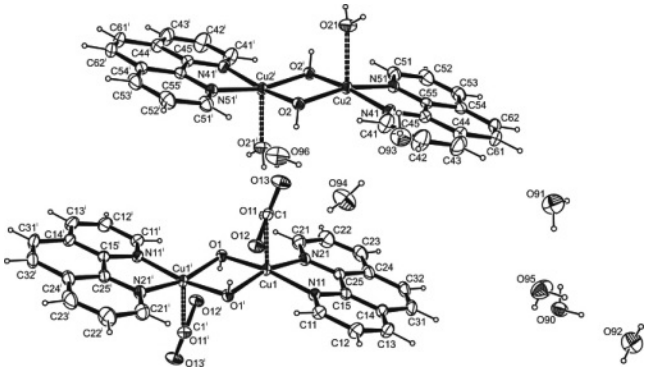
Crystal structure of bis((μ$_2$-hydroxo)-aqua-(1,10-phenanthroline-κ^2*N,N'*)-copper(II))bis((μ$_2$-hydroxo)-(carbonato-κ*O*)-(1,10-phenanthroline-κ^2*N,N'*)-copper(II)) tetradecahydrate, $C_{50}H_{64}Cu_4N_8O_{26}$

Candyce Clark, Bereneice Sephton, Abigail Sephton, Travis Dugmore, Matthew Hickson and Richard Betz*

Nelson Mandela Metropolitan University, Summerstrand Campus, Department of Chemistry, University Way, Summerstrand, PO Box 77000, Port Elizabeth 6031, South Africa

Received July 24, 2014, accepted March 12, 2015, available online March 19, 2015, CCDC no. 1267/4274



Abstract

$C_{50}H_{64}Cu_4N_8O_{26}$, triclinic, $P\bar{1}$ (no. 2), a = 11.0000(3) Å, b = 11.2890(3) Å, c = 12.4370(4) Å, α = 107.976(1)°, β = 90.676(1)°, γ = 95.937(1)°, V = 1459.6 Å^3, Z = 1, $R_{gt}(F)$ = 0.0262, $wR_{ref}(F^2)$ = 0.0727, T = 200 K.

Table 1. Data collection and handling.

Crystal:	blue platelets, size 0.134×0.304×0.309 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	15.30 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	56.66°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	26401, 7271
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6132
$N(param)_{refined}$:	462
Programs:	SHELX, WinGX, MERCURY, PLATON [7–10]

Source of material

The compound was prepared upon reacting copper(II) acetate with 1,10-phenanthroline in a mixture of aqueous sodium hydroxide and acetone. Crystals suitable for the diffraction study evolved upon prolonged storage of the reaction vessel at ambient conditions with contact to air.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(C). All oxygen-bound H atoms were located on a difference Fourier map and refined freely.

Discussion

Coordination compounds of copper show a broad variation in colour over the range from blue to green in aqueous solution. In the solid state, the colours often seem to deviate substantially. The latter can be rationalized in terms of changing coordination spheres upon the transition from the dissolved into the solid state as well as by simply assuming concentration effects – i.e. intensification of the colour upon crystallization from solution. A research project was designed to elucidate the rules that influence on the absorption spectra of transition metal coordination compounds that – on a broader scale – will allow for the quantification of the simple qualitative crystal field and molecular orbital description of d-d transitions and, ultimately, the tailoring of compounds with defined UV/Vis spectra. As metrical parameters play a key role in this context, bond lengths and distances between the respective central atoms and their bonding partners are to be determined by means of single-crystal diffraction studies. At the beginning of the project, simple compounds of copper(II) were chosen as a starting point, among others, the title compound. The molecular and crystal structure of the decahydrate of the salt has been reported earlier [1]. Additionally, two further compounds featuring the same set-up of mixed-charge-type copper(II) coordination compounds have been characterized structurally, one containing 2,6-dihydroxbenzoate [2] and one containing pyridine-3-olate [3] as additional anionic moieties in the crystal lattice. The results of the structural analysis show the presence of an ionic compound. The cation is a centrosymmetric dinuclear copper(II) coordination compound. The two penta-coordinate central atoms are connected by two bridging hydroxido ligands. The respective square-pyramidal coordination polyhedron around each central atoms is completed by a chelating 1,10-phenanthroline ligand as well as an aquo ligand each in both apical position, the latter two in relative *trans* configuration to each other. The two copper atoms are displaced by about 0.22 Å from the least-squares plane as constituted by the donor atoms of the coordination polyhedron's basal plane. A conformational analysis of the five-membered chelate rings according to Cremer & Pople [4] is precluded by the small puckering amplitude (τ = 3.8°). The anion is a centrosymmetric dinuclear copper(II) coordination compound as well. The coordination environment is square-pyramidal as well with the same set of ligands in the basal plane, however, the apical ligands are monodentate *O*-coordinating carbonato ligands. The displacement of the two central atoms from the coordination polyhedron's basal plane (as described for the cation) is found around 0.25 Å in this case. As is the case for the cation, a Cremer & Pople analysis [4] of the chelate rings is hampered by the small puckering amplitude (τ = 3.0°). The two central Cu–O–Cu–O rings appear as rhombs with the larger angles invariably found on the oxygen atoms. The respective Cu–O–Cu angle in the anion is smaller than the corresponding angle in the cation (95.02(5)° and 96.14(5)°, respectively). The dis-

