Redetermination of the crystal structure of aqua-methanol-bis[μ_2-*N*-(3-carboxylsalicylidene)-*N'*-(salicylaldehyde)-1,2-ethylenediamine-*N*,*N'*,*O*,*O*,*O'*,*O'*]dicopper(II)-magnesium(II) — methanol (1:1), $[MgCu_2(H_2O)(CH_3OH)(C_{17}H_{13}N_2O_4)_2] \cdot CH_3OH$

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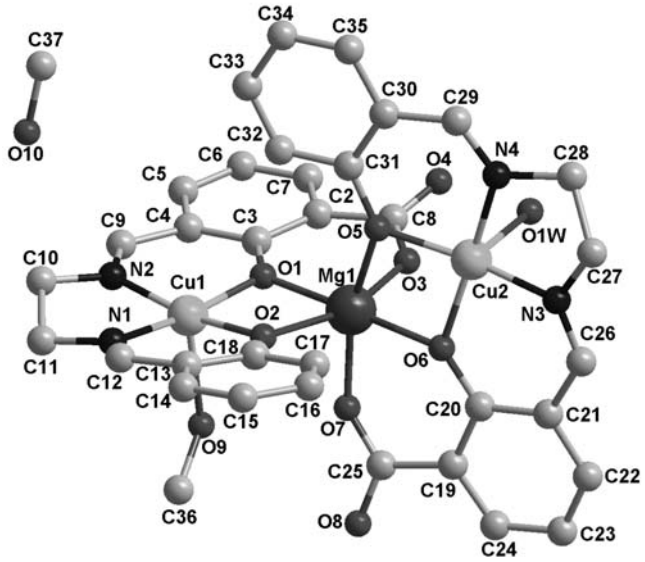

Abstract

$C_{36}H_{36}Cu_2MgN_4O_{11}$, monoclinic, $P12_1/c1$ (no. 14), a = 11.8256(2) Å, b = 15.4144(2) Å, c = 19.4318(3) Å, β = 98.041(1)°, V = 3507.3 Å^3, Z = 4, $R_{gt}(F)$ = 0.035, $wR_{ref}(F^2)$ = 0.082, T = 296 K.

Source of material

The radical mononuclear complex *N*-(3-carboxylsalicylidene)-*N'*-(salicylaldehyde-1,2-ethylenediamine)copper(II) (HCuL) was synthesized by the procedure in the literature [1]. After slow diffusion of ammonia gas into the reaction mixture of HCuL (0.03 mmol), magnesium chloride (0.015 mmol) and 5 ml methanol in a sealed system, red prismatic crystals were obtained after allowing the solution to stand at room temperature for several weeks. Chemical analysis — found: C, 51.01 %; H, 4.35 %; N, 6.63 %; calculated for $C_{36}H_{36}N_4O_{11}Cu_2Mg$: C, 50.74 %; H, 4.26 %; N, 6.57 %.

Experimental details

All the hydrogen atoms on C and O atoms of the methanol were located on the calculated positions with d(C—H) = 0.93 - 0.97 Å, U_{iso}(H) = 1.2 or 1.5 U_{eq}(C,O). The positions of the water H atoms were obtained from a difference Fourier map and refined freely.

Discussion

Schiff bases containing phenol oxygen groups are known to be versatile organic ligands, which can chelate as well as bridge metal ions to construct discrete and extended structures. On the other hand, a successful strategy in obtaining the desired spin topology is the "complex as ligand" approach. Thus the Schiff base mononuclear complexes containing phenol oxygen groups are particularly suitable for designing heterobimetallic complexes and have played an important role in the development of molecular magnetism [2-5]. The symmetrical double Schiff base ligands, resulting from the reaction of 3-carboxylsalicylaldehyde with different diamines easily yield discrete heterodinuclear complexes with the Cu(II) ion coordinated in the N_2O_2 site and the other one 3*d* or 4*f* cation in the O_2O_2 site [6-9]. However, owing to synthetic difficulties, only a few asymmetrical Schiff base complexes have been both structurally and magnetically characterized [10-12]. This observation prompted us to extend the synthesis, through stepwise processes, of ligands including an inner asymmetrical trianionic tetradentate N_2O_2 coordination site from the reaction of salicylaldehyde and 3-carboxylsalicylaldehyde with different diamines. In the previous paper, we have synthesized and characterized two asymmetrical double Schiff base-Cu(II) mononuclear complexes and their transition metal heterotrinuclear complexes through "the complex as ligand" approach [1,13]. We reported the space group of the title complex to be *Pc* [14]. Later, R. E. Marsh suggested, that the correct space group should be $P2_1/c$ [15]. Recently, we re-synthesized the title complex by diffusion method of ammonia gas different from the previous paper [14] and obtained better diffraction data.

