

The novel ligand 4'-phenyl-3,2':6',3''-terpyridine (**L**) and the supramolecular structure of the dinuclear complex $[\text{Zn}_2(\mu\text{-L})(\text{acac})_4] \cdot \text{H}_2\text{O}$ (acac = acetylacetonato)

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A B S T R A C T

The new terpyridyl ligand 4'-phenyl-3,2':6',3''-terpyridine (**L**) reacts with $\text{Zn}(\text{acac})_2$ to produce the dizinc complex $[\text{Zn}_2(\mu\text{-L})(\text{acac})_4] \cdot \text{H}_2\text{O}$ (**1**) (acac = acetylacetonato). The analysis of the crystal structure of this zero-dimensional (0D) complex shows the existence of two $\text{Zn}(\text{acac})_2$ centers bridged symmetrically by one $\mu\text{-L}$ ligand. The key role played by the acac and **L** ligands and the guest water molecule allows the generation of a series of intermolecular hydrogen bonds of the O-H/O, C-H/O and C-H/ π type which give rise to a 3D supramolecular array. The observed C-H/ π interactions are so widespread that all the π -rings present in the structure, viz., those belonging to the **L** ligand as well as the acetylacetonato chelate rings, participate as hydrogen bond acceptors.

Keywords:

Polypyridine complexes
Supramolecular structure
C-H/ π interaction
C-H/O interaction
Hydrogen bond

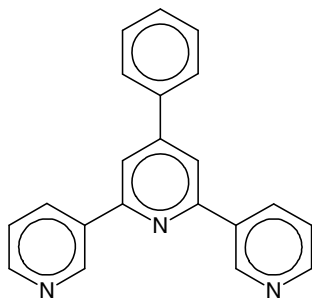
The tridentate ligand 2,2':6'2''-terpyridine and its derivatives bonded to a metal have been well studied in the area of supramolecular chemistry [1,2]. Recently, as an extension in the exploration of this type of metal-binding domains, symmetric divergent and 4'-functionalized terpyridine have been used in the formation of coordination architectures [3,4]. Indeed, the scarcely reported examples on this subject include only the 4,4'' ligands 4'-phenyl-4,2':6',4''-terpyridine and 4'-(4'''-octyloxyphenyl)-4,2'-6',4''-terpyridine and their coordination to ZnCl_2 generating polymeric 1D helical networks, which exhibit intermolecular C-H/Cl hydrogen bonds [3,4]. In this context, with the aim on going further in the understanding of the bonding properties of this new class of terpyridyl derivatives, we report the synthesis and characterization of the novel 3,3'' ligand 4'-phenyl-3,2':6',3''-terpyridine (**L**) (Scheme 1) and the supramolecular structure of its reaction product with $\text{Zn}(\text{acac})_2$ the dizinc complex $[\text{Zn}_2(\mu\text{-L})(\text{acac})_4] \cdot \text{H}_2\text{O}$ (**1**). The weak hydrogen bonds of the CH/ π type have been extensively studied in the past years [5]. Despite this, only recently the specific presence of the chelating acac ligand have been introduced as an additional factor to be considered in the analysis of the hydrogen bond interactions in metal complexes. In fact, Zarić et al. [6] have evaluated the noncovalent interactions of the C-H/ π type between the coordinated acac ligand and phenyl rings, on the basis of the crystal structures from the Cambridge Structural Database and by quantum chemical calculations. It was concluded that the chelat-

ing acac shows two types of interactions, one by using either its CH and/or CH_3 groups (hydrogen bond donor) and the other one involving the π -system of the chelate ring (as a hydrogen bond acceptor). It was also inferred that the strength of the acac ligand as H-bond donor depends on the acid hardness of the metal centres; complexes with soft Lewis acids metals centers have tendency to produce stronger interactions than those with hard ones. The application of these concepts to the construction of the supramolecular assembly of the molecules of **1** allows to understand the form in which the structure expands to reach a three-dimensional array.

