A neutral dicopper(III) bis(μ-oxo) complex from a copper(I) ethylene iminophosphanamide and O₂†

Bernd F. Straub, Frank Rominger and Peter Hofmann*

Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany. E-mail: ph@phindigo.oci.uni-heidelberg.de

The copper(I) ethylene complex [Bu$^t_2$P(NSiMe₃)₂-κ²*N*]Cu(η²-C₂H₄) reacts with O₂, yielding an uncharged dinuclear copper(III) bis(μ-oxo) species, which has been fully characterized, *e.g.* by single-crystal X-ray diffraction.

Tyrosinase, the longest known monooxygenase, activates dioxygen for transforming phenols to catechols and quinones.[1] Similar to hemocyanin, the oxygen transport protein of invertebrates, tyrosinase contains a dinuclear copper site, where each copper atom is coordinated by three histidine imidazole ligands.[2] A great number of model complexes have been synthesized to realize different coordination modes of dioxygen in dinuclear copper complexes and to understand their reactivity.[3] Amine, pyridine, imidazole and pyrazole derivatives have been utilized as ligands. The coordination number at copper, the steric demand of ligands as well as counter ions, temperature and solvent have been varied in order to correlate ligand features with spectroscopic, structural, kinetic and thermodynamic data of the resulting (μ-η²:η²)peroxo,[3,4] μ-1,2-peroxo[5] and bis(μ-oxo)[6] dicopper complexes. Despite intense research directed towards ligand effects in copper dioxygen chemistry, neither extremely electron-rich and basic ligands nor four-membered chelate systems have been investigated.

We have introduced the anionic iminophosphanamide ligand [Bu$^t_2$P(NSiMe₃)₂]⁻ into copper(I) coordination chemistry.[7] Its basicity is many orders of magnitude higher than that of any ligand used in copper dioxygen chemistry so far. In addition, the small N–Cu–N bite angle of the neutral d¹⁰ fragment [Bu$^t_2$P(N-SiMe₃)₂-κ²*N*]Cu of *ca.* 78° leads to increased Lewis acidity of the copper center, provides better back-bonding capability and stabilizes the copper(III) oxidation state.[7,8]

The copper(I) ethylene complex **1**[7] is oxidized by O₂, yielding a brown crystalline precipitate of bis(μ-oxo) complex **2** (Scheme 1).‡ The reaction is irreversible; no ethylene complex **1** could be detected upon addition of C₂H₄ to a solution of **2**.

The low solubility of **2** in various solvents is in contrast to the extremely high solubility of the precursor complex **1**. A 444 nm absorption maximum of **2** is characteristic for a bis(μ-oxo) dicopper chromophore.[3,6] Formation of a butterfly (μ-η²:η²)peroxo dicopper(II) complex, which also would show an absorption band at 420–490 nm,[9] is hampered by the bulky trimethylsilyl groups (*viz.* Fig. 1) and so far an out-of-plane distortion could only be enforced by linkers between the ligand units. Even in concentrated solutions, no absorption bands at 340–370 nm 500–600 nm, indicative of the presence of a (μ-η²:η²)peroxo complex, could be observed. Thus, a nearly thermoneutral equilibrium of **2** with its (μ-η²:η²)peroxo isomer, as reported for some dicationic analogues,[3,6a] can be ruled out.[3,4] ²⁹Si{¹H} and ³¹P{¹H} NMR spectra of **2** at room temperature are in accordance with a diamagnetic low-spin d⁸-ML₄ copper(III) species. The respective low-field shifts, unprecedented among all other derivatives synthesized so far, indicate a distinct net charge transfer from the [Bu$^t_2$P-(NSiMe₃)₂-κ²*N*]Cu fragment to the oxygen atoms.[7,10] An antiferromagnetically coupled bis(μ-hydroxo) dicopper(II) complex is ruled out for **2** by IR spectroscopy and LT-FAB[11] mass spectrometry, which reveals stepwise fragmentation of the bis(μ-oxo) complex **2**.† At ambient temperature, complex **2** decomposes within minutes in solution and within days in the solid state. This decomposition occurs independently of the solvent (pentane, toluene or CDCl₃), leading to a copper(II) species (λ_{max} = 640 nm, $\varepsilon \approx 10^2$ M⁻¹ cm⁻¹), which possibly results from an intramolecular process. The product remains unidentified so far.

