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Antiferromagnetic Adducts of Copper(II) Propionate with Pyridyl Nitronyl Nitroxides

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Copper(II) propionate was reacted with 2-(4-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide (*p*-nitpy), 2-(3-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide (*m*-nitpy), and 2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide (*o*-nitpy) to isolate three complexes, which were characterized by measurements of the infrared and electronic spectra, as well as the magnetic susceptibilities. Single-crystal X-ray analyses reveal that the former two complexes are adducts of dimeric copper(II) propionate, $[Cu_2(pro)_4(p\text{-nitpy})_2]$ (**1**) (Hpro = C_2H_5COOH) and $[Cu_2(pro)_4(m\text{-nitpy})_2]$ (**2**), and that the latter complex is bis(picolinato)copper(II) dihydrate ($\mathbf{3}\cdot 2H_2O$).

There has been considerable interest in metal complexes with nitronyl nitroxides.[1] One of the fascinating strategies toward designing metal nitroxide complexes is the use of metal carboxylates as a metal source. Recently, some efforts to make nitroxide adducts have been made with a combination of metal carboxylates and nitronyl nitroxide radicals.[2—9] However, in the case of copper(II) carboxylates, none of them were successful in producing such compounds, except for nitroxide adducts of copper(II) trichloroacetate, reported by Doedens et al.[10,11] The magnetic property of the nitroxide adduct of copper(II) carboxylates should be interesting, because they provide a novel example of a linear 1/2-1/2-1/2-1/2 spin system. In the only few reported adducts, all of the dinuclear skeletons differ from the well-known dimeric copper(II) acetate structure, and the geometries of the copper atoms are distorted trigonal bipyramidal, resulting in the diamagnetic property of these adducts.[10b] In this study, we tried to obtain new adducts of copper(II) carboxylate and nitronyl nitroxides, in which the dinuclear copper(II) structure with a square-pyramidal coordination about the two copper atoms is maintained by a reaction of copper(II) propionate $[Cu_2(pro)_4]$ (Hpro = C_2H_5COOH) and nitronyl nitroxides having a pyridyl group, 2-(4-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide (*p*-nitpy), 2-(3-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide (*m*-nitpy), and 2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide (*o*-nitpy). The isolated complexes were characterized by measurements of the infrared and electronic spectra and the magnetic susceptibilities. We report here on our findings concerning this system.

Experimental

Synthesis of the Complexes. 2-(4-Pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide (*p*-nitpy), 2-(3-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide (*m*-nitpy), and 2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide (*o*-nitpy) were synthesized according to a method reported in the literature.[12]

The starting material, copper(II) propionate, was prepared as follows.

$[Cu_2(pro)_4]$. To a stirred solution of sodium propionate (9.60 g, 100 mmol) in distilled water (30 cm^3) was added copper(II) nitrate trihydrate (12.04 g, 49.83 mmol). A white-blue precipitate immeadiately formed, which was filtered, washed by distilled water, and dried in vacuo over P_2O_5. Recrystallization was carried out from acetonitrile. Dark-blue crystals were deposited. They were filtered off and dried in vacuo over P_2O_5: Yield 8.36 g (40%). Found: C, 34.25; H, 4.96%. Calcd for $C_{12}H_{20}Cu_2O_8$: C, 34.37; H, 4.81%. FT-IR (KBr) 1589 (COO^-), 1424 (COO^-) cm^{-1}.

$[Cu_2(pro)_4(p\text{-nitpy})_2]$(1). Copper(II) propionate (42 mg, 0.10 mmol) was dissolved in 20 cm^3 of acetonitrile; then, *p*-nitpy (47 mg, 0.20 mmol) was added. After the solution had been filtered, the filtrate was kept at room temperature for one month. Dark-green columnar crystals were deposited and collected by filtration and dried in vacuo over P_2O_5: Yield, 73 mg (82%). Found: C, 48.47; H, 5.91; N, 9.61%. Calcd for $C_{36}H_{52}Cu_2N_6O_{12}$: C, 48.81; H, 5.69; N, 9.49%. FT-IR (KBr) 3100 (CH), 1619 (COO^-), 1432 (COO^-), 1373 (NO) cm^{-1}.

