Crystal structure of (μ-4,4′-bipyridine-*N*,*N*′)bis(*N*,*N*′-ethylene-bis(salicylaldiminato))dizinc(II) methanol disolvate, $Zn_2(C_{10}H_8N_2)(C_{16}H_{14}N_2O_2)_2 \cdot 2CH_3OH$

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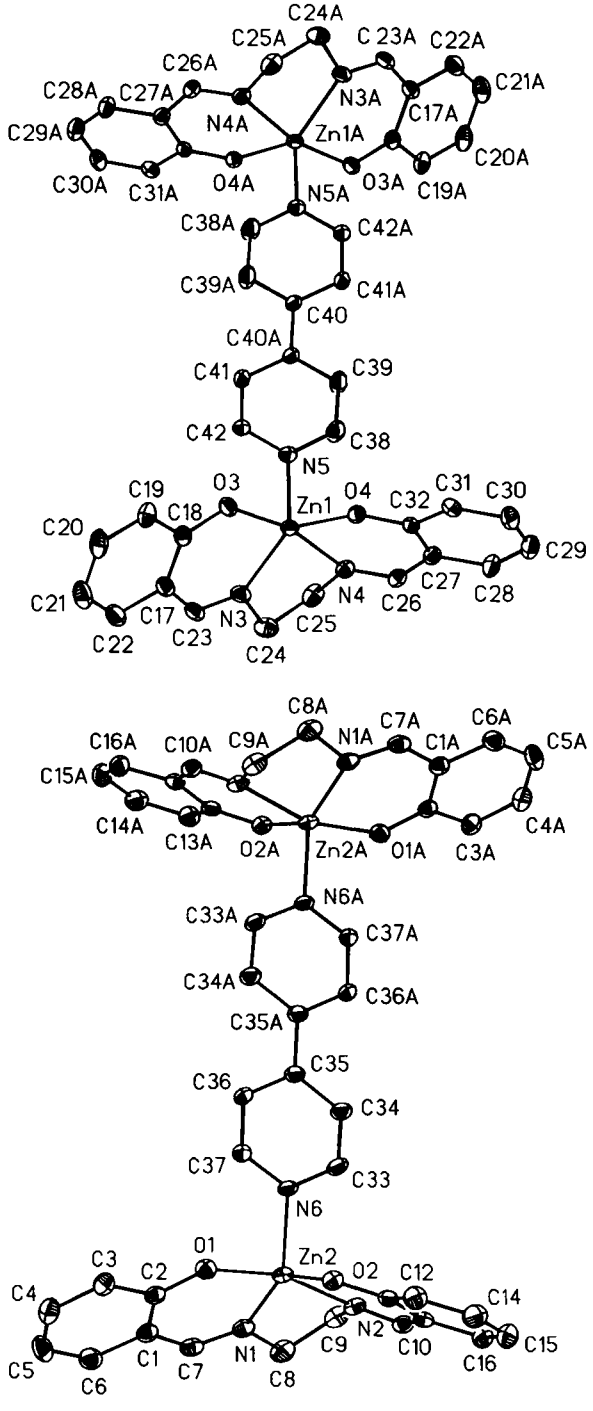

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Abstract

$C_{44}H_{44}N_6O_6Zn_2$, monoclinic, $P12_1/c1$ (no. 14), a = 8.954(1) Å, b = 21.265(3) Å, c = 21.770(3) Å, β = 92.272(2)°, V = 4142.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.079, $wR_{ref}(F^2)$ = 0.256, T = 291 K.

Source of material

$Zn(CH_3COO)_2 \cdot 4H_2O$ (0.122 g, 0.5 mmol) and NH_4SCN (0.192 g, 1 mmol) were refluxed in anhydrous methanol (10 mL) for 50 min and then was added 20 mL methanol solution of freshly distilled salicylaldehyde and ethylenediamine. The mixture was stirred for 3 h, then was added 10 mL methanol solution of 4,4′-bipyridine, further stirred for 2 h and then filtered. The resulting clear solution was diffused with diethyl ether vapor at room temperature for two weeks. Block-shaped yellow crystals were formed, collected by filtration and dried in air (yield 0.423 g, 48 %).
Elemental analysis – found: C, 59.82 %; H, 4.67 %; N, 9.60 %; calc. for $C_{44}H_{44}N_6O_6Zn_2$: C, 59.75 %; H, 4.98 %; N, 9.51 %.

Experimental details

While the hydroxyl H atom was refined, the other H atoms were added geometrically.