The solid-state structure of **2** reveals a perfectly planar bis(μ-oxo) dicopper unit (Fig. 1).§ Compound **2** represents the first neutral bis(μ-oxo) dicopper complex, that has been structurally characterized; all other bis(μ-oxo) dicopper complexes are dicationic.[3,6] The Cu–Cu distance of 2.906(1) Å has no precedent and is distinctly longer than Cu–Cu distances reported for bis(μ-oxo) dicopper cores so far.[6] The O–O
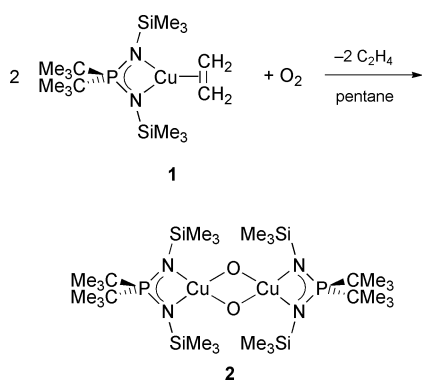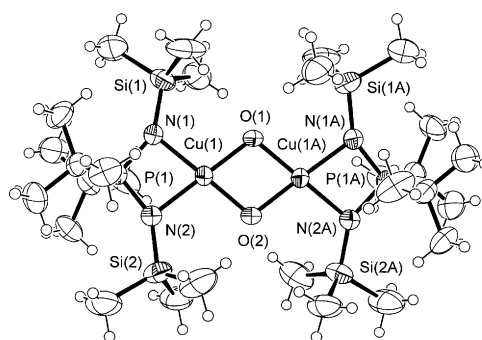

Scheme 1

Fig. 1 ORTEP diagram of the solid state structure of **2**.‡ Distances and bond lengths (Å): O(1)–O(2) 2.338(6), Cu(1)–Cu(1A) 2.906(1), Cu(1)–N(1) 1.976(4), Cu(1)–N(2) 1.980(4), Cu(1)–O(1) 1.865(3), Cu(1)–O(2) 1.864(3), P(1)–N(1) 1.607(4), P(1)–N(2) 1.605(4), Si(1)–N(1) 1.726(4), Si(2)–N(2) 1.723(4). Bond angles (°): P(1)–N(1)–Si(1) 148.2(3), P(1)–N(2)–Si(2) 148.0(3), N(1)–P(1)–N(2) 100.7(2), P(1)–N(1)–Cu(1) 91.0(2), P(1)–N(2)–Cu(1) 90.9(2), N(1)–Cu(1)–N(1A) 77.4(2), O(1)–Cu(1)–O(2) 77.6(2), Cu(1)–O(1)–Cu(1A) 102.3(2), Cu(1)–O(2)–Cu(1A) 102.4(2). Dihedral angles (°): Cu(1)–O(1)–Cu(1A)–O(2) 0.0, N(1)–Cu(1)–O(1)–O(2) −173.7(1), N(2)–Cu(1)–O(2)–O(1) −175.2(1).
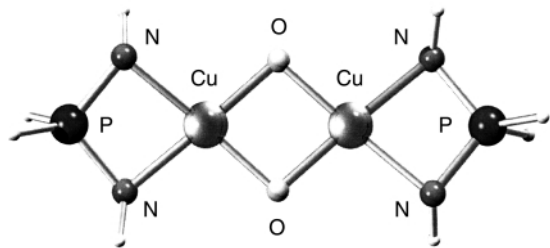
Fig. 2 Ball-and-stick plot of the model complex [{H$_2$P(NH)$_2$–κ^{2}N}$_2$Cu$_2$(μ-O)$_2$] **3** [B3LYP/6–311+G(2d,p), NIMAG = 0].§ Distances and bond lengths (Å): O–O 2.330, Cu–Cu 2.739, Cu–N 1.969, Cu–O 1.798, P–N 1.613. Bond angles (°): N–P–N 99.55, P–N–Cu 91.52, N–Cu–N 77.41, O–Cu–O 80.77, Cu–O–Cu 99.23. Dihedral angles (°): Cu–O–Cu′–O′ 0.0, N–Cu–O–O′ 174.2. NBO charges: Cu +1.40, O –0.93, N –1.32, P +1.55.

