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Synthesis, crystal structures, and electronic spectra of (1,8-naphthyridine)$Re^I(CO)_3Cl$ and [(1,8-naphthyridine)Cu^I(DPEPhos)]PF_6

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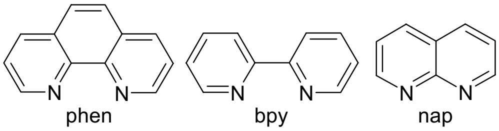
Abstract

Two 1,8-naphthyridine (nap) metal complexes (nap)$Re^I(CO)_3Cl$ (**1**) and [(nap)Cu^I(DPEPhos)]PF_6 (**2**) were synthesized and characterized by NMR-, emission, and absorption spectroscopy, elemental analysis, mass spectrometry, and X-ray structural analysis. In both complexes, the nap ligand coordinates with both N atoms to the metal centre in a bidentate manner. **1** and **2** exhibit a broad phosphorescence in solid state at $T = 300$ K, which is completely quenched in solution at r.t. In addition, the gas-phase structures of both complexes were optimized at the B3LYP/6-31G(d,p) level of theory.

Keywords: Naphthyridine; Rhenium; Copper; Electronic spectra; Photoluminescence

1,8-Naphthyridine (nap) is well established in coordination chemistry and a great number of metal complexes bearing nap as ligand have been published previously [1,2]. Nap and its derivatives can act as monodentate [3–6], bidentate [5–8] and dinuclear bridging [3,5,9–11] ligands. Due to this variability of binding and the ease of preparation, the nap moiety is a versatile building block for several ligand systems [12–18] yielding complexes which display interesting structural [3–10], magnetic, [9] luminescent, [17] catalytic [11,19] and electrochemical [8,13,18,20] properties. For instance, nap is frequently used as a bridging ligand in Rh^I- and Ni^{II}-complexes, where a close metal contact is achieved by the geometrical demand of the ligand. In the monodentate binding pattern, the free N atom can act as an additional reaction site for another ligand (e.g. CO [8,20]) or for substrates during redox reactions. This enables the pre-orientation of reaction partners during a catalytic cycle, which could enhance the catalytic efficiency. Furthermore, nap easily interchanges between mono- and bidentate coordination and thus can provide a free coordination site at a catalytically active metal centre [8].

Nevertheless, little is known about the photophysical properties of complexes containing the unsubstituted nap ligand. To probe the ability to generate luminescent compounds, two examples with (nap)$Re^I(CO)_3Cl$ (**1**) and [(nap)Cu^I(DPEPhos)]PF_6 (**2**) (DPEPhos = bis[2-(diphenylphosphino)phenyl]ether) were prepared and characterized. Analogous complexes containing 1,10-phenanthroline (phen) and 2,2′-bipyridine (bpy) instead of nap have been investigated thoroughly. They exhibit intense photo- and electroluminescence and have demonstrated their applicability in organic light emitting devices (OLEDs) [21–29].



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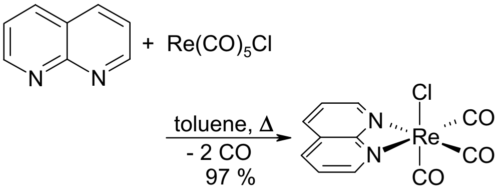
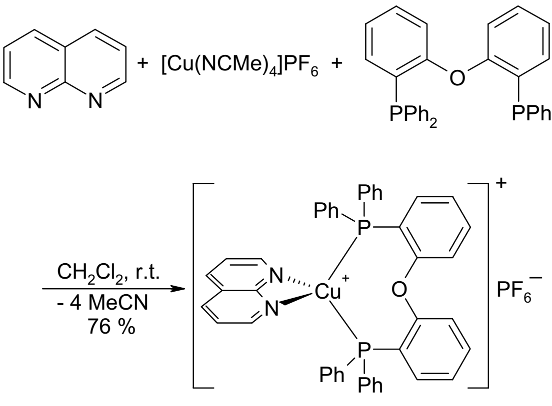
Complex **1** was prepared from nap and $Re(CO)_5Cl$ in boiling toluene in almost quantitative yields (Eq. (1)) [30]. The copper complex is obtained in good yields (76%) from nap, DPEPhos and $[Cu(NCMe)_4]PF_6$ in DCM solution (Eq. (2)) [31]. Both compounds are yellow powders and are stable in the solid state and solutions under aerobic conditions. Complex **1** is soluble in polar organic solvents (MeCN, DCM, $CHCl_3$), whereas complex **2** is only modestly soluble in hot MeCN. Their identities were confirmed by elemental analyses, mass spectrometry and NMR spectroscopy [30,31].



