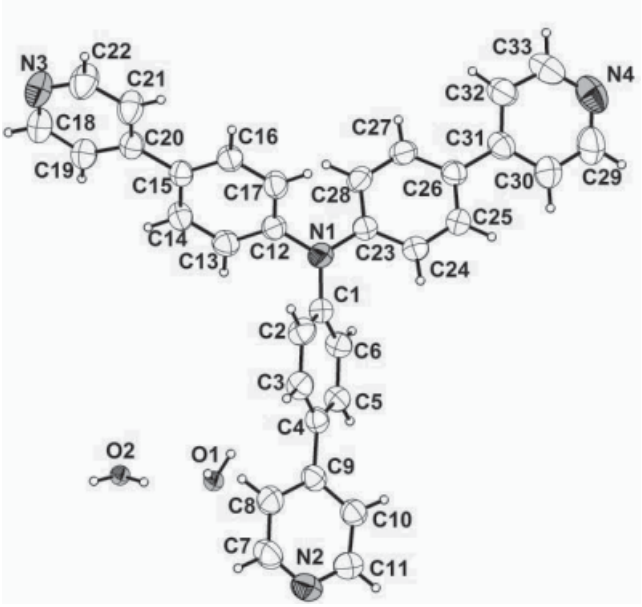
Crystal structure of tris(4-(pyridin-4-yl)phenyl)amine dihydrate, $(C_{33}H_{24}N_4)\cdot 2(H_2O)$, $C_{33}H_{28}N_4O_2$

Lei Cao[I], Le Zhou[*, I], Guo-Hui Kang[II], Chuan-Sheng Ruan[II] and Bao-Ming Ji[III]

[I] College of Science, Northwest Agriculture and Forestry University, YangLing 712100, Shaanxi Province, P. R. China
[II] College of Chemistry and Molecular Engineering, Zheng Zhou University, Zheng Zhou 450001, Henan Province, P. R. China
[III] College of Chemistry and Chemical Engineering, Luo Yang Normal University, Luo Yang 471022, Henan Province, P. R. China

Received January 11, 2013, accepted April 09, 2013, available online June 28, 2013, CCDC no. 1267/3998



Abstract

$C_{33}H_{28}N_4O_2$, monoclinic, $P2_1/c$ (no. 14), a = 10.263(8) Å, b = 23.48(2) Å, c = 12.28(1) Å, β = 114.498(9)°, V = 2692.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.0451, $wR_{ref}(F^2)$ = 0.1189, T = 296 K.

Table 1. Data collection and handling.

Crystal:	yellow blocks, size 0.17×0.25×0.33 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.80 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	20298, 5002
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3657
$N(param)_{refined}$:	352
Programs:	SHELX [8]

Source of material

To a mixture of tris(4-iodo- phenyl)amine (3.115 g, 5 mmol), $Pd(PPh_3)_4$ (0.578 g, 0.5 mmol), pyridine-4-boronic acid (2.215 g, 18 mmol), 1 M Cs_2CO_3 (15 mL, 15 mmol) and 1,4-dioxane (45 mL) were degassed with a steady stream of N_2 for 15 min at room temperature. The reaction mixture was then heated to reflux for 24 h under N_2. After cooling to room temperature, the reaction mixture was extracted by $CHCl_3$ (3 × 100 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by silica gel column chromatography with EtOAc as eluent to give the target compound as yellow solid (1.856 g, 77.82%). The single crystal for the X-ray diffraction study was obtained from a chloroform solution.

* Correspondence author (e-mail: zhoulechem@yahoo.com.cn)

Experimental details

All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were assigned with common isotropic displacement factors U_{iso}(H) = 1.2 U_{eq}(C) or 1.5 U_{eq}(O), and included in the final refinement by using geometrical restraints, with C–H distances of 0.93 Å.

