

## The three-dimensional intermolecular network formed *via* water molecules in *trans*-bis(nitrito- $\kappa$ N)tetrakis(pyridine- $\kappa$ N)ruthenium(II) dihydrate

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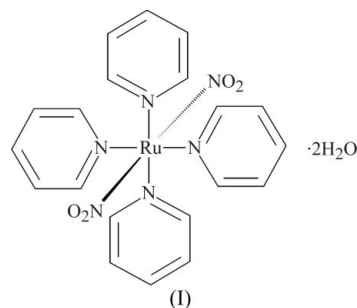
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The molecular geometry of the tetragonal crystal structure of the title compound,  $[\text{Ru}(\text{NO}_2)_2(\text{C}_5\text{H}_5\text{N})_4]\cdot 2\text{H}_2\text{O}$ , differs from that previously determined by powder diffraction [Schaniel *et al.* (2010). *Phys. Chem. Chem. Phys.* **12**, 6171–6178]. In the  $[\text{Ru}(\text{NO}_2)_2(\text{C}_5\text{H}_5\text{N})_4]$  molecule, the Ru atom lies at the intersection of three twofold axes (Wyckoff position 8*b*). It is coordinated by four N atoms of the pyridine rings, as well as by two N atoms of *N*-nitrite groups. The last two N atoms are located on a twofold axis (Wyckoff position 16*f*). The O atoms of the water molecules are situated on a twofold axis (Wyckoff position 16*e*). Short intermolecular contacts are observed in the crystal structure, *viz.* N—O...OW and N—O...H—OW contacts between nitrite and water, and weak C—H...OW hydrogen bonds between pyridine and water. Thus, the intercalated water molecules act as bridges connecting the *trans*- $[\text{Ru}(\text{NO}_2)_2(\text{py})_4]$  molecules into a three-dimensional network.

### Comment

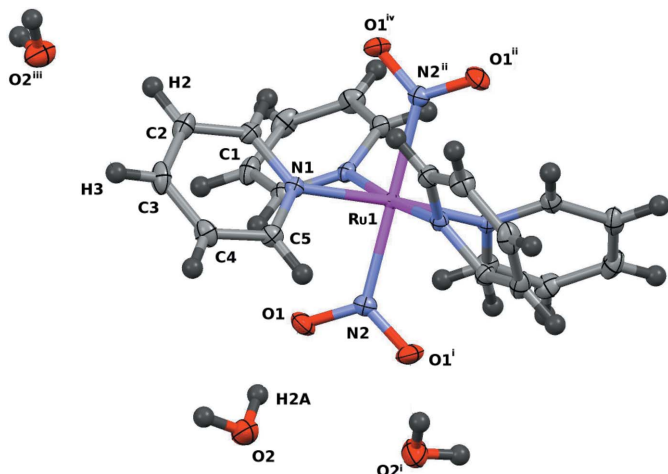
Nitrosyl complexes have attracted great interest over the past ten years because they present reversible linkage isomerization under light irradiation between *M*—N—O and *M*—O—N forms, where *M* is a metal atom (Fe, Co, Ru, Ni *etc.*) (Coppens *et al.*, 2002, and references therein). The prototype compound is  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$  (Hauser *et al.*, 1977). Another kind of reversible photochemical transformation is reported between *N*-nitrite (*M*—NO<sub>2</sub>) and *O*-nitrite (*M*—ONO) molecules. The *N*-nitrite form of the molecule can usually be obtained during the synthesis of the corresponding nitrosyl complex *M*—N—O. The prototype compound exhibiting *N*-nitrite to *O*-nitrite linkage isomerization is  $[\text{Co}(\text{NO}_2)-$

$(\text{NH}_3)_5]\text{Cl}_2$  (Grenthe & Nordin, 1979), but detailed crystallographic studies of these two kinds of materials are still limited because of difficulties in obtaining good single crystals and partial photochemical transformations (Coppens *et al.*, 2002). A notable exception now exists in the family of nitrosyl complexes: *trans*- $[\text{RuCl}(\text{py})_4(\text{NO})](\text{PF}_6)_2\cdot 0.5\text{H}_2\text{O}$  recently became a model system for the structural analysis of the two isomeric configurations of the NO ligand (Cormary *et al.*, 2009), since the phototransformation from linear Ru—N—O [the so-called GS (ground state)] to linear Ru—O—N [the so-called MS1 (metastable 1) state] is complete or quasi-complete in the single-crystal structure of the complex.