$[Cu_2(pro)_4(m\text{-nitpy})_2]$(2). To a solution of copper(II) propionate (42 mg, 0.10 mmol) in acetonitrile (10 cm^3), *m*-nitpy (47 mg, 0.20 mmol) was added. The solution was then filtered. After the filtrate was allowed to stand at room temperature for one month, dark-green columns resulted, which were filtered and dried in vacuo over P_2O_5: Yield, 72 mg (81%). Found: C, 48.52; H, 6.01; N, 9.47%.

Calcd for $C_{36}H_{52}Cu_2N_6O_{12}$: C, 48.81; H, 5.69; N, 9.49%. FT-IR (KBr) 3094 (CH), 1616 (COO^-), 1430 (COO^-), 1373 (NO) cm^{-1}.

$[Cu_2(pic)_2]$ (Hpic = C_5H_4NCOOH) (3). To a solution of copper(II) propionate (101 mg, 0.241 mmol) in acetonitrile (7 cm^3), *o*-nitpy (121 mg, 0.516 mmol) was added. The solution was then filtered. After the filtrate was allowed to stand at room temperature for two weeks, blue crystals resulted, which were filtered and dried in vacuo over P_2O_5: Yield, 15 mg (16%). Found: C, 46.89; H, 2.62; N, 9.16%. Calcd for $C_{12}H_8CuN_2O_4$: C, 46.83; H, 2.62; N, 9.10%. FT-IR (KBr) 3471 (OH), 3075 (CH), 1646 (COO^-), 1350 (COO^-) cm^{-1}.

Measurements. Carbon, hydrogen, and nitrogen analyses were carried out using a Perkin-Elmer 2400 Series II CHNS/O Analyzer. Infrared spectra were measured with a JASCO MFT-2000 FT-IR Spectrometer in the 4000—600 cm^{-1} region. The electronic spectra were measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer (Model UV-3100). The temperature dependence of the magnetic susceptibilities was measured with a Quantum Design MPMS-5S SQUID susceptometer operating at a magnetic field of 0.5 T between 4.5 and 300 K. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants.[13] The effective magnetic moments were calculated from the equation $\mu_{\mathrm{eff}} = 2.828\sqrt{\chi_{\mathrm{A}}T}$, where χ_{A} is the atomic magnetic susceptibility.

X-Ray Crystal Structure Analyses. Each crystal was sealed in a glass capillary together with the mother liquor and mounted on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-$K\alpha$ radiation at 25±1 °C. The unit-cell parameters were determined by a least-squares refinement based on 25 reflections with $20 \leq 2\theta \leq 30$ °. Intensitiy data were corrected for Lorentz-polarization effects and for absorption. The structures were solved by direct methods and refined by full-matrix least-squares methods using the weighting scheme $w = 1/[\sigma^2(|F_0|)+(0.02|F_0|)^2+1.0]$. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were inserted at their calculated positions and fixed at their positions. All of the calculations were carried out on a VAX station 4000 90A computer using a MolEN program package.[14]