1

(1)



2

(2)

Single crystals of **1** suitable for structure determination by X-ray diffraction were obtained from $CHCl_3/Et_2O$. The compound crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ molecules in the unit cell [32]. Although the complexes in crystals of **1** show no crystallographically imposed symmetry, they closely approach a mirror symmetry with a mirror plane including Re1, Cl1, and C9. Nap acts as a bidentate ligand and the Re–N distances are almost identical [2.232(3) and 2.236(2) Å]. Thus, the Re(I) atom exists in a distorted octahedral environment defined by a *facial* arrangement of the three carbonyl groups, the chloride atom and the two nitrogen atoms of the nap ligand (Fig. 1). The distortion from the ideal octahedral symmetry essentially arises from the sterical demand of the chelating nap ligand with its small bite angle.

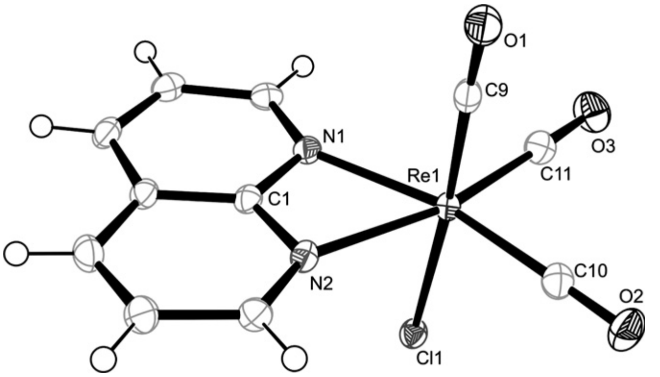


Fig. 1. Crystal structure of **1** (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Re1–N1 2.232(3), Re1–N2 2.236(2), Re1–Cl1 2.4937(8), Re1–C9 1.921(3), Re1–C10 1.929(4), Re1–C11 1.915(3), N1–Re1–N2 60.12(10), N1–Re1–C11 105.28, C10–Re1–C11 87.89(15), Cl1–Re1–N1 83.33(6), Cl1–Re1–C9 176.27(10), Re1–N1–C1 95.1(2), Re1–N2–C1 94.91(17).

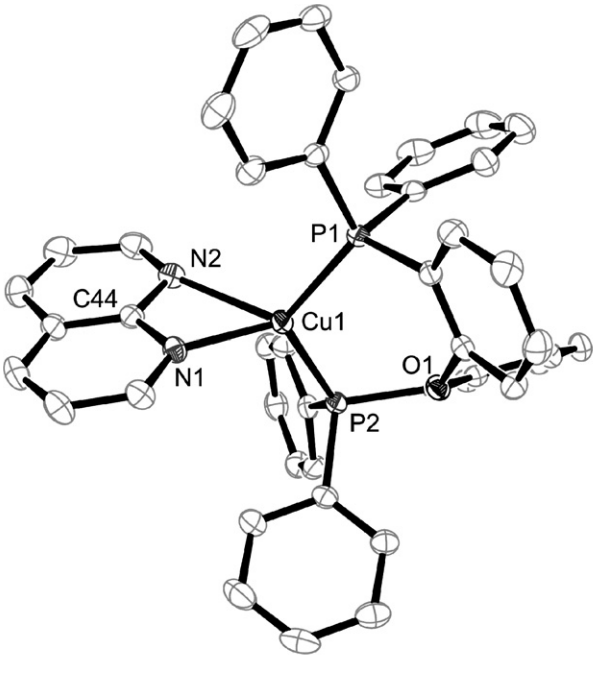


Fig. 2. Crystal structure of the cation in crystals of **2** (H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Cu1–N1 2.0254(15), Cu1–N2 2.5633(16), Cu1–P1 2.2426(5), Cu1–P2 2.2706(5), N1–Cu1–N2 58.31, P1–Cu1–P2 116.62(2), P1–Cu1–N1 127.31(4), Cu1–N1–C44 105.98(11), Cu1–N2–C44 82.34(10).