We report here the crystal structure of the *N*-nitrite form of *trans*- $[\text{Ru}(\text{NO}_2)_2(\text{py})_4]\cdot 2\text{H}_2\text{O}$ , (I), which is an intermediate product obtained during the synthesis of *trans*- $[\text{RuCl}(\text{py})_4(\text{NO})](\text{PF}_6)_2\cdot 0.5\text{H}_2\text{O}$  (Schaniel *et al.*, 2007). High-quality yellow single crystals of (I) were obtained and the tetragonal space group  $I4_1acd$  ( $Z = 8$ ) was determined. This crystal structure differs from the powder structure previously determined in the orthorhombic space group  $Pna2_1$ ,  $Z = 4$  (Schaniel *et al.*, 2010). In that work, the *trans*- $[\text{Ru}(\text{NO}_2)_2(\text{py})_4]$  molecular geometry showed discrepancies with parameters derived from density functional theory (DFT) (Delley, 2006), which was discussed alongside the powder structure. Analysis of the single-crystal data reported here leads to a geometry for *trans*- $[\text{Ru}(\text{NO}_2)_2(\text{py})_4]$  that is in good agreement with the DFT calculations performed for the free molecule. In addition, the single-crystal data enable discussion of the intermolecular interactions between *trans*- $[\text{Ru}(\text{NO}_2)_2(\text{py})_4]$  and intercalated water.

The molecular geometry of *trans*- $[\text{Ru}(\text{NO}_2)_2(\text{py})_4]$  differs significantly from that previously determined from powder data. The Ru atom lies at the intersection of three twofold axes (Wyckoff position 8*b*) and is coordinated by four N atoms (labeled N1) of the pyridine rings, as well as by two N atoms (labeled N2) of *N*-nitrite groups. The last two N atoms are located on a twofold screw axis (Wyckoff position 16*f*). Thus, there is only one symmetry-independent pyridine ring and consequently a unique value for the Ru1—N1 bond length. The two O atoms of the *N*-nitrite group are symmetry equivalent and there are unique values for the Ru1—N2 and N2—O1 bond lengths (Fig. 1 and Table 1). Differences between the single-crystal structure and the previous powder structure are also clear from both bond length and angles values. In particular, the pyridine N—Ru distance (Ru1—N1) is longer than the nitrite N—Ru distance (Ru1—N2), while


**Figure 1**

The structure of a *trans*-[Ru(NO<sub>2</sub>)<sub>2</sub>(py)<sub>4</sub>] molecule and the symmetry-equivalent neighbouring water molecules, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i)  $-y + \frac{1}{4}, -x + \frac{1}{4}, -z + \frac{1}{4}$ ; (ii)  $-x, -y + \frac{1}{2}, z$ ; (iii)  $x - \frac{1}{2}, -y, z$ ; (iv)  $y - \frac{1}{4}, x + \frac{1}{4}, -z + \frac{1}{4}$ ]

the powder structure led to the opposite result (see Table 1). As mentioned above, DFT calculations are in agreement with the present single-crystal structure (Table 1). Moreover, the Ru1–N2 bond length reported here [2.0496 (17) Å] is not surprising when compared with values obtained from other nitro compounds of ruthenium, for example, 2.033 (4) Å at 293 K in [Ru(tpy)(dpk)(NO<sub>2</sub>)]ClO<sub>4</sub> (tpy is 2,2':6',2''-terpyridine and dpk is di-2-pyridyl ketone; Sarkar *et al.*, 2005), and 2.088 (1) and 2.091 (2) Å at 90 and 200 K, respectively, in [Ru(bpy)(NO)(NO<sub>2</sub>)](PF<sub>6</sub>)<sub>2</sub> (bpy is 2,2'-bipyridine; Kovalevsky *et al.*, 2005). Another significant difference between the present single-crystal structure and the previous powder structure concerns the angular values involving the NO<sub>2</sub> group. The Ru1–N2–O1 and O1–N2–O1<sup>i</sup> [symmetry code: (i)  $-y + \frac{1}{4}, -x + \frac{1}{4}, -z + \frac{1}{4}$ ] angles differ by between *ca* 5 and 18° (Table 1 and Fig. 1). In contrast, comparison between the

*trans*-[Ru(NO<sub>2</sub>)<sub>2</sub>(py)<sub>4</sub>] molecular geometry determined here from single-crystal data (Table 1, column 2) and that calculated from DFT (Table 1, column 3) (Schaniel *et al.*, 2010) again shows good agreement. Thus, the present single-crystal structure validates the DFT calculations.