The ligand **L** was prepared in a similar way to that of its isomer 4'-phenyl-4,2':6',4''-terpyridine from 3-acetylpyridine and benzaldehyde [3], but the crude product was purified by vacuum column chromatography over silica gel [7]. The new compound was characterized by satisfactory elemental analysis, FT-IR spectrum, mass spectrum and ^1H , ^{13}C NMR spectra [7]. The assignment of the resonance signals of protons was established by coupling constants proton spectrum and ^1H - ^1H COSY-45. The five phenyl protons can be readily distinguished from the other for the characteristic AA'BB'X pattern in the region 7.52–7.81 ppm. The two protons of the central pyridine ring appear as a sharp singlet at 7.96 ppm. Those protons of the 3-pyridyl groups show an expected low field broad singlet at 9.39 ppm due to two H-2 protons, while the six remaining protons of these rings H-4, H-5 and H-6 were assigned to the chemical shifts of 8.51, 7.46 and 8.71 ppm, respectively.

The ligand **L** reacts with $\text{Zn}(\text{acac})_2$ in a methanol solution to produce light yellow crystals of **1**, which are unstable when taken out

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Scheme 1. The sketch of ligand **L**.

of the mother liquor where it seems the solvated water is lost [8]. Single crystal X-ray diffraction at 123 K [9], shows that **1** consists of a bis-monodentate **L** ligand bridging two $\{Zn(acac)_2\}$ fragments through its 3-pyridyl N atoms, the whole assembly being halved by a two fold axis for what only half of the group is crystallographically independent. As illustrated in Fig. 1, the resulting $(\mu-L)\{Zn(acac)_2\}_2$ branched unit is externally closed, at both sides, by a strong H-bonded hydration water that bridges two acac O atoms ($O1W \cdots O12$ 3.045(3) Å) to configure finally a 16-membered ring. Each Zn center has a 4 + 1 coordination sphere; four sites are provided by two different acac groups coordinated in the usual chelating form through their carbonyl O donor, the planar groups subtending an angle of 69.9(1)° to each other. The fifth site of the coordination polyhedron is occupied by a 3-pyridyl N atom from the **L** ligand. The geometry around Zn1 is an almost perfect trigonal bipyramid, with an apical $O13-Zn1-O22$ angle of 175.5(1)° and the apical bonds deviating less than 2.6(1)° from the normal to the

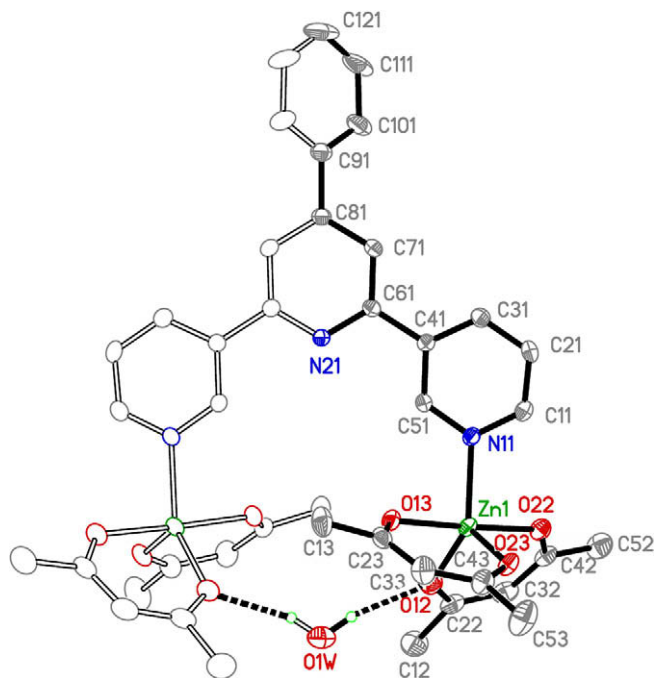


Fig. 1. Molecular diagram of **1**, with anisotropic displacement ellipsoids drawn at a 40% probability level. Independent atoms represented as labeled full ellipsoids in full bonds. H atoms attached to carbon were removed for clarity. The heavy broken lines represent hydrogen bonds. Selected bond lengths (Å) and bond angles (°): Zn1–O23 1.979(2), Zn1–O12 1.987(2), Zn1–O13 2.031(2), Zn1–O22 2.044(2), Zn1–N11 2.092(2), O23–Zn1–O12 113.07(9), O23–Zn1–O13 91.72(9), O12–Zn1–O13 89.42(9), O23–Zn1–O22 92.72(9), O12–Zn1–O22 89.47(9), O13–Zn1–O22 175.50(8), O23–Zn1–N11 113.67(9), O12–Zn1–N11 133.23(9), O13–Zn1–N11 87.60(9), O22–Zn1–N11 89.99(9), O1W···O12 3.045(3), H1W···O12 2.24(3), O1W–H1W···O12 161(4).

equatorial base. The three pyridine-based rings of the **L** ligand form a nearly planar structure; each outer pyridyl group is twisted with respect to the central one, subtending a dihedral angle of 6.46°. In contrast, the dihedral angle between the central ring and phenyl group amounts 44.42°.

