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Synthetic Analogues of Nitrite Adducts of Copper Proteins: Characterization and Interconversion of Dicopper(I,I) and -(I,II) Complexes Bridged Only by NO$_2^-$

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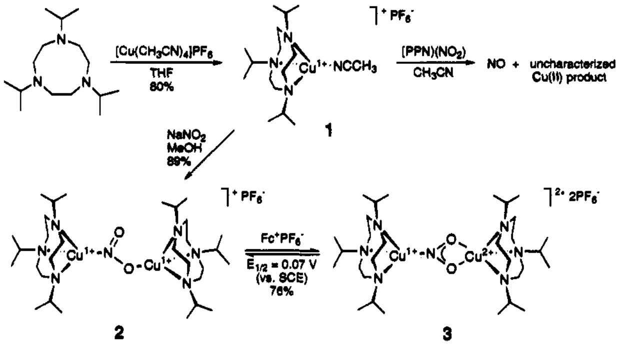
Copper-containing enzymes from bacteria catalyze the reduction of nitrite (NO$_2^-$) to NO, N$_2$O, and/or N$_2$ during biological denitrification, a key process in the global nitrogen cycle.[1–4] It has been proposed that the mechanism of nitrite reduction by copper nitrite reductases involves initial coordination of NO$_2^-$ to a single active site copper ion, presumed to be in the +1 oxidation state, followed by dehydration to generate a reactive copper nitrosyl species.[5–9] Nitrite adducts have also been implicated during studies of nitrogen oxide interactions with other copper proteins, the proposed NO$_2^-$ complex of the mixed valence (semimet, Cu^{I}Cu^{II}) form of hemocyanin being a noteworthy and controversial case.[10,11] Although synthetic modeling studies have provided structural and spectroscopic analogues for Cu(II)–(NO$_2^-$) interactions in proteins,[12–15] nitrite complexed to Cu(I) ions in mono- or dinuclear complexes has not been identified. We have therefore begun to pursue Cu(I)–(NO$_2^-$) species as targets for synthetic, spectroscopic, and mechanistic investigation as part of our efforts to unravel the fundamental chemistry underlying the interactions of nitrogen oxides with copper sites in biological and heterogeneous catalytic systems.[12,15–18] Here we report the isolation, structural characterization, and redox interconversions of novel nitrite-bridged Cu(I)Cu(I) and Cu(I)Cu(II) complexes that model putative biological intermediates and exhibit unusual structural and spectroscopic features.

Scheme 1



The starting material for our synthetic studies is [(*i*-Pr$_3$TACN)Cu(CH$_3$CN)]PF$_6$ (**1**), which was isolated in 80% yield from the reaction of [Cu(CH$_3$CN)$_4$]PF$_6$ with *i*-Pr$_3$TACN (1,4,7-triisopropyl-1,4,7-triazacyclononane)[19] in THF (Scheme 1).[20] Treatment of **1** with (PPN)(NO$_2$) in CH$_3$CN resulted in slow (>1 day) oxidation of the complex to an uncharacterized Cu(II)-containing species and generation of 1 equiv of NO gas (GC), a common type of reaction[21] that nonetheless models the activity of nitrite reductases.[5–8] In contrast, addition of excess NaNO$_2$ to a solution of **1** in MeOH yielded a yellow solution, from which yellow crystals of a unique dicopper(I) complex, [(*i*-Pr$_3$TACN)$_2$Cu$_2$(μ_2-(η^1-*N*:η^1-*O*)-NO$_2$)]PF$_6$ (**2**), were isolated in 89% yield.[20]

An X-ray crystal structure determination confirmed the dimeric formulation for **2**, which represents the first example of a copper(I)–nitrite complex (Figure 1).[22] Both Cu(I) ions adopt C_{3v}-distorted tetrahedral geometries characterized by small intraligand N$_L$–Cu–N$_L$ angles (N$_L$ = *i*-Pr$_3$TACN nitrogen; average 85.4°) and large N$_L$–Cu–N(O)$_{\text{nitrite}}$ angles (average 128.2°). The bridging nitrite ion coordinates to one Cu(I) ion via its N atom, an interaction characterized by a rather short bond distance of 1.899(2) Å, and to the other metal center via the *syn* lone pair of one O atom (O(2)). The entire Cu–(μ_2-NO$_2$)–Cu unit is coplanar. Internuclear distances of 2.786(2) and 2.820(2) Å from O(1) to Cu(1) and Cu(2), respectively, suggest that the bonding between these atoms is weak or nonexistent. This description is corroborated by the copper coordination geometries that are relatively unperturbed from C_{3v} symmetry and the observation that the N(1)–O(1) bond length is ~0.04 Å shorter than the N(1)–O(2) distance [1.235(3) Å vs 1.279(3) Å, respectively]. Similar μ_2-(η^1-*N*:η^1-*O*)-nitrite geometries have been identified in polynuclear complexes of other transition metals, but because of the presence of additional bridging ligands in

