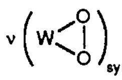
formed[23] via a binuclear oxo-bridged peroxo intermediate.[24]

Oxopolytungstates **1** and **2** behave as 2:1 elecrolytes (250 and 240 Ω^{-1} cm^2 M^{-1}) in acetonitrile.[25] The IR band at 980 cm^{-1} in the spectra of **1** and **2** can be assigned to the $\nu(W{=}O)_{asym}$ vibration, while those at 815 cm^{-1} (**1**) and 820 cm^{-1} (**2**) are attributable to the $\nu(W{-}O{-}W)_{asym}$ vibration in the polytungstate unit. The corresponding symmetric band appears at 440 cm^{-1}. The $\nu(W_6{-}O)$ vibration involving each of the six tungsten atoms about O(10) appears at 360 cm^{-1} for **1** and at 365 cm^{-1} for **2**. The two species also show identical UV–vis absorption spectra; 295 nm (ϵ = 1120 for **1** and 970 for **2**), assigned to the $O_{p\pi} \rightarrow W_{d\pi}$ LMCT transition.

Peroxometalates **3** and **4**, previously unknown, show $\nu(W{=}O)_{asym}$ vibrations at 960 and 950 cm^{-1}, respectively. The band at 840 cm^{-1} in **3** and **4** is attributable to the $\nu(O{-}O)_{asym}$ vibration, which, however, appears at 854 and 852 cm^{-1}, respectively, in their Raman spectra. The Raman spectra show that the $\nu(W{=}O)_{asym}$ vibration is found at 953 cm^{-1} for **3** and at 944 cm^{-1} for **4**. The strong IR band at 540 cm^{-1} in both compounds may be attributed to



vibration. In the Raman spectra this vibration appears at 561 cm^{-1} in **3** and 550 cm^{-1} in **4**. UV–vis spectra (Nujol mull) show a single absorption band for both: at 357 nm for **3** and 340 nm for **4**. This band can be attributed to a $O_2^{2-}\ \pi^* \rightarrow W_{d\pi}$ LMCT transition.[26] The X-ray powder diffraction patterns of **3** and **4** indicate that they are possibly isostructural.

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Registry No. **1**, 65599-15-7; **2**, 67316-62-5; **3**, 25464-03-3; **4**, 23273-38-3; Na_2WO_4, 13472-45-2.

Supplementary Material Available: Listings of all crystal data and details of the refinement, anisotropic thermal parameters for non-hydrogen atoms, and bond angles and distances for the PPN cation (3 pages); a listing of structure factor amplitudes (38 pages). Ordering information is given on any current masthead page.

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Synthesis and Structures of (2,9-Dimethyl-1,10-phenanthroline)(acetonitrile)copper(I) Perchlorate and Hexafluorophosphate. A Correlation between Bond Angles and Bond Distances in T- and Y-Shaped Three-Coordinate Copper(I) Complexes

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Coordination number 3 is a rare coordination number in transition-metal complexes, because the metal atom can usually serve as an acceptor to stronger Lewis bases.[1] Such a metal atom is coordinatively unsaturated. The copper(I) in $Na_2[Cu(CN)_3]\cdot 3H_2O$[2] is a typical example of regular trigonal-planar geometry with the angles of 120°. Several other examples of three-coordination, $[Cu(Me_3PS)Cl]_3$,[3a] $[Cu(Br)(PPh_3)_2]$,[3b] $[Cu(SPh)_3]PPh_4$,[3c] $[Cu(etu)_3]BF_4$ (etu = ethylenethiourea),[3d] $[Cu(tmtu)_3]BF_4$[3d] (tmtu = tetramethylthiourea), $[Cu(SPMe_3)_3]ClO_4$,[3e] $[Cu(tpt)_2Cl]$[3f] (tpt = tetrahydro-1*H*-pyrimidine-2-thione), $[Cu_2I_2(tmpip)_2]$[3g] (tmpip = 2,2,6,6-tetramethylpiperidine) and $[Cu(2\text{-}Me\text{-}py)_3]ClO_4$,[4] have been verified by X-ray studies. In all examples, the geometry approximates an equilateral triangle with the copper atom at the center as expected for sp^2 hybridization. Recently, three-coordinate T-shaped copper(I) complexes in which one of the bond angles around copper(I) is remarkably larger than 120° have been synthesized.[5,6] The most striking feature of this geometry is that the middle Cu–donor atom distance is quite a bit longer than the terminal bond distances. In contrast to the T-shaped geometry, we have synthesized three-coordinate Y-shaped copper(I) complexes $[Cu(dmp)(CH_3CN)]ClO_4$ (dmp = 2,9-dimethyl-1,10-phenanthroline) and $[Cu(dmp)(CH_3CN)]PF_6$ in which one of the bond angles about the copper atom is remarkably smaller than 120°. The structure of the Y-shaped complex in this paper has been determined by a single-crystal structure analysis, and the relationship between the bond distance and the bond angle has been discussed.