Crystals of **2** obtained from $MeCN/Et_2O$ are triclinic, with space group $P\bar{1}$ ($Z = 4$). The copper atom is coordinated by nap and DPEPhos in a distorted tetrahedral environment (Fig. 2). There are no sub-van der Waals contacts between the oxygen of the phosphine ligand and the copper centre. Whereas the Cu–P bond lengths are comparable [Cu1–P1 2.2426(5) Å, Cu1–P2 2.2706(5) Å], the nap coordination is highly asymmetric [Cu1–N1 2.0254(15) Å, Cu1–N2 2.5633(16) Å]. The differences of the Cu–N bond length as well as of the Cu–N–C44 angles [<(Cu1–N1–C44) 105.98(11)°, <(Cu1–N2–C44) 82.34(10)°] mark the transition from a bidentate to a monodentate or bridging coordination pattern of the nap ligand. By contrast, only one set of protons (and only one phosphor species of the DPEPhos ligand) is observed in the NMR spectra of **2**, showing a dynamic behaviour in solution equilibrating the positions [3,5]. In fact, there are examples for a bridging coordination geometry of the nap ligand in similar copper complexes (e.g.$[Cu_2(nap)_2(dppm)(MeCN)](PF_6)_2$ with dppm = bis(diphenylphosphino)methane) [10]. The averaged Cu1–N_{nap} distance of 2.025(1) Å of the latter complex is the same as the Cu1–N1 contact in **2**. In $[Cu(bpnap)(PPh_3)_2]PF_6$ (bpnap = 2,7-bis(2-pyridyl)-1,8-naphthyridine), the copper atom is also complexed by two nitrogen atoms, one stemming from nap and the other one from the pyridine moiety [14].

The nap ligand exhibits a structured absorption at $\lambda_{max} = 297$, 303, 308 nm ($\lg\varepsilon = 3.69$, 3.74, 3.72) and 257 nm ($\lg\varepsilon = 3.63$) in $CHCl_3$ (Fig. S1), which is in accordance with the published values [33]. Complex **1** exhibits the lowest energy band at $\lambda_{max} = 415$ ($\lg\varepsilon = 3.25$) and transitions which appear near the free ligand absorption ($\lambda_{max} = 276$, 301, 313 nm; $\lg\varepsilon = 4.18$, 3.93, 3.79) (Fig. 3). The lower energy absorption at 415 nm is assignable to a MLCT Re(dπ)→nap(π*) transition. The higher energy band can be associated with LC(π–π*) electronic transitions localized mainly on the nap ligand. These two absorption features are well known for Re(I) complexes of the form $(N\cap N)Re(CO)_3Cl$ ($N\cap N$ e.g. 1,10-phenanthroline, 2,2′-bipyridine, etc.) [22]. In addition, DFT calculations confirm the interpretation that the highest occupied molecular orbital (HOMO) is metal centred and the highest unoccupied molecular orbital (LUMO) is ligand centred (Fig. 4) [34].

Typically, heteroleptic Cu(I) complexes containing $N\cap N$ and DPEPhos ligands exhibit ligand centred features in the UV and a broad MLCT band in the 350–450 nm spectral range [23,25,26]. In compound **2** the signals in the UV spectral region appear at $\lambda_{max} = 301$ and 224 nm ($\lg\varepsilon = 4.22$, 4.80). In contrast to the known Cu(I) complexes, a very weak low energy MLCT band occurs in the usual MLCT absorption range ($\lambda_{max} = 380$ nm, $\lg\varepsilon = 1.87$, not depicted in Fig. 5). The observed ε value seems to be too small for a typical singlet ground state→^{1}MLCT transition, therefore further investigations are required. Thus, although the substance is yellow in the solid state the acetonitrile solution is colourless. A possible reason for this behaviour might be the transient displacement of one of the nap's nitrogen atoms by a solvent molecule. The DFT calculation of the ground state structure of **2** roughly reproduces the coordination mode of the X-ray structure. The nap ligand is also coordinated in an asymmetric, almost monodentate manner, but the Cu–N and Cu–P bonds are too long (Fig. S2 and Table S2). The difference in structures may be the result of a flat potential surface for the nap coordination. Therefore, the calculated results are not reliable to draw conclusion regarding the electronic situation in the complex.