Crystallographic data: for **1**; $C_{36}H_{52}Cu_2N_6O_{12}$. $F.W.$ = 887.93, triclinic, space group $P\bar{1}$, $a = 7.289(2)$, $b = 10.086(2)$, $c = 14.780(3)$ Å, $\alpha = 82.72(2)$, $\beta = 82.19(2)$, $\gamma = 73.61(2)°$, $V = 1028.3(4)$ $Å^3$, $Z = 1$, $D_m = 1.44$, $D_c = 1.43$ $g\,cm^{-3}$, μ (Mo $K\alpha$) = 10.99 cm^{-1}, crystal dimensions $0.30\times0.40\times0.55$ mm^3, 3611 reflections measured ($2\theta_{\max} = 50°$), 2880 [$I \geq 3\sigma(I)$] used in the refinement, $R = \sum||F_0|-|F_c||/\sum|F_0| = 0.030$, $R_w = [\sum w(|F_0|-|F_c|)^2/\sum w|F_0|^2]^{1/2} = 0.034$. For **2**; $C_{36}H_{52}Cu_2N_6O_{12}$, $F.W.$ = 887.93, triclinic, space group $P\bar{1}$, $a = 9.282(3)$, $b = 10.627(3)$, $c = 11.907(3)$ Å, $\alpha = 110.64(2)$, $\beta = 96.63(2)$, $\gamma = 104.75(2)°$, $V = 1035.3(6)$ $Å^3$, $Z = 1$, $D_m = 1.42$, $D_c = 1.43$ $g\,cm^{-3}$, μ (Mo $K\alpha$) = 10.92 cm^{-1}, crystal dimensions $0.35\times0.45\times0.60$ mm^3, 3635 reflections measured ($2\theta_{\max} = 50°$), 2877 [$I \geq 3\sigma(I)$] used in the refinement, $R = 0.040$, $R_w = 0.048$. For **3**·$2H_2O$; $C_{12}H_{12}CuN_2O_6$, $F.W.$ = 343.78, triclinic, space group $P\bar{1}$, $a = 5.136(2)$, $b = 7.641(2)$, $c = 9.232(3)$ Å, $\alpha = 74.88(2)$, $\beta = 84.28(2)$, $\gamma = 71.47(3)°$, $V = 331.6(2)$ $Å^3$, $Z = 1$, $D_m = 1.86$, $D_c = 1.72$ $g\,cm^{-3}$, μ (Mo $K\alpha$) = 16.77 cm^{-1}, crystal dimensions $0.17\times0.20\times0.35$ mm^3, 1158 reflections measured ($2\theta_{\max} = 50°$), 1123 [$I \geq 3\sigma(I)$] used in the refinement, $R = 0.030$, $R_w = 0.043$. The X-ray analyses data have been deposited as Document No. 73059 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 14806–148038.

Table 1. Selected Interatomic Distances (l/Å) and Bond Angles (ϕ/°) with Their Estimated Standard Deviations in Parentheses

$[Cu_2(pro)_4(p\text{-nitpy})_2]$ (**1**)			
Cu–Cu′ [a]	2.628(1)	Cu–N1	2.189(2)
Cu–O1	1.966(3)	O5–N2	1.271(3)
Cu–O2′	1.979(3)	O6–N3	1.274(4)
Cu–O3	1.960(2)	O5–O6″ [b]	3.920(3)
Cu–O4′	1.966(2)	O6–O6* [c]	3.847(3)
Cu′–Cu–O1	82.39(7)	O1–Cu–N1	96.9(1)
Cu′–Cu–O2′	85.83(6)	O2′–Cu–O3	89.2(1)
Cu′–Cu–O3	84.17(7)	O2′–Cu–O4′	88.2(1)
Cu′–Cu–O4′	83.93(7)	O2′–Cu–N1	94.91(9)
Cu′–Cu–N1	179.19(7)	O3–Cu–O4′	168.0(1)
O1–Cu–O2′	168.18(9)	O3–Cu–N1	96.17(8)
O1–Cu–O3	90.5(1)	O4′–Cu–N1	95.75(8)
O1–Cu–O4′	89.6(1)		
$[Cu_2(pro)_4(m\text{-nitpy})_2]$ (**2**)			
Cu–Cu′ [d]	2.631(1)	Cu–N1	2.192(3)
Cu–O1	1.970(3)	O5–N2	1.267(5)
Cu–O2′	1.961(2)	O6–N3	1.283(4)
Cu–O3	1.972(2)	O5–O5″ [e]	4.423(5)
Cu–O4′	1.980(3)	O6–O6* [f]	4.275(5)
Cu′–Cu–O1	83.5(1)	O1–Cu–N1	95.2(1)
Cu′–Cu–O2′	84.5(1)	O2′–Cu–O3	89.3(1)
Cu′–Cu–O3	83.51(9)	O2′–Cu–O4′	89.2(1)
Cu′–Cu–O4′	84.69(9)	O2′–Cu–N1	96.8(1)
Cu′–Cu–N1	178.67(8)	O3–Cu–O4′	168.2(1)
O1–Cu–O2′	168.0(1)	O3–Cu–N1	96.3(1)
O1–Cu–O3	89.3(1)	O4′–Cu–N1	95.5(1)
O1–Cu–O4′	89.8(1)		
$[Cu(pic)_2]\cdot2H_2O$(**3**·$2H_2O$)			
Cu–O1	1.942(2)	O3···O3″ [g]	2.852(5)
Cu–N	1.964(2)	O3···O3* [h]	2.766(5)
O2···O3	2.915(4)		
O1–Cu–N	83.47(8)	O1–Cu–N′ [i]	96.53(8)

