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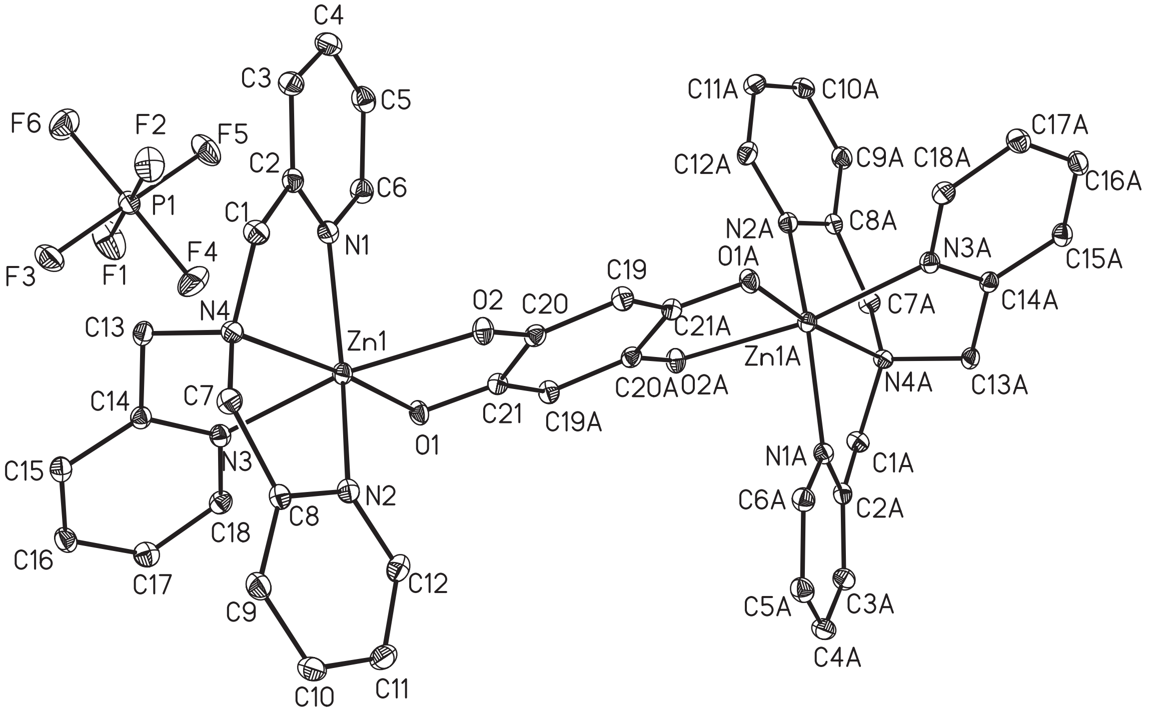
Crystal structure of (3,6-dioxocyclohexa-1,4-diene-1,4-bis(olato)-κ^4*O*,*O′*:*O″*,*O‴*)-bis(tris(2-pyridylmethyl)amine-κ^4*N*,*N′*,*N″*,*N‴*))-dizinc(II) bis(hexafluorophosphate(V)), $C_{42}H_{38}F_{12}N_8O_4P_2Zn_2$



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Abstract

$C_{42}H_{38}F_{12}N_8O_4P_2Zn_2$, monoclinic, $P2_1/c$ (no. 14), $a = 11.470(2)$ Å, $b = 16.221(3)$ Å, $c = 11.548(2)$ Å, $\beta = 91.03(3)°$, $V = 2148.3(7)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0365$, $wR_{ref}(F^2) = 0.0905$, $T = 123(2)$ K.