Discussion

The N-centered triangular ligands have played an important role in metal-organic frameworks (MOFs) not only beacause they can more easily meet with geometric requirement of metal ions but also they can serve as 3-connected nodes that are prone to form aesthetic topogical structures [1-6]. As a N-centered triangular ligand, tris(4-(pyridin-4-yl)phenyl)amine have been used in building MOFs with outstanding properties [7]. A view of the molecular structure of the title compound is given in the figure. The asymmetric unit of the title compound contains one tris(4-(pyridin-4-yl)phenyl)amine molecule and two water molecules. The dihedral angles between the phenyl rings are 80.3(1)°, 67.4(2)°, 63.7(2)°, respectively. The average dihedral angles between the phenyl rings and its adjacent pyridinyl rings are 41.9(1)°, 10.1(1)°, 21.1(1)°, respectively. The C–$N_{central}$–C angles are 120.55°, 117.49°, 121.91°, respectively. The short $N_{central}$–C bond lengths are 1.426(2) Å, 1.431(2) Å, 1.406(2) Å, respectively. Two tris(4-(pyridin-4-yl)phenyl)amine molecules are connected into dimers by four water molecules through two intermolecular O–H···N hydrogen bonds and one intermolecular O–H···O hydrogen bond: O2–H4W···O1 (d(H4W···O1) = 2.09 Å, d(O2···O1) = 2.907 Å, and the angle of O2–H4W···O1 is 162.4°); O2–H3W···N3 (d(H3W···N3) = 2.09 Å, d(O2···N3) = 2.890 Å, and the angle of O2–H3W···N3 is 156.4°); O1–H2W···N4 (d(H2W···N4) = 2.05 Å, d(O1···N4) = 2.884 Å, and the angle of O1–H2W···N4 is 169.0°). The dimers are further linked into a two-dimensional nets structure by intermolecular O–H···N hydrogen bonds: O1–H1W···N2 (d(H1W···N2) = 2.04 Å, d(O1···N2) = 2.872 Å, and the angle of O1–H1W···N2 is 167.4°).

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	4*e*	0.6960	0.2320	0.1556	0.059
H(3)	4*e*	0.8600	0.3048	0.2104	0.058
H(5)	4*e*	0.7316	0.3539	0.4626	0.051
H(6)	4*e*	0.5622	0.2824	0.4041	0.052
H(7)	4*e*	1.0554	0.4792	0.2595	0.076
H(8)	4*e*	0.8908	0.4072	0.2064	0.070

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(10)	4*e*	0.9932	0.3813	0.5546	0.059
H(11)	4*e*	1.1589	0.4522	0.5958	0.067
H(13)	4*e*	0.3595	0.2821	0.0764	0.059
H(14)	4*e*	0.2250	0.2733	–0.1261	0.058
H(16)	4*e*	0.3281	0.1084	–0.1078	0.056
H(17)	4*e*	0.4600	0.1167	0.0953	0.057
H(18)	4*e*	–0.0530	0.2494	–0.5047	0.075
H(19)	4*e*	0.0775	0.2614	–0.3046	0.063
H(21)	4*e*	0.2397	0.1058	–0.2955	0.073
H(22)	4*e*	0.1038	0.0995	–0.4959	0.085
H(24)	4*e*	0.6800	0.1758	0.4494	0.061

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(25)	4*e*	0.6414	0.1164	0.5806	0.063
H(27)	4*e*	0.2433	0.0863	0.3397	0.058
H(28)	4*e*	0.2785	0.1474	0.2090	0.057
H(29)	4*e*	0.5397	0.0266	0.8455	0.095
H(30)	4*e*	0.5775	0.0855	0.7146	0.080
H(32)	4*e*	0.2526	0.0086	0.4500	0.074
H(33)	4*e*	0.2232	–0.0466	0.5913	0.090
H(1W)	4*e*	0.2449	0.5403	0.4234	0.115
H(2W)	4*e*	0.3221	0.5504	0.3613	0.115
H(3W)	4*e*	0.0538	0.6485	0.2003	0.184
H(4W)	4*e*	0.1237	0.6229	0.2984	0.184