a) Prime refers to the equivalent position (−x, −y, 2 − z).
b) Double prime refers to the equivalent position (1 + x, y, z).
c) Star refers to the equivalent position (1 − x, −y, 1 − z).
d) Prime refers to the equivalent position (2 − x, −y, 2 − z).
e) Double prime refers to the equivalent position (1 − x, −y, 1 − z). f) Star refers to the equivalent position (1 − x, 1−y, 1 − z). g) Double prime refers to the equivalent position (1 − x, −y, −1 −z). h) Star refers to the equivalent position (2 − x, −y, −1 −z). i) Prime refers to the equivalent position (−x, −y, −z).

Results and Discussion

Doedens et al described that the presence of a halogen substituent in copper(II) carboxylates appeared necessary for nitroxide adduct formation, because no analogous product could be obtained with unsubstituted copper(II) acetate.[10] However, when we treated copper(II) propionate with 2-(4-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide (*p*-nitpy) in acetonitrile, a nitroxide adduct **1** was isolated. The X-ray crystal structure of **1** shows that it is a nitroxide adduct $[Cu_2(pro)_4(p\text{-nitpy})_2]$, as shown in Fig. 1. The complex has a crystallographic inversion center at the center of the Cu_2 core. The Cu–Cu′ distance [2.628(1) Å)] is significantly longer than those of $[Cu_2(pro)_4(H_2O)_2]$ [2.575(4), 2.589(5), and 2.620(3) Å][15] and in the range of those found in the reported adducts of copper(II) propionate $[Cu_2(pro)_4L_2]$ (L = pyridine, picolines) [2.631(1)—2.647(4) Å].[16—19] It is to be noted that each nitronyl nitroxide is coordinated to the copper atom via the pyridyl group of *p*-nitpy with a Cu–N1 distance of 2.189(2) Å. The coordination geometry of the copper atom is a square pyramid, as normally found in the adducts of copper(II) acetate. The successful isolation of the adduct of copper(II) propionate with a square-pyramidal coordination may be ascribed to the presence of the pyridyl group of the nitronyl nitroxide, which is a good donor as the axial ligation. During the course of the present work,[20] the analogous, $[Cu_2(CH_3COO)_4(p\text{-nitpy})_2]$, $[Cu_2((CH_3)_3CCOO)_4(p\text{-nitpy})_2]$, and $[Cu_2(C_6H_5CH_2COO)_4(m\text{-nitpy})_2]$, were reported.[21] These complexes have very similar dinuclear structures to that of **1**. In **1**, the basal Cu–O distances range from 1.960(2) to 1.979(3) Å, which are within the normal range in the copper(II) propionate adducts [Cu–O 1.954(9)—1.981(2) Å].[16—19] The copper atom is displaced toward the apical pyridyl-nitrogen atom from the basal O1–O3–O2′–O4′ plane by 0.20 Å. The N–O bond lengths of the *p*-nitpy moiety are 1.271(3) and 1.274(4) Å for N2–O5 and N3–O6, respectively. These values are in the range observed for nitronyl nitroxide radicals.[7] The closest intermolecular contacts [O5···O6 (1+x, y, z) 3.920(3) Å, O6···O6 (1−x, −y, 1−z) 3.847(3) Å] between uncoordinated N–O groups are not expected to mediate strong exchange interactions, but may be considered to cause a weak intermolecular radical–radical interaction (Fig. 2). In the infrared spectrum of **1**, the $\nu_{as}(COO)$ and $\nu_s(COO)$ bands appear at 1619 and 1432 cm^{-1}, respectively, as in the case of $[Cu_2(pro)_4]$ [$\nu_{as}(COO)$ 1589, $\nu_s(COO)$ 1424 cm^{-1}]. The separation between the $\nu_{as}(COO)$ and $\nu_s(COO)$ frequencies are diagnostic of *syn-syn* bridging of carboxylato ligands.[22] The diffuse reflectance spectrum of **1** is shown in Fig. 3 together with those of copper(II) propionate and *p*-nitpy. The intense band at 371 nm is characteristic of copper(II) carboxylate dimers.[23] In the visible region, a broad band with multiple peaks appears at around 675 nm, and can be assigned as d-d transition bands. The multiple peaks (494, 565, 629 nm) may come from superimposition with the spectrum

