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fac-/mer-[RuCl₃(NO)(P–N)] (P–N = [*o*-(*N*,*N*-dimethylamino)phenyl]diphenylphos-phine): Synthesis, characterization and DFT calculations

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ABSTRACT

Complex *fac*-[RuCl₃(NO)(P–N)] (1) was synthesized from the reaction of [RuCl₃(H₂O)₂(NO)] and the P–N ligand, *o*-[(*N*,*N*-dimethylamino)phenyl]diphenylphosphine) in refluxing methanol solution, while complex *mer*,*trans*-[RuCl₃(NO)(P–N)] (2) was obtained by photochemical isomerization of (1) in dichloromethane solution. The third possible isomer *mer*,*cis*-[RuCl₃(NO)(P–N)] (3) was never observed in direct synthesis as well as in photo- or thermal-isomerization reactions. When refluxing a methanol solution of complex (2) a thermally induced isomerization occurs and complex (1) is regenerated.

The complexes were characterized by NMR (${}^{31}P{}^{1}H$), ${}^{15}N{}^{1}H$ and ${}^{1}H$), cyclic voltammetry, FTIR, UV–Vis, elemental analysis and X-ray diffraction structure determination. The ${}^{31}P{}^{1}H$ NMR revealed the presence of singlet at 35.6 for (1) and 28.3 ppm for (2). The ${}^{1}H$ NMR spectrum for (1) presented two singlets for the methyl hydrogens at 3.81 and 3.13 ppm, while for (2) was observed only one singlet at 3.29 ppm. FTIR Ru–NO stretching in KBr pellets or CH₂Cl₂ solution presented 1866 and 1872 cm⁻¹ for (1) and 1841 and 1860 cm⁻¹ for (2). Electrochemical analysis revealed a irreversible reduction attributed to Ru^{II}–NO⁴ \rightarrow Ru^{II}–NO⁰ at -0.81 V and -0.62 V, for (1) and (2), respectively; the process Ru^{II} \rightarrow Ru^{III}, as expected, is only observed around 2.0 V, for both complexes.

Studies were conducted using ¹⁵NO and both complexes were isolated with ¹⁵N-enriched NO. Upon irradiation, the complex *fac*-[RuCl₃(NO)(P–N)] (1) does not exchange ¹⁴NO by ¹⁵NO, while complex *mer,trans*-[RuCl₃(NO)(P–N)] (2) does. Complex *mer,trans*-[RuCl₃(¹⁵NO)(P–N)] (2') was obtained by direct reaction of *mer,trans*-[RuCl₃(NO)(P–N)] (2) with ¹⁵NO and the complex *fac*-[RuCl₃(¹⁵NO)(P–N)] (1') was obtained by thermal-isomerization of *mer,trans*-[RuCl₃(¹⁵NO)(P–N)] (2').

DFT calculation on isomer energies, electronic spectra and electronic configuration were done. For complex (1) the HOMO orbital is essentially Ru (46.6%) and Cl (42.5%), for (2) Ru (57.4%) and Cl (39.0%) while LUMO orbital for (1) is based on NO (52.9%) and is less extent on Ru (38.4%), for (2) NO (58.2%) and Ru (31.5%).

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1. Introduction

Two events have made nitric oxide (NO) one of the most studied small molecules. In 1992, NO was considered the molecule of the year by Science and the 1998s Nobel Prize in physiology or medicine awarded to Robert Furchgott, Ferid Murad and Louis Ignarro for the discovery of NO as a signaling molecule in biological systems. After theses events, an impressive number of works have been published dealing with properties and applications of NO containing transition metal complexes [1–17]. Therefore ruthenium is of crucial importance in the NO chemistry and probably

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is one of the most studied transition metal with NO in coordination compounds [1–28]. The chemistry of this successful association has been explored by chemists focusing on different aspects. The most explored aspect is the use of such complexes as NO controlled releasing or scavenger compounds [1,2]. Many other insights have been explored, ranging from electronic and molecular structure [3–6,29–33] to catalysis [7–9]. Recently, application of ruthenium-nitrosyl complexes as anticancer agent has emerged [10–13].

In general, ruthenium/nitrosyl complexes are associated with co-ligands such as pyridines [3], salen [2,14], amines [15–18], porphyrins [15,34–39] and diphosphines [12,19–26]. The chemistry of ruthenium/nitrosyl complexes with chelated P–N ligands is rare, and only two works can be found in the literature so far [27,28].

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In this work, we present the synthesis, characterization of fac/mer-[RuCl₃(NO)(P–N)] (P–N = o-[(N,N-dimethylamino)phenyl]diphenylphosphine)). These complexes were characterized by FTIR, NMR (³¹P{¹H}, ¹⁵N{¹H}, ¹H), cyclic voltammetry, UV–Vis, X-ray diffraction studies and elemental analysis. X-ray structure for (**1**) has been published previously [28], although will be presented to enlighten the discussion. ¹⁵N-enriched nitrosyl complexes were also isolated. Density functional theory was also applied in an attempt to understand the electronic structure of these compounds.

2. Experimental methods

2.1. Measurements

The IR spectra were recorded on a FTIR Bomem-Michelson 102 spectrometer in the 4000–400 cm⁻¹ region using solid samples pressed in KBr pellets or dichloromethane solution in a CaF₂ crystal with path length of 1 mm. NMR spectra ($^{31}P{^1H}$, $^{15}N{^1H}$ and ^{1}H)

Table 1Crystal data and structures refinement.