The most conspicuous feature of the structure of **1** is its packing, organized in a “hierarchical” disposition of interactions strengths (or levels) leading to different types of well differentiated arrays. Thus, in a first level we find the (strong) H-bonds generating chains (1D structures) which run along (010); in a second level, a mixture of (middle strength) non-conventional C–H/O bonds and C–H/ π interactions which laterally join the former chains into 2D frameworks parallel to (001); and in a third final level, a variety of (weaker) C–H/ π contacts which connect layers into a 3D structure. In this way, the hydrogen-bonded 16-membered ring of **1**, as shown in Fig. 1, can be considered as the basic building unit for the 1D array. This comes from the visualization that the crystallization water molecule plays a fundamental double role in the “first level” interactions giving raise to this 1D substructure. First, as mentioned above, acting as a donor for two symmetric H-bonds directed towards O-acac atoms. Second, as an acceptor of the H-bond donated by the outermost C–H group of a neighbor phenyl ring, to produce a perfect linear C–H···O arrangement ($C121-H121 \cdots O1W$ 180°) (Fig. 2). This intermolecular interaction promotes a head-to-tail packing of the basic cyclic structures to give a clear 1D H-bonded chain parallel to the *b* axis (heavy broken lines in Fig. 2). These one-dimensional H-bonded chains are further connected into 2D structures by a combination of interchain CH/O and CH/ π hydrogen bonds: two CH(pyridyl)/O(acac), one CH(pyridyl)/ π (phenyl ring) and one CH(pyridyl)/ π (chelate-acac ring). All these four “second level” interactions are represented in Fig. 2 as simple broken lines and their geometric parameters are given in the legend. One of the CH(pyridyl)/O(acac) connections, $C31H31 \cdots O23$, corresponds to the major component of a bifurcated hydrogen bond and the other one to a single contact, $C71H71 \cdots O23$, nevertheless the bond distances and angles of both CH/O links [$C31 \cdots O23$, 3.282 Å, 143°; $C71 \cdots O23$, 3.473 Å, 161°] are within the expected range for this class of H-bonds [10]. Similarly, the CH(pyridyl)/ π (phenyl ring) interaction in **1** agree with the results obtained elsewhere [11] through a crystallographic database (CSD) survey on transition metal compounds, and where the short distance H(donor)···C(acceptor) between aromatic groups has been used as a parameter. More specifically, this contact correspond in **1** to the $H11 \cdots C111$ pair with a H···C distance of 2.708 Å, which is very similar to the observed average value (2.86 ± 0.13) [11]. However, it has been also settled that the C–H donor groups tend to be oriented toward the centroid of the phenyl ring [11,12]. In this regard, the C–H···Ph interaction is usually described as C–H···Cg (Cg refers to the centroid of the phenyl ring) and in our case is designated as $C11-H11 \cdots Cg5$ (Fig. 2). The last interaction in this second level set, comes from the minor component, $C31-H31 \cdots Cg1$, of the above alluded bifurcated hydrogen bond, which involves as H-donor a 3-pyridyl group and the π -system of the acetylacetonato chelate ring as acceptor (Fig. 2). It has been observed that the donor/acceptor steric effects produce a shorter linkage distance H···centroid(chelate-acac ring) in square-planar complexes than those in the more sterically crowded octahedral complexes [6]. The $H31 \cdots Cg1$ distance of 2.82 Å in **1** correlates well with a five-coordinated environment around the Zn(II) cation, since is shorter than the values found in octahedral complexes with metal(II) centers (>3.05 Å) [6].

