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Time-resolved Laue diffraction of excited species at atomic resolution: 100 ps single-pulse diffraction of the excited state of the organometallic complex Rh₂(µ-PNP)₂(PNP)₂·BPh₄

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The polychromatic Laue technique has been applied in 100 ps delay synchrotron pump–probe experiments of the triplet excited state of a Rh(I) dinuclear complex. The observed contraction of the Rh–Rh distance of 0.154 (13) Å is less than predicted by a series of theoretical calculations, a difference attributed to the constraining effect of the crystal lattice.

In the past few years time-resolved (TR) pump–probe diffraction studies of µs and sub-µs lifetime species at synchrotron sources have developed from much a discussed prospect to an increasingly realistic technique, both in macromolecular crystallography[1,2] and in the study of short-lived excited states in chemistry.[3–6] Especially the latter require maximal accuracy as the shift in individual atoms in the complex of interest have to be precisely determined. Because of this such studies have until the present made use of monochromatic radiation. Processing of monochromatic data does not involve analysis of the wavelength dependence of the scattering process and of the detector response and avoids the broadening of the reflection maxima inherent in the Laue technique. However, use of monochromatic radiation implies a very inefficient use of the photons in the synchrotron beam and thus longer X-ray probe periods, thereby limiting the time-resolution that can be achieved and the lifetimes that are accessible.

We report here the first time-resolved atomic-resolution Laue study of an organometallic complex with improved accuracy compared with previous monochromatic studies. In this work the wavelength dependence of the polychromatic technique was circumvented by application of the *RATIO*-method, in which the information extracted from the synchrotron experiment are the ratios of the light-on and light-off intensities of the individual reflections.[7] No changes in cell dimensions, which could affect the ratio method, occurred on excitation, as checked by careful analysis of each of the individual frames. The ratios are subsequently used with a set of monochromatic data collected at a conventional source at the same temperature to derive the light-on intensities for calculation of photodifference maps. Integration is performed with the Seed-Skewness method,[8,9] which does not require a regular spot-shape as no profile fitting is used. The refinement of the excited-state (ES) structure is performed with the program Laser2010 which is based on the experimental ON–OFF ratios as primary observables.[10]

The structure and photochemistry of Rh₂(µ-PNP)₂(PNP)₂·BPh₄, where PNP = CH₃N(P(OCH₃)₂)₂ and Ph = phenyl (**1**) (Fig. 1) and related salts was first studied by Mague and coworkers.[11,12] Strong emission on excitation with 337 nm light, attributed to a photo-excited triplet state was observed at low temperatures. In the α-polymorph of (**1**) a change in the emission from two bands at 730 and 780 nm to a single band at 780 nm is observed on heating above 50 K. The change is attributed to a thermal transition to a second triplet state conformer.[11]

The α-polymorphic modification of the title compound crystallizes with one formula in the unit cell of the monoclinic crystals (space group $P2_1/n$). Because of a broadening of the spot shape on cooling due of strain in the specimen crystals, the experiment was performed at 225 K.† The temperature of the experiment reported here implies that the excited state with the 780 nm emission was studied. The resulting shortening of the emission lifetime monitored at 790 nm from the value of 46.5(3) µs reported at 10 K does not affect the current experiment as the delay between the 35 ps pump and 100 ps probe pulses was only 100 ps.
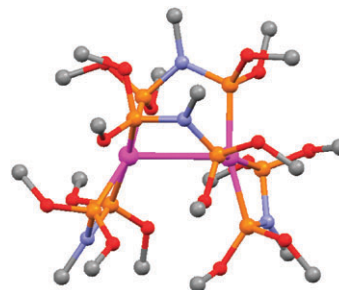

Fig. 1 Molecular structure of the cation of (**1**). Rh: purple, P: orange, N: blue, O:red, C: gray.

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Two data sets of three runs each were collected at 12 keV and at 15 keV undulator settings respectively ($\Delta E/E$ = 7%).‡ To maximize the part of the sample exposed to the laser beam small crystals of about 40 × 30 × 10 μ were selected. Consistence of the data was checked by plotting the experimental ratios of different runs against each other in 'correlation plots'. Since none of the data sets were complete due to limited lifetime of the crystals during repeated laser exposure, photo-difference maps are incomplete but nevertheless indicated significant shifts of the Rh atoms. Refinements with the Laser program[10] were done on the combined three 12 keV sets and the combined 15 keV sets, followed by a joint refinement on all six sets of data. No merging is required in this procedure as the program Laser allows simultaneous refinement on several data sets on the same sample.[10] Each of the PNP ligands in the excited state was treated as a rigid body, which was allowed to rotate and translate in the crystal. As the results of the 12 and 15 keV refinements gave closely similar Rh–Rh shortenings and the final all-data refinement was intermediate between the first two refinements, only the latter using 2256 unique reflections is reported here. Possible temperature differences are taken into account in the Laser program by introduction of a overall temperature-scale-factor k_B which multiplies the experimental atomic displacement parameters (ADP's).[13] However, in the current study temperature increases are moderate as single-pulse diffraction images were recorded k_B factors averaged 1.23 for the 12 keV and 1.12 for the 15 keV experiments which were recorded with lower laser power; The excited-state populations averaged over each of the 3 sets are 6.6% (12 keV) and 4.7% (15 keV). Resulting GS and ES Rh–Rh bond distances are listed in Table 1. The Rh(1) atom in the crystal moves mostly perpendicular to the bond direction by 0.170(14) Å, while the Rh(2) atom moves towards Rh(1) by 0.156(12) Å, leading to a Rh–Rh distance contraction of 0.154(13) Å. The combined effect corresponds to a rotation of the Rh–Rh bond axis in the crystal of 2.5°. The individual changes in position of the P atoms are generally not significant given the large standard deviations in the rigid-body rotational angles. However, for the terminal ligands the average Rh–P distance increases by ∼0.06 Å. This is not the case for bridging ligands, which seem to follow the shifts of the Rh atoms on excitation. The atomic shifts are illustrated in Fig. 2.