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(22) The crystal of **2** selected for data collection was mounted in the cold stream (128 K) of a Siemens P4 diffractometer equipped with a LT-2 low-temperature apparatus. The radiation employed was Ni-filtered Cu Kα from a Siemens rotating anode source operating at 15 kW. A linear decay of 2.7% in the intensities of three standard reflections was observed during data collection, and the data were scaled to adjust for this decay. The structure was solved in the space group $P\bar{1}$ using direct and difference Fourier methods. Hydrogens were added geometrically and refined by use of a riding model and fixed isotropic thermal parameters. Refinement was by full-matrix least-squares methods, with anisotropic thermal parameters for all non-hydrogen atoms. The final difference map was featureless. Crystal data: triclinic, space group $P\bar{1}$ (No. 2), at 128 K, a = 10.736(1) Å, b = 13.710(1) Å, c = 14.566(1) Å, α = 74.380(7)°, β = 76.130(8)°, γ = 73.270(8)°, V = 1946.6(3) Å^3, Z = 2, R = 0.033, and R_w = 0.040 for 4412 reflections with $F > 4\sigma(F)$ and 433 parameters.

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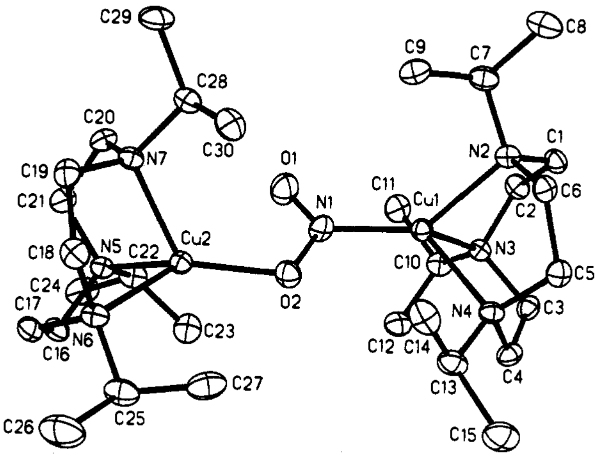

Figure 1. Computer generated representation of the cation in the X-ray structure of $[(i\text{-Pr}_3\text{TACN})_2\text{Cu}_2(\mu_2\text{-}(\eta^1\text{-}N{:}\eta^1\text{-}O)\text{-NO}_2)]\text{PF}_6$ (**2**) (50% ellipsoids, hydrogen atoms not shown for clarity). Selected intramolecular distances (Å) and angles (deg): Cu(1)–N(1), 1.899(2); Cu(1)–N(2), 2.156(2); Cu(1)–N(3), 2.117(3); Cu(1)–N(4), 2.178(2); Cu(2)–O(2), 1.968(2); Cu(2)–N(5), 2.137(3); Cu(2)–N(6), 2.157(3); Cu(2)–N(7), 2.152(2); O(1)–N(1), 1.235(3); O(2)–N(1), 1.279(3); N(1)–Cu(1)–N(2), 133.5(1); N(1)–Cu(1)–N(3), 129.4(1); N(2)–Cu(1)–N(3), 85.6(1); N(1)–Cu(1)–N(4), 122.1(1); N(2)–Cu(1)–N(4), 84.2(1); N(3)–Cu(1)–N(4), 86.1(1); O(2)–Cu(2)–N(5), 132.7(1); O(2)–Cu(2)–N(6), 130.9(1); N(5)–Cu(2)–N(6), 84.8(1); O(2)–Cu(2)–N(7), 121.1(1); N(5)–Cu(2)–N(7), 86.9(1); N(6)–Cu(2)–N(7), 84.8(1); Cu(2)–O(2)–N(1), 117.7(7); Cu(1)–N(1)–O(1), 124.1(2); Cu(1)–N(1)–O(2), 119.8(2); O(1)–N(1)–O(2), 116.0(2).