The asymmetric unit of the title crystal structure consists of one heterotrinuclear neutral complex $[CuL(H_2O)]Mg[CuL(CH_3OH)]$ and one uncoordinated methanol molecule. The structure of the neutral trinuclear molecule is similar to those of the reported complexes [1] with four phenolato oxygen atoms acting as bridges between one central Mg(II) and two outer Cu(II) ions. The outer Cu ions have a classical square pyramidal environment N_2O_3 with an oxygen atom from a coordinated water or methanol molecule occupying the axial position. The Cu—N distances are in the range of 1.915(23) - 1.924(2) Å, while the Cu—O distances are in the range of 1.911(2) - 2.443(2) Å. The bond lengths of axial bonds Cu1—O9 (2.443 Å), Cu2—O1W (2.405 Å) are much longer than those of the equatorial bonds for the weaker coordination action of solvent molecules. The Cu1, Cu2 are pulled out of the equatorial planes by 0.164, 0.138 Å, respectively. In addition, the two equatorial planes of two outer Cu2 ions in the trinuclear

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molecule are almost perpendicular with the dihedral angle of 85.5°. The central Mg(II) ion is located in a distorted octahedral environment consisted by four phenolato oxygen and two carboxylic oxygen atoms from two terminal CuL^- moieties. The bond lengths between Mg(II) ion and four phenolato oxygen atoms (2.0881 - 2.1346 Å) are longer than that between Mg(II) ion and two carboxylate oxygen atoms (1.9983 -2.0699 Å). This result is similar to other heterometallic trinuclear Schiff base complexes probably because phenolato oxygen atoms are bridging [1].

Table 1. Data collection and handling.

Crystal:	red block, size 0.28 × 0.30 × 0.32 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	13.00 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ/ω
$2\theta_{max}$:	56.12°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	61281, 8462
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5994
$N(param)_{refined}$:	499
Programs:	SHELXS-97, SHELXL-97 [16]