The experimental contraction of the Rh–Rh bond in this Rh(I) complex is considerably less than observed in the time-resolved study of the [Rh(II)₂(1,8-diisocyano-p-menthane)₄]$^{2+}$ ion, for which a contraction of 0.85(5) Å from a much longer ground state Rh–Rh bond length of 4.496(1) Å was observed, compared with a theoretical shortening of 1.54 Å.[14]

Theoretical DFT calculations (Table 2) with two different functionals predict a much larger Rh–Rh distance shortenings than observed, as also found for [Rh(II)₂(1,8-diisocyano-p-menthane)₄] (2). The difference may be at least in part attributed to the constraining influence of the crystal lattice,

Table 1 Experimental Rh–Rh bond length changes on excitation

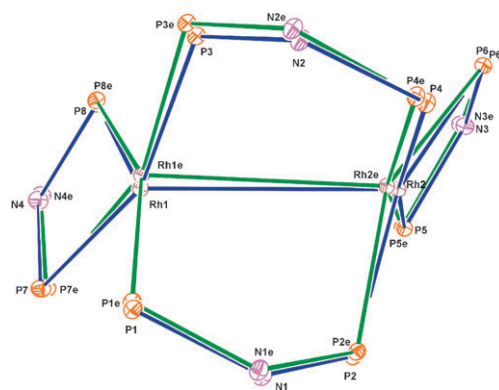| Atom1	Atom2	GS geometry Distance/Å	ES geometry	Δ
Rh1	Rh2	3.1805(2)	3.027(13)	−0.154(13)

Fig. 2 Structural changes on excitation. Ground state (blue lines) and excited triplet state (green lines).

Table 2 (a) Theoretical Rh–Rh bond lengths obtained with the B3LYP functional (Å). (b) Theoretical Rh–Rh bond lengths obtained with the BP86 functional (Å)

(a) Gaussian[17]

Basis set	GS	ES	Δ
LANL2DZ	3.670	3.031	0.639
6-31G*	3.620	3.138	0.482
6-311G*	3.667	3.115	0.552
WTBS	3.774	3.268	0.506

(b) Gaussian

Basis set	GS	ES	Δ
LANL	3.364	2.941	0.423
6-31G*	3.386	3.057	0.329
6-311G*	3.439	3.069	0.370
WTBS	3.650	3.186	0.464

ADF[18]

	GS	ES	Δ
DZ	3.407	3.035	0.372
DZP	3.431	3.102	0.329

as suggested by our QMMM study on the excited state of a Zn complex in which a shell of molecules surrounding the excited molecule were treated by molecular mechanics.[15] Preliminary QMMM studies on (1), to be described elsewhere, give an improved value for the Rh–Rh distance and almost quantitative agreement with experiment for its shortening on excitation. The effect of the crystal lattice on geometry is also evident from the 0.19 Å difference (from 3.2727(5) to 3.082(4) Å) between the room temperature Rh–Rh separations observed in the triflate and β-tetraphenylborate salts of the Rh₂(μ-PNP)₂(PNP)₂ cation reported by Mague.[12] The QMMM study shows the shortening to be a result of promotion of an antibonding electron to a weakly bonding pσ orbital, similar to our earlier studies on binuclear Pt and Rh complexes.[14,16]

We conclude that the improved Laue technique can be used for the atomic resolution determination of molecular excited states in crystals. Experimental standard deviations in the current study are smaller than those in previous monochromatic results while the experiment was completed in a much shorter time span. The improvement is evident from the standard deviation of 0.013 Å for the Rh–Rh bond length obtained in

the present study, which may be compared with 0.05 Å for the standard deviation of this distance in a previous monochromatic study of a Rh(II) binuclear complex.[14] In addition single pulse experiments allow much better time resolution than the monochromatic stroboscopic method and are applicable to species with lifetimes of nanoseconds or less as the pump–probe delay can be minimized as done in the current study.

Notes and references

† Cell dimensions at 225 K: $a = 13.8117$ Å $b = 19.9538$ Å $c = 28.1469$ Å $\alpha = 90°$ $\beta = 90.189°$ $\gamma = 90°$.
‡ To improve counting statistics three single pulse–probe cycles were accumulated on each frame. For the subsequent analysis each ratio was based on 10-ON and 10-OFF frames.

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