these cases, metal coordination to the *anti* oxygen lone pair is observed instead of to the *syn* lone pair as seen for **2**.[23-25]

Cyclic voltammetry of **2** in 0.5 M Bu_4NPF_6 in CH_2Cl_2 revealed an electrochemically quasi-reversible ($\Delta E_p = 110$ mV, scan rate $= 0.1$ V/s) and chemically reversible ($i_{pa}/i_{pc} \approx 1$) oxidation with $E_{1/2} = 0.07$ V vs SCE.[26] Coulometric experiments verified that the electrochemical process involves reversible transfer of one electron per dicopper pair; the cyclic voltammogram of the product of stoichiometric oxidation (initial scan cathodic) matches that of **2** (initial scan anodic). The oxidation product was isolated as red-brown crystals in 76% yield by treatment of a CH_2Cl_2 solution of **2** with ferrocenium hexafluorophosphate and identified as $[(i\text{-Pr}_3\text{TACN})_2\text{Cu}_2(\mu_2\text{-}(\eta^1\text{-}N{:}\eta^2\text{-}O,O)\text{-NO}_2)](\text{PF}_6)_2$ (**3**) from analytical, spectroscopic, and preliminary X-ray crystallographic data (Scheme 1).[20,27] A localized, mixed valent $\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}$ formulation for **3** is suggested by the presence of an axial signal with four Cu hyperfine features ($g_\perp = 2.07$, $g_\parallel = 2.24$, $A_\parallel = 130$ G) in its X-band EPR spectrum that integrated for 46(2)% of the total copper at 77 K, as well as by the differing copper ion geometries identified from the initial X-ray structural results (tetrahedral and square pyramidal for the N-bound and O,O-bound centers, respectively). The $\eta^1\text{-}N{:}\eta^2\text{-}O,O$ nitrite bridge is an aspect of the structure of **3** that, to our knowledge, has no precedent in transition metal chemistry.[28] An intense optical absorption band with $\lambda_{\max} = 444$ nm (ϵ 2500 $\text{M}^{-1}\ \text{cm}^{-1}$) is a distinctive signature of the complex which may arise from a CT transition involving the nitrite bridge; resonance Raman spectroscopic experiments designed to uncover the nature of this absorption feature, as well as the vibrational modes of the unique $\mu\text{-NO}_2^-$ moiety, are underway.

With the isolation and characterization of compounds **2** and **3**, we have provided key structural benchmarks useful for comparison to data acquired for copper–nitrite adducts in proteins. Specific precedence now exists for coordination of NO_2^- to Cu(I) via its N or O atoms and for bridging of NO_2^- between Cu(I) and Cu(I) or Cu(II) ions, interaction modes that may be important in copper nitrite reductase reaction pathways[5-8] and in the binding of nitrite to other multicopper proteins.[10] The redox-initiated changes in bridging modes between $\eta^1\text{-}N{:}\eta^1\text{-}O$ and $\eta^1\text{-}N{:}\eta^2\text{-}O,O$ during the interconversion of **2** and **3** is a particularly intriguing feature of their chemistry that is in some respects akin to the "carboxylate shift" identified in metal–carboxylate complex structures and postulated to be kinetically important in polymetalloproteins.[29] It remains to be seen whether shifts in nitrite binding modes such as that exhibited by the **2**/**3** system are significant in nitrogen oxide activation pathways in biology.

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Supplementary Material Available: Analytical and spectroscopic data for **1**–**3** and structure determination summary with tables of bond lengths, bond angles, atomic coordinates, and thermal parameters for **2** (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(27) A preliminary X-ray structure determination clearly confirmed the presence of the $\text{Cu}_2(\mu_2\text{-}(\eta^1\text{-}N{:}\eta^2\text{-}O,O)\text{-NO}_2)$ core in **3**, but disorder involving the PF_6^- counterions and the $i\text{-Pr}_3\text{TACN}$ ligands has hindered complete solution of the structure. Some relevant crystal data: orthorhombic, space group *Pnma* (No. 62), at 297 K, $a = 25.677(9)$ Å, $b = 11.13(1)$ Å, $c = 16.44(1)$ Å, $V = 4698(5)$ Å^3, $Z = 4$, $R = 0.137$, and $R_w = 0.135$ for 1182 reflections with $F > 2\sigma(F)$ and 145 parameters.

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