Discussion

The chemistry of metal complexes with multi-dentate ligands such as salicylaldehyde Schiff bases has gained much interest because of their use as models in biological systems and organic reactions, catalysis and making desirable the widest range of ways to modify liquid crystal compounds, nano-devices and machines [1-4]. Zinc is an essential element for human, which plays a central, if still only dimly understood, role in a number of healing processes probably acting as a convenient source of bioactive Zn^{2+} (aq). 4,4′-bipyridine is an excellent rodlike bifunctional ligand and has been extensively employed as the rigid organic building block for the construction of infinite 1D, 2D, 3D coordination polymeric frameworks [5-7]. The study of zinc(II) complex involving an aromatic Schiff base as the primary ligand, 4,4′-bipyridine as the secondary ligand acting as a bridging mode can serve as useful models for gaining a better understanding of enzyme-metal ion-substrate complexes that play an important role in metalloenzyme-catalyzed biochemical reactions.
The crystal structure of the complex is found to contain two discrete crystallographically independent dinuclear centrosymmetric zinc(II) complex units bridged through the 4,4′-bipyridine with a Zn···Zn separation of 11.28 Å (figure, top). Each Zn(II) ion is five-coordinated by three nitrogen and two oxygen atoms, forming a distorted square pyramid with the terminal nitrogen atom from 4,4′-bipyridine located at the apical position. Two nitrogen atoms are from the deprotonated ethylenediamine part, and two oxygen atoms from the salicylaldehyde hydroxyl group, which lead to one

five- and two six-membered rings around the Zn(II) ion. The salicylaldehyde Schiff base molecule exists as a dianion, acting as a bidentate chelate ligand. The atoms O1, O2, N1 and N2 form a square, and the central ion deviates by 0.470 Å from the mean plane of the four atoms. The bond lengths Zn2—O1, Zn2—O2, Zn1—O3 and Zn1—O4 are 1.979(5) Å, 1.991(5) Å, 1.977(5) Å, 1.992(4) Å, respectively, which are little shorter than those of Zn(II) complexes of two salicylaldehyde amino acid Schiff bases [8]. The bond lengths Zn2—N1, Zn2—N2, Zn1—N3 and Zn1—N4 are 2.097(6) Å, 2.104(6) Å, 2.086(6) Å and 2.105(6) Å, respectively. While the bond length Zn2—N6 is 2.100(5) Å, which is close to those of Zn—N (from the base-square) and to the apical Zn—N bond found in zinc(II) complexes of $[Zn(Him_2Py)(N_3)_2]_2$ with an N5 donor group [9], but is longer than those in some other Zn(II) complexes [10]. The angles N6–Zn2–N2, N1–Zn2–N6 and O1–Zn2–N6 are 98.5(2)°, 96.7(2)°, and 111.3(2)°, respectively. The dihedral angle between the plane of C33-C34-C35-C36-C37-N6 and the plane of C1-C2-C3-C4-C5-C6 is 100.2°. Zn(II) ion maximum deviations of above the mean plane of C1-C2-C3-C4-C5-C6 and plane of C12-C13-C14-C15-C16-C17 are both 0.062 Å.

Two methanol molecules were connected to two oxygen atoms from the salicylaldehyde hydroxyl group via the hydrogen bonds, O6–H6′···O4, and O5–H6···O2, the bond lengths and angles are both 2.755(9) Å, 153(15)°. The two adjacent 4,4′-bipyridine plane in the same layer are almost perpendicular, on closer inspection, the distance between the two nearest parallel bipyridine ring centroids is found to be 21.77 Å, thus, there is no significant interactions between the ligands.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.17 × 0.24 × 0.31 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	12.14 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	23974, 9424
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 6093
$N(param)_{refined}$:	530
Programs:	SHELXS-97 [11], SHELXL-97 [12]