* Correspondence author (e-mail: Richard.Betz@nmmu.ac.za)

tance between the two copper atoms in the cation is measured at 2.8904(4) Å while the corresponding distance in the anion is only slightly shorter at 2.8920(4) Å. These values are invariably longer than the ones reported for the decahydrate of the salt [1]. In comparison to other dinuclear compounds featuring penta-coordinate copper as the central atom with a *N,N′,O,O′,O″* donor set of atoms and a central Cu–O–Cu–O ring whose metrical parameters have been deposited with the Cambridge Structural Database [5], these values are still among the shortest ever reported. The oblate cation as well as the oblate anion are nearly parallel to each other with the least-squares planes as defined by the non-hydrogen atoms of the aromatic ligands in the cation as well as the anion, respectively, enclosing an angle of 0.92(5)° only. The carbonato ligand adopts a nearly perpendicular conformation with respect to the plane of the anion it is part of the corresponding least-squares planes intersect at an angle of 87.14(4)°. A total of 14 water molecules are also present in the crystal structure. In the crystal, classical hydrogen bonds of the O–H···O type can be observed next to C–H···O contacts whose range falls below the sum of van-der-Waals radii of the atoms participating in them [6]. Both bridging hydroxido ligands establish hydrogen bonds to two different oxygen atoms of the carbonato ligand while the third oxygen atom of the latter also serves as acceptor for one of the hydrogen bonds established by the aquo ligand of the cation. The water molecules form hydrogen bonds to all different types of oxygen atoms present in the structure forming a complicated layered network containing rings of various sizes. The C–H···O contacts are supported by two hydrogen atoms on the cation and six hydrogen atoms on the anion as donors and have oxygen atoms of water molecules as well as one of the oxygen atoms of a carbonato ligand as acceptor. In total, the entities of the title compound are connected to a three-dimensional network in the crystal. The shortest intercentroid distance between two centers of gravity was measured at 3.4785(10) Å only and is apparent in between the central ring of the 1,10-phenanthroline ligand on the anion and its symmetry-generated equivalent in a neighbouring molecule.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(11)	2*i*	0.2765	0.8780	0.5844	0.028
H(12)	2*i*	0.3817	0.7657	0.6773	0.036
H(13)	2*i*	0.2764	0.6079	0.7343	0.037
H(21)	2*i*	–0.2753	0.7640	0.4546	0.032
H(22)	2*i*	–0.4014	0.6034	0.4920	0.042
H(23)	2*i*	–0.3210	0.4780	0.5862	0.040
H(31)	2*i*	0.0711	0.4752	0.7357	0.038
H(32)	2*i*	–0.1320	0.4302	0.6844	0.038
H(211)	2*i*	0.038(2)	0.278(2)	–0.210(2)	0.041(7)
H(212)	2*i*	0.141(2)	0.266(2)	–0.182(2)	0.025(6)
H(41)	2*i*	0.3217	0.4501	0.0767	0.037
H(42)	2*i*	0.4682	0.3648	0.1585	0.047
H(43)	2*i*	0.4095	0.1952	0.2232	0.044
H(51)	2*i*	–0.2181	0.2253	–0.0174	0.029
H(52)	2*i*	–0.3030	0.0585	0.0416	0.036
H(53)	2*i*	–0.1810	–0.0334	0.1396	0.035

