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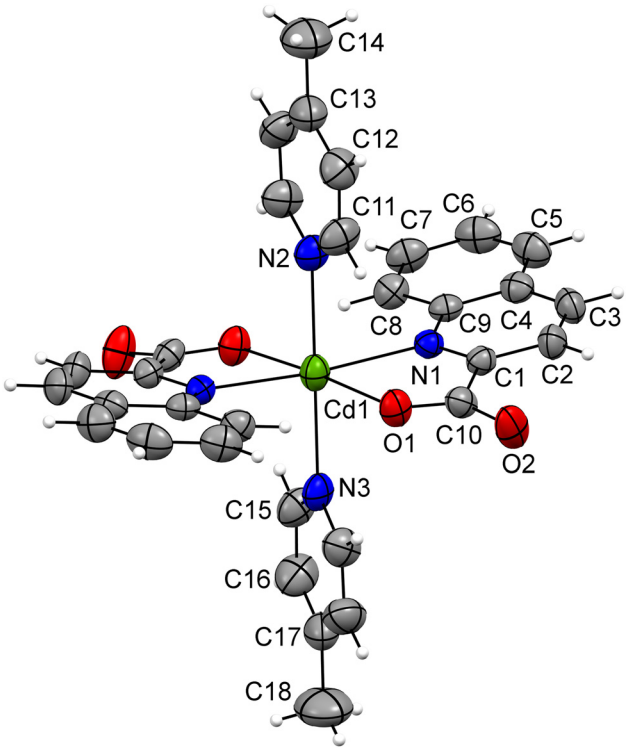
The crystal structure of *trans*-[bis(4-methylpyridine-κN) bis(quinoline-2-carboxylato- κ^2N,O)cadmium(II)], $C_{32}H_{26}CdN_4O_4$



https://doi.org/10.1515/ncrs-2022-0515
Received November 6, 2022; accepted December 3, 2022; published online December 14, 2022

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Abstract
$C_{32}H_{26}CdN_4O_4$, tetragonal, $P4_12_12$ (no. 92), a = 13.7308(6) Å, c = 15.1806(7) Å, V = 2862.1(3) Å^3, Z = 4, $R_{gt}(F)$ = 0.0359, $wR_{ref}(F^2)$ = 0.0693, T = 296(2) K.

CCDC no.: 2224185

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless prism
Size:	0.42 × 0.39 × 0.25 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.81 mm^{-1}
Diffractometer, scan mode:	Oxford Xcalibur2 Sapphire 3, φ and ω
θ_{max}, completeness:	30.0°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	25832, 4170, 0.035
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2738
$N(param)_{refined}$:	192
Programs:	CrysAlis CCD, CrysAlis RED [1], Shelx [2, 3], Mercury [4]

Source of material

The water-containing complex $[Cd(quin)_2(H_2O)_2]$ was prepared as reported previously [5]. A 4-picoline solution (5 mL) of $[Cd(quin)_2(H_2O)_2]$ (0.05 g, 0.10 mmol) was prepared by a gentle heating and left to stand at room temperature to slowly evaporate. The colorless crystals were formed in a couple of days, filtered off, washed with mother liquor and dried in air. Yield: 0.03 g (43%).

Experimental details

The positions of hydrogen atoms belonging to the Csp^2 and Csp^3 carbon atoms were geometrically optimized applying the riding model (Csp^2—H, 0.93 Å; U_{iso}(H) = 1.2U_{eq}(C) and