Finally, in a series of five C–H··· π contacts (our “third hierarchical level”) involving the acetylacetonato ligand, the 2D layers interact with their upward/downward neighbors to form an infinite 3D network (Fig. 3). Here, only the $C33-H33 \cdots Cg3$ (3-pyridyl) interaction presents the CH(acac) group as H-donor. The $C33 \cdots Cg3$ bond length of 3.99 Å is centred within the reported range of 3.73–4.25 Å

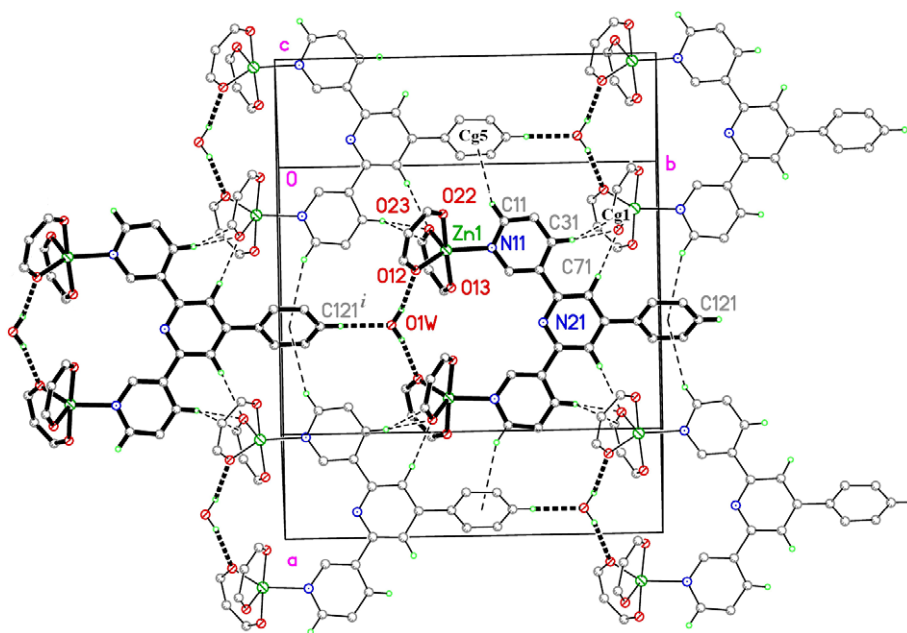


Fig. 2. Packing view parallel to (001) showing first and second level interactions in **1**. Chains run horizontally, parallel to [010]. H-bonds of the first level type drawn in heavy broken lines; second level ones, in simple broken lines. All the methyl groups and those H atoms not involved in the interactions were removed for clarity. Intermolecular hydrogen bonds (a) first level type: C121ⁱ...O1W, 3.256(8) Å, 180°; (b) second level type: C31ⁱⁱ...O23, 3.282(4) Å, 143°; C71ⁱⁱⁱ...O23, 3.473(4) Å, 161°; C11ⁱⁱⁱ...Cg5, 4.07 Å, 154°; C31ⁱⁱ...Cg1, 3.58 Å, 140°. [Ring centroid codes: (Cg1): Zn1, O12, C22, C32, C42, O22; (Cg5): C91, C101, C111, C121, C111^{iv}, C101^{iv}. Symmetry codes: (i) $x, -1 + y, z$; (ii) $0.5 - x, -0.5 + y, 0.5 - z$; (iii) $0.5 - x, 0.5 + y, 0.5 - z$; (iv) $1 - x, y, 0.5 - z$].

for complexes with metals of borderline Lewis acid hardness like Zn(II) [6]. All the four remaining interactions have the CH₃ group as H-bond donor, two of them are directed towards individual pyridyl groups (C52–H52C...Cg3; C12–H12C...Cg4) and the other two towards individual acac-chelate rings (C13–H13B...Cg1; C52–H52B...Cg2). The previously communicated interval of the H(methyl)...Cg(pyridyl) distances goes from 2.2 to 4.1 Å [6]. In **1**, both values are clearly inside this wide range, 3.06 (H52C...Cg3)

and 2.91 (H12C...Cg4) Å. Very close to these values appear those of the two H(methyl)...Cg(acac-chelate) interactions, 3.02 (H13B...Cg1) and 2.90 (H52B...Cg2) Å. This kind of interaction that occurs between two acac moieties has not been characterized pre-