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(61)	2*i*	0.2345	0.0399	0.2530	0.038
H(62)	2*i*	0.0325	–0.0376	0.2250	0.036
H(901)	2*i*	0.300(2)	0.107(2)	0.739(2)	0.042(7)
H(902)	2*i*	0.218(2)	0.105(2)	0.669(2)	0.042(8)
H(911)	2*i*	0.395(3)	0.024(2)	0.385(3)	0.09(1)
H(912)	2*i*	0.471(3)	0.116(2)	0.438(1)	0.06(1)
H(921)	2*i*	0.478(2)	0.099(2)	0.842(2)	0.06(1)
H(922)	2*i*	0.469(2)	0.005(2)	0.756(2)	0.055(9)
H(931)	2*i*	0.745(1)	0.445(2)	0.068(2)	0.038(7)
H(932)	2*i*	0.639(3)	0.401(4)	0.032(2)	0.15(2)
H(941)	2*i*	0.637(2)	0.693(2)	0.245(3)	0.07(1)
H(942)	2*i*	0.613(3)	0.578(2)	0.198(4)	0.15(2)
H(951)	2*i*	0.521(2)	0.279(2)	0.629(2)	0.044(8)
H(952)	2*i*	0.602(2)	0.207(3)	0.595(2)	0.07(1)
H(961)	2*i*	0.363(2)	0.730(2)	0.150(2)	0.045(8)
H(962)	2*i*	0.465(3)	0.690(4)	0.145(4)	0.16(2)