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Cd1	0.26919 (2)	0.26919 (2)	0.500000	0.05077 (13)
N1	0.27305 (19)	0.25344 (18)	0.65508 (15)	0.0404 (6)
N2	0.1454 (2)	0.1454 (2)	0.500000	0.0563 (10)
N3	0.3924 (2)	0.3924 (2)	0.500000	0.0565 (11)
O1	0.38640 (18)	0.16074 (18)	0.53001 (16)	0.0551 (6)
O2	0.47571 (19)	0.0976 (2)	0.63754 (18)	0.0758 (9)
C1	0.3384 (2)	0.1878 (2)	0.6803 (2)	0.0417 (8)
C2	0.3475 (2)	0.1567 (2)	0.7671 (2)	0.0538 (10)
H2	0.393813	0.110202	0.782269	0.065*
C3	0.2881 (3)	0.1952 (3)	0.8292 (2)	0.0564 (10)
H3	0.293419	0.174984	0.887502	0.068*
C4	0.2189 (2)	0.2648 (2)	0.8061 (2)	0.0493 (9)
C5	0.1545 (3)	0.3091 (3)	0.8677 (3)	0.0650 (10)
H5	0.156900	0.290935	0.926692	0.078*
C6	0.0900 (3)	0.3772 (3)	0.8414 (3)	0.0698 (12)
H6	0.048519	0.405414	0.882528	0.084*
C7	0.0847 (3)	0.4059 (3)	0.7529 (3)	0.0628 (10)
H7	0.040118	0.453275	0.735728	0.075*
C8	0.1451 (3)	0.3644 (2)	0.6916 (3)	0.0532 (9)
H8	0.141124	0.383273	0.632912	0.064*
C9	0.2125 (2)	0.2938 (2)	0.7174 (2)	0.0440 (9)
C10	0.4066 (3)	0.1447 (3)	0.6097 (2)	0.0489 (8)
C11	0.1667 (3)	0.0511 (3)	0.4972 (3)	0.0687 (10)
H11	0.232003	0.033366	0.494796	0.082*
C12	0.0985 (3)	−0.0218 (3)	0.4977 (4)	0.0729 (11)
H12	0.118145	−0.086585	0.496538	0.087*
C13	0.0011 (4)	0.0011 (4)	0.500000	0.0710 (13)
C14	−0.0763 (4)	−0.0763 (4)	0.500000	0.111 (2)
H14A[a]	−0.127635	−0.057877	0.539550	0.166*
H14B[a]	−0.048540	−0.136973	0.518863	0.166*
H14C[a]	−0.102093	−0.083419	0.441587	0.166*
C15	0.3719 (3)	0.4861 (3)	0.5107 (3)	0.0688 (11)
H15	0.307083	0.503615	0.518812	0.083*
C16	0.4405 (4)	0.5588 (4)	0.5104 (4)	0.0820 (12)
H16	0.421399	0.623308	0.517321	0.098*
C17	0.5366 (3)	0.5366 (3)	0.500000	0.0752 (16)
C18	0.6148 (4)	0.6148 (4)	0.500000	0.129 (3)
H18A[a]	0.662609	0.599887	0.544108	0.193*
H18B[a]	0.585705	0.676791	0.512687	0.193*
H18C[a]	0.645430	0.617066	0.443205	0.193*

[a]Occupancy: 0.5.

Csp^3(methyl)—H, 0.96 Å; U_{iso}(H) = 1.5U_{eq}(C), respectively). The methyl H atoms (attached to the C14 and C18 atoms) are disordered about the twofold axis and their site occupancy factors were set to 0.5 during refinement. This disorder was refined by using a PART-1 instruction.