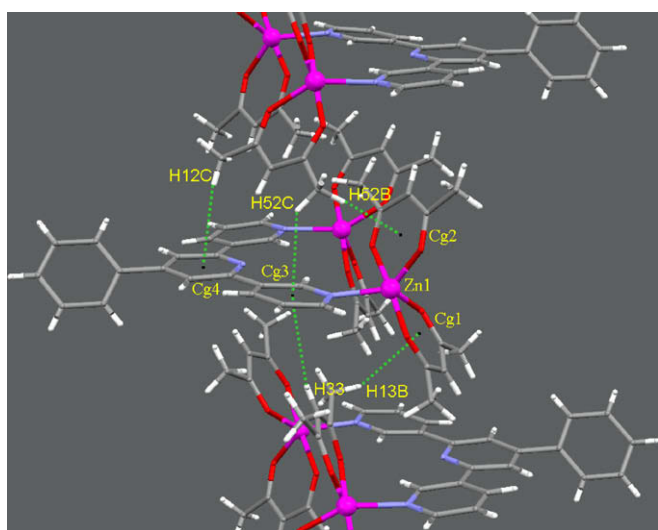


Fig. 3. Packing diagram showing the third level CH/π interactions in **1**, involving the H-donor (CH, CH₃) and the π-donor (chelate ring) groups of the acetylacetonato ligand. Intermolecular hydrogen bonds (third level type): C33^{iv}...Cg3, 3.99 Å, 167°; C52^v...Cg3, 3.76 Å, 131°; C12^v...Cg4, 3.78 Å, 151°; C13^{iv}...Cg1, 3.78 Å, 137°; C52^v...Cg2, 3.82 Å, 160°. [Ring centroid codes: (Cg1): Zn1, O12, C22, C32, C42, O22; (Cg2): Zn1, O13, C23, C33, C43, O23; (Cg3): N11, C11, C21, C31, C41, C51; (Cg4): N21, C61, C71, C81, C71^{vi}, C61^{vi}. Symmetry codes: (iv) $x, 1 - y, 0.5 + z$; (v) $x, 1 - y, -0.5 + z$; (vi) $1 - x, y, 1/2 - z$].

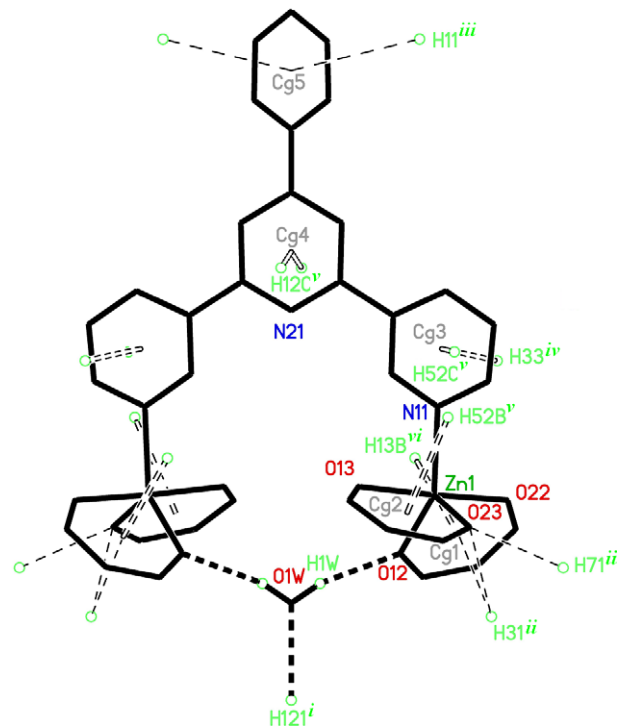


Fig. 4. Schematic representation of a single unit of complex **1**, showing all those noncovalent interactions in which the structure acts as an acceptor. All the methyl groups and those H atoms not involved in the interactions were removed for clarity. H-bonds of the first level type drawn in heavy broken lines; second level ones, in simple broken lines; third level ones, in double broken lines.

viously, but its similitude with the H(methyl)-Cg(pyridyl) assembly, evidenced through the comparison of their observed bond distances, induce us to assume the existence of a similar type of weak contact. As a summary, Fig. 4 displays all the noncovalent contacts accepted by a single unit of complex **1**.

Acknowledgements

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Appendix A. Supplementary material

CCDC 693795 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.inoche.2008.09.009](https://doi.org/10.1016/j.inoche.2008.09.009).