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

Atom	Site	x	y	z	U_{iso}
H(5)	4e	0.1490	0.8554	0.8887	0.247
H(3)	4e	1.0443	0.7219	1.0008	0.075
H(4)	4e	1.0327	0.6203	1.0350	0.087
H(5A)	4e	0.8625	0.5500	0.9922	0.099
H(6A)	4e	0.7004	0.5829	0.9149	0.089
H(7)	4e	0.5969	0.6566	0.8473	0.072
H(8A)	4e	0.4420	0.7285	0.7925	0.087
H(8B)	4e	0.5729	0.7239	0.7467	0.087
H(9A)	4e	0.4684	0.8183	0.7242	0.080
H(9B)	4e	0.4506	0.8348	0.7941	0.080
H(10)	4e	0.6545	0.8721	0.6848	0.065
H(13)	4e	1.1911	0.9162	0.7843	0.083
H(14)	4e	1.2337	0.9676	0.6942	0.098
H(15)	4e	1.0472	0.9748	0.6178	0.100
H(16)	4e	0.8230	0.9321	0.6310	0.082
H(19)	4e	0.5160	1.0077	0.2894	0.079
H(20)	4e	0.5360	1.0340	0.3905	0.094
H(21)	4e	0.3862	0.9861	0.4619	0.105
H(22)	4e	0.2245	0.9084	0.4304	0.085
H(23)	4e	0.1023	0.8487	0.3568	0.071
H(24A)	4e	−0.0651	0.7958	0.2859	0.093
H(24B)	4e	0.0695	0.7483	0.2876	0.093
H(25A)	4e	−0.0487	0.7281	0.1949	0.083
H(25B)	4e	−0.0740	0.8000	0.1810	0.083
H(26)	4e	0.1268	0.6892	0.1364	0.062
H(28)	4e	0.2859	0.6377	0.0717	0.083
H(29)	4e	0.5038	0.6257	0.0229	0.095
H(30)	4e	0.6892	0.7009	0.0362	0.094
H(31)	4e	0.6548	0.7882	0.0950	0.071
H(33)	4e	0.6075	0.9457	0.8393	0.079
H(34)	4e	0.4950	1.0184	0.8982	0.079
H(36)	4e	0.6084	0.9161	1.0462	0.099
H(37)	4e	0.7141	0.8444	0.9826	0.085
H(38)	4e	0.1892	0.8495	0.0598	0.123
H(39)	4e	0.0951	0.9066	−0.0222	0.128
H(41)	4e	−0.0095	1.0422	0.0936	0.067
H(42)	4e	0.0921	0.9820	0.1728	0.065
H(43A)	4e	0.3809	0.8018	0.9347	0.169
H(43B)	4e	0.2719	0.7579	0.8963	0.169
H(43C)	4e	0.2152	0.7934	0.9540	0.169
H(44A)	4e	0.8216	0.9410	0.2026	0.160
H(44B)	4e	0.7288	0.8966	0.2440	0.160
H(44C)	4e	0.6506	0.9533	0.2099	0.160
H(6′)	4e	0.62(2)	0.859(7)	0.168(4)	0.2(1)