distance of 2.338(6) Å is unexceptional.[6] The Cu–N bond lengths of 1.980(4) and 1.976(4) Å underline the presence of copper(III), consistent with all spectroscopic data even in the absence of K-edge X-ray absorption investigations.[12] The minimally elongated Si–N bonds compared to ethylene complex **1** can be attributed to the reduced negative partial charge of the nitrogen atoms in **2**. For the first time, the neutral species **2** offers an opportunity to compare theoretical and experimental geometries without Coulomb repulsion artifacts, which are a problem for calculations of gas-phase dications.

Full B3LYP 6-311+G(2d,p) geometry optimization of the simplified model complex [{H$_2$P(NH)$_2$-κ^{2}N}$_2$Cu$_2$(μ-O)$_2$] **3** accurately reproduces the PN$_2$Cu geometry.¶ The Cu$_2$O$_2$ core is similar to that of the dicationic bis(μ-oxo) dicopper(III) complexes,[3,6] however, the calculation underestimates the Cu–O bond length by 0.066 Å and the Cu–Cu distance by 0.167 Å compared to the solid-state structure of **2** (Fig. 2).

From CASSCF and DFT calculations as well as from orbital arguments for the dicationic model [{(H$_3$N)$_3$Cu}$_2$(μ-O)$_2$]$^{2+}$, Tolman and coworkers have rationalized that the energy surface for elongating the Cu$_2$O$_2$ core of bis(μ-oxo) copper complexes in the Cu–Cu direction, with concomitant decrease of the O–O distance, is flat.[13] This is corroborated by a single-point calculation for model **3** with the experimental Cu$_2$O$_2$ geometry of **2**, leading to an increase in energy of only 19.4 kJ mol^{-1}. Thus steric interactions in the solid-state structure of real system **2** and the need for a still higher level of theory may explain the discrepancy between the Cu$_2$O$_2$ cores of the computed model **3** and of **2**. By contrast, accurate [(H$_3$N)$_6$Cu$_2$O$_2$]$^{2+}$ geometries were obtained even with modest basis sets.[13] However, such studies on dications may benefit from a mutual cancellation of errors due to an underestimation of bond lengths by small basis sets§ and bond enlargement by repulsive Coulomb forces, respectively.

Related to the well documented small isomerization barrier between dicationic bis(μ-oxo) copper(III) and (μ-η^2:η^2)peroxo copper(II) complexes,[3,6a] a relative stabilization of the bis(μ-oxo) core in **2** can be expected from the electronic stabilization of high copper oxidation states by the iminophosphanamide ligand and the lack of intramolecular Coulomb repulsion, which would favor the peroxo isomer.[11] We expect compound **2** to allow further interesting model studies.

Notes and references

‡ *Synthesis of* **2**: 421 mg of ethylene complex **1**[7] (1.02 mmol) are dissolved in 50 ml of pentane in a Schlenk tube under an argon atmosphere. The Schlenk tube is sealed with a CaCl$_2$ drying tube, the solution is heated to reflux and subsequently cooled to −25 °C. Upon cooling, atmospheric dioxygen is automatically drawn into the Schlenk tube through the CaCl$_2$ drying tube. Dark brown crystals grow from the brown solution. After 20 h, the mother liquor is removed, the crystals are washed with pentane and dried at 10^{-3} mbar. 295 mg (0.37 mmol, 72%) of **2** are isolated; 87–88 °C color change to green, mp 126 °C (decomp.); IR (KBr/cm^{-1}): ν/cm^{-1} 2951m, 2901m, 1478w, 1396w, 1363w, 1248m, 1149m, 1115s, 845s, 756m, 691m, 633m; UV (pentane, c ≈ 0.4 mM): $λ_{max}$/nm 256 (≈ 315 sh), 444 ($ε$ 10^4 M^{-1}