Table 3. continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	2*i*	0.00209(2)	0.87422(2)	0.50571(2)	0.0189(1)	0.0135(1)	0.0164(1)	0.00178(8)	0.00061(8)	0.00682(8)
O(1)	2*i*	–0.1172(1)	0.9719(1)	0.4657(1)	0.0188(6)	0.0143(5)	0.0190(6)	0.0019(5)	–0.0014(5)	0.0055(5)
O(11)	2*i*	0.0692(1)	0.7982(1)	0.3341(1)	0.0167(6)	0.0223(6)	0.0164(6)	0.0009(5)	0.0007(5)	0.0041(5)
O(12)	2*i*	0.2612(1)	0.8882(1)	0.3785(1)	0.0203(7)	0.0235(6)	0.0219(6)	–0.0022(5)	–0.0016(5)	0.0027(5)
O(13)	2*i*	0.2174(1)	0.7273(1)	0.2212(1)	0.0216(7)	0.0299(7)	0.0215(6)	–0.0003(5)	0.0047(5)	–0.0026(5)
N(11)	2*i*	0.1130(1)	0.7871(1)	0.5812(1)	0.0259(8)	0.0173(7)	0.0159(7)	0.0048(6)	0.0024(6)	0.0068(6)
N(21)	2*i*	–0.1232(1)	0.7367(1)	0.5235(1)	0.0257(8)	0.0163(7)	0.0201(7)	0.0021(6)	0.0032(6)	0.0067(6)
C(1)	2*i*	0.1825(2)	0.8049(2)	0.3106(1)	0.0201(9)	0.0156(8)	0.0164(8)	0.0010(6)	–0.0007(6)	0.0078(6)
C(11)	2*i*	0.2325(2)	0.8124(2)	0.6057(2)	0.028(1)	0.0233(9)	0.0204(8)	0.0048(7)	–0.0004(7)	0.0073(7)
C(12)	2*i*	0.2960(2)	0.7457(2)	0.6619(2)	0.032(1)	0.032(1)	0.029(1)	0.0081(9)	–0.0054(8)	0.0102(9)
C(13)	2*i*	0.2343(2)	0.6519(2)	0.6943(2)	0.047(1)	0.029(1)	0.0216(9)	0.0161(9)	–0.0020(8)	0.0100(8)
C(14)	2*i*	0.1082(2)	0.6212(2)	0.6682(2)	0.041(1)	0.0198(9)	0.0156(8)	0.0109(8)	0.0043(7)	0.0069(7)
C(15)	2*i*	0.0517(2)	0.6916(2)	0.6104(1)	0.032(1)	0.0159(8)	0.0149(8)	0.0063(7)	0.0058(7)	0.0049(6)
C(21)	2*i*	–0.2411(2)	0.7135(2)	0.4931(2)	0.028(1)	0.0247(9)	0.030(1)	0.0006(8)	0.0024(8)	0.0103(8)
C(22)	2*i*	–0.3172(2)	0.6175(2)	0.5154(2)	0.031(1)	0.032(1)	0.041(1)	–0.0055(9)	0.0031(9)	0.0118(9)
C(23)	2*i*	–0.2701(2)	0.5438(2)	0.5712(2)	0.041(1)	0.023(1)	0.035(1)	–0.0055(9)	0.0112(9)	0.0094(8)
C(24)	2*i*	–0.1457(2)	0.5667(2)	0.6058(2)	0.041(1)	0.0165(8)	0.0228(9)	0.0023(8)	0.0101(8)	0.0063(7)
C(25)	2*i*	–0.0757(2)	0.6645(2)	0.5793(1)	0.031(1)	0.0155(8)	0.0162(8)	0.0043(7)	0.0068(7)	0.0054(6)
C(31)	2*i*	0.0344(2)	0.5227(2)	0.6956(2)	0.057(2)	0.0212(9)	0.0220(9)	0.0136(9)	0.0094(9)	0.0124(8)
C(32)	2*i*	–0.0858(2)	0.4964(2)	0.6657(2)	0.055(1)	0.0161(9)	0.026(1)	0.0054(9)	0.0132(9)	0.0104(8)
Cu(2)	2*i*	0.03731(2)	0.38696(2)	0.01525(2)	0.0174(1)	0.0145(1)	0.0181(1)	0.00025(8)	–0.00048(8)	0.00728(8)
O(2)	2*i*	0.1109(1)	0.5552(1)	0.0290(1)	0.0168(6)	0.0153(6)	0.0208(6)	0.0008(5)	–0.0001(5)	0.0063(5)
O(21)	2*i*	0.0881(1)	0.3074(1)	–0.1615(1)	0.0213(7)	0.0318(8)	0.0182(6)	0.0069(6)	–0.0014(5)	0.0000(6)
N(41)	2*i*	0.1807(1)	0.3323(1)	0.0858(1)	0.0243(8)	0.0214(7)	0.0203(7)	0.0018(6)	–0.0011(6)	0.0098(6)
N(51)	2*i*	–0.0512(1)	0.2355(1)	0.0460(1)	0.0230(8)	0.0165(7)	0.0180(7)	0.0018(6)	0.0029(6)	0.0060(6)
C(41)	2*i*	0.2970(2)	0.3795(2)	0.1008(2)	0.026(1)	0.034(1)	0.037(1)	–0.0017(8)	–0.0037(8)	0.0201(9)
C(42)	2*i*	0.3851(2)	0.3297(2)	0.1509(2)	0.026(1)	0.048(1)	0.049(1)	–0.001(1)	–0.009(1)	0.024(1)
C(43)	2*i*	0.3505(2)	0.2296(2)	0.1888(2)	0.035(1)	0.041(1)	0.040(1)	0.008(1)	–0.010(1)	0.020(1)