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}
Zn(1)	4e	0.25208(8)	0.85522(3)	0.19319(3)	0.0447(4)	0.0405(4)	0.0409(4)	−0.0016(3)	0.0058(3)	0.0060(3)
Zn(2)	4e	0.77805(8)	0.82198(4)	0.85011(3)	0.0411(4)	0.0543(5)	0.0413(4)	−0.0011(3)	0.0033(3)	−0.0140(3)
O(1)	4e	0.8896(5)	0.7754(2)	0.9159(2)	0.055(3)	0.055(3)	0.058(3)	−0.005(2)	−0.006(2)	−0.006(2)
O(2)	4e	0.9573(5)	0.8644(2)	0.8180(2)	0.047(2)	0.059(3)	0.052(3)	−0.008(2)	0.002(2)	−0.004(2)
O(3)	4e	0.3546(6)	0.9253(2)	0.2370(2)	0.068(3)	0.058(3)	0.047(3)	−0.012(2)	0.014(2)	−0.006(2)
O(4)	4e	0.4268(5)	0.8209(2)	0.1503(2)	0.050(2)	0.044(2)	0.050(3)	−0.006(2)	0.009(2)	−0.003(2)
O(5)	4e	0.236(1)	0.8466(7)	0.8829(6)	0.095(6)	0.26(1)	0.141(9)	−0.036(8)	−0.016(6)	0.06(1)
O(6)	4e	0.695(1)	0.8848(5)	0.1589(5)	0.110(6)	0.133(7)	0.137(8)	−0.042(6)	0.043(6)	−0.045(6)
N(1)	4e	0.6455(6)	0.7419(3)	0.8340(3)	0.047(3)	0.069(4)	0.050(3)	−0.009(3)	−0.004(2)	−0.015(3)
N(2)	4e	0.6624(6)	0.8448(3)	0.7671(3)	0.044(3)	0.069(4)	0.046(3)	0.005(3)	0.002(2)	−0.015(3)
N(3)	4e	0.1321(7)	0.8373(3)	0.2715(3)	0.056(3)	0.061(4)	0.054(4)	−0.010(3)	0.015(3)	0.008(3)
N(4)	4e	0.1378(6)	0.7719(3)	0.1685(3)	0.043(3)	0.046(3)	0.063(4)	−0.003(2)	0.006(2)	0.004(3)
N(5)	4e	0.1468(7)	0.9091(3)	0.1241(3)	0.065(3)	0.045(3)	0.043(3)	0.005(3)	−0.002(2)	0.006(2)
N(6)	4e	0.6701(6)	0.8874(3)	0.9054(3)	0.058(3)	0.051(3)	0.043(3)	0.001(3)	0.013(2)	−0.014(2)
C(1)	4e	0.7720(8)	0.6741(4)	0.9087(3)	0.052(4)	0.063(4)	0.052(4)	−0.007(3)	0.015(3)	−0.006(3)
C(2)	4e	0.8769(7)	0.7171(3)	0.9342(3)	0.047(3)	0.060(4)	0.045(4)	−0.002(3)	0.014(3)	−0.007(3)
C(3)	4e	0.9742(8)	0.6946(4)	0.9826(4)	0.055(4)	0.076(5)	0.059(5)	−0.003(4)	0.007(3)	0.002(4)
C(4)	4e	0.9673(9)	0.6334(4)	1.0033(4)	0.064(5)	0.089(6)	0.066(5)	0.008(4)	0.008(4)	0.019(5)
C(5)	4e	0.866(1)	0.5913(4)	0.9780(5)	0.087(6)	0.059(5)	0.103(8)	−0.001(5)	0.025(6)	0.024(5)
C(6)	4e	0.770(1)	0.6112(4)	0.9319(4)	0.084(6)	0.064(5)	0.077(6)	−0.015(4)	0.019(5)	−0.008(4)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(7)	4e	0.6614(8)	0.6887(4)	0.8602(4)	0.053(4)	0.067(5)	0.061(5)	−0.017(3)	0.011(3)	−0.020(4)
C(8)	4e	0.5366(9)	0.7468(4)	0.7816(4)	0.063(5)	0.091(6)	0.063(5)	−0.020(4)	−0.013(4)	−0.014(4)
C(9)	4e	0.5148(8)	0.8147(4)	0.7651(4)	0.040(3)	0.100(6)	0.060(5)	−0.001(4)	−0.003(3)	−0.009(4)
C(10)	4e	0.7158(8)	0.8703(3)	0.7203(3)	0.050(4)	0.062(4)	0.050(4)	0.015(3)	0.001(3)	−0.009(3)
C(11)	4e	0.8621(8)	0.8968(3)	0.7171(3)	0.065(4)	0.042(3)	0.051(4)	0.013(3)	0.011(3)	−0.008(3)
C(12)	4e	0.9749(8)	0.8921(3)	0.7656(3)	0.059(4)	0.043(3)	0.052(4)	0.003(3)	0.009(3)	−0.010(3)
C(13)	4e	1.1145(9)	0.9191(4)	0.7543(4)	0.066(5)	0.068(5)	0.074(5)	−0.016(4)	0.007(4)	−0.006(4)
C(14)	4e	1.141(1)	0.9497(4)	0.7001(5)	0.091(6)	0.077(6)	0.078(6)	−0.029(5)	0.022(5)	−0.011(5)
C(15)	4e	1.029(1)	0.9540(4)	0.6543(5)	0.105(7)	0.075(6)	0.071(6)	0.002(5)	0.026(5)	0.011(5)