Table I. Crystallographic Details for **1** and **2**

	1	**2**
formula	$CuClC_{16}H_{15}O_4N_3$	$CuPF_6C_{16}H_{15}N_3$
fw	412.3	457.8
space group	$P2_1/c$	$P1$
a, Å	11.9101 (9)	11.305 (4)
b, Å	19.987 (1)	12.479 (5)
c, Å	7.636 (1)	7.669 (4)
α, deg		87.91 (5)
β, deg	108.159 (9)	106.42 (4)
γ, deg		117.69 (3)
Z	4	2
temp, K	296	296
λ, Å	0.71069 (Mo Kα)	1.54178 (Cu Kα)
ρ_{cal}, g/cm^3	1.585	1.665
μ, cm^{-1}	14.46	31.29
$F(000)$	840	460
R^a	0.051	0.077
$R_w{}^b$	0.056	0.105

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_c|^2]^{1/2}$.

Experimental Section

$[Cu(dmp)(CH_3CN)]ClO_4$ (1). A solution of 2,9-dimethyl-1,10-phenanthroline (dmp) (50 μmol, 10.4 mg) and 1,5-cyclooctadiene (1.5 mmol, 0.18 mL) in methanol (5 mL) was added to tetrakis (acetonitrile)copper(I) perchlorate (50 μmol, 16.4 mg) under argon. Then, ca. 1 mL of the solution was sealed in a glass tube and left at −10 °C. After

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Table II. Positional Parameters and Their Estimated Standard Deviations for $[Cu(dmp)(CH_3CN)]ClO_4$[a]

atom	x	y	z	B(eq), Å^2
Cu	0.7351 (1)	0.14144 (6)	0.1743 (2)	5.57 (3)
Cl	1.1967 (2)	0.0814 (1)	0.2548 (3)	5.48 (6)
O(1)	1.2650 (7)	0.0636 (6)	0.149 (1)	13.6 (3)
O(2)	1.0917 (6)	0.0463 (4)	0.199 (1)	10.5 (3)
O(3)	1.2616 (9)	0.0656 (6)	0.432 (1)	14.0 (4)
O(4)	1.1765 (8)	0.1460 (4)	0.246 (2)	17.1 (5)
N(1)	0.5918 (5)	0.1842 (4)	−0.0048 (9)	4.2 (2)
N(2)	0.7830 (5)	0.2385 (3)	0.2398 (8)	3.8 (2)
N(3)	0.8010 (7)	0.0572 (4)	0.2322 (9)	5.1 (2)
C(1)	0.4960 (7)	0.1568 (4)	−0.123 (1)	4.5 (2)
C(2)	0.4079 (8)	0.1948 (5)	−0.240 (1)	5.6 (3)
C(3)	0.4159 (7)	0.2643 (5)	−0.240 (1)	4.9 (2)
C(4)	0.5157 (7)	0.2936 (4)	−0.113 (1)	4.3 (2)
C(5)	0.5996 (7)	0.2522 (4)	0.001 (1)	3.7 (2)
C(6)	0.7021 (7)	0.2818 (4)	0.134 (1)	3.8 (2)
C(7)	0.7134 (7)	0.3509 (4)	0.148 (1)	4.7 (2)
C(8)	0.8119 (8)	0.3754 (4)	0.287 (1)	5.2 (2)
C(9)	0.8913 (7)	0.3322 (5)	0.397 (1)	5.3 (2)
C(10)	0.8776 (7)	0.2624 (5)	0.366 (1)	4.8 (2)
C(11)	0.5310 (7)	0.3649 (5)	−0.103 (1)	5.0 (2)
C(12)	0.6259 (9)	0.3919 (5)	0.025 (1)	5.8 (3)
C(13)	0.4865 (9)	0.0804 (5)	−0.121 (1)	6.8 (3)
C(14)	0.9710 (9)	0.2156 (5)	0.472 (1)	6.2 (3)
C(15)	0.9047 (9)	−0.0581 (5)	0.291 (1)	6.6 (3)
C(16)	0.8446 (8)	0.0064 (4)	0.258 (1)	4.5 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table III. Selected Bond Distances and Angles for $[Cu(dmp)(CH_3CN)]ClO_4$

