. As refinement of the two data sets gave essentially identical results, they were combined in a single refinement. The final excited state Rh–Rh distance is 3.64(5) Å, compared with the ground state value of 4.5153 (3) Å (90 K) and 4.496(1) Å at 17 K (this work), corresponding to a shortening of 0.86(5) Å, by far the largest structural change on excitation observed by atomic-resolution time-resolved diffraction methods. In addition, a rotation of 13(1)° of the molecule on excitation in the crystal is observed. Excited state populations refined to 1.9% (532 nm excitation) and 2.5% (355 nm) in the two crystals respectively. Though this is clearly sufficient for refinement of the Rh positions, it prevents determination of the changes in the positions of the lighter atoms. Increasing the laser power led to breakdown of the crystals before sufficient data could be collected. Methods to increase X-ray flux and thus reduce exposure time are currently being explored.

The large contraction of the Rh–Rh distance may be related to the shallowness of the Rh–Rh potential in the complex which has a Rh–Rh ground-state stretching frequency of only 28 cm^{-1}. The relatively long ground-state bond length of the diisocyanomenthane complex has been attributed to the stiffness of the ligand, compared to more flexible bridging ligands like 1,6-diisocyanohexane. Nevertheless, the Rh–Rh bond formed on the $d\sigma^* \rightarrow p\sigma$ excitation is sufficiently strong to cause a very large reduction in the Rh–Rh separation on excitation.

The results may be compared with theoretical predictions. DFT calculations performed with the ADF program[10] (ZORA relativistic approach, VWNBLYP density functional, Slater-type triple-ζ basis set for Rh, double-ζ with polarization function basis set for the other atoms), show a shallow potential energy minimum and a Rh–Rh bond length of 4.647 Å shortening to 3.107 Å on excitation with an increase in Mayer bond order[11] from 0.019 to 0.863 calculated with the program of Bridgeman and Empson.[12] Thus, the contraction calculated theoretically is considerably larger than actually observed in the crystal. A reduced distortion in the crystal was also observed by TR diffraction for $[Cu(I)(dmp)(dppe)][PF_6]$ (dmp = 2,9-dimethylphenanthroline, dppe = 1,2-bis (diphenylphosphino)ethane), which flattens on excitation. However, in the latter case a considerable change in the shape of the molecule occurs, while a contraction as occurs for Rh–Rh should be less impeded by the molecular environment. The theoretical excited state structure (Fig. 3) shows a movement of the CN group of the isocyano ligand to accommodate the Rh–Rh distance contraction, but little change in the more rigid menthane part of the ligand.

We conclude that the time-resolved crystallographic methods now becoming available have the potential to considerably increase our insight in a broad range of photochemical processes.
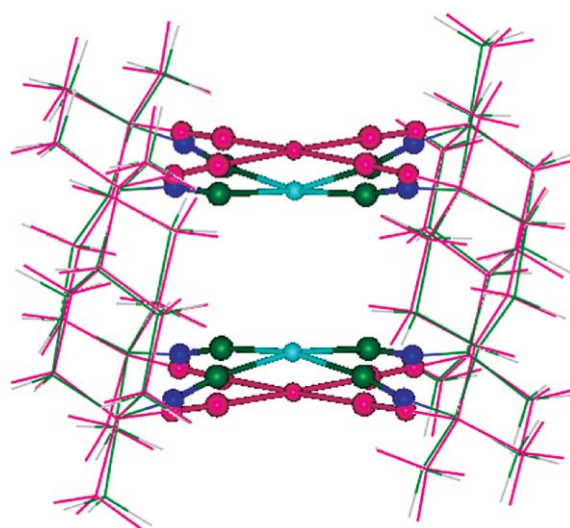
Fig. 3 Theoretical ground state (in pink) and excited state (green and blue colors) geometries of the $[Rh_2(1,8\text{-diisocyanomenthane})_4]^{2+}$ complex.

Notes and references

† Crystal data for $Rh_2(dimen)_4(PF_6)_2 \cdot CH_3CN$: Cell dimensions at 17 K: $a = 9.4407(6)$ Å, $b = 13.4608(6)$ Å, $c = 13.6781(8)$ Å, $\alpha = 61.9167(7)°$, $\beta = 84.9358(8)°$, $\gamma = 75.068(1)°$, $V = 1480.7(3)$ Å^3, Space group P$\bar{1}$, $Z = 1$ (half a molecule in the asymmetric unit). CCDC [CCDC NUMBER(S)]. See http://www.rsc.org/suppdata/cc/b4/b409463h/ for crystallographic data in .cif or other electronic format.

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