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4*e*	0.6106(2)	0.24972(7)	0.2733(1)	0.0429(9)	0.0420(9)	0.0392(9)	–0.0020(7)	0.0152(8)	0.0016(7)
C(2)	4*e*	0.7017(2)	0.25681(8)	0.2165(2)	0.053(1)	0.057(1)	0.042(1)	–0.0032(9)	0.0226(8)	–0.0079(8)
C(3)	4*e*	0.8006(2)	0.30042(8)	0.2500(2)	0.047(1)	0.060(1)	0.046(1)	–0.0022(8)	0.0253(8)	0.0001(8)
C(4)	4*e*	0.8136(2)	0.33796(7)	0.3415(1)	0.0390(9)	0.0424(9)	0.0419(9)	0.0032(7)	0.0162(8)	0.0060(7)
C(5)	4*e*	0.7236(2)	0.32993(7)	0.3999(1)	0.0460(9)	0.0410(9)	0.0429(9)	0.0009(7)	0.0214(8)	–0.0017(7)
C(6)	4*e*	0.6226(2)	0.28671(7)	0.3653(2)	0.0446(9)	0.0446(9)	0.047(1)	–0.0014(8)	0.0248(8)	–0.0010(8)
C(7)	4*e*	1.0439(2)	0.45876(9)	0.3198(2)	0.063(1)	0.063(1)	0.069(1)	–0.009(1)	0.031(1)	0.015(1)
C(8)	4*e*	0.9433(2)	0.41562(8)	0.2869(2)	0.055(1)	0.068(1)	0.051(1)	–0.009(1)	0.0191(9)	0.0097(9)
C(9)	4*e*	0.9206(2)	0.38485(7)	0.3744(2)	0.0407(9)	0.0430(9)	0.050(1)	0.0025(7)	0.0196(8)	0.0057(8)
C(10)	4*e*	1.0041(2)	0.40009(7)	0.4922(2)	0.053(1)	0.048(1)	0.049(1)	–0.0014(8)	0.0227(9)	0.0026(8)
C(11)	4*e*	1.1035(2)	0.44322(8)	0.5161(2)	0.055(1)	0.053(1)	0.058(1)	–0.0039(9)	0.0220(9)	–0.0053(9)
C(12)	4*e*	0.4225(2)	0.20027(7)	0.1074(1)	0.0441(9)	0.0460(9)	0.0395(9)	–0.0042(7)	0.0180(8)	0.0002(7)
C(13)	4*e*	0.3526(2)	0.24687(7)	0.0398(2)	0.060(1)	0.0396(9)	0.048(1)	–0.0007(8)	0.0232(9)	–0.0043(8)
C(14)	4*e*	0.2724(2)	0.24156(7)	–0.0822(2)	0.055(1)	0.044(1)	0.046(1)	0.0060(8)	0.0214(9)	0.0060(8)
C(15)	4*e*	0.2609(2)	0.18985(7)	–0.1407(1)	0.0396(9)	0.0453(9)	0.0392(9)	0.0012(7)	0.0196(7)	0.0031(7)
C(16)	4*e*	0.3334(2)	0.14351(7)	–0.0712(2)	0.056(1)	0.0419(9)	0.042(1)	0.0013(8)	0.0205(8)	–0.0022(8)
C(17)	4*e*	0.4129(2)	0.14835(7)	0.0510(2)	0.055(1)	0.0422(9)	0.043(1)	0.0068(8)	0.0169(8)	0.0041(8)
C(18)	4*e*	0.0065(2)	0.21983(9)	–0.4619(2)	0.058(1)	0.074(1)	0.050(1)	0.013(1)	0.016(1)	0.013(1)
C(19)	4*e*	0.0852(2)	0.22753(8)	–0.3407(2)	0.052(1)	0.056(1)	0.049(1)	0.0071(9)	0.0198(9)	0.0036(9)
C(20)	4*e*	0.1759(2)	0.18467(7)	–0.2723(1)	0.0429(9)	0.053(1)	0.0405(9)	0.0019(8)	0.0209(8)	0.0035(8)
C(21)	4*e*	0.1806(2)	0.13606(9)	–0.3353(2)	0.073(1)	0.064(1)	0.042(1)	0.017(1)	0.020(1)	–0.0003(9)
C(22)	4*e*	0.0976(2)	0.1327(1)	–0.4568(2)	0.084(2)	0.076(1)	0.045(1)	0.013(1)	0.021(1)	–0.008(1)
C(23)	4*e*	0.4834(2)	0.16855(7)	0.3141(1)	0.047(1)	0.0396(9)	0.0400(9)	–0.0027(7)	0.0162(8)	–0.0017(7)
C(24)	4*e*	0.5914(2)	0.15823(7)	0.4268(2)	0.043(1)	0.049(1)	0.051(1)	–0.0071(8)	0.0115(8)	0.0037(8)
C(25)	4*e*	0.5679(2)	0.12214(7)	0.5052(2)	0.051(1)	0.050(1)	0.046(1)	–0.0036(8)	0.0092(8)	0.0055(8)
C(26)	4*e*	0.4386(2)	0.09383(7)	0.4762(2)	0.053(1)	0.0390(9)	0.043(1)	–0.0024(8)	0.0202(8)	–0.0022(7)
C(27)	4*e*	0.3314(2)	0.10438(7)	0.3628(2)	0.049(1)	0.053(1)	0.044(1)	–0.0118(8)	0.0192(8)	–0.0070(8)
C(28)	4*e*	0.3526(2)	0.14099(7)	0.2838(2)	0.047(1)	0.055(1)	0.0357(9)	–0.0063(8)	0.0125(8)	–0.0038(8)
C(29)	4*e*	0.4798(3)	0.0231(1)	0.7646(2)	0.090(2)	0.093(2)	0.057(1)	0.006(2)	0.034(1)	0.018(1)
C(30)	4*e*	0.5039(2)	0.05890(9)	0.6860(2)	0.075(1)	0.073(1)	0.051(1)	–0.007(1)	0.024(1)	0.008(1)
C(31)	4*e*	0.4182(2)	0.05536(7)	0.5636(2)	0.061(1)	0.0417(9)	0.051(1)	0.0015(8)	0.0288(9)	–0.0007(8)
C(32)	4*e*	0.3125(2)	0.01391(8)	0.5304(2)	0.082(1)	0.050(1)	0.060(1)	–0.010(1)	0.036(1)	–0.0031(9)
C(33)	4*e*	0.2962(3)	–0.01962(9)	0.6168(2)	0.098(2)	0.053(1)	0.090(2)	–0.011(1)	0.057(2)	0.000(1)
N(1)	4*e*	0.5044(2)	0.20613(6)	0.2336(1)	0.0538(9)	0.0510(8)	0.0369(8)	–0.0123(7)	0.0150(7)	–0.0011(6)
N(2)	4*e*	1.1254(2)	0.47285(6)	0.4327(2)	0.056(1)	0.0502(9)	0.072(1)	–0.0046(7)	0.0295(9)	0.0019(8)
N(3)	4*e*	0.0098(2)	0.17315(8)	–0.5219(1)	0.067(1)	0.086(1)	0.0439(9)	0.011(1)	0.0149(8)	0.0026(9)
N(4)	4*e*	0.3775(2)	–0.01589(8)	0.7335(2)	0.104(2)	0.071(1)	0.077(1)	0.006(1)	0.056(1)	0.016(1)
O(1)	4*e*	0.2855(2)	0.56730(6)	0.4031(1)	0.094(1)	0.0626(9)	0.094(1)	–0.0250(8)	0.0601(9)	–0.0262(8)
O(2)	4*e*	0.0426(2)	0.6388(1)	0.2625(2)	0.102(1)	0.201(2)	0.075(1)	0.025(1)	0.047(1)	0.045(1)