Table 3. continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(44)	2*i*	0.2278(2)	0.1788(2)	0.1763(2)	0.036(1)	0.0222(9)	0.0214(9)	0.0058(8)	–0.0037(8)	0.0071(7)
C(45)	2*i*	0.1463(2)	0.2326(2)	0.1225(1)	0.030(1)	0.0172(8)	0.0154(8)	0.0037(7)	0.0005(7)	0.0054(7)
C(51)	2*i*	–0.1676(2)	0.1892(2)	0.0235(2)	0.025(1)	0.0201(9)	0.0269(9)	0.0007(7)	0.0039(7)	0.0066(7)
C(52)	2*i*	–0.2189(2)	0.0888(2)	0.0581(2)	0.029(1)	0.0234(9)	0.034(1)	–0.0030(8)	0.0094(8)	0.0071(8)
C(53)	2*i*	–0.1470(2)	0.0347(2)	0.1157(2)	0.041(1)	0.0187(9)	0.027(1)	–0.0012(8)	0.0130(8)	0.0073(8)
C(54)	2*i*	–0.0222(2)	0.0802(2)	0.1396(2)	0.039(1)	0.0163(8)	0.0170(8)	0.0033(8)	0.0077(8)	0.0052(7)
C(55)	2*i*	0.0212(2)	0.1820(2)	0.1027(1)	0.029(1)	0.0142(8)	0.0138(8)	0.0034(7)	0.0037(7)	0.0032(6)
C(61)	2*i*	0.1806(2)	0.0759(2)	0.2149(2)	0.052(1)	0.024(1)	0.025(1)	0.0105(9)	–0.0032(9)	0.0135(8)
C(62)	2*i*	0.0614(2)	0.0296(2)	0.1978(2)	0.053(1)	0.0185(9)	0.0222(9)	0.0067(9)	0.0053(9)	0.0104(7)
O(90)	2*i*	0.2536(1)	0.1482(1)	0.7244(1)	0.0270(8)	0.0274(7)	0.0272(8)	0.0051(6)	–0.0036(6)	0.0010(6)
O(91)	2*i*	0.4422(2)	0.0776(2)	0.3774(2)	0.037(1)	0.042(1)	0.040(1)	–0.0076(8)	–0.0008(7)	0.0148(8)
O(92)	2*i*	0.4321(2)	0.0413(2)	0.8081(2)	0.0326(9)	0.041(1)	0.049(1)	–0.0025(8)	0.0023(8)	0.0131(8)
O(93)	2*i*	0.6785(1)	0.4377(1)	0.0870(1)	0.0258(8)	0.0323(8)	0.0280(7)	0.0003(6)	0.0060(6)	0.0079(6)
O(94)	2*i*	0.5858(2)	0.6376(2)	0.2347(2)	0.0329(9)	0.0316(9)	0.046(1)	–0.0006(7)	0.0061(7)	0.0003(8)
O(95)	2*i*	0.5558(2)	0.2460(2)	0.5757(1)	0.0331(9)	0.058(1)	0.0316(9)	0.0158(8)	0.0015(7)	0.0140(8)
O(96)	2*i*	0.4230(2)	0.7255(2)	0.1169(1)	0.0220(8)	0.047(1)	0.0318(8)	–0.0007(7)	0.0044(6)	0.0039(7)

Acknowledgments. The authors thank Musiegh Madatt for helpful discussions.

References

1. Zheng, Y.-Q.; Lin, J.-L.: Synthesis and Crystal Structure of $[Cu_2(H_2O)_2(phen)_2(OH)_2][Cu_2(phen)_2(OH)_2(CO_3)_2]\cdot 10H_2O$ with phen = 1,10-phenanthroline. Z. Anorg. Allg. Chem. **627** (2001) 1647–1651.
2. You, Z.-L.; Liu, W.-S.; Zhu, H.-L.; Fun, H.-K.: Syntheses, crystal structures, and cytochrome P450-like hydroxylation property of two novel copper(II) complexes. Trans. Met. Chem. **30** (2005) 1–4.
3. Iglesias, S.; Castillo, O.; Luque, A.; Roman, P.: Inclusion of organic
5. Allen, F. H.: The Cambridge Structural Database: a quarter of a million crystal structures and rising. Acta Crystallogr. **B58** (2002) 380–388.
6. Bondi, A.: van der Waals Volumes and Radii. J. Phys. Chem. **68** (1964) 441–451.
7. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
8. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. **45** (2012) 849–854.
9. Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P.A.: Mercury CSD 2.0 - new features for the visualization and investigation of crystal structures. J. Appl. Crystallogr. **41** (2008) 466–470.
10. Spek, A. L.: Structure validation in chemical crystallography. Acta Crystallogr. **D65** (2009) 148–155.