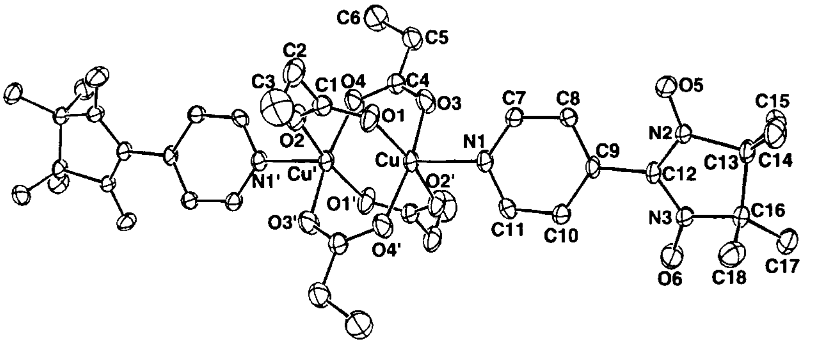

Fig. 1. ORTEP drawing of the structure of $[Cu_2(pro)_4(p\text{-nitpy})_2]$ (**1**) showing the 35% probability thermal ellipsoids and atom labeling scheme. Hydrogen atoms are omitted for clarity. Primed and unprimed atoms are related by the inversion.

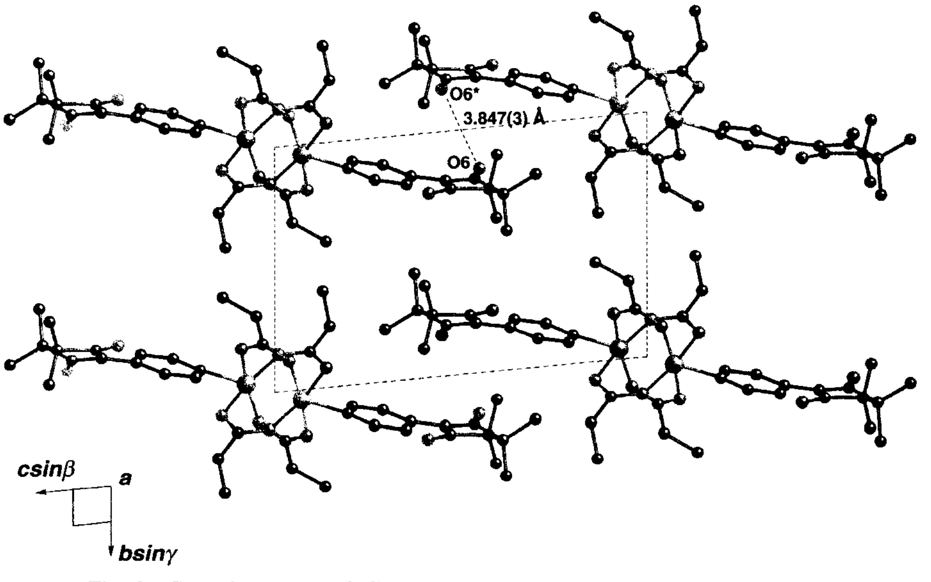

Fig. 2. Crystal structure of $[Cu_2(pro)_4(p\text{-nitpy})_2]$ (**1**) viewed along the *a* axis.