	Bond Distance (Å)		
Cu–N(1)	2.015 (6)	Cu–N(2)	2.039 (7)
Cu–N(3)	1.852 (7)	C(5)–N(1)	1.36 (1)
C(5)–C(6)	1.45 (1)	C(6)–N(2)	1.361 (9)
C(16)–N(3)	1.13 (1)	C(15)–C(16)	1.46 (1)
	Bond Angle (deg)		
N(1)–Cu–N(2)	82.9 (2)	N(1)–Cu–N(3)	139.0 (3)
N(2)–Cu–N(3)	137.7 (3)	C(2)–C(1)–C(13)	120.9 (7)
C(9)–C(10)–C(14)	120.1 (7)	C(13)–C(1)–N(1)	116.9 (7)
C(14)–C(10)–N(2)	119.4 (8)	C(6)–C(5)–N(1)	117.6 (6)
Cu–N(1)–C(1)	130.5 (6)	C(5)–C(6)–N(2)	116.3 (7)
C(1)–N(1)–C(5)	117.9 (6)	C(15)–C(16)–N(3)	178 (1)
Cu–N(2)–C(10)	129.3 (6)	Cu–N(1)–C(5)	111.5 (4)
Cu–N(3)–C(16)	175.1 (8)	Cu–N(2)–C(6)	111.5 (5)
C(6)–N(2)–C(10)	119.2 (7)		

4 days, pale yellow crystals of $[Cu(dmp)(CH_3CN)]ClO_4$ suitable for X-ray diffraction studies were obtained.

$[Cu(dmp)(CH_3CN)]PF_6$ (2). A solution of dmp (50 μmol, 10.4 mg) and 1,5-cyclooctadiene (1.5 mmol, 0.18 mL) in methanol (5 mL) was added to tetrakis(acetonitirle)copper(I) hexafluorophosphate (50 μmol, 18.6 mg) under argon. Then, ca 1 mL of the solution was sealed in a glass tube and left at −10 °C. After 2 days pale, yellow crystals of $[Cu(dmp)(CH_3CN)]PF_6$ suitable for X-ray diffraction studies were obtained.

X-ray Data Collection. A single crystal (0.2 × 0.2 × 0.2 mm) of compound **1** was glued on top of a glass fiber and studied on an Enraf-Nonius CAD4 automatic diffractometer. Preliminary investigation revealed the crystals to be monoclinic. Unit cell parameters were determined from a least-squares fit of 25 accurately centered reflections. Intensities were gathered in an ω–2θ scan model. Lorentz, polarization, and absorption corrections were applied. Of the 3741 unique reflections measured, 1145 were considered observed ($F_o > 3\sigma(F_o)$) and were used in the subsequent structure analysis. The Laue class and the axial dimensions were confirmed with oscillation photographs. From the systematic absences, the space group was uniqely determined to be $P2_1/c$.

A single crystal (0.3 × 0.3 × 0.3 mm) of compound **2** was glued on top of a glass fiber and studied on an Rigaku AFC-5B automatic diffractometer. Preliminary investigation revealed the crystals to be triclinic. Unit cell parameters were determined from a least-squares fit of 25 accurately centered reflections. All independent reflections within the range $2\theta < 120°$ were collected in an ω–2θ scan mode. The intensity date were converted to F_o data in the usual manner. No absorption corrections were applied. The reflections of 2394 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Crystal data and details of data collection are given in Table I.

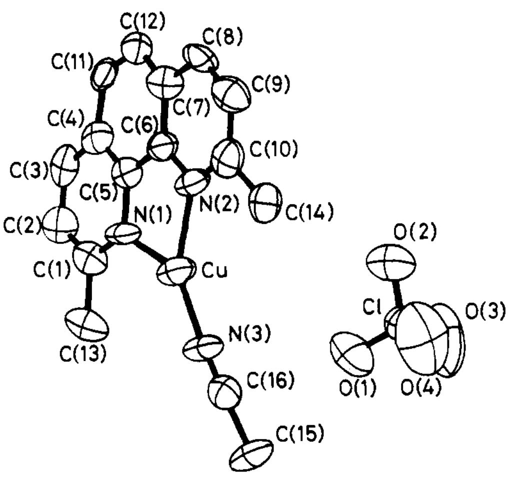


Figure 1. Molecular structure of $[Cu(dmp)(CH_3CN)]ClO_4$ showing 50% probability thermal ellipsoids.

