

Short Communication

Crystal Structure of Aquadinitrato-(2,9-dimethyl-1,10-phenanthroline)copper(II)

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Several complexes of copper(I) with 2,9-dimethyl-1,10-phenanthroline (dmp) as ligand have been structurally characterized.¹ Reports on corresponding complexes of copper(II) are, on the other hand, relatively rare. To our knowledge crystal structures of four such complexes with one dmp ligand in the coordination sphere {[Cu(dmp)(H₂O)Cl₂], [Cu(dmp)(glygly)]·5H₂O, [Cu(dmp)(dmc)₂] (where dmc=2,5-dimethoxycinnamate) and [Cu(dmp)(tmhd)(NO₃)] (where tmhd=2,2,6,6-tetramethyl-3,5-heptadione)}^{2–5} and one with two dmp ligands ([Cu(dmp)₂(NO₃)](C₂Cl₃O₂)·C₂HCl₃O₂)⁶ have been published thus far. The methyl groups of the dmp ligand put some constraints on possible coordination geometries in the complexes. Planar trigonal as well as tetrahedral geometries, which stabilize copper(I) relative to copper(II), will obviously be easily attainable.⁷ However, with the well known plasticity of the copper(II) ion in mind, one would expect that stable copper(II) complexes with a variety of irregular coordination geometries might be formed with dmp in the ligand sphere. The present paper reports the crystal structure of a new copper(II)–dmp compound, [Cu(dmp)(H₂O)(NO₃)₂].

Experimental

Preparation of compound. A warm saturated aqueous solution containing 1 mmol (0.208 g) of 2,9-dimethyl-1,10-phenanthroline (dmp) was added to an aqueous solution of 1 mmol (0.241 g) of Cu(NO₃)₂·3H₂O. Slow evaporation at room temperature yielded green, needle-shaped crystals suitable for X-ray analysis.

X-Ray data collection, structure determination and refinement. Diffraction data were collected at 104 K with an Enraf-Nonius CAD-4 diffractometer, equipped

with a liquid-nitrogen cooling device, using graphite-monochromated Mo K α radiation ($\lambda=0.71073$ Å). Crystal parameters and refinement results are compiled in Table 1. A total of 2828 unique reflections were recorded in the range $2 < \theta < 25^\circ$. Three reference reflections, monitored during the data collection, decreased in average by 1.6%. The data were corrected for Lorentz and polarization effects, for linear decay, and for absorption based on psi-scan measurements of 7 reflections.

The structure was solved by direct methods,⁸ and refined

Table 1. Crystallographic data for [Cu(dmp)(H₂O)(NO₃)₂].

Chem. formula	C ₁₄ H ₁₄ CuN ₄ O ₇
FW	413.83
Space group	P2 ₁ /c (No. 14)
a/Å ^a	7.662(1)
b/Å	20.359(6)
c/Å	11.642(2)
$\beta/^\circ$	117.6(2)
V/Å ³	1609.3(1.1)
Z	4
ρ (calcd.)/g cm ⁻³	1.708
$\lambda/\text{Å}$	0.71073
μ/cm^{-1}	14.046
Max–min transmission (%) ^b	99.89–86.72
T/K	104
Max. $2\theta/^\circ$	50
No. of unique reflections	2828
No. of refl. in refinement, N_0	1776 ($I > 2\sigma$)
Parameters refined, N_v	292
Extinction coefficient	$4.48 \cdot 10^{-7}$
$R = (\sum F_o - F_c / \sum F_o)$	0.048
$R_w = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$	0.049
$S = [\sum w(F_o - F_c)^2 / (N_0 - N_v)]^{1/2}$	1.274
k in weighting scheme ^c	0.04

^a Cell dimensions based on setting angles of 25 reflections ($17 < 2\theta < 42^\circ$). ^b Empirical absorption correction based on psi scans of 7 reflections. ^c Function minimized $\sum [w(|F_o| - |F_c|)^2]$, $w = 4F_o^2 / [\sigma_c^2 + (kF_o^2)^2]$, where σ_c is the standard deviation in F^2 based on counting statistics alone.