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

Atom	Site	x	y	z	U_{iso}
H(10)	4*e*	0.3021	0.8383	0.1212	0.149
H(12)	4*e*	0.3219	0.6521	0.2737	0.056
H(9)	4*e*	0.4675	0.6050	–0.0137	0.057
H(17)	4*e*	0.7548	0.6499	0.3847	0.058
H(11A)	4*e*	0.2507	0.6325	0.1604	0.074
H(11B)	4*e*	0.2987	0.5389	0.1502	0.074
H(7)	4*e*	0.9347	0.6019	–0.0160	0.073
H(14)	4*e*	0.3693	0.6832	0.3899	0.066
H(15)	4*e*	0.4941	0.7027	0.4893	0.076
H(10A)	4*e*	0.3078	0.5966	0.0450	0.071
H(10B)	4*e*	0.3381	0.6895	0.0755	0.071
H(6)	4*e*	0.7877	0.5968	–0.1064	0.097
H(5)	4*e*	0.6035	0.5942	–0.0832	0.080
H(16)	4*e*	0.6883	0.6865	0.4859	0.072
H(29)	4*e*	1.0011	0.9444	0.3250	0.060
H(26)	4*e*	1.1634	0.6089	0.4836	0.057
H(22)	4*e*	1.1666	0.4611	0.4902	0.061
H(24)	4*e*	0.9468	0.3087	0.3748	0.053
H(23)	4*e*	1.1003	0.3249	0.4601	0.062
H(28A)	4*e*	1.1311	0.8919	0.4177	0.074
H(28B)	4*e*	1.1916	0.8285	0.3710	0.074
H(27A)	4*e*	1.2090	0.7553	0.4727	0.072
H(27B)	4*e*	1.0871	0.7837	0.4878	0.072
H(32)	4*e*	0.6863	0.7585	0.1718	0.061
H(34)	4*e*	0.7135	1.0163	0.1601	0.078
H(35)	4*e*	0.8636	1.0138	0.2476	0.069
H(33)	4*e*	0.6245	0.8881	0.1220	0.073
H(1WA)	4*e*	1.0871	0.6657	0.2229	0.068
H(36A)	4*e*	0.4932	0.4319	0.2573	0.101
H(36B)	4*e*	0.5537	0.3463	0.2387	0.101
H(36C)	4*e*	0.4402	0.3762	0.1934	0.101
H(37A)	4*e*	0.3009	0.9685	0.0912	0.131
H(37B)	4*e*	0.3912	0.9456	0.0421	0.131
H(37C)	4*e*	0.4264	0.9450	0.1229	0.131
H(1WB)	4*e*	1.138(2)	0.734(1)	0.240(1)	0.048(8)
H(9A)	4*e*	0.643(1)	0.443(2)	0.195(1)	0.07(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}
O(10)	4*e*	0.3359(3)	0.8469(2)	0.0878(1)	0.139(3)	0.072(2)	0.095(2)	0.010(2)	0.047(2)	–0.015(1)
Cu(1)	4*e*	0.55902(2)	0.60110(2)	0.17557(2)	0.0257(2)	0.0485(2)	0.0368(2)	0.0030(1)	0.0008(1)	0.0015(1)
Cu(2)	4*e*	0.97624(2)	0.70615(2)	0.33630(2)	0.0349(2)	0.0369(2)	0.0457(2)	–0.0039(1)	0.0006(1)	–0.0039(1)
Mg(1)	4*e*	0.81116(6)	0.59936(5)	0.23770(4)	0.0269(4)	0.0345(4)	0.0323(4)	0.0018(3)	0.0009(3)	0.0023(3)
O(1)	4*e*	0.7061(1)	0.6024(1)	0.14329(7)	0.0279(8)	0.0459(9)	0.0297(8)	0.0024(7)	0.0028(6)	0.0036(7)
O(2)	4*e*	0.6451(1)	0.6177(1)	0.26647(8)	0.0286(8)	0.0477(9)	0.0357(9)	0.0028(7)	0.0055(7)	–0.0021(7)
O(3)	4*e*	0.9380(1)	0.6000(1)	0.17969(8)	0.0312(9)	0.059(1)	0.0396(9)	0.0047(8)	0.0057(7)	0.0038(8)
O(6)	4*e*	0.9219(1)	0.5877(1)	0.32964(8)	0.0338(9)	0.0338(8)	0.0381(9)	0.0001(7)	–0.0021(7)	0.0029(7)