Empirical formula $C_{20}H_{20}N_2OPCl_3Ru$ $C_{20}H_{20}N_2OPCl_3Ru$ Formula weight 542.77 542.77 Temperature (K) 150(2) 293(2) Wavelength (Å) 0.71073 0.71073 Crystal system orthorhombic orthorhombic Space group $P2_12_12_1$ $P2_12_12_1$ unit cell dimensions a (Å) 9.3629(1) 8.7986 (1) b (Å) 14.6378(2) 15.2385(3) (C) c (Å) 15.3757(3) 16.2248(2) Volume (Å^3) 2107.27(6) 2175.38(6) Z 4 4 Date (mg/m ³) 1.711 1.657 Absorption coefficient 1.214 1.176 (mm ⁻¹) 7000 1088 1088 Crystal size (mm ³) 0.315 × 0.309 × 0.296 0.47 × 0.23 × 0.15 Theta range for data 3.43-27.5 3.42-27.48 collection (°) 11 -11 < h < 11 Independent reflections 99.7% 99.442 Reflections collected 15 860 <th></th> <th>fac-[RuCl₃(NO)(P–N)] [28]</th> <th>mer,trans- [RuCl₃(NO)(P–N)]</th>		fac-[RuCl ₃ (NO)(P–N)] [28]	mer,trans- [RuCl ₃ (NO)(P–N)]
Formula weight Temperature (K)542.77542.77Temperature (K)150(2)293(2)Wavelength (Å)0.710730.71073Crystal systemorthorhombicorthorhombicSpace group $P_{21}_{21}_{21}$ $P_{21}_{21}_{21}$ Unit cell dimensionsa8.7986 (1)a (Å)9.3629(1)8.7986 (2)b (Å)14.6378(2)15.2385(3)c (Å)15.3757(3)16.2248(2)Volume (Å ³)2107.27(6)2175.38(6)Z44D_{calc} (mg/m ³)1.7111.657Absorption coefficient1.2141.176(mm ⁻¹) $F(0 0 0)$ 10881088Crystal size (mm ³)0.315 × 0.309 × 0.2960.47 × 0.23 × 0.15Theta range for data collection (°) $3.43-27.5$ $3.42-27.48$ Index ranges $-12 \leqslant h \leqslant 11$ $-11 \leqslant h \leqslant 11$ $-19 \leqslant k \approx 18$ $-19 \leqslant k \leqslant 19$ $-19 \leqslant l < 19$ $-21 \leqslant l \leqslant 18$ Reflections collected15 86016 965Independent reflections6aussianGaussianMaximum and minimum transmission0.754 and 0.6550.830 and 0.622Maximum and minimum transmissionSetux-97Shetx-97Refinement methodFull-matrix least- squares on F^2 Squares on F^2 Computing ⁴ Coutert, HKL Denzo and Scalepack 	Empirical formula	C20H20N2OPCl3Ru	C20H20N2OPCl3Ru
Temperature (K) 150(2) 293(2) Wavelength (Å) 0.71073 0.71073 Crystal system orthorhombic orthorhombic Space group P_{2} (2,12,1 P_{2} (2,12,1 Unit cell dimensions a (Å) 9.3629(1) 8.7986 (1) a (Å) 9.3629(1) 8.7986 (1) b (Å) 14.6378(2) 15.2385(3) c (Å) 15.3757(3) 16.2248(2) Volume (Å ³) 2107.27(6) 2175.38(6) Z 4 4 D _{calc} (mg/m ³) 1.711 1.657 Absorption coefficient 1.214 1.176 (mm ⁻¹) 7000 1088 1088 Crystal size (mm ³) 0.315 × 0.309 × 0.296 0.47 × 0.23 × 0.15 Theta range for data 3.43-27.5 3.42-27.48 collection (°) 11 -11 ≤ h ≤ 11 Index ranges -12 ≤ h ≤ 11 -11 ≤ h ≤ 19 -19 ≤ k ≤ 18 -19 ≤ k ≤ 19 -21 ≤ 1 ≤ 18 Reflections collected 15 860 16 965 Independent reflections Gaussian 0.830 and 0.622	Formula weight	542.77	542.77
Wavelength (Å)0.710730.71073Crystal systemorthorhombicorthorhombicSpace group $P_2_{12}_{12}_{1}$ $P_{2}_{21}_{21}_{1}$ Unit cell dimensionsa(Å)9.3629(1)8.7986 (1)a (Å)9.3629(1)8.7986 (1)b (Å)14.6378(2)15.2385(3)c (Å)15.3757(3)16.2248(2)Volume (Å3)2107.27(6)2175.38(6)Z44Date (mg/m ³)1.7111.657Absorption coefficient1.2141.176(mm ⁻¹)11.657F(0 0 0)10881088Crystal size (mm ³)0.315 × 0.309 × 0.2960.47 × 0.23 × 0.15Theta range for data3.43-27.53.42-27.48collection (°)1-11 Index ranges $-12 < h < 11$ $-11 < h < 11$ $-19 < k < 18$ $-19 < k < 19$ $-19 < l < l < 18$ 15 86016 965Independent reflections4828 [R(int) = 0.0258]4942 [R(int) = 0.0230]Completeness to theta = 27.5°4828 [R(int) = 0.0258]4942 [R(int) = 0.0230]Absorption correctionGaussianGaussianMaximum and minimum transmission0.754 and 0.6550.830 and 0.622Refinement methodFull-matrix least- squares on F^2 Suttus-97Data/restraints/ parameters4828/0/2564942/0/256Goodness-of-fit on F^2 1.1041.147Final R indices [I > $2\sigma(I)$] $R_1 = 0.0231$, $R_1 = 0.0316$, $WR_2 = 0.0565$ $WR_2 = 0.0818$	Temperature (K)	150(2)	293(2)
Crystal system orthorhombic orthorhombic Space group $P_{2_12_12_1}$ $P_{2_12_12_1}$ Unit cell dimensions a (Å) 9.3629(1) 8.7986 (1) a (Å) 14.6378(2) 15.2385(3) c c (Å) 15.3757(3) 16.2248(2) Volume (Å ³) 2107.27(6) 2175.38(6) Z 4 4 4 D_{cate} (mg/m ³) 1.711 1.657 Absorption coefficient 1.214 1.176 (mm ⁻¹) F(0 0 0) 1088 1088 Crystal size (mm ³) 0.315 × 0.309 × 0.296 0.47 × 0.23 × 0.15 3.42–27.48 collection (°) Index ranges $-12 \leqslant h \leqslant 11$ $-11 \leqslant h \leqslant 11$ $-19 \leqslant k \leqslant 19$ $-19 \leqslant k \leqslant 19$ $-19 \leqslant k \leqslant 18$ $-19 \leqslant k \leqslant 19$ $-19 \leqslant l \leqslant 19$ $-21 \leqslant l \leqslant 18$ r19 $-19 \leqslant k \leqslant 19$ $-19 \leqslant k \leqslant 19$ $-19 \leqslant l \leqslant 19$ $-21 \leqslant l \leqslant 18$ r19 $-9 < k \leqslant 19$ $-19 \leqslant k \leqslant 19$ $-19 \leqslant l \leqslant 19$ $-21 \leqslant l \leqslant 8$ R[(int) = 0.0258] 4942 [R(int) = 0.0230] Godiessian Gaussian Gaussian	Wavelength (Å)	0.71073	0.71073
Space group Unit cell dimensions $P2_{12}_{12}_{1}$ $P2_{12}_{12}_{1}$ a (Å)9.3629(1)8.7986 (1) b (Å)14.6378(2)15.2385(3) c (Å)15.3757(3)16.2248(2)Volume (Å ³)2107.27(6)2175.38(6) Z 44 D_{calc} (mg/m ³)1.7111.657Absorption coefficient (mm ⁻¹)1.2141.176 $F(0 0 0)$ 10881088Crystal size (mm ³)0.315 × 0.309 × 0.2960.47 × 0.23 × 0.15Theta range for data collection (°)3.43-27.53.42-27.48Index ranges $-12 \leq h \leq 11$ $-19 \leq k \leq 18$ $-19 \leq k \leq 18$ $-19 \leq k \leq 19$ $-19 \leq l < 19$ $-21 < l < 18$ Reflections collected Independent reflections4828 [R(int) = 0.0258] 99.7%4942 [R(int) = 0.0230] 99.4%Refinement method transmissionFull-matrix least- squares on F^2 couputing ^a Gaussian Couleer, HKL Denzo and ScalepackRefinement method final R indices $[I > 2\sigma(I)]$ R ₁ = 0.0231, $R_1 = 0.0238,$ $R_1 = 0.0321,$ $R_2 = 0.0565$ M2 = 0.0818 $R_1 = 0.0321,$ $R_2 = 0.0569$ R indices (all data) $R_1 = 0.0231,$ $R_2 = 0.0569$ $R_2 = 0.0821$ Absolute structure parameter0.0071(6)0.0143(10)Largest difference peak and hole0.0071(6)0.0143(10)	Crystal system	orthorhombic	orthorhombic