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The cationic title complex together with the counter anion is shown in the figure (symmetry code: A = 2−*x*, −*y*, 2−*z*). Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Brown block
Size:	0.10 × 0.08 × 0.06 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	13.0 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{max}$, completeness:	55.2°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	20116, 4916, 0.039
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4638
$N(param)_{refined}$:	317
Programs:	SHELX [1], PLATON [2], Bruker programs [3],

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Source of material

The title complex was prepared as following procedures: a methanolic solution (10.0 mL) of the ligand tri(2-pyridylmethyl)amine (TPA) (0.2 mmol) was added into a MeOH solution (10 mL) of $ZnCl_2$ (0.2 mmol). Then, 2,5-dihydroxy-1,4-benzoquinone (DHBQ, 0.1 mmol) and triethylamine (0.4 mmol) as well as $NaPF_6$ (0.2 mmmol) were added into the above mentioned mixture. The mixture was refluxed for 1 h, it was filtered and the resulting solution was kept at room temperature for about several days, producing brown block shaped crystals of the title compound with a yield of 82.0%. Elemental analysis calculated for $C_{42}H_{38}F_{12}N_8O_4P_2Zn_2$: C, 44.27%; H, 3.36%; N, 9.83%; found: C, 44.32%; H, 3.31%; N, 9.88%.

Experimental details

All H atoms bond to C atoms were introduced using the HFIX command in the SHELXL program [1], with the value of 0.93 Å or 0.96 Å for C—H bond distances. All H atoms were allowed for as riding atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for hydrogen atoms. The structure was checked using PLATON [2].

Comment

It is well known that the design and synthesis of molecule-based functional materials with interesting topological molecular structures and novel properties have been paid much attentions in the past several decades [4–7]. Up to date, a larger number of new compounds have been prepared and their structures have been investigated in detail, especially their crystal structures have been determined through single crystal X-ray diffraction technique, which provides important basis for the clear elucidation of new phenomenon and full establishment of relationship between structure and property. Futhermore, some new important scientific results involving magnetic, optical, catalytic and electric properties and pure structure science have been reported [8–10]. For the design of new complexes the selection of suitable coordination ligands and the central metal ions as well as the bridging ligands usually play important roles. Multi-nitrogen organic compounds are common ligands which have been widely investigated. In these tris(2-pyridylmethyl)amine ligand (TPA) four nitrogen atoms have been usually exploited as capping tetradentate ligands for assembling low-dimensional complexes [11–13]. In addition, 2,5-dihydroxy-1,4-benzoquinone (DHBQ) and its derivatives can be employed as the bridging ligands [14, 15]. Herein, we report the crystal structure of a new 2,5-dioxy-1,4-benzoquinone-bridged binuclear complex $C_{42}H_{38}F_{12}N_8O_4P_2Zn_2$ using TPA terminal capping ligand.