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- [7] *Synthesis of 4'-phenyl-3,2':6',3''-terpyridine (L)*: A mixture of 3-acetylpyridine (2.42 g, 0.02 mol), benzaldehyde (1.06 g, 0.01 mol) and NaOH (1.3 g) in water (15 mL) and ethanol (15 mL) was stirred for three days after which water (100 mL) was added to give an amorphous white mass which was separated by filtration, washed with plenty of water and dried in oven at 100 °C for a couple of hours. The obtained white cake was treated with ammonium acetate (12 g) in refluxing ethanol (80 mL) for 20 h. The resulting orange colored solution was reduced in volume to its third part and treated with water (100 mL). The precipitate was filtered up and redissolved in hot ethanol (40 mL). The cooled solution gave a yellowish microcrystalline substance, which was treated again with hot ethanol to yield a white precipitate. The crude product was purified by vacuum column chromatography over silica gel (EtOAc/*n*-hexane 15%). The less polar product was recrystallized (dichloromethane/hexane) to give a white solid of **L**. Yield: 20%. M.p. 219–221 °C. Anal. Calcd. for C₂₁H₁₅N₃: C, 81.53; H, 4.89; N, 13.58%. Found: C, 81.60; H, 4.99; N, 13.39%. IR (KBr, cm⁻¹): 1607, 1550, 1405, 1023, 808, 759, 697. ¹H NMR (200 MHz, CDCl₃, 298 K): δ = 9.39 (br s, 2H), 8.71 (br d, 2H, *J* = 4.8 Hz), 8.51 (dt, 2H, *J* = 8.2, 1.8 Hz), 7.96 (s, 2H), AA'BB'X system observed at 7.52–7.61 (3H) and 7.72–7.81 (2H), 7.46 (2H, dd, 8.2, 4.8 Hz). ¹³C-PND and ¹³C-DEPT NMR (50 MHz, CDCl₃, 298 K): 155.3 (C_{quat}), 150.8 (C_{quat}), 150.2 (CH), 148.4 (CH), 138.2 (C_{quat}), 134.4 (C_{quat}), 129.4 (CH), 129.2 (CH), 127.1 (CH), 123.6 (CH), 117.7 (CH). HRMS (FAB⁺) calcd for C₂₁H₁₅N₃ [M + 1]⁺ 310.1344, found 310.1351, MS (EI⁺, 70 eV), for C₂₁H₁₅N₃ ([M]⁺) 309 (100%), 308 (36%), 231 (7%).
- [8] *Synthesis of [Zn₂(L)(acac)₄]·H₂O (1)*: To a hot solution of **L** (7.8 mg, 0.025 mmol) in methanol (3.0 ml) was added Zn(acac)₂ (99.7 mg, 0.378 mmol). The resultant solution was cooled at room temperature in a closed vessel and after standing for several hours a crystalline solid was formed. After selecting suitable crystals for X-ray analysis, the rest of the product was collected by filtration, washed with methanol and dried at room temperature. The resulting light yellow crystals become opaque when exposed to air, due to that the compound easily released the guest H₂O molecule to form a partially dehydrated compound. (19.0 mg, 88.9% yield). Anal. Calcd. for C₄₁H₄₅N₉O₉Zn₂: C, 57.62; H, 5.31; N, 4.92. Found: C, 58.01; H, 5.02; N, 5.03%.
- [9] Crystal data were collected on a Bruker Smart CCD diffractometer at 123 K using Mo K α radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined by full-matrix least squares on *F*² using the SHELXS-97 software. All non-hydrogen atoms were refined anisotropically; the water hydrogen was found in a difference Fourier and refined with restraints; those bound to carbon were instead idealized. The structural analysis was performed with the help of the multipurpose PLATON program. Crystallographic data for C₄₁H₄₃N₉O₈Zn₂·H₂O (**1**): *M_w* = 854.54, monoclinic, space group C2/c, *a* = 16.9967(13) Å, *b* = 17.2414(13) Å, *c* = 14.2974(11) Å, *Z* = 2, β = 108.616(2)°, *V* = 3970.6(5) Å³, *D_c* = 1.430 g/cm³, μ = 1.226 mm⁻¹, *F*(000) = 1776, crystal size: 0.31 × 0.17 × 0.09 mm, of 11,307 reflections collected, 4289 were independent of which 3096 had *I* > 2 σ (*I*) [*R*_{int}] = 0.040]. The *R* values are *R*₁ = 0.0497, and *wR*₂ = 0.1150 [*I* > 2 σ (*I*)] and GOOF = 1.166, max/min residual electron density: 0.654/−0.454 eÅ⁻³.
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