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by full-matrix least-squares methods. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were located in a difference Fourier map, and were isotropically refined. An extinction parameter was included and adjusted in the final stages of refinement. The refinement including 1776 reflections with $I > 2\sigma$ converged at $R = 0.048$ and $R_w = 0.049$.

All calculations were carried out with programs in the MolEN system.⁹ Neutral atomic scattering factors were used,¹⁰ and anomalous scattering terms were included in F_{calc} .¹¹ Atomic coordinates of non-hydrogen atoms are listed in Table 2, bond distances and angles in Tables 3 and 4. Supplementary material contains coordinates of hydrogen atoms, anisotropic thermal parameters, bond

Table 2. Atomic coordinates for [Cu(dmp)(H₂O)(NO₃)₂].

Atom	x	y	z
Cu	0.06478(9)	0.14774(3)	0.20281(6)
O(1)	-0.1691(5)	0.1803(2)	0.2186(3)
O(31)	0.0814(5)	0.2366(2)	0.1421(3)
O(32)	-0.0546(6)	0.2998(2)	-0.0246(3)
O(33)	-0.1451(6)	0.1972(2)	-0.0398(4)
O(41)	0.2210(5)	0.1102(2)	0.1201(3)
O(42)	0.4701(5)	0.1706(2)	0.2494(4)
O(43)	0.5014(5)	0.1025(2)	0.1170(3)
N(1)	0.0213(6)	0.0546(2)	0.2404(4)
N(2)	0.2641(6)	0.1453(2)	0.4112(4)
N(3)	-0.0433(6)	0.2442(2)	0.0225(4)
N(4)	0.3999(6)	0.1287(2)	0.1637(4)
C(1)	0.1338(7)	0.0354(3)	0.3649(5)
C(2)	-0.0990(8)	0.0123(3)	0.1511(5)
C(3)	-0.1115(8)	-0.0534(3)	0.1868(5)
C(4)	0.0012(8)	-0.0731(3)	0.3121(5)
C(5)	0.1298(8)	-0.0295(3)	0.4064(5)
C(6)	0.2511(8)	-0.0466(3)	0.5381(5)
C(7)	0.3733(9)	-0.0022(3)	0.6237(5)
C(8)	0.3804(8)	0.0643(3)	0.5852(5)
C(9)	0.5041(8)	0.1136(3)	0.6701(5)
C(10)	0.5009(8)	0.1746(3)	0.6244(5)
C(11)	0.3800(7)	0.1902(3)	0.4935(5)
C(12)	0.2626(7)	0.0831(3)	0.4560(5)
C(13)	-0.2170(8)	0.0360(3)	0.0161(5)
C(14)	0.3748(8)	0.2574(3)	0.4427(5)

Table 3. Bond distances (in Å) for [Cu(dmp)(H₂O)(NO₃)₂].

Atoms	Distance	Atoms	Distance
Cu–O(1)	1.997(4)	C(1)–C(5)	1.412(8)
Cu–O(31)	1.968(4)	C(1)–C(12)	1.440(7)
Cu–O(41)	2.004(5)	C(2)–C(3)	1.418(8)
Cu–N(1)	2.009(5)	C(2)–C(13)	1.484(7)
Cu–N(2)	2.188(3)	C(3)–C(4)	1.366(7)
O(31)–N(3)	1.281(5)	C(4)–C(5)	1.400(7)
O(32)–N(3)	1.242(6)	C(5)–C(6)	1.420(7)
O(33)–N(3)	1.236(6)	C(6)–C(7)	1.350(7)
O(41)–N(4)	1.279(6)	C(7)–C(8)	1.435(9)
O(42)–N(4)	1.231(6)	C(8)–C(9)	1.420(7)
O(43)–N(4)	1.255(7)	C(8)–C(12)	1.402(7)
N(1)–C(1)	1.356(6)	C(9)–C(10)	1.345(9)
N(1)–C(2)	1.334(6)	C(10)–C(11)	1.405(7)
N(2)–C(11)	1.324(7)	C(11)–C(14)	1.484(8)
N(2)–C(12)	1.371(8)		

Table 4. Bond angles (in °) for [Cu(dmp)(H₂O)(NO₃)₂].