Unit cell dimensions $a(A)$ 9.3629(1) 8.7986 (1) $b(A)$ 14.6378(2) 15.2385(3) $c(A)$ 15.3757(3) 16.2248(2) Volume (Å ³) 2107.27(6) 2175.38(6) Z 4 4 $D_{calc} (mg/m^3)$ 1.711 1.657 Absorption coefficient (mm ⁻¹) 1.214 1.176 $F(0 0 0)$ 1088 1088 Crystal size (mm ³) 0.315 × 0.309 × 0.296 0.47 × 0.23 × 0.15 Theta range for data collection (°) 104x ranges $-12 \le h \le 11$ $-11 \le h \le 11$ $-19 \le k \le 18$ $-19 \le k \le 19$ $-19 \le l \le 19$ $-19 \le l \le 18$ Reflections collected 15 860 16 965 Independent reflections 4828 [R(int) = 0.0258] 4942 [R(int) = 0.0230] Ompleteness to 99.7% 99.4% theta = 27.5° Absorption correction Gaussian Gaussian Maximum and minimum 0.754 and 0.655 0.830 and 0.622 transmission Full-matrix least-squares on F^2 squares on F^2 Computing ^a Coutecr, HKL Denzo and Scalepack sheix-97, ShetxL-97	Space group	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$
a (Å) 9.3629(1) 8.7986 (1) b (Å) 14.6378(2) 15.2385(3) c (Å) 15.3757(3) 16.2248(2) Volume (Å ³) 2107.27(6) 2175.38(6) Z 4 4 D_{calc} (mg/m ³) 1.711 1.657 Absorption coefficient (mm ⁻¹) 1.214 1.176 $f(0 0 0)$ 1088 1088 Crystal size (mm ³) 0.315 × 0.309 × 0.296 0.47 × 0.23 × 0.15 Theta range for data collection (°) 1.12 + h < 11	Unit cell dimensions		
$\begin{array}{ccccc} b \ (Å) & 14.6378(2) & 15.2385(3) \\ c \ (Å) & 15.3757(3) & 16.2248(2) \\ Volume \ (Å^3) & 2107.27(6) & 2175.38(6) \\ Z & 4 & 4 \\ D_{calc} \ (mg/m^3) & 1.711 & 1.657 \\ Absorption coefficient & 1.214 & 1.176 \\ (mm^{-1}) & & & & & \\ F(0 \ 0 \ 0) & 1088 & 1088 \\ Crystal size \ (mm^3) & 0.315 \times 0.309 \times 0.296 \\ O \ 0) & 0.88 & 1088 \\ Crystal size \ (mm^3) & 0.315 \times 0.309 \times 0.296 \\ Index \ range for \ data & 3.43-27.5 & 3.42-27.48 \\ collection \ (^\circ) & & & \\ Index \ ranges & -12 \leqslant h \leqslant 11 & -11 \leqslant h \leqslant 11 \\ -19 \leqslant k \leqslant 18 & -19 \leqslant k \leqslant 19 \\ -19 \leqslant l \leqslant 18 & -19 \leqslant k \leqslant 19 \\ -19 \leqslant l \leqslant 19 & -21 \leqslant l \leqslant 18 \\ Reflections \ collected & 15 \ 860 & 16 \ 965 \\ Independent \ reflections \\ Completeness \ to & 99.7\% & 99.4\% \\ theta = 27.5^\circ & & & & \\ Absorption \ correction & Gaussian & Gaussian \\ Maximum \ and \ minimum \\ transmission \\ Refinement \ method & Full-matrix \ least- \\ squares \ on \ F^2 & squares \ on \ F^2 \\ Computing^a & Collect, \ HKL \ Denzo \ and \ Scalepack \\ Sheexs-97, \ Sheexl-97 & Sheexl-97 \\ parameters & & & \\ Goodness-of-fit \ on \ F^2 & 1.104 & 1.147 \\ Final \ R \ indices \ (all \ data) & R_1 = 0.0231, \\ R \ indices \ (all \ data) & R_1 = 0.0231, \\ R \ indices \ (all \ data) & R_1 = 0.0238, \\ R \ indices \ (all \ data) & R_1 = 0.0238, \\ R \ indices \ (all \ data) & R_1 = 0.0238, \\ R \ indices \ (all \ data) & R_1 = 0.0238, \\ R \ indices \ (all \ data) & R_1 = 0.0238, \\ R \ indices \ (all \ data) & R_1 = 0.0238, \\ R \ indices \ (all \ data) & R_1 = 0.0238, \\ R \ indices \ (all \ data) & R_1 = 0.0238, \\ R \ indices \ (all \ data) & R_1 = 0.0238, \\ R \ indices \ (all \ data) & R_1 = 0.0238, \\ R \ indices \ (all \ data) & R_1 = 0.0238, \\ R \ indices \ (all \ data) & R_1 = 0.0238, \\ R \ indices \ (all \ data) & R_1 = 0.0238, \\ R \ indices \ (all \ data) & R_1 = 0.0238, \\ R \ indices \ (all \ data) & R_1 = 0.0238, \\ R \ indices \ (all \ data) & R_1 = 0.0238, \\ R \ indices \ (all \ data) & R_1 = 0.0238, \\ R \ indices \ (all \ data) & R_1 = 0.0238, \\ R \ indices \ (all \ data) & R_1 = 0.0238, \\ R \ indices \ (all \$	a (Å)	9.3629(1)	8.7986 (1)
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Volume (\hat{A}^3) 2107.27(6) 2175.38(6) Z 4 4 D_{calc} (mg/m ³) 1.711 1.657 Absorption coefficient (mm ⁻¹) 1.214 1.176 $F(0 0 0)$ 1088 1088 Crystal size (mm ³) 0.315 × 0.309 × 0.296 0.47 × 0.23 × 0.15 Theta range for data collection (°) 3.43–27.5 3.42–27.48 Index ranges $-12 \le h \le 11$ $-11 \le h \le 11$ $-19 \le k \le 18$ $-19 \le k \le 19$ $-19 \le k \le 19$ $-19 \le l \le 19$ $-21 \le l \le 18$ 19 Reflections collected 15 860 16 965 Independent reflections 99.7% 99.4% theta = 27.5° Absorption correction Gaussian Gaussian Maximum and minimum transmission Full-matrix least-squares on F^2 squares on F^2 Refinement method Full-matrix least-squares on F^2 squares on F^2 Computing ^a Coulect, HKL Denzo and Scalepack and Scalepack Shelexs-97, Shelext-97 Shelexs-97, Shelext-97 Shelexs-97, Shelext-97 Data/restraints/ $4828/0/256$ 4942/0/256 parameters </td <td><i>c</i> (Å)</td> <td>15.3757(3)</td> <td>16.2248(2)</td>	<i>c</i> (Å)	15.3757(3)	16.2248(2)
Z 4 4 $D_{calc} (mg/m^3)$ 1.711 1.657 Absorption coefficient (mm ⁻¹) 1.214 1.176 $F(0\ 0\ 0)$ 1088 1088 Crystal size (mm ³) 0.315 × 0.309 × 0.296 0.47 × 0.23 × 0.15 Theta range for data collection (°) 1.12 < $h < 11$ $-11 < h < 11$ Index ranges $-12 < h < 11$ $-11 < h < 11$ $-19 < k < 18$ $-19 < k < 19$ $-21 < l < 18$ Reflections collected 15 860 16 965 Independent reflections 4828 [R(int) = 0.0258] 4942 [R(int) = 0.0230] Completeness to theta = 27.5° Gaussian Gaussian Gaussian Maximum and minimum transmission Full-matrix least- squares on F^2 Full-matrix least- squares on F^2 Computing ^a Coulect, HKL Denzo and Scalepack Scalepack SHEIXS-97, SHEIXL-97 SHEIXS-97, SHEIXL-97 Data/restraints/ parameters $R_1 = 0.0231$, $R_1 = 0.0231$, $R_1 = 0.0316$, $R_2 = 0.0565$ $R_2 = 0.0818$ R indices (all data) $R_1 = 0.0238$, $R_1 = 0.0238$, $R_1 = 0.03210$, $R_2 = 0.0569$ $R_2 = 0.0821$ Absolute structure parameter $0.04(2)$ $-0.03(3)$ Absolute structu	Volume (Å ³)	2107.27(6)	2175.38(6)