Analysis of the intermolecular interactions in (I) shows that the solvent water molecules act as bridges connecting the *trans*-[Ru(NO<sub>2</sub>)<sub>2</sub>(py)<sub>4</sub>] complexes into a three-dimensional supramolecular network *via* (i) short O–H···O hydrogen bonds connecting the NO<sub>2</sub> group and water, and (ii) weak C–H···O hydrogen bonds between pyridine rings and intercalated water (Table 2, and Figs. 1 and 2). Until now, the role of such close intermolecular contacts has not been discussed in the *N*-nitrite to *O*-nitrite photochemical process. One reason is that high-quality single-crystal data for such materials is largely missing and therefore DFT studies are usually limited to the intramolecular level (Schaniel *et al.*, 2010). The single-crystal structure presented here could be used to undertake calculations beyond this level for a deeper understanding of the photochemical reaction. Indeed, IR spectroscopic investigations on powder samples (Schaniel *et al.*, 2010) showed that, using light of wavelength 325 nm, about 50% of the *trans*-[Ru(NO<sub>2</sub>)<sub>2</sub>(py)<sub>4</sub>] molecules can be switched from the N-bound Ru–NO<sub>2</sub> to the O-bound Ru–ONO configuration below *T* = 250 K. The reverse transformation is also observed with light in the wavelength range 405–442 nm. Further investigation of these photochemical reactions will be performed on the single crystals.

## Experimental

*trans*-[Ru(NO<sub>2</sub>)<sub>2</sub>(py)<sub>4</sub>]·2H<sub>2</sub>O powder was prepared as described previously (Schaniel *et al.*, 2007, and references therein). The pale-yellow powder was dissolved in ethanol ( $2.10 \times 10^{-5}$  mol in 10 ml) and a few drops of water were added. Good-quality yellow needle-shaped single crystals of (I) were obtained after slow evaporation over a period of a few days.

### Crystal data

[Ru(NO<sub>2</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>4</sub>]·2H<sub>2</sub>O  
*M<sub>r</sub>* = 545.52  
 Tetragonal, *I*4<sub>1</sub>/acd  
*a* = 16.3418 (2) Å  
*c* = 16.6448 (2) Å  
*V* = 4445.07 (9) Å<sup>3</sup>

*Z* = 8  
 Mo *K*α radiation  
 $\mu$  = 0.76 mm<sup>-1</sup>  
*T* = 120 K  
 0.21 × 0.11 × 0.09 mm

### Data collection

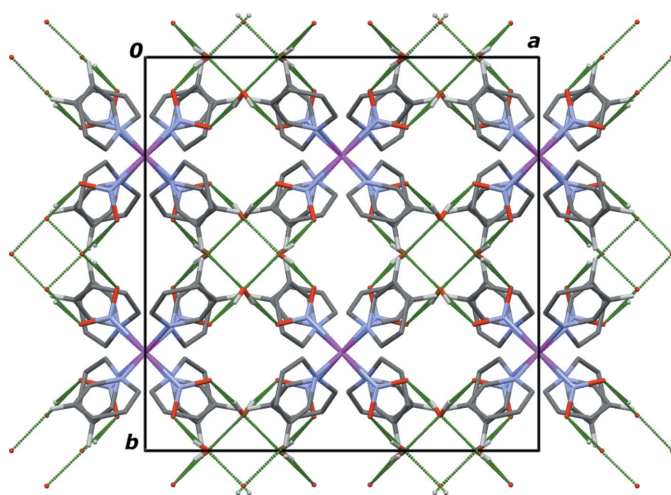
Oxford Xcalibur diffractometer  
 with Sapphire 3 CCD area  
 detector  
 Absorption correction: analytical  
 (PLATON; Spek, 2009)  
*T<sub>min</sub>* = 0.886, *T<sub>max</sub>* = 0.941

17299 measured reflections  
 1221 independent reflections  
 907 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.030

### Refinement

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.018  
*wR*(*F*<sup>2</sup>) = 0.049  
*S* = 1.01  
 1221 reflections  
 80 parameters  
 1 restraint

H atoms treated by a mixture of  
 independent and constrained  
 refinement  
 $\Delta\rho_{\max}$  = 0.26 e Å<sup>-3</sup>  
 $\Delta\rho_{\min}$  = -0.39 e Å<sup>-3</sup>


**Figure 2**

A projection of the *trans*-[Ru(NO<sub>2</sub>)<sub>2</sub>(py)<sub>4</sub>] and water molecules in the *ab* plane, showing the three-dimensional supramolecular network. Hydrogen bonds are shown as dotted lines.