References

1. Wu, H.; Liu, B.; Yang, J.; Liu, H. Y.; Ma, J. F.: A new type of entangled motif: from 2D polyrotaxane layers to a 3D polythreaded framework. CrystEngComm. **13** (2011) 3661-3664.
2. Wu, H.; Liu, H. Y.; Liu, Y. Y.; Yang, J.; Liu, B.; Ma, J. F.: An unprecedented 2D → 3D metal-organic polyrotaxane framework constructed from cadmium and a flexible star-like ligand. Chem. Commun. **47** (2011) 1818-1820.
3. Wu, H.; Yang, J.; Su, Z. M.; Batten, S. R.; Ma, J. F.: An Exceptional 54-Fold Interpenetrated Coordination Polymer with 10^3-srs Network Topology. J. Am. Chem. Soc. **133** (2011) 11406-11409.
4. Yao, X. Q.; Cao, D. P.; Hu, J. S.; Li, Y. Z.; Guo, Z. J.; Zheng, H. G.: Chiral and Porous Coordination Polymers Based on an N-Centered Triangular Rigid Ligand Cryst. Growth Des. **11** (2011) 231-239.
5. Pan, Z. R.; Xu, J.; Zheng, H. G.; Huang, K. X.;Li, Y. Z.; Guo, Z. J.; Batten, S. R.: Three New Heterothiometallic Cluster Polymers with Fascinating Topologies. Inorg. Chem. **48** (2009) 5772-5778.
6. Wu, H.; Liu, H. Y.; Liu, B.; Yang, J.; Liu, Y. Y.; Ma, J. F.; Liu, Y. Y.; Bai, H, Y.: Two unprecedented 3D metal-organic polyrotaxane frameworks based on a new flexible tri(imidazole) ligand. CrystEngComm. **13** (2011) 3402-3407.
7. Zhang, M, D.; Di, C, M.; Qin, L.; Yao, X, Q.; Li, Y, Z.; Guo, Z, J.; Zheng, H. G.: Diverse Structures of Metal-Organic Frameworks Based on a New Star-Like Tri(4-pyridylphenyl)amine Ligand. Cryst.Growth Des. **12** (2012) 3957-3963.
8. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.