$\begin{array}{ccccccc} D_{\rm calc} (\rm mg/m^3) & 1.711 & 1.657 \\ Absorption coefficient (\rm mm^{-1}) & 1.214 & 1.176 \\ (\rm mm^{-1}) & 1.214 & 1.176 \\ (\rm mm^{-1}) & 1.214 & 1.176 \\ (\rm mm^{-1}) & 0.315 \times 0.309 \times 0.296 & 0.47 \times 0.23 \times 0.15 \\ Theta range for data & 3.43-27.5 & 3.42-27.48 \\ collection (°) & & & & & & \\ Index ranges & -12 \leqslant h \leqslant 11 & -11 \leqslant h \leqslant 11 \\ -19 \leqslant k \leqslant 18 & -19 \leqslant k \leqslant 19 \\ -19 \leqslant l \leqslant 19 & -21 \leqslant l \leqslant 18 \\ Reflections collected & 15 860 & 16 965 \\ Independent reflections & 4828 [R(int) = 0.0258] & 4942 [R(int) = 0.0230] \\ Completeness to & 99.7\% & 99.4\% \\ theta = 27.5^{\circ} & 4828 [R(int) = 0.0255] & 4942 [R(int) = 0.0230] \\ Completeness to & 99.7\% & 99.4\% \\ theta = 27.5^{\circ} & Gaussian & Gaussian \\ Maximum and minimum & 0.754 and 0.655 & 0.830 and 0.622 \\ transmission & & & & \\ Refinement method & Full-matrix least- & squares on F^2 \\ Computing^a & Collectr, HKL Denzo and \\ Scalepack & and Scalepack \\ SHELXS-97, SHELXL-97 & SHELXS-97, SHELXL-97 \\ Data/restraints/ & 4828/0/256 & 4942/0/256 \\ parameters & & & & \\ Goodness-of-fit on F^2 & 1.104 & 1.147 \\ Final R indices [I > 2\sigma(I)] & R_1 = 0.0231, & R_1 = 0.0316, \\ wR_2 = 0.0565 & wR_2 = 0.0818 \\ R indices (all data) & R_1 = 0.0238, & R_1 = 0.0321, \\ wR_2 = 0.0569 & wR_2 = 0.0821 \\ o.04(2) & -0.03(3) \\ parameter \\ Extinction coefficient & 0.0071(6) & 0.0143(10) \\ Largest difference peak \\ and hole & -0.659 e A^{-3} & -0.445 e A^{-3} \\ \end{array} \right$	Ζ	4	4
Absorption coefficient (mm ⁻¹) 1.214 1.176 $F(0 0 0)$ 1088 1088 Crystal size (mm ³) 0.315 × 0.309 × 0.296 0.47 × 0.23 × 0.15 Theta range for data collection (°) 3.43–27.5 3.42–27.48 Index ranges $-12 \le h \le 11$ $-11 \le h \le 11$ $-19 \le k \le 18$ $-19 \le k \le 19$ $-21 \le l \le 18$ $-19 \le l \le 19$ $-21 \le l \le 18$ $-19 \le k \le 19$ $-19 \le l \le 19$ $-21 \le l \ge 18$ $-19 \le k \le 19$ $-19 \le l \le 19$ $-21 \le l \ge 18$ $-19 \le k \le 19$ $-19 \le l \ge 19$ $-21 \le l \ge 18$ $-19 \le k \le 19$ $-19 \le l \ge 19$ $-21 \le l \ge 18$ $-9 \le k \le 19$ $-19 \le l \ge 19$ $-21 \le l \ge 18$ $-9 \le l \le 13$ Reflections collected 15 860 16 965 Independent reflections Gaussian Gaussian Maximum and minimum transmission 0.754 and 0.655 0.830 and 0.622 Refinement method Full-matrix least- squares on F^2 squares on F^2 Computing ^a Collect, HKL Denzo and Scalepack Sheixs-97, Sheixl-97 parameters Goodness-of-fit on F^2 1.104 1.147 <td>$D_{\text{calc}} (\text{mg/m}^3)$</td> <td>1.711</td> <td>1.657</td>	$D_{\text{calc}} (\text{mg/m}^3)$	1.711	1.657
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Absorption coefficient	1.214	1.176
$F(0 \ 0 \ 0)$ 1088 1088 Crystal size (mm ³) 0.315 × 0.309 × 0.296 0.47 × 0.23 × 0.15 Theta range for data collection (°) 3.43–27.5 3.42–27.48 Index ranges $-12 \le h \le 11$ $-11 \le h \le 11$ $-19 \le k \le 18$ $-19 \le k \le 19$ $-19 \le k \le 19$ $-19 \le l \le 19$ $-21 \le l \le 18$ $19 \le k \le 19$ $-19 \le l \le 19$ $-21 \le l \le 18$ $19 \le l \le 19$ $-19 \le l \le 19$ $-21 \le l \le 18$ 10230 Completeness to togo y-7% 99.4% 99.4% Absorption correction Gaussian Gaussian Maximum and minimum transmission 0.754 and 0.655 0.830 and 0.622 Refinement method Full-matrix least-squares on F^2 $Coulact, HKL Denzo and Scalepack and Scalepack SHELXS-97, SHELXL-97 Shelxs-97, SHELXL-97 SHELXS-97, SHELXL-97 SHELXS-97, SHELXL-97 Data/restraints/ 4828/0/256 4942/0/256 parameters Goodness-of-fit on F^2 1.104 1.147 Final R findices [I > 2\sigma(I)] R_1 = 0.0231, R_1 = 0.0316, WR_2 = 0.0565 WR_2 = 0.0818 R indices (all data) R_1 = 0.0238, R_1 = 0.0321, WR_2 = 0.0565 $	(mm^{-1})		
Crystal size (mm ³) $0.315 \times 0.309 \times 0.296$ $0.47 \times 0.23 \times 0.15$ Theta range for data collection (°) $3.43-27.5$ $3.42-27.48$ Index ranges $-12 \le h \le 11$ $-11 \le h \le 11$ $-19 \le k \le 18$ $-19 \le k \le 19$ $-21 \le l \le 18$ $-19 \le l \le 19$ $-21 \le l \le 18$ $-19 \le k \le 19$ $-19 \le l \le 19$ $-21 \le l \le 18$ $-19 \le k \le 19$ $-19 \le l \le 19$ $-21 \le l \le 18$ $4942 \ [R(int) = 0.0230]$ Completeness to 99.7% 99.4% theta = 27.5° Absorption correction Gaussian Gaussian Maximum and minimum transmission $0.754 \text{ and } 0.655$ $0.830 \text{ and } 0.622$ Refinement method Full-matrix least-squares on F^2 $Coulecr, HKL Denzo \text{ and } Scalepack$ Sheizx-97, SHEIXL-97 SHEIXS-97, SHEIXL-97 SHEIXS-97, SHEIXL-97 Data/restraints/ $4828/0/256$ $4942/0/256$ parameters $0.0231,$ $R_1 = 0.0316,$ $WR_2 = 0.0565$ $WR_2 = 0.0818$ $R_1 = 0.0316,$ R indices (all data) $R_1 = 0.0238,$ $R_1 = 0.0321,$ $WR_2 = 0.0569$ $WR_2 = 0.0821$ $0.04(2)$ $-0.03(3)$ </td <td>F(0 0 0)</td> <td>1088</td> <td>1088</td>	F(0 0 0)	1088	1088
Theta range for data collection (°) $3.43-27.5$ $3.42-27.48$ Index ranges $-12 \le h \le 11$ $-19 \le k \le 18$ $-19 \le k \le 19$ $-19 \le l \le 19$ $-21 \le l \le 18$ $-11 \le h \le 11$ $-19 \le k \le 19$ $-21 \le l \le 18$ Reflections collected15 86016 965Independent reflections $4828 [R(int) = 0.0258]$ $99.7%$ 99.4% Completeness to theta = 27.5° 99.7% 99.4% Absorption correctionGaussian 0.754 and 0.655Gaussian 0.830 and 0.622Refinement method transmissionFull-matrix least- squares on F^2 $Coupert, HKL Denzo andScalepackSHELXS-97, SHELX-97Full-matrix least-squares on F^2Data/restraints/parameters4828/0/2564942/0/256Parameters0.0231,WR_2 = 0.0565R_1 = 0.0316,WR_2 = 0.0818R indices (all data)parameterR_1 = 0.0238,R_1 = 0.0321,WR_2 = 0.0569R_2 = 0.0821Absolute structureparameter0.04(2)-0.03(3)ParameterExtinction coefficient0.0071(6)0.0143(10)Largest difference peakand hole0.589 and-0.6592.044 and-0.445$	Crystal size (mm ³)	$0.315\times0.309\times0.296$	$0.47 \times 0.23 \times 0.15$