**Table 1**

Selected experimental and calculated bond distances and angles (Å, °) for the [Ru(NO<sub>2</sub>)<sub>2</sub>(py)<sub>4</sub>] molecule.

| Bond length/angle          | Experimental (this work) | Calculated <sup>a</sup> | Experimental (powder data) <sup>a</sup>   |
|----------------------------|--------------------------|-------------------------|---|
| Ru1–N1(pyridine)           | 2.0989 (12)              | 2.12 and 2.13           | 2.07 (2), 2.13 (2), 2.00 (2) and 2.08 (2) |
| Ru1–N2( <i>N</i> -nitrite) | 2.0496 (17)              | 2.10                    | 2.23 (2) and 2.22 (2)                     |
| N2–O1                      | 1.2582 (13)              | 1.27                    | 1.12 (4), 1.18 (4), 1.14 (4) and 1.15 (3) |
| O1–N2–O1 <sup>i</sup>      | 116.56 (17)              | 117.8                   | 122 (3) and 135 (3)                       |
| N2–Ru1–N2 <sup>ii</sup>    | 180                      | 179.9                   | 175.2 (10)                                |
| N1–Ru1–N1 <sup>i</sup>     | 175.37 (6)               | 179.4                   | 177.0 (9) and 177.8 (9)                   |
| Ru1–N2–O1                  | 121.72 (9)               | 120.8 and 121.3         | 111 (2), 110 (2), 113 (2) and 118 (2)     |

Reference: (a) Schaniel *et al.* (2010). Symmetry codes: (i)  $-y + \frac{1}{2}, -x + \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $-x, -y + \frac{1}{2}, z$ .

**Table 2**

Intermolecular distances and angles (Å, °) shorter than the sum of the van der Waals radii in the *trans*-[Ru(NO<sub>2</sub>)<sub>2</sub>(py)<sub>4</sub>].2H<sub>2</sub>O crystal structure.

The van der Waals radii sums are: O...O = 3.04 Å and O...H = 2.72 Å (Bondi, 1964).

|  | Intermolecular distance | Angle      |
|--|-------------------------|------------|
| Between an <i>N</i> -nitrite group and water |                         |            |
| N2–O1...O2                                   | 2.8427 (13)             | 114.72 (7) |
| O2–H2A...O1                                  | 1.969 (18)              | 168.9 (16) |
| Between pyridine and water                   |                         |            |
| C2–H2...O2 <sup>iii</sup>                    | 2.44                    | 144        |

Symmetry code: (iii)  $x - \frac{1}{2}, -y, z$ .

All H atoms were located in a difference Fourier synthesis, but those attached to C atoms were treated as riding on their parent C atoms, with C–H = 0.93 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The H atoms of the water molecule were refined semi-freely by introducing a distance restraint of 0.84 (2) Å while constraining  $U_{\text{iso}}(\text{H})$  values to  $1.5U_{\text{eq}}(\text{O})$ .

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2004); data reduc-

tion: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MX3053). Services for accessing these data are described at the back of the journal.

## References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Coppens, P., Novozhilova, I. & Kovalevsky, A. (2002). *Chem. Rev.* **102**, 861–883.
- Cormary, B., Malfant, I., Valade, L., Buron-Le Cointe, M., Toupet, L., Todorova, T., Delley, B., Schaniel, D., Mockus, N., Woike, T., Fejfarová, K., Petříček, V. & Dušek, M. (2009). *Acta Cryst.* **B65**, 612–623.
- Delley, B. (2006). *Mol. Simul.* **32**, 117–123.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Grenthe, I. & Nordin, E. (1979). *Inorg. Chem.* **18**, 1869–1874.
- Hauser, U., Oestreich, V. & Rohrwerk, H. D. (1977). *Z. Phys. A.* **280**, 17–25.
- Kovalevsky, A. Y., King, G., Bagley, K. A. & Coppens, P. (2005). *Chem. Eur. J.* **11**, 7254–7264.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Oxford Diffraction (2004). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171.26. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
- Sarkar, S., Sarkar, B., Chanda, N., Kar, S., Mobin, S. M., Fiedler, J., Kaim, W. & Kumar Lahiri, G. (2005). *Inorg. Chem.* **44**, 6092–6099.
- Schaniel, D., Cormary, B., Malfant, I., Valade, L., Woike, T., Delley, B., Krämer, K. W. & Güdel, H. U. (2007). *Phys. Chem. Chem. Phys.* **9**, 3717–3724.
- Schaniel, D., Mockus, N., Woike, T., Klein, A., Sheptyakov, D., Todorova, T. & Delley, B. (2010). *Phys. Chem. Chem. Phys.* **12**, 6171–6178.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.