Atoms	Angle	Atoms	Angle
O(1)–Cu–O(31)	86.5(2)	O(41)–N(4)–O(43)	117.9(4)
O(1)–Cu–O(41)	158.8(1)	O(42)–N(4)–O(43)	121.4(5)
O(1)–Cu–N(1)	92.7(2)	N(1)–C(1)–C(5)	122.1(4)
O(1)–Cu–N(2)	95.8(2)	N(1)–C(1)–C(12)	118.2(5)
O(31)–Cu–O(41)	91.5(2)	C(5)–C(1)–C(12)	119.7(4)
O(31)–Cu–N(1)	172.4(1)	N(1)–C(2)–C(3)	119.8(4)
O(31)–Cu–N(2)	106.9(2)	N(1)–C(2)–C(13)	118.5(5)
O(41)–Cu–N(1)	86.6(2)	C(3)–C(2)–C(13)	121.7(4)
O(41)–Cu–N(2)	105.0(2)	C(2)–C(3)–C(4)	119.6(5)
N(1)–Cu–N(2)	80.7(2)	C(3)–C(4)–C(5)	121.2(5)
Cu–O(31)–N(3)	111.2(3)	C(1)–C(5)–C(4)	116.4(4)
Cu–O(41)–N(4)	117.8(3)	C(1)–C(5)–C(6)	119.5(4)
Cu–N(1)–C(1)	114.7(3)	C(4)–C(5)–C(6)	124.1(5)
Cu–N(1)–C(2)	124.3(3)	C(5)–C(6)–C(7)	121.0(5)
C(1)–N(1)–C(2)	120.9(5)	C(6)–C(7)–C(8)	121.0(5)
Cu–N(2)–C(11)	132.5(4)	C(7)–C(8)–C(9)	124.1(4)
Cu–N(2)–C(12)	108.5(3)	C(7)–C(8)–C(12)	119.6(5)
C(11)–N(2)–C(12)	118.9(4)	C(9)–C(8)–C(12)	116.3(5)
O(31)–N(3)–O(32)	117.0(4)	C(8)–C(9)–C(10)	119.6(5)
O(31)–N(3)–O(33)	119.6(4)	C(9)–C(10)–C(11)	121.3(5)
O(32)–N(3)–O(33)	123.4(4)	N(2)–C(11)–C(10)	120.9(5)
O(41)–N(4)–O(42)	120.7(5)	N(2)–C(11)–C(14)	117.6(4)
C(10)–C(11)–C(14)	121.5(5)	N(2)–C(12)–C(8)	123.1(5)
N(2)–C(12)–C(1)	117.8(4)	C(1)–C(12)–C(8)	119.1(5)

lengths and angles involving hydrogen atoms, hydrogen bond parameters, least-squares planes, and structure factor tables.

Results and Discussion

The structure consists of neutral [Cu(dmp)(H₂O)(NO₃)₂] complex units (Fig. 1). The coordination geometry of copper may best be described as distorted square pyramidal, with dmp in unsymmetrical bidentate coordination mode occupying the apical and one equatorial position [Cu–N = 2.188(3) and 2.009(5) Å], and two monodentate nitrate ions [Cu–O = 1.968(4) and 2.004(5) Å] and one water molecule [Cu–O = 1.997(4) Å] occupying the other equatorial positions. The bond angles in the copper coordination sphere reveal a significant trigonal distortion of the square pyramid, the τ -value used to describe the degree of trigonal distortion being 0.23.¹² The Cu^{II} ion is displaced from the mean equatorial plane of the square pyramid towards the apical N(2) (by 0.25 Å), as is typically found in this coordination geometry.