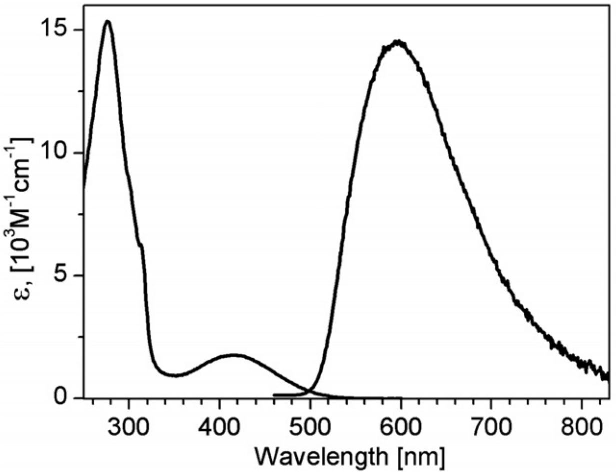


Fig. 3. Electronic absorption (in $CHCl_3$ solution, left axis) and emission (solid state, 300 K, $\lambda_{exc} = 450$ nm, right axis) spectrum of $(nap)Re^I(CO)_3Cl$.

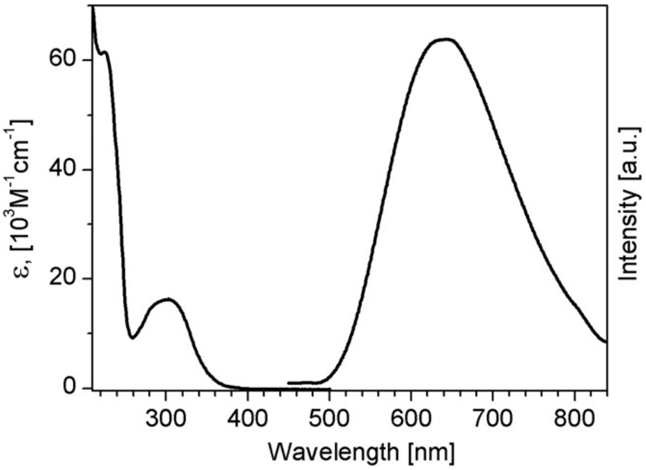


Fig. 5. Electronic absorption (in MeCN solution, left axis) and emission (solid state, 300 K, $\lambda_{exc} = 400$ nm, right axis) spectrum of $[(nap)Cu^I(DPEPhos)]PF_6$.

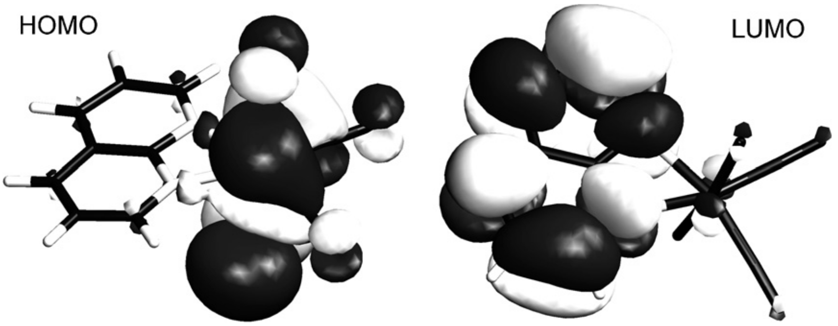


Fig. 4. Contour plots of the highest occupied and lowest unoccupied molecular orbital (DFT calculation at the B3LYP/6-31G(d,p) level).