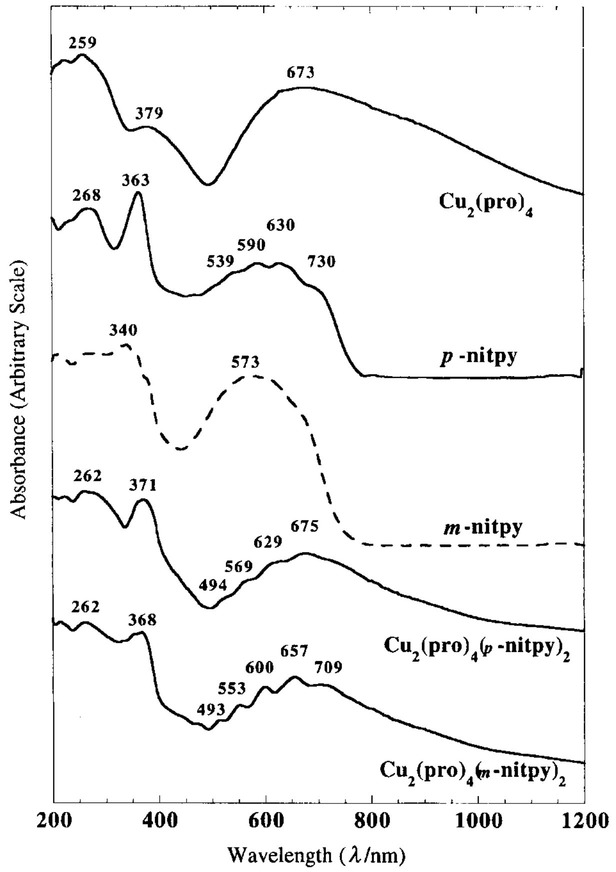

Fig. 3. Diffuse reflectance spectra of nitronyl nitroxides, copper(II) propionate and its adducts.

of the p-nitpy radical. The magnetic property of **1** is different from those of Doedens et al.'s compounds.[10,11] The effective magnetic moment of **1** is 3.17 B.M. per molecule at room temperature. This is lower than the spin-only value (3.46 B.M.) for non-interacting 1/2-1/2-1/2-1/2 spins. The magnetic moment gradually decreases from room temperature to ca. 25 K, then decreases rapidly with lowering of temperature, and reaches a value of 1.42 B.M. at 4.5 K (Fig. 4). A plot of χ_M^{-1} vs. temperature shows that the magnetic data of **1** follow the Curie–Weiss law, $\chi_M = C/(T-\theta)$, with θ values of −7.5 and −204 K for temperature ranges of 4.5—125 and 150—300 K, respectively. This suggests that the magnetic behavior is antiferromagnetic as a whole. However, the magnetic behavior is different from those of the usual adducts of copper(II) carboxylate dimers, which show a monotonous decrease of the magnetic moment with lowering the temperature.[24] This may come from an additional magnetic interaction between the nitronyl nitroxide and copper atom to a strong antiferromagnetic interaction between the two copper atoms, although the magnetic coupling between the nitroxide radical and the copper atom through the pyridyl group should be weak. In the present case, the radical-radical interaction also can not be neglected, because a significant antiferromagnetic interaction was often observed when uncoordinated N–O groups of the radicals were at relatively short distances (3.5—4.0 Å) from each other.[25] Therefore, we estimated the interaction by introducing the Weiss temperature to the susceptibility equation based on a model consisting of a dinuclear copper(II) unit and two mononuclear radicals,

$$\chi_M = (2Ng^2\beta^2/kT)\,[3+\exp(-2J/kT)]^{-1} + C/(T-\theta) + 2N\alpha, \quad (1)$$