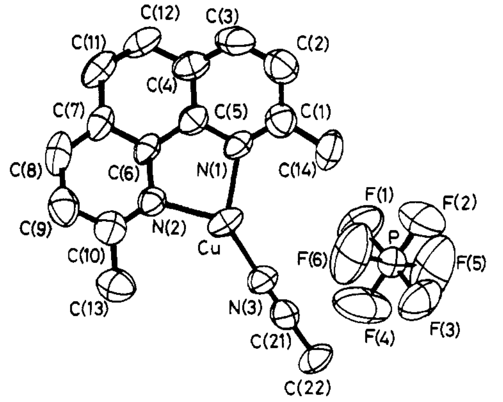


Figure 2. Molecular structure of $[Cu(dmp)(CH_3CN)]PF_6$ showing 50% probability thermal ellipsoids. Selected bond distances (Å) and angles Cu–N(1) = 2.023 (6), Cu–N(2) = 2.010 (4), Cu–N(3) = 1.850 (6), N(3)–C(16) = 1.115 (9); N(1)–Cu–N(2) = 83.1 (2), N(1)–Cu–N(3) = 138.0 (2), N(2)–Cu–N(3) = 138.8 (2), Cu–N(3)–C(16) = 174.3 (7).

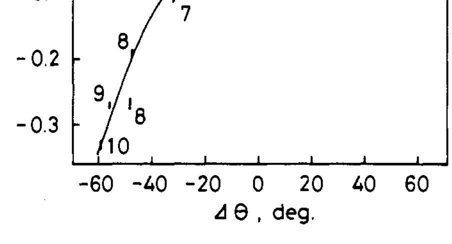
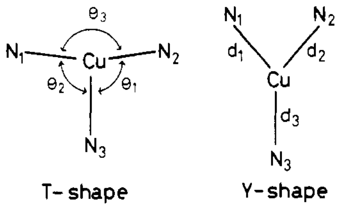


Figure 3. Correlation between bond distances (Δd) and bond angles ($\Delta\theta$) for three-coordinate copper(I) complexes with only nitrogen donor atoms, where $\Delta d = (d_1 + d_2)/2 - d_3$ and $\Delta\theta = (\theta_1 + \theta_2)/2 - \theta_3$ (see Figure 4): (1) $[Cu_2(TPEN)](BF_4)$[9a]; (2) $[Cu(dmp)(CH_3CN)]PF_6$; (3) $[Cu(dmp)(CH_3CN)]ClO_4$; (4) $[Cu_2L(CH_3CN)_2](ClO_4)_2$[5b]; (5) $Na_2[Cu(CN)_3]$[2] (a typical three-coordinate copper(I) complex, although the donor atoms are carbon); (6) $[Cu(2\text{-}Me\text{-}py)_3](ClO_4)$[4]; (7) $[Cu_2(HB(Me_2pz)_3)_2]$[9b]; (8) $[Cu_2(m\text{-}XYL(py))](PF_6)_2$[5a]; (9) $[Cu_2(mxyN_6)](BF_4)_2$[5c]; (10) $[Cu(Bpy2)](PF_6)$.[5d]



T-shape Y-shape

Figure 4. T- and Y-shaped complexes.

Solution and Refinement of the Structure. The positions of the copper atoms were obtained via direct methods using the MULTAN program. Fourier syntheses were then calculated to determine the positions of the remaining atoms. The structure was refined by full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were placed in calculated positions, but their parameters were not refined. Finally two cycles of refinement led to convergence at $R = \sum[|F_o| - |F_c|]/\sum|F_o| = 0.0507$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_c|^2]^{1/2} = 0.0561$, $w = [\sigma^2(F) + (0.02F)^2]$, $S = 1.57$, and $\Delta e = 0.35$ e Å^{-3} for **1**, and the largest shift/esd at final cycle was 0.86. The fractional positional parameters for non-hydrogen atoms for **1** are given in Table II, and selected bond distances and angles are listed in Table III.

Results and Discussion

The overall structure of $[Cu(dmp)(CH_3CN)]ClO_4$ consists of two units, a $[Cu(dmp)(CH_3CN)]^+$ cation and uncoordinated ClO_4^- anion, as shown in Figure 1. The copper(I) complex is three-coordinate and has an approximately Y-shaped planar geometry. This is the second case of a three-coordinate Y-shaped copper(I) complex. The angles around copper, N(1)-Cu-N(2) = 82.9 (2)°, N(1)-Cu-N(3) = 139.0(3)°, and N(2)-Cu-N(3) = 137.7 (3)°, sum to 359.6 (3) Å, since the copper atoms lies 0.065 (1) Å from the plane defined by the three nitrogen atoms. The angle of 84.4 (3)° is much smaller than 120°, whereas two other angles, 139.0 (3) and 137.7 (4)°, are larger than 120°. Such a stereochemistry is unusual for copper(I) since trigonal planar is the preferred geometry of three-coordinate d^{10} metal complexes, and this must represent a compromise between ideality and the limits of stretch of the dmp ligand. Y-Shaped coordination probably offers rather little stabilization of copper compared with the regular sp^3 trigonal hybridization.