In chloroform solution at room temperature, the free nap ligand shows a structured blue emission at $\lambda_{em} = 388$ and 407 nm with shoulders on both the high and low energy sides at 369 and 430 nm (Fig. S1). Complexes **1** and **2** exhibit a broad, structureless and weak emission in solid state at $T = 300$ K (**1**: $\lambda_{em} = 594$ nm; **2**: $\lambda_{em} = 638$ nm). Their emission decay times are in the microsecond regime. These findings are well established for analogous metal complexes and indicate phosphorescence from ^{3}MLCT or MLCT perturbed ^{3}LC states [22–27]. However, the emissions of both complexes are completely quenched in solution at room temperature. For **2**, a nucleophilic attack by oxygen at the copper centre is feasible because DPEPhos is capable of functioning as a tridentate ligand [35], but intramolecular exciplex quenching seems to be improbable [26]. Furthermore, solvent-induced quenching which involves a transient increase in the coordination number of the copper centre is widely found for MLCT states of Cu(I) complexes [27,28]. Nevertheless, for both complexes the most likely mechanism is vibrational deactivation of the excited state due to the fluxional behaviour of the nap ligand. Even at a temperature of 77 K the emission of **2** is completely quenched in acetonitrile, whereas **1** features an emission at $\lambda_{em} = 604$ nm in 2-methyltetrahydrofuran.

Acknowledgements

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Appendix A. Supplementary material

CCDC 654659 and 654654 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.09.010.

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[30] *Preparation of* $(nap)Re^I(CO)_3Cl$, **1**: The preparation was performed according to a previously reported method with minor modifications [2]. $Re(CO)_5Cl$ (150 mg, 0.41 mmol) and 1,8-naphthyridine (54 mg, 0.41 mmol) were dissolved in degassed toluene and heated to reflux for 3 h. After cooling to room temperature, the yellow precipitate was filtered and dried in vacuum. Yield: 173 mg (0.40 mmol, 97%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 9.09$ (dd, $^3J_{HH} = 4.66$, $^4J_{HH} = 1.65$ Hz, 1H, C2/7-H), 8.53 (dd, $^3J_{HH} = 8.51$, $^4J_{HH} = 1.65$ Hz, 1H, C4/5-H), 7.79 (dd, $^3J_{HH} = 8.51$, $^3J_{HH} = 4.66$ Hz, 1H, C3/6-H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): $\delta = 152.9$ (s, C2/7), 137.3 (s, C4/5), 125.5 (s, C3/6), quaternary Cs not detected; MS (EI): m/z (%) = 130.0 $[nap]^+$ (100), 351.9 $[M{-}3CO]^+$ (3.3), 379.9 $[M{-}2CO]^+$ (1.3), 407.9 $[M{-}CO]^+$ (1.7), 435.9 $[M]^+$ (1.3); MS (ESI): m/z (%) = 130.9 $[nap + H]^+$ (14), 442.0 $[M{-}Cl{+}MeCN]^+$ (100); UV/vis ($CHCl_3$): $\lambda(\lg\varepsilon) = 415$ (3.25), 313 (sh, 3.79), 301 (sh, 3.93), 276 nm (4.18); EA $[C_{11}H_6N_2O_3Re]Cl$ calc.: C 30.31, H 1.39, N 6.43, found: C 30.31, H 1.52, N 6.42; MF: $C_{11}H_6N_2O_3ReCl$; MW = 435.84 g/mol.