cm^{-1}); ^{1}H NMR (268 K, toluene-d$_8$, 300.13 MHz): $δ$ 1.11 [d, $^3J_{PH}$ 14.5 Hz, C(CH$_3$)$_3$, 36H], 0.45 [s + sat, $^1J_{CH}$ 117 Hz, Si(CH$_3$)$_3$; 36H]; ^{13}C{^{1}H} NMR (298 K, C$_6$D$_6$, 75.47 MHz): $δ$ 27.30 [d, $^2J_{PC}$ 2 Hz, C(CH$_3$)$_3$], 5.38 [d, $^3J_{PC}$ 2 Hz, Si(CH$_3$)$_3$], C(CH$_3$)$_3$ not found because of low solubility and too rapid decomposition of **2** at room temperature; ^{29}Si{^{1}H} NMR (DEPT) (298 K, CDCl$_3$, 99.36 MHz): $δ$ −4.3 (d + sat, $^2J_{PSi}$ 7 Hz); ^{31}P{^{1}H} NMR (268 K, toluene-d$_8$, 121.50 MHz): $δ$ 82.6 (s + sat, $^2J_{PSi}$ 7 Hz); LT-FAB[11] (toluene) (%): m/z 798.3 (63) [M$^+$], 781.3 (73) [M − OH$^-$], 768.3 (85) [M$^+$ − CH$_2$O], 767.3 (80) [M − CH$_3$O$^-$], 711.2 (35) [M$^+$ − Bu^t − CH$_2$O], 631.3 (100) [(LH)$_2$Cu$^+$ + H − SiMe$_3$], 305.3 (88) [LH$^+$ − Me], correct isotopic pattern; Anal. C$_{28}$H$_{72}$N$_4$Cu$_2$P$_2$Si$_4$: calc: C, 42.13; H, 9.09; N, 7.02; P, 7.76; found: C, 42.51; H 9.05; N, 7.07; P, 7.64%.

§ Single crystals suitable for X-ray diffraction analysis were obtained by slow oxidation of **1** in a pentane solution at −25 °C with trace amounts of dioxygen in argon. Higher temperatures or air as oxidant only led to microcrystalline material. Data were collected on a Bruker SMART CCD instrument[14,15] *Crystal data* for **2**: C$_{28}$H$_{72}$Cu$_2$N$_4$O$_2$P$_2$Si$_4$, M = 798.28, monoclinic, space group $C2/c$ $μ$ = 1.186 mm^{-1}, $R1$ = 0.058, $wR2$ = 0.140 (observed reflections), a = 28.4009(7), b = 11.2930(3), c = 16.9370(5) Å, $β$ = 126.604(1)°, V = 4360.9(2) Å^3, T = 200(2) K, Z = 4, half a molecule per asymmetric unit, 21976 reflections measured 4991 independent (R_{int} = 0.0629). CCDC 182/1720. See http://www.rsc.org/suppdata/cc/b0/ b004173o/ for crystallographic files in .cif format.

¶ For the DFT calculations, the empirically parametrized B3LYP[16] method within the Gaussian 98 (Revision A.5) package[17] was used. Restricted and unrestricted energy calculations of singlet **3** yield identical energies (−4338.1224 E_h). an unrestricted single point calculation of triplet **3** leads to an energy 105.4 kJ mol^{-1} above the singlet [B3LYP 6-31G(d): 102.2 kJ mol^{-1}]. Cu–Cu distance of **3**: B3LYP 6-31G(d): 2.685 Å; B3LYP 3-21G: 2.649 Å. NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter and F. Weinhold.

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