C(16)	4e	0.896(1)	0.9288(4)	0.6623(4)	0.079(5)	0.067(5)	0.059(5)	0.011(4)	0.014(4)	0.003(4)
C(17)	4e	0.2657(8)	0.9105(4)	0.3392(3)	0.055(4)	0.066(4)	0.045(4)	0.014(3)	0.005(3)	0.002(3)
C(18)	4e	0.3564(7)	0.9395(3)	0.2951(3)	0.047(3)	0.054(4)	0.052(4)	0.009(3)	0.001(3)	−0.007(3)
C(19)	4e	0.4566(9)	0.9870(4)	0.3172(4)	0.057(4)	0.060(4)	0.082(5)	0.007(3)	0.006(4)	−0.019(4)
C(20)	4e	0.468(1)	1.0032(5)	0.3776(5)	0.068(5)	0.083(6)	0.083(6)	0.008(4)	−0.019(5)	−0.037(5)
C(21)	4e	0.379(1)	0.9742(5)	0.4207(4)	0.095(7)	0.107(8)	0.058(5)	0.028(6)	−0.017(5)	−0.028(5)
C(22)	4e	0.282(1)	0.9285(4)	0.4016(4)	0.081(5)	0.085(6)	0.047(4)	0.016(5)	0.004(4)	0.000(4)
C(23)	4e	0.1589(8)	0.8629(4)	0.3247(3)	0.062(4)	0.074(5)	0.043(4)	0.003(4)	0.015(3)	0.008(3)
C(24)	4e	0.027(1)	0.7848(4)	0.2666(4)	0.071(5)	0.076(6)	0.089(7)	−0.023(4)	0.030(5)	0.012(5)
C(25)	4e	−0.0047(8)	0.7696(4)	0.1992(4)	0.045(4)	0.057(4)	0.105(7)	−0.006(3)	0.009(4)	−0.003(4)
C(26)	4e	0.1869(8)	0.7248(3)	0.1394(3)	0.053(4)	0.042(3)	0.059(4)	−0.003(3)	−0.002(3)	−0.002(3)
C(27)	4e	0.3282(8)	0.7227(3)	0.1108(3)	0.056(4)	0.045(3)	0.051(4)	0.005(3)	−0.003(3)	−0.001(3)
C(28)	4e	0.358(1)	0.6689(4)	0.0756(4)	0.076(5)	0.052(4)	0.079(6)	0.007(4)	0.008(4)	−0.014(4)
C(29)	4e	0.489(1)	0.6609(4)	0.0472(5)	0.093(6)	0.060(5)	0.086(6)	0.010(5)	0.018(5)	−0.016(4)
C(30)	4e	0.599(1)	0.7064(4)	0.0550(4)	0.088(6)	0.076(6)	0.074(6)	0.009(5)	0.036(5)	−0.012(5)
C(31)	4e	0.5777(9)	0.7591(4)	0.0899(3)	0.067(4)	0.063(4)	0.050(4)	0.000(3)	0.020(3)	0.004(3)
C(32)	4e	0.4412(7)	0.7699(3)	0.1179(3)	0.058(4)	0.044(3)	0.033(3)	0.008(3)	0.000(3)	0.003(3)
C(33)	4e	0.6061(9)	0.9394(4)	0.8816(3)	0.082(5)	0.074(5)	0.040(4)	0.024(4)	0.005(3)	−0.010(3)
C(34)	4e	0.5390(9)	0.9833(4)	0.9169(3)	0.079(5)	0.068(5)	0.051(4)	0.027(4)	0.003(4)	−0.011(4)
C(35)	4e	0.5350(8)	0.9765(3)	0.9798(3)	0.068(4)	0.050(4)	0.050(4)	−0.004(3)	0.014(3)	−0.009(3)
C(36)	4e	0.605(1)	0.9230(4)	1.0040(4)	0.149(9)	0.060(5)	0.041(4)	0.025(5)	0.033(5)	0.000(3)
C(37)	4e	0.669(1)	0.8801(4)	0.9654(4)	0.112(7)	0.053(4)	0.049(4)	0.022(4)	0.018(4)	0.000(3)
C(38)	4e	0.148(1)	0.8888(4)	0.0670(4)	0.18(1)	0.065(5)	0.058(5)	0.060(6)	−0.024(6)	0.002(4)
C(39)	4e	0.091(2)	0.9229(4)	0.0173(4)	0.21(1)	0.066(5)	0.046(5)	0.063(7)	−0.022(6)	−0.007(4)
C(40)	4e	0.0299(8)	0.9808(3)	0.0265(3)	0.070(4)	0.036(3)	0.043(3)	0.004(3)	−0.004(3)	0.002(3)
C(41)	4e	0.0304(8)	1.0028(3)	0.0854(3)	0.074(5)	0.044(3)	0.051(4)	0.017(3)	0.003(3)	−0.002(3)
C(42)	4e	0.0908(8)	0.9660(3)	0.1330(3)	0.072(4)	0.046(3)	0.045(4)	0.007(3)	0.001(3)	0.003(3)
C(43)	4e	0.279(1)	0.7960(7)	0.9198(6)	0.105(8)	0.14(1)	0.098(9)	−0.023(8)	0.015(7)	−0.011(8)
C(44)	4e	0.726(1)	0.9215(6)	0.2072(6)	0.112(8)	0.106(8)	0.105(9)	−0.031(7)	0.028(7)	−0.035(7)

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