Index ranges $-12 \leqslant h \leqslant 11$ $-19 \leqslant k \leqslant 18$ $-19 \leqslant l \leqslant 19$ $-19 \leqslant l \leqslant 19$ $-21 \leqslant l \leqslant 19$ $-21 \leqslant l \leqslant 18$ Reflections collected15 86016 965Independent reflections4828 [R(int) = 0.0258]4942 [R(int) = 0.0230]Completeness to theta = 27.5°99.7%99.4%Absorption correctionGaussianGaussianMaximum and minimum transmission0.754 and 0.6550.830 and 0.622Refinement methodFull-matrix least- squares on F^2 Squares on F^2 Computing ^a Collect, HKL Denzo and Scalepack HELXS-97, SHELXL-97Collect, HKL Denzo and Scalepack SHELXS-97, SHELXL-97Data/restraints/ parameters1.1041.147Final R indices [$l > 2\sigma(l)$] $R_1 = 0.0231$, $R_1 = 0.0238$, $R_1 = 0.0321$, $WR_2 = 0.0565$ $WR_2 = 0.0818$ R indices (all data) $R_1 = 0.0238$, $R_1 = 0.0321$, $WR_2 = 0.0569$ $WR_2 = 0.0821$ Absolute structure parameter0.04(2) $-0.03(3)$ parameter extinction coefficient0.0071(6)0.0143(10)Largest difference peak and hole0.589 and $-0.659 e^{-3}$ $-0.445 e^{-3}$	Theta range for data collection (°)	3.43–27.5	3.42-27.48
$\begin{array}{cccc} -19 \leqslant k \leqslant 18 & -19 \leqslant k \leqslant 19 \\ -19 \leqslant l \leqslant 19 & -21 \leqslant l \leqslant 18 \\ \text{Independent reflections} \\ \text{Completeness to} \\ \text{theta} = 27.5^{\circ} \\ \text{Absorption correction} \\ \text{Maximum and minimum} \\ \text{transmission} \\ \text{Refinement method} \\ \text{Refinement method} \\ \text{Full-matrix least-} \\ \text{squares on } F^2 \\ \text{Computing}^a \\ \text{CouleCT, HKL Denzo and} \\ \text{Scalepack} \\ \text{SHELXS-97, SHELXL-97} \\ \text{SHELXS-97, SHELXL-97} \\ \text{Data/restraints/} \\ \text{parameters} \\ \text{Goodness-of-fit on } F^2 \\ \text{Goodness-of-fit on } F^2 \\ \text{Rindices (all data)} \\ R indices (all data) \\ \text{Absolute structure} \\ parameter \\ \text{Extinction coefficient} \\ \text{Extinction coefficient} \\ \text{Dotaf(fict method)} \\ \text{Dotaf(fict method)} \\ \text{Coule Structure} \\ Coule Struc$	Index ranges	$-12 \leqslant h \leqslant 11$	$-11 \leq h \leq 11$
$\begin{array}{cccc} -19 \leqslant l \leqslant 19 & -21 \leqslant l \leqslant 18 \\ \mbox{Reflections collected} & 15 860 & 16 965 \\ \mbox{Independent reflections} & 4828 [R(int) = 0.0258] & 4942 [R(int) = 0.0230] \\ \mbox{Ompleteness to} & 99.7\% & 99.4\% \\ \mbox{Intera = 27.5^{\circ}} & & & & & & & & & & & & & & & & & & $		$-19 \leqslant k \leqslant 18$	$-19 \leqslant k \leqslant 19$
Reflections collected15 86016 965Independent reflections4828 [$R(int) = 0.0258$]4942 [$R(int) = 0.0230$]Completeness to99.7%99.4%theta = 27.5°GaussianGaussianMaximum and minimum transmission0.754 and 0.6550.830 and 0.622Refinement methodFull-matrix least- squares on F^2 squares on F^2 ComputingaCollect, HKL Denzo and ScalepackCollect, HKL Denzo and 		$-19 \leqslant l \leqslant 19$	<i>−</i> 21 <i>≤l ≤</i> 18
Independent reflections4828 $[R(int) = 0.0258]$ 4942 $[R(int) = 0.0230]$ Completeness to99.7%99.4%theta = 27.5°99.7%99.4%Absorption correctionGaussianGaussianMaximum and minimum0.754 and 0.6550.830 and 0.622transmissionFull-matrix least-squares on F^2 Refinement methodFull-matrix least-squares on F^2 Computing ^a Collect, HKL Denzo andCollect, HKL Denzo andScalepackand ScalepackparametersSHELXS-97, SHELXL-97Data/restraints/4828/0/2564942/0/256parameters0.0316,Goodness-of-fit on F^2 1.1041.147Final R índices $[I > 2\sigma(I)]$ $R_1 = 0.0231$, $R_1 = 0.0316$, $R'_2 = 0.0565$ $R_2 = 0.0818$ RR indices (all data) $R_1 = 0.0238$, $R_1 = 0.0321$, $wR_2 = 0.0569$ $wR_2 = 0.0821$ 0.04(2) $-0.03(3)$ parameter0.0071(6)0.0143(10)Largest difference peak0.589 and2.044 andand hole -0.659 e Å ⁻³ -0.445 e Å ⁻³	Reflections collected	15 860	16 965
Completeness to theta = 27.5°99.7%99.4%Absorption correction Maximum and minimum transmissionGaussianGaussian 0.754 and 0.6550.830 and 0.622Refinement method transmissionFull-matrix least- squares on F^2 Full-matrix least- squares on F^2 Computing ^a Collect, HKL Denzo and Scalepack HELXS-97, SHELXL-97Collect, HKL Denzo and Scalepack SHELXS-97, SHELXL-97Data/restraints/ parameters4828/0/2564942/0/256Goodness-of-fit on F^2 1.1041.147Final R índices [$I > 2\sigma(I)$] w $R_2 = 0.0565$ $R_1 = 0.0316$, w $R_2 = 0.0818$ R indices (all data) $R_1 = 0.0238$, $R_1 = 0.0321$, w $R_2 = 0.0821$ Absolute structure parameter0.04(2)-0.03(3)Parameter0.0071(6)0.0143(10)Largest difference peak and hole0.589 and $-0.659 e Å^{-3}$ -0.445 e Å^{-3}	Independent reflections	4828 [R(int) = 0.0258]	4942 [R(int) = 0.0230]
Absorption correction Maximum and minimum transmissionGaussian 0.754 and 0.655Gaussian 0.830 and 0.622Refinement methodFull-matrix least- squares on F^2 Full-matrix least- squares on F^2 ComputingaCollect, HKL Denzo and Scalepack SHELXS-97, SHELXL-97Collect, HKL Denzo and Scalepack SHELXS-97, SHELXL-97Data/restraints/ parameters4828/0/2564942/0/256Goodness-of-fit on F^2 1.1041.147Final R indices $[I > 2\sigma(I)]$ parameter $R_1 = 0.0231$, $WR_2 = 0.0565$ $R_1 = 0.0321$, $WR_2 = 0.0818$ R indices (all data) $R_1 = 0.0238$, $R_1 = 0.0321$, $WR_2 = 0.0569$ $WR_2 = 0.0821$ Absolute structure parameter0.004(2) $-0.03(3)$ Extinction coefficient and hole0.0589 and -0.659 e Å ⁻³ -0.445 e Å ⁻³	Completeness to theta = 27.5°	99.7%	99.4%
Maximum and minimum transmission0.754 and 0.6550.830 and 0.622Refinement methodFull-matrix least- squares on F^2 Full-matrix least- squares on F^2 ComputingaCollect, HKL Denzo and 	Absorption correction	Gaussian	Gaussian