[31] *Preparation of* $[(nap)Cu^I(DPEPhos)]PF_6$, **2**: 1,8-naphthyridine (50 mg, 0.38 mmol), $[Cu^I(NCMe)_4]PF_6$ (143 mg, 0.38 mmol) and bis[2-(diphenylphosphino)phenyl]ether (207 mg, 0.38 mmol) were dissolved in degassed methylene chloride and heated to reflux for 3 h. The solution was concentrated and diethyl ether was added to precipitate the product. The suspension was filtered and recrystallized from $MeCN/Et_2O$ yielding yellow crystals. Once precipitated the complex is almost insoluble in DCM and $CHCl_3$ and modestly soluble in hot MeCN. Yield: 253 mg (0.29 mmol, 76%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 9.07$ (br, 1H, C2/7-H), 8.51 (br, 1H, C4/5-H), 7.61 (dd, C3/6-H), 7.24 – 7.44 (m, 20 H), 6.91 – 7.03 (m, 4 H) 6.69 – 6.74 (m, 2H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): $\delta = 157.7$ (dd, $J_{CP} = 6.27$ Hz C2/7), 137.4 (br, C4/5), 133.8 (s), 133.2 (dd, $J_{CP} = 8.11$ Hz), 131.6 (s), 131.0 (dd, $J_{CP} = 16.43$ Hz), 129.8 (s), 128.4 (dd, $J_{CP} = 4.79$ Hz), 124.4 (s, C3/6), 123.42 (dd, $J_{CP} = 14.75$ Hz), 119.8 (s); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = -13.14$ (s, DPEPhos), -143.16 (septet, $J_{PF} = 704$ Hz, $(PF_6)^-$); MS (ESI): m/z (%) = 601.1 $[(DPEPhos)Cu^I]^+$ (53), 642.1 $[(DPEPhos)Cu^I + MeCN]^+$ (100) 731.2 $[(DPEPhos)Cu]^+$ (35); EA $[C_{44}H_{34}N_2OP_2Cu]$ PF_6 calc.: C 60.25, H 3.91, N 3.19, found: C 60.36, H 3.97, N 3.18; UV/vis (MeCN): $\lambda(\lg\varepsilon) = 380$ (1.87), 301 (4.22), 224 nm (4.80); MF: $[C_{44}H_{34}N_2OP_2Cu]$ PF_6; MW = 877.19 g/mol.

[32] *Crystal structure determination*: Crystals of compounds **1** and **2** were used for data collection on a STOE-IPDS diffractometer [36] with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SIR-97) [37] and refined by full-matrix least squares on F^2 (SHELXL-97 [38]). The H atoms were calculated geometrically and a riding model was applied during the refinement process. *Crystal data for* **1**: $C_{11}H_6ClN_2O_3Re$, $M = 435.84$, translucent yellow prism, $0.19 \times 0.15 \times 0.10$, triclinic, space group $P\bar{1}$, $a = 7.0534(8)$ Å, $b = 8.7475(10)$ Å, $c = 10.8185(13)$ Å, $\alpha = 85.954°$, $\beta = 87.449(14)°$, $\gamma = 70.873(13)°$, $V = 628.91(14)$ Å^3, $\rho_{calc} = 2.302$ g cm^{-3}, $Z = 2$, $\mu = 9.873$ mm^{-1}, $T = 123$ K, θ range = 2.47 – 26.89°, 6884 reflections collected, 2486 [$R(int) = 0.0234$] unique reflections, 2438 observed reflections [$I > 2\sigma(I)$], 163/0 parameters refined/restraint, absorption correction: analytical from crystal shape, T_{min}, $T_{max} = 0.3498$, 0.1316, σ_{fin} (max/min) = 1.267/−0.966 e Å^{-3}, R_1 [$I \geqslant 2\sigma(I)$] = 0.0171, $wR_2 = 0.0443$. *Crystal data for* **2**: $C_{44}H_{34}CuN_2OP_2$, F_6P, $M = 877.19$, yellow prism, $0.22 \times 0.16 \times 0.10$, monoclinic, space group $P2_1/c$, $a = 11.0828(8)$ Å, $b = 28.827(2)$ Å, $c = 12.6691(10)$ Å, $\beta = 103.440(9)°$, $V = 3936.7(5)$ Å^3, $\rho_{calc} = 1.480$ g cm^{-3}, $Z = 4$, $\mu = 0.744$ mm^{-1}, $T = 123$ K, θ range = 1.89–25.78°, 49592 reflections collected, 7372 [$R(int) = 0.0302$] unique reflections, 6567 observed reflections [$I > 2\sigma(I)$], 514/0 parameters refined/restraint, absorption correction: analytical from crystal shape, T_{min}, $T_{max} = 0.9576$, 0.9033, σ_{fin} (max/min) = 0.523/−0.341 e Å^{-3}, R_1 [$I \geqslant 2\sigma(I)$] = 0.0309, $wR_2 = 0.0875$.

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