Each nitrate, although described above as monodentate with one strong Cu–O bond, is oriented such that one of the other oxygen atoms makes a close contact to copper [Cu...O(33) = 2.715(4) Å and Cu...O(42) = 2.931(4) Å]. The presence of Cu...O contacts of this length are often referred to as semi-coordination.¹³ Addison *et al.* consider nitrate ligands as unsymmetrically bidentate if the metal–oxygen distances differ by 0.2–0.8 Å.¹⁴ Using this definition one of the nitrate groups would be regarded as unsymmetrically bidentate, and O(33) would complete an elongated, distort-

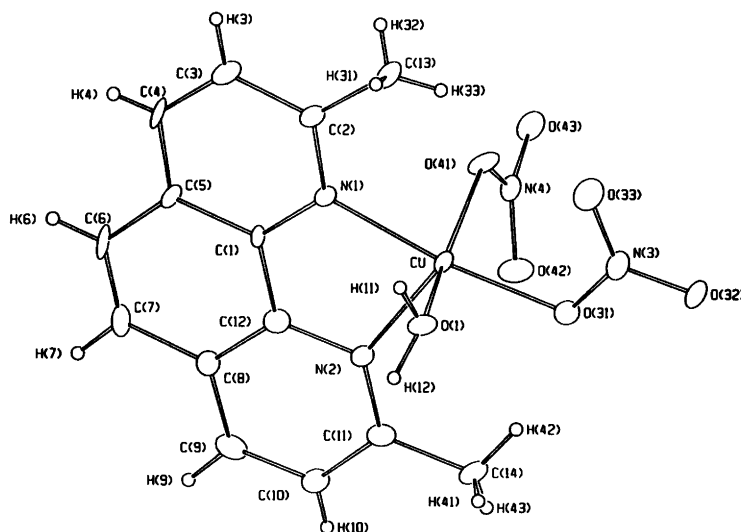


Fig. 1. View of $[\text{Cu}(\text{dmp})(\text{H}_2\text{O})(\text{NO}_3)_2]$ with the atomic numbering used. Thermal ellipsoids are plotted at the 50% probability level.

ted octahedral coordination sphere for copper [$\text{N}(2)-\text{Cu}\cdots\text{O}(33)=159.2(2)^\circ$]. In each nitrate the bond between nitrogen and the strongly coordinated oxygen is significantly longer than the other N–O bonds. The nitrate ions are connected through hydrogen bonds to the coordinated water molecules in neighbouring molecules [$\text{O}(32)\cdots\text{O}(1)(x, 1/2-y, z-1/2)=2.728(5) \text{ \AA}$, $\text{O}(43)\cdots\text{O}(1)(x+1, y, z)=2.741(5) \text{ \AA}$].

The coordination geometry of the present compound is similar to those found in three of the other structurally fully characterized complexes where copper(II) is bonded to one dmp ligand.^{2,3,5} Both in $[\text{Cu}(\text{dmp})(\text{H}_2\text{O})\text{Cl}_2]$,² $[\text{Cu}(\text{dmp})(\text{glygly})\cdot 5\text{H}_2\text{O}]$,³ and $[\text{Cu}(\text{dmp})(\text{tmhd})(\text{NO}_3)]$ ⁵ distorted square pyramidal geometries are found, the distortions towards trigonal bipyramidal geometries are slightly more pronounced (τ -values of 0.26, 0.27 and 0.25, respectively) than in the present compound. In each case the dmp ligand is asymmetric bidentate with equatorial and apical Cu–N bond distances of 1.982(9), 2.236(11) Å,² 2.013(2), 2.263(2) Å,³ and 2.030(3), 2.266(3) Å,⁵ respectively. In $[\text{Cu}(\text{dmp})(\text{dmc})_2]$, on the other hand, the copper coordination geometry is significantly different.⁴ The asymmetry in the dmp coordination is much less pronounced [Cu–N=1.988(4) and 2.045(3) Å] and both nitrogen atoms occupy equatorial positions in a square pyramid which possesses a large tetrahedral distortion. A small deviation from symmetrical coordination of dmp to copper(II) is also found in $[\text{Cu}(\text{dmp})_2(\text{NO}_3)](\text{C}_2\text{Cl}_3\text{O}_2)\cdot\text{C}_2\text{HCl}_3\text{O}_2$.⁶ In this context it should be noted that unsubstituted 1,10-phenanthroline (phen) also binds in a close to symmetrical bidentate mode in $[\text{Cu}(\text{phen})(\text{NO}_3)_2]$ and $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_2(\text{NO}_3)]$.¹⁵

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