Refinement methodFull-matrix least- squares on F^2 Full-matrix least- squares on F^2 Computing ^a Collect, HKL Denzo and Scalepack HELX=97, SHELXL-97Collect, HKL Denzo and Scalepack SHELX=97, SHELXL-97Data/restraints/ parameters4828/0/2564942/0/256Goodness-of-fit on F^2 1.1041.147Final R índices $[I > 2\sigma(I)]$ R indices (all data) $R_1 = 0.0231$, $R_1 = 0.0238$, $R_2 = 0.0565$ $R_2 = 0.0818$ R indices (all data)0.04(2)-0.03(3)parameterUnder the structure Data (10)0.0071(6)Largest difference peak and hole0.589 and $-0.659 e Å^{-3}$ 2.044 and $-0.445 e Å^{-3}$	Maximum and minimum transmission	0.754 and 0.655	0.830 and 0.622
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Refinement method	Full-matrix least-	Full-matrix least-
$\begin{array}{cccc} {\rm Computing}^{\rm a} & {\rm Collect, HKL Denzo and } & {\rm Collect, HKL Denzo and } & {\rm Scalepack} & {\rm and Scalepack} & {\rm and Scalepack} & {\rm SHELXS-97, SHELXL-97} & {\rm SHELXS-97, SHELXL-97} & {\rm SHELXS-97, SHELXL-97} & {\rm Data/restraints/} & {\rm 4828/0/256} & {\rm 4942/0/256} & {\rm parameters} & {\rm Goodness-of-fit on } F^2 & {\rm 1.104} & {\rm 1.147} & {\rm Final } R \ {\rm indices } [l > 2\sigma(l)] & R_1 = 0.0231, & R_1 = 0.0316, & {\rm wR}_2 = 0.0565 & {\rm wR}_2 = 0.0818 & {\rm R} & {\rm indices } ({\rm ald } {\rm data}) & R_1 = 0.0238, & R_1 = 0.0321, & {\rm wR}_2 = 0.0569 & {\rm wR}_2 = 0.0821 & {\rm O.04(2)} & {\rm -0.03(3)} & {\rm parameter} & {\rm Extinction coefficient} & {\rm 0.0071(6)} & {\rm 0.0143(10)} & {\rm Largest difference peak} & {\rm 0.589 \ and} & {\rm 2.044 \ and} & {\rm and \ hole} & {\rm -0.659 \ ell}^{-3} & {\rm -0.445 \ ell}^{-3} & {\rm Collect, HKL Denzo and Scalepack} & {\rm Collect, HKL Denzo and Scalepack} & {\rm and \ bole} & {\rm -0.659 \ ell}^{-3} & {\rm -0.445 \ ell}^{-3} & {\rm Collect, HKL Denzo and Scalepack} & {\rm Collect, HKL Denzo and Scalepack} & {\rm Collect, HKL Denzo and Scalepack} & {\rm and \ collech and \ c$		squares on F^2	squares on F ²
$\begin{array}{cccc} Scalepack & and Scalepack \\ SHELXS-97, SHELXL-97 & SHELXL-97 \\ Data/restraints/ & 4828/0/256 & 4942/0/256 \\ parameters & & & & & & \\ Goodness-of-fit on F^2 & 1.104 & 1.147 \\ Final R indices [l > 2\sigma(l)] R1 = 0.0231, R1 = 0.0316, wR_2 = 0.0565 wR_2 = 0.0818R indices (all data) R1 = 0.0238, R1 = 0.0321, wR_2 = 0.0569 wR_2 = 0.0821Absolute structure 0.04(2) -0.03(3)parameter & & & & \\ Extinction coefficient 0.0071(6) 0.0143(10) \\ Largest difference peak and hole -0.659 e Å^{-3} -0.445 e Å^{-3} \\ \end{array}$	Computing ^a	COLLECT, HKL Denzo and	Collect, HKL Denzo
$\begin{array}{c c} & SHELXS-97, SHELXL-97 \\ Data/restraints/ & 4828/0/256 & 4942/0/256 \\ parameters & & & & \\ Goodness-of-fit on F^2 & 1.104 & 1.147 \\ Final R indices [I > 2\sigma(I)] & R_1 = 0.0231, & R_1 = 0.0316, \\ wR_2 = 0.0565 & wR_2 = 0.0818 \\ R indices (all data) & R_1 = 0.0238, & R_1 = 0.0321, \\ wR_2 = 0.0569 & wR_2 = 0.0821 \\ Absolute structure & 0.04(2) & -0.03(3) \\ parameter & & \\ Extinction coefficient & 0.0071(6) & 0.0143(10) \\ Largest difference peak & 0.589 and & 2.044 and \\ and hole & -0.659 e Å^{-3} & -0.445 e Å^{-3} \end{array}$		Scalepack	and Scalepack
$\begin{array}{llllllllllllllllllllllllllllllllllll$		SHELXS-97, SHELXL-97	SHELXS-97, SHELXL-97
Goodness-of-fit on F^2 1.104 1.147 Final R índices $[I > 2\sigma(I)]$ $R_1 = 0.0231$, $R_1 = 0.0316$, $wR_2 = 0.0565$ $wR_2 = 0.0818$ R indices (all data) $R_1 = 0.0238$, $R_1 = 0.0321$, $wR_2 = 0.0821$ $wR_2 = 0.0569$ $wR_2 = 0.0821$ Absolute structure $0.04(2)$ $-0.03(3)$ parameter Extinction coefficient $0.0071(6)$ $0.0143(10)$ Largest difference peak 0.589 and 2.044 and and hole	Data/restraints/ parameters	4828/0/256	4942/0/256
Final R índices $[I > 2\sigma(I)]$ $R_1 = 0.0231$, $R_1 = 0.0316$, $wR_2 = 0.0565$ $wR_2 = 0.0818$ R indices (all data) $R_1 = 0.0238$, $R_1 = 0.0321$, $wR_2 = 0.0821$ Absolute structure $0.04(2)$ $-0.03(3)$ parameter Extinction coefficient $0.0071(6)$ $0.0143(10)$ Largest difference peak 0.589 and 2.044 and and hole -0.659 e Å ⁻³	Goodness-of-fit on F^2	1.104	1.147
$ \begin{array}{ccc} & wR_2 = 0.0565 & wR_2 = 0.0818 \\ R \text{ indices (all data)} & R_1 = 0.0238, & R_1 = 0.0321, \\ wR_2 = 0.0569 & wR_2 = 0.0821 \\ Absolute structure & 0.04(2) & -0.03(3) \\ parameter & & & \\ Extinction coefficient & 0.0071(6) & 0.0143(10) \\ Largest difference peak & 0.589 \text{ and} & 2.044 \text{ and} \\ and hole & -0.659 \text{ e} \text{ Å}^{-3} & -0.445 \text{ e} \text{ Å}^{-3} \end{array} $	Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0231$,	$R_1 = 0.0316$,
R indices (all data) $R_1 = 0.0238$, $wR_2 = 0.0321$, $wR_2 = 0.0569$ $wR_2 = 0.0821$ Absolute structure $0.04(2)$ $-0.03(3)$ parameter Extinction coefficient $0.0071(6)$ $0.0143(10)$ Largest difference peak 0.589 and 2.044 and and hole -0.659 e Å ⁻³ -0.445 e Å ⁻³		$wR_2 = 0.0565$	$wR_2 = 0.0818$
$wR_2 = 0.0569$ $wR_2 = 0.0821$ Absolute structure $0.04(2)$ $-0.03(3)$ parameter Extinction coefficient $0.0071(6)$ $0.0143(10)$ Largest difference peak 0.589 and 2.044 and and hole -0.659 e Å ⁻³ -0.445 e Å ⁻³	R indices (all data)	$R_1 = 0.0238,$	$R_1 = 0.0321$,
Absolute structure 0.04(2) -0.03(3) parameter		$wR_2 = 0.0569$	$wR_2 = 0.0821$
parameter 0.0071(6) 0.0143(10) Largest difference peak 0.589 and 2.044 and and hole $-0.659 \text{ e} \text{ Å}^{-3}$ $-0.445 \text{ e} \text{ Å}^{-3}$	Absolute structure	0.04(2)	-0.03(3)
Largest difference peak 0.589 and 2.044 and and hole $-0.659 \text{ e} \text{ Å}^{-3}$ $-0.445 \text{ e} \text{ Å}^{-3}$	Extinction coefficient	0.0071(6)	0.0143(10)
and hole $-0.659 \text{ e} \text{ Å}^{-3}$ $-0.445 \text{ e} \text{ Å}^{-3}$	Largest difference peak	0.589 and	2.044 and
	and hole	–0.659 e Å ^{–3}	−0.445 e Å ^{−3}