O(5)	4*e*	0.8493(1)	0.7278(1)	0.26612(9)	0.0356(9)	0.0303(8)	0.053(1)	0.0010(7)	0.0025(8)	0.0026(7)
N(2)	4*e*	0.4745(2)	0.6095(1)	0.0837(1)	0.032(1)	0.050(1)	0.046(1)	0.0013(9)	–0.0062(9)	0.006(1)
N(1)	4*e*	0.4132(2)	0.6172(1)	0.2062(1)	0.028(1)	0.056(1)	0.055(1)	0.0029(9)	0.001(1)	–0.004(1)
O(7)	4*e*	0.7936(1)	0.4705(1)	0.24648(8)	0.0405(9)	0.0368(9)	0.0409(9)	0.0010(7)	–0.0053(7)	0.0028(7)
N(3)	4*e*	1.0817(2)	0.6852(1)	0.4188(1)	0.039(1)	0.053(1)	0.043(1)	–0.007(1)	0.001(1)	–0.011(1)
O(8)	4*e*	0.7831(2)	0.3406(1)	0.2918(1)	0.049(1)	0.0361(9)	0.067(1)	–0.0054(8)	–0.0016(9)	0.0039(9)
N(4)	4*e*	1.0197(2)	0.8258(1)	0.3487(1)	0.042(1)	0.041(1)	0.060(1)	–0.009(1)	0.012(1)	–0.010(1)
O(4)	4*e*	1.0375(2)	0.6318(2)	0.0962(1)	0.040(1)	0.130(2)	0.057(1)	–0.016(1)	0.013(1)	0.006(1)
C(3)	4*e*	0.7279(2)	0.6007(1)	0.0783(1)	0.040(1)	0.031(1)	0.032(1)	–0.005(1)	0.004(1)	–0.0004(9)
C(2)	4*e*	0.8418(2)	0.6034(2)	0.0630(1)	0.042(1)	0.041(1)	0.036(1)	–0.010(1)	0.009(1)	–0.003(1)
C(4)	4*e*	0.6380(2)	0.5980(2)	0.0215(1)	0.045(2)	0.050(1)	0.035(1)	–0.013(1)	–0.001(1)	–0.000(1)
C(18)	4*e*	0.6025(2)	0.6417(1)	0.3233(1)	0.036(1)	0.033(1)	0.040(1)	0.001(1)	0.009(1)	0.000(1)
C(13)	4*e*	0.4840(2)	0.6534(2)	0.3251(1)	0.035(1)	0.038(1)	0.051(2)	0.002(1)	0.012(1)	–0.003(1)
C(12)	4*e*	0.3969(2)	0.6414(2)	0.2667(1)	0.030(1)	0.048(2)	0.064(2)	0.004(1)	0.013(1)	–0.003(1)
C(9)	4*e*	0.5180(2)	0.6045(2)	0.0276(1)	0.047(2)	0.050(2)	0.040(1)	–0.009(1)	–0.013(1)	0.006(1)
C(8)	4*e*	0.9465(2)	0.6124(2)	0.1161(1)	0.038(1)	0.046(1)	0.044(1)	0.000(1)	0.011(1)	–0.001(1)
C(17)	4*e*	0.6766(2)	0.6558(2)	0.3849(1)	0.041(2)	0.062(2)	0.042(1)	0.005(1)	0.006(1)	–0.004(1)
C(11)	4*e*	0.3174(2)	0.6002(2)	0.1514(2)	0.027(1)	0.088(2)	0.068(2)	0.004(1)	–0.002(1)	–0.011(2)
C(7)	4*e*	0.8599(3)	0.6012(2)	–0.0062(1)	0.057(2)	0.085(2)	0.045(2)	–0.025(2)	0.018(1)	–0.013(2)
C(14)	4*e*	0.4471(2)	0.6762(2)	0.3886(2)	0.046(2)	0.062(2)	0.063(2)	0.004(1)	0.022(1)	–0.010(1)
C(15)	4*e*	0.5209(3)	0.6881(2)	0.4480(2)	0.068(2)	0.074(2)	0.052(2)	0.006(2)	0.026(2)	–0.014(2)
C(10)	4*e*	0.3522(2)	0.6280(2)	0.0827(2)	0.037(2)	0.071(2)	0.063(2)	0.011(1)	–0.014(1)	0.002(2)