where J is the exchange integral for the two copper(II) ions, θ is the Weiss temperature to account for the weak interaction between the radical and copper atom and/or the radical–radical interaction, and the other symbols have their usual meanings. The best fitting parameters were obtained by fixing $N\alpha$ at 60×10^{-6} cm^3 mol^{-1}. The obtained values are $J = -213$ cm^{-1}, $g = 2.34$, $\theta = -8.2$ K, and $C = 0.871$ cm^3 Kmol^{-1}. The J value means a strong antiferromagnetic interaction between the two copper atoms, and is comparable to those of copper(II) propionate and its adducts ($J = -150$—200 cm^{-1}).[23,26,27] A negative θ value suggests that the interaction between the nitroxide radical and the copper atom and/or the radical-radical interaction are antiferromagnetic. Therefore, antiferromagnetic interactions are dominant in this system. A similar magnetic behavior was observed for related adducts: $[Cu_2(CH_3COO)_4(p\text{-nitpy})_2]$, $[Cu_2((CH_3)_3CCOO)_4(p\text{-nitpy})_2]$, and $[Cu_2(C_6H_5CH_2COO)_4(m\text{-nitpy})_2]$.[21]

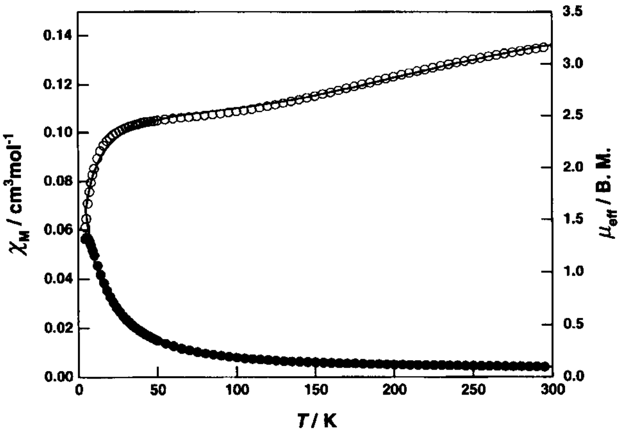

Fig. 4. Magnetic susceptibility data (●) and effective magnetic moments (○) of $[Cu_2(pro)_4(p\text{-nitpy})_2]$ (**1**).

Similarly, a reaction of copper(II) propionate with 2-(3-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxyl 3-oxide led to a dark-green solution and subsequent isolation of a dinuclear adduct $[Cu_2(pro)_4(m\text{-nitpy})_2]$ (**2**) as dark-green crystals. The X-ray crystallography of **2** shows a dinuclear structure similar to that of **1**, having a crystallographic inversion center at the center of the Cu_2 core (Fig. 5). The Cu–Cu′ distance is 2.631(1) Å. The coordination geometry of each copper atom is square-pyramidal and the equatorial Cu–O distances are 1.961(2)—1.980(3) Å. The apical position is occupied by the pyridyl nitrogen atom of m-nitpy with a Cu–N1 distance of 2.192(3) Å. The copper atom is displaced toward the apical nitrogen atom from the basal plane by 0.20 Å. The N–O distances (N2–O5 1.267(5) and N3–O6 1.283(4) Å) confirm the free-radical character of the