^a Data collection, data processing, structure solution and structure refinement, respectively.

were acquired at room temperature on a Bruker AVANCE 400 NMR spectrometer, operating at 9.4 T, equipped with a 5 mm multinuclear direct detection probe. The ³¹P{¹H} NMR spectra were obtained in CH₂Cl₂ (D₂O capillary was inserted in the solution), while ¹H and ¹⁵N{¹H} NMR spectra were obtained in CDCl₃. The ³¹P, ¹⁵N and ¹H NMR chemical shifts are given in parts per million related to H₃PO₄ (85%, capillary), CH₃NO₂ (neat, capillary) and TMS (tetramethylsilane, internal), respectively. The coupling constants are given in Hertz, and the splitting of hydrogen, phosphorus and nitrogen signals are defined as s, singlet; d, doublet; m, multiplet. EPR spectra were measured at 77 K on a Bruker EMX-micro EPR spectrometer, operating at X band, equipped with a rectangular TE₁₀₂ resonator cavity. Cyclic voltammetry (CV) experiments were carried out at room temperature in CH₂Cl₂ or CH₃CN containing 0.1 M [Bu₄N]ClO₄ (TBAP) (Fluka Purum) (in these conditions, Half-wave potential for ferrocene is 0.423 V) using a PARC 273 (Princeton Applied Research). The working and auxiliary electrodes were stationary Pt foils; the reference electrode was Ag/AgCl in a Luggin capillary probe filled with the electrolyte solution (TBAP in CH₂Cl₂ or CH₃CN). The electronic spectra were obtained from dichloromethane solution of the complexes in guartz cuvettes with path length of 1 cm, with concentrations ranging from 10^{-6} to 10^{-2} on a Hewlett-Packard diode array 8452A spectrophotometer. The elemental analyses were performed on a Fisons CHNS-O, EA 1108 Element analyser.