C(6)	4*e*	0.7724(3)	0.5979(3)	–0.0608(2)	0.080(2)	0.131(3)	0.036(2)	–0.046(2)	0.018(2)	–0.016(2)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(5)	4*e*	0.6631(3)	0.5964(2)	–0.0466(1)	0.065(2)	0.100(3)	0.033(1)	–0.033(2)	–0.002(1)	–0.005(2)
C(16)	4*e*	0.6368(3)	0.6781(2)	0.4458(2)	0.058(2)	0.077(2)	0.044(2)	0.004(2)	0.005(1)	–0.010(1)
C(21)	4*e*	1.0589(2)	0.5287(2)	0.4195(1)	0.036(1)	0.052(2)	0.031(1)	0.003(1)	0.003(1)	0.000(1)
C(29)	4*e*	0.9702(2)	0.8895(2)	0.3153(2)	0.056(2)	0.034(1)	0.066(2)	–0.011(1)	0.029(2)	–0.011(1)
C(19)	4*e*	0.9244(2)	0.4344(2)	0.3483(1)	0.032(1)	0.038(1)	0.035(1)	0.005(1)	0.008(1)	0.006(1)
C(20)	4*e*	0.9675(2)	0.5192(2)	0.3643(1)	0.028(1)	0.042(1)	0.029(1)	0.004(1)	0.0054(9)	0.003(1)
C(25)	4*e*	0.8272(2)	0.4142(2)	0.2921(1)	0.032(1)	0.036(1)	0.040(1)	0.004(1)	0.007(1)	0.001(1)
C(30)	4*e*	0.8703(2)	0.8837(2)	0.2638(1)	0.046(2)	0.034(1)	0.053(2)	0.000(1)	0.025(1)	0.002(1)
C(31)	4*e*	0.8162(2)	0.8052(2)	0.2406(1)	0.041(1)	0.034(1)	0.047(1)	0.004(1)	0.020(1)	0.004(1)
C(26)	4*e*	1.1077(2)	0.6107(2)	0.4448(1)	0.036(1)	0.066(2)	0.037(1)	0.003(1)	–0.005(1)	–0.006(1)
C(22)	4*e*	1.1063(2)	0.4546(2)	0.4544(1)	0.041(2)	0.069(2)	0.039(1)	0.009(1)	–0.006(1)	0.007(1)
C(24)	4*e*	0.9754(2)	0.3640(2)	0.3854(1)	0.047(2)	0.045(1)	0.043(1)	0.005(1)	0.007(1)	0.010(1)
C(23)	4*e*	1.0664(2)	0.3733(2)	0.4372(1)	0.048(2)	0.057(2)	0.048(2)	0.013(1)	–0.002(1)	0.017(1)
C(28)	4*e*	1.1271(2)	0.8349(2)	0.3963(2)	0.049(2)	0.056(2)	0.079(2)	–0.017(1)	0.005(2)	–0.021(2)
C(27)	4*e*	1.1307(3)	0.7654(2)	0.4517(2)	0.052(2)	0.063(2)	0.062(2)	–0.009(1)	–0.005(1)	–0.022(2)
C(32)	4*e*	0.7235(2)	0.8095(2)	0.1874(1)	0.054(2)	0.039(1)	0.060(2)	0.009(1)	0.009(1)	0.006(1)
C(34)	4*e*	0.7389(3)	0.9638(2)	0.1803(2)	0.089(2)	0.043(2)	0.069(2)	0.023(2)	0.033(2)	0.018(2)
C(35)	4*e*	0.8287(3)	0.9619(2)	0.2323(2)	0.079(2)	0.034(1)	0.068(2)	0.002(1)	0.039(2)	0.001(1)
C(33)	4*e*	0.6859(3)	0.8872(2)	0.1576(2)	0.067(2)	0.056(2)	0.062(2)	0.021(2)	0.014(2)	0.012(2)
O(1W)	4*e*	1.1166(2)	0.6890(1)	0.2590(1)	0.039(1)	0.046(1)	0.051(1)	0.0013(8)	0.0071(8)	–0.0012(9)
O(9)	4*e*	0.5739(2)	0.4430(1)	0.1768(1)	0.044(1)	0.058(1)	0.055(1)	–0.0046(9)	–0.0032(9)	0.0046(9)
C(36)	4*e*	0.5102(3)	0.3956(2)	0.2200(2)	0.063(2)	0.074(2)	0.061(2)	–0.013(2)	–0.005(2)	0.017(2)
C(37)	4*e*	0.3659(3)	0.9330(3)	0.0858(2)	0.074(3)	0.091(3)	0.091(3)	0.004(2)	–0.004(2)	0.003(2)

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