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

Atom	x	y	z	$U_{\text{iso}}{}^*/U_{\text{eq}}$
Zn1	0.840189(19)	0.076767(13)	0.711571(18)	0.01657(9)
P1	0.38403(5)	0.08552(3)	0.78740(5)	0.02214(13)
F1	0.32313(17)	0.15444(10)	0.86378(14)	0.0519(5)
F2	0.44543(13)	0.01763(9)	0.70837(12)	0.0364(3)
F3	0.37593(15)	0.14588(8)	0.67702(12)	0.0403(4)
F4	0.50830(14)	0.12388(11)	0.82069(14)	0.0486(4)
F5	0.39376(14)	0.02541(9)	0.89594(11)	0.0392(4)
F6	0.26042(13)	0.04717(11)	0.75133(14)	0.0436(4)
N1	0.72189(14)	−0.02089(10)	0.73550(14)	0.0182(3)
N2	0.97244(14)	0.13182(10)	0.60921(14)	0.0185(3)
N3	0.73628(14)	0.18529(10)	0.67050(14)	0.0179(3)
N4	0.77588(14)	0.04880(10)	0.53041(13)	0.0165(3)
C1	0.75156(18)	−0.04034(12)	0.52928(17)	0.0201(4)
H1A	0.8233	−0.0703	0.5164	0.024*
H1B	0.6977	−0.0530	0.4660	0.024*
C2	0.69974(17)	−0.06798(12)	0.64217(17)	0.0185(4)
C3	0.63657(18)	−0.14046(12)	0.64886(18)	0.0225(4)
H3	0.6211	−0.1716	0.5827	0.027*
C4	0.59659(18)	−0.16590(13)	0.75589(19)	0.0253(4)
H4	0.5544	−0.2146	0.7626	0.030*
C5	0.62045(18)	−0.11788(13)	0.85231(18)	0.0243(4)
H5	0.5952	−0.1339	0.9250	0.029*
C6	0.68276(17)	−0.04541(13)	0.83860(18)	0.0220(4)
H6	0.6979	−0.0126	0.9032	0.026*
C7	0.86314(18)	0.07390(12)	0.44532(17)	0.0201(4)
H7A	0.8235	0.0988	0.3792	0.024*
H7B	0.9037	0.0253	0.4182	0.024*
C8	0.95180(16)	0.13461(12)	0.49463(17)	0.0183(4)
C9	1.01453(18)	0.18676(13)	0.42339(18)	0.0240(4)
H9	0.9993	0.1880	0.3440	0.029*
C10	1.10015(19)	0.23688(13)	0.4723(2)	0.0278(5)
H10	1.1419	0.2731	0.4264	0.033*
C11	1.12267(18)	0.23240(13)	0.5900(2)	0.0266(4)
H11	1.1806	0.2648	0.6244	0.032*
C12	1.05761(17)	0.17906(13)	0.65541(18)	0.0226(4)
H12	1.0732	0.1756	0.7346	0.027*
C14	0.67972(16)	0.18154(12)	0.56769(16)	0.0172(4)
C13	0.66592(17)	0.09603(12)	0.51756(17)	0.0193(4)
H13A	0.6040	0.0673	0.5570	0.023*
H13B	0.6443	0.1000	0.4362	0.023*
C15	0.63544(17)	0.25110(12)	0.51242(17)	0.0205(4)
H15	0.5972	0.2467	0.4410	0.025*
C16	0.64919(17)	0.32732(13)	0.56570(18)	0.0228(4)
H16	0.6214	0.3750	0.5300	0.027*
C17	0.70498(18)	0.33115(13)	0.67285(18)	0.0239(4)
H17	0.7138	0.3813	0.7111	0.029*
C18	0.74750(17)	0.25896(12)	0.72232(17)	0.0204(4)
H18	0.7852	0.2618	0.7942	0.024*
C19	1.04370(18)	−0.07384(12)	0.94386(17)	0.0194(4)
H19	1.0702	−0.1213	0.9076	0.023*
C20	0.98441(16)	−0.01355(12)	0.87799(16)	0.0180(4)
C21	0.93671(16)	0.06383(12)	0.93883(17)	0.0181(4)
O1	0.88071(12)	0.11481(9)	0.87468(12)	0.0204(3)
O2	0.96676(12)	−0.01778(9)	0.77056(11)	0.0203(3)

The asymmetric unit consists of half of a cationic complex and one hexafluorophosphate anion. In the dinuclear title Zn(II) complex $DHBQ^{2-}$ acts as bridging and tetradentate TPA as the terminal capping ligand. Its structure consists of the cationic $[Zn_2(TPA)_2(DHBQ)]^{2+}$ unit and two PF_6^- as the counter anions. The Zn(II) ion in the title complex is six-coordinated by four nitrogen atoms from the capping ligand TPA and two oxygen atoms of $DHBQ^{2-}$ ligand at two *cis* positions, forming a distorted octahedral coordination geometry. The $Zn—N_{pyridine}$ bond lengths are very similar and are within the narrow scope of 2.1073(17) to 2.1735(16) Å, which are slightly shorter than that of the $Zn—N_{amine}$ bond length of 2.2519(16) Å [12]. The Zn—O bond length is 2.0282(14) Å, which is significantly shorter than those of the neighboring $Zn—O_{benzoquinone}$ bond length (2.2111(14) Å) [13]. The two C—O bond lengths are 1.255(2) Å and 1.276(2) Å, respectively. The three important bond angles around the Zn(II) ion are 169.58(6)° for O2—Zn1—N3, 171.84(6)° for O1—Zn1—N4 and 148.48(6)° for N1—Zn1—N2. The bond angle of O1—Zn1—O2 is 77.68(6)°. The above mentioned bond parameters clearly indicate that the Zn(II) ion adopts significantly distorted octahedral geometry. All the bond parameters in the title complex are comparable with those of complex $C_{25}H_{22}Cl_2N_4O_5Zn$ [16].

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