2.2. X-ray diffraction data

Crystal data for complexes (1) and (2) (Table 1): formula weight = 542.77, orthorhombic, $P2_12_12_1$. For (1) a = 9.3629(1) Å, b = 14.6378(2) Å, c = 15.3757(3) Å, V = 2107.27 Å³, Z = 4, $D_{calc} = 1000$ 1.711 g cm^{-3} , R(wR) = 0.0231(0.0565) for 15 860 reflections $[I > 2\sigma(I)]$, and for (2) a = 8.7986(1) Å, b = 15.2385(3) Å, c = 16.2248(2) Å, V = 2175.38 Å³, Z = 4, $D_{calc} = 1.657$ g cm⁻³, R(wR) =0.0316(0.0818) for 16 965 reflections $[I > 2\sigma(I)]$. X-ray diffraction data collection using the COLLECT program [40] was performed on an Enraf-Nonius Kappa-CCD diffractometer utilizing graphitemonochromated Mo Ka radiation (0.71073 Å). Final unit cell parameters were based on all reflections. Integration and scaling of the reflections were performed with the HKL Denzo-Scalepack system of programs [41]. A Gaussian absorption correction was applied [42]. The structure was solved by direct methods using SHELXS-97 [43]. The model was refined by full-matrix least-squares on F2 with SHELXL-97 [44]. All hydrogen atoms were stereochemically positioned and refined with the riding model.

2.3. Method of calculation

Calculations were performed with GAUSSIAN 03 program [45]. The DFT and TDDFT methods were used with the B3LYP functional [46-48]. In the calculations the PCM solvent model was used [49], with dichloromethane (DCM) as the solvent. The PCM calculations were performed on the optimized geometries without solvent. The DGauss DZVP [50] basis sets were employed for ruthenium with two additional polarization f functions with the exponents 1.9472 and 0.7489. These basis sets are of the form (18s12p9d2f)/[6s5p3d2f]. For C, N, O, P, Cl and H the standard 6-31G* basis set was employed. The specified basis set has already been successfully applied to the calculations for other ruthenium complexes [51]. Natural orbital bond (NBO) population analysis [52] was used for calculating the atomic charges, bond orders and for characterization of the Ru-NO bonding. The molecular structures were depicted by the program MOLDEN [53]. Molecular orbitals were drawn with the use of program GOPENMOL [54].

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