To our knowledge there is only one report of an acetonitrile for the three-coordinate copper(I) complex,[5b] where a Cu-N(CH_3CN) distance of 1.92 (2) Å is found. The present complex has a short Cu-N(CH_3CN) distance of 1.852 (7) Å. This is also remarkably short compared with the Cu-N(CH_3CN) distances (1.94-2.002 (3) Å) for four-coordinate copper(I) complexes[7] and (1.91 (5)-2.322 (4) Å) for five-coordinate copper(II) complexes.[8] The Cu-N(CH_3CN) distance is furthermore shorter than the those (1.890 (8)-2.295 (7) Å) reported for $[CuN_3]^+$ type complexes,[5,9] and the shorter end of the range (1.847 (17)-2.006 (22) Å) for the two-coordinate copper(I) complexes of $[CuN_2]^+$ type.[10] Thus, a short middle bond distance in a Y-shaped copper(I) structure is noteworthy. On the other hand, the other two Cu-N(dmp) distances of 2.015 (6) and 2.039 (7) Å are longer than the middle bond distance and can be compared with the range (1.890 (8)-2.295 (7) Å) for $[CuN_3]^+$ type complexes.[5,9] The structure of the hexafluorophosphate derivative $[Cu(dmp)(CH_3CN)]PF_6$ is essentially the same as that of the perchlorate derivative as shown in Figure 2.

It has been found for T-shaped copper(I) complexes that the middle bond distance is longer than the two terminal bond distances.[5,6] Figure 3 shows a plot of the difference in angles, $\Delta\theta$, against that in bond distances, Δd, in the three-coordinate copper(I) complexes with nitrogen donor atoms so far reported, where $\Delta\theta = (\theta_1 + \theta_2)/2 - \theta_3$ and $\Delta d = (d_1 + d_2)/2 - d_3$ (Figure 4). The positive value of $\Delta\theta$ increases as a copper(I) varies from regular trigonal-planar geometry to Y-shaped geometry, whereas the negative value increases as the copper(I) varies from the regular trigonal-planar geometry to T-shaped geometry. A good correlation between Δd and $\Delta\theta$ in Figure 3 demonstrates that the metal-donor atom distances depend on the bond angles around the copper in three-coordinate copper(I) complexes. For example, the middle bond distance, d_3, lengthens as the angle opposite the bond, θ_3, approaches 180° from 120° and shortens as θ_3 approaches 0° from 120°. A similar correlation can be expected for the series Y- and T-shaped copper(I) complexes with other donor atom sets[6] such as N_2O and N_2S.

Thus, the unusual bond angles in the three-coordinate copper(I) complexes with low symmetry such as Y- and T-shaped geometries are compensated for by regulating their bond distances.

Registry No. **1**, 123148-39-0; **2**, 123148-40-3; tetrakis(acetonitrile)copper(I) perchlorate, 14057-91-1; tetrakis(acetonitrile)copper(I) hexafluorophosphate, 64443-05-6.

Supplementary Material Available: For $[Cu(dmp)(CH_3CN)]ClO_4$ and $[Cu(dmp)(CH_3CN)]PF_6$, tables of atomic parameters for non-hydrogen atoms, fractional coordinates and isotropic thermal parameters for hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, bond lengths and valence angles, and torsion angles (7 pages); tables of observed and calculated structure factors for $[Cu(dmp)(CH_3CN)]ClO_4$ and $[Cu(dmp)(CH_3CN)]PF_6$ (7 pages). Ordering information is given on any current masthead page.

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Contribution from the Fuzhou Laboratory of Structural
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A Novel Polynuclear Mo-Cu Cluster from Tetrathiomolybdate: Preparation and Structure of $(Et_4N)_2[Mo_2Cu_5S_8(S_2CNMe_2)_3]\cdot 2H_2O$

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Tetrathiomolybdate is a fundamental unit of some molybdoenzymes and exists in many biological systems.[1,2] It reacts with copper compounds to form various types of Mo-Cu-S complexes, such as $[MoS_4CuL]^{2-}$,[3] $[MoS_4(CuL)_2]^{2-}$,[3,4] $[MoS_4(CuL)_3]^{2-}$,[4,5]

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