Comment

Quinoline-2-carboxylic acid (2-quinaldic acid, quinH) is an efficient chelating reagent for various metal ions and is, thus, used in the gravimetric analysis of metal(II) ions [6]. Metal complexes with 2-quinaldic acid have been extensively studied, as the crystal structures of 2-quinaldate complexes of transition metals, 12th group metals, platinum group metals, lanthanoids and main group metals have been reported [7]. The 2-quinaldate as a ligand may have attracted such an interest due to the fact that it has a role in a tryptophan metabolism [8] and several of its metabolites participate as signaling agents in neuronal pathways, revealing to be crucial in brain neuropathology [9]. The 2-quinaldic acid also reveals a potential application in the removal and recovery of aluminum(III) ions from environmental waste sites [10]. Previously, we have prepared $[Cd(quin)_2(H_2O)_2]$ by a reaction of cadmium(II) acetate and 2-quinaldic acid in a water/ethanol solution [5]. The respective DMSO-containing complex, $[Cd(quin)_2(DMSO)_2]$, was obtained by a prolonged recrystallization of $[Cd(quin)_2(H_2O)_2]$ from DMSO solution, revealing to be a *trans*-isomer (the DMSO molecules bound in the octahedral axial positions) [5]. In the meantime, a water-containing complex $[Cd(quin)_2(H_2O)_2]$ was also obtained by a hydrothermal procedure which allowed formation of its single crystals and a determination of its crystal structure, showing to be a *cis*-isomer [9]. Therefore, the additional *O*-donor ligands (DMSO vs. water) in the respective cadmium(II) complexes can be placed either in *trans*- or *cis*-positions [5, 9]. We wanted to check the type of isomer (*cis* vs. *trans*) that can be obtained if a suitable *N*-donor ligand is used e.g. 4-methylpyridine (4-picoline). With this goal in mind, we recrystallized the water-containing complex $[Cd(quin)_2(H_2O)_2]$ from a 4-picoline solution to obtain the title compound.

Since the Cd1, N2, N3, C13, C14, C17 and C18 atoms are placed on a twofold axis along [110], the asymmetric unit of the title compound is composed of one half of a cadmium(II) ion, one 2-quinaldate ion and two halves of two independent 4-picoline molecules. The cadmium(II) ion is octahedrally coordinated by two *N,O*-chelating 2-quinaldate ligands (via respective N1 and N1^i atoms (Cd1—N1, 2.365(2) Å) and carboxylate O1 and O1^i atoms (Cd1—O1, 2.239(2) Å), symmetry code (i): *y*, *x*, −*z*+1) in the equatorial plane and by two 4-picoline molecules (via respective N2 and N3 atoms (Cd1—N2, 2.404(4) Å and Cd1—N3, 2.393(4) Å)) in the axial positions, giving a *trans*-isomer (N2—Cd1—N3, 180°). The bond angles around cadmium(II) ion corresponding to the *trans* pairs of donor atoms are in the range of 174.4(1)–180°, whilst those corresponding to the *cis* pairs are in the range of 73.77(8)–106.45(8)°, revealing a distorted octahedral coordination. Such a distortion from an ideal geometry is also clearly seen in the small value of the bite angle O1—Cd1—N1 (73.77(8)°). The 2-quinaldate pyridine ring

(defined by the atoms N1/C1/C2/C3/C4/C9) and the corresponding five-membered chelate ring (defined by the atoms Cd1/O1/C10/C1/N1) are almost co-planar, with a value of a dihedral angle between those rings of 6.4(2)°. There are no classical hydrogen bonds in the crystal packing of the title compound and the molecules are assembled into a 3–D structure by C—H···π interactions only. These interactions are formed in between 4-picoline C12 atoms and centroids (cg) of 2-quinaldate pyridine rings N1/C1/C2/C3/C4/C9 (C···cg, 3.857(4) Å; C—H···Cg, 168°). There are only three structurally related cadmium(II) complexes with *N,O*-chelating 2-quinaldate known from the literature, containing either water molecules (in *cis*-position) [9] or DMSO molecules [5] or 4-(1-naphthylvinyl)pyridine [11] molecules in *trans*-position. Consequently, the Cd—N and Cd—O bond lengths (N and O atoms from 2-quinaldate) are comparable not only to the corresponding bond lengths in those compounds, but also in cadmium(II) complexes with picolinate [12], 6-methylpicolinate [13, 14], 3-hydroxypicolinate [15, 16] and 5-hydroxypicolinate [17] ligands.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: This research was funded by the Ministry of Science, Education and Sports of the Republic of Croatia (grant no. 119–1193079–1332) and the open access paper charge was funded by the Faculty of Chemistry and Technology, University of Split institutional funding.
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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