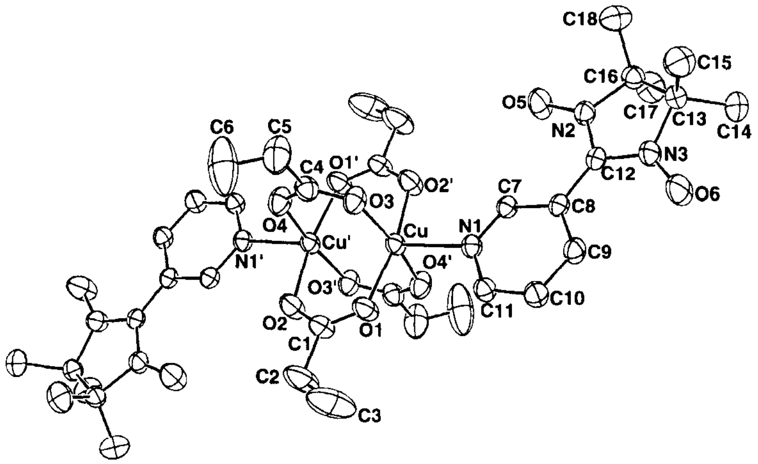

Fig. 5. ORTEP drawing of the structure of [$Cu_2(pro)_4$(*m*-nitpy)$_2$] (**2**) showing the 35% probability thermal ellipsoids and atom labeling scheme. Hydrogen atoms are omitted for clarity. Primed and unprimed atoms are related by the inversion.

m-nitpy ligand. The closest intermolecular contacts between the N–O groups are O5···O5 (1−x, −y, 1−z) 4.423(5) Å and O6···O6 (1−x, 1−y, 1−z) 4.275(5) Å (Fig. 6). The *syn-syn* bridging form of the carboxylate groups can be confirmed by the infrared spectrum of **2** [ν_{as}(COO) 1616, ν_s(COO) 1430 cm^{-1}]. The diffuse reflectance spectrum of **2** is similar to that of **1**, and shows an intense band characteristic of copper(II) carboxylate dimers at 368 nm and a broad band with multiple peaks at around 657 nm. The magnetic property of **2** is also similar to that of **1**, as shown in Fig. 7. The magnetic moment of **2** gradually decreases from room temperature (3.16 B.M.) to ca. 20 K, then decreases rapidly and reaches a value of 1.76 B.M. at 4.5 K. The χ_M^{-1} vs. T plot of **2** follows the Curie–Weiss law with θ values of −4.5 and 245 K for the temperature ranges 4.5—110 and 150—300 K, respectively. The best fit by equation 1 gave the following parameters: $J = -182$ cm^{-1}, $g = 2.33$, $\theta = -3.6$ K, and $C = 0.756$ cm^3 Kmol^{-1} for **2**.

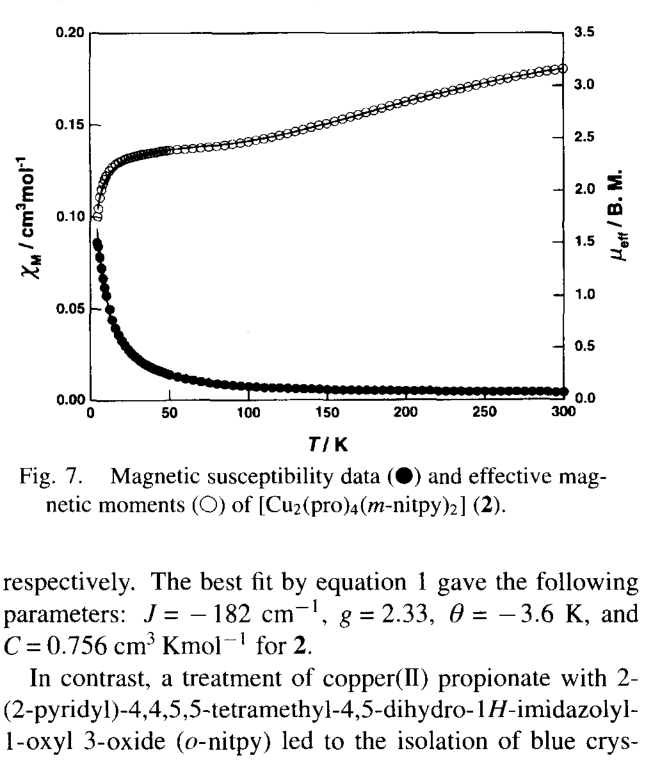

Fig. 7. Magnetic susceptibility data (●) and effective magnetic moments (○) of [$Cu_2(pro)_4$(*m*-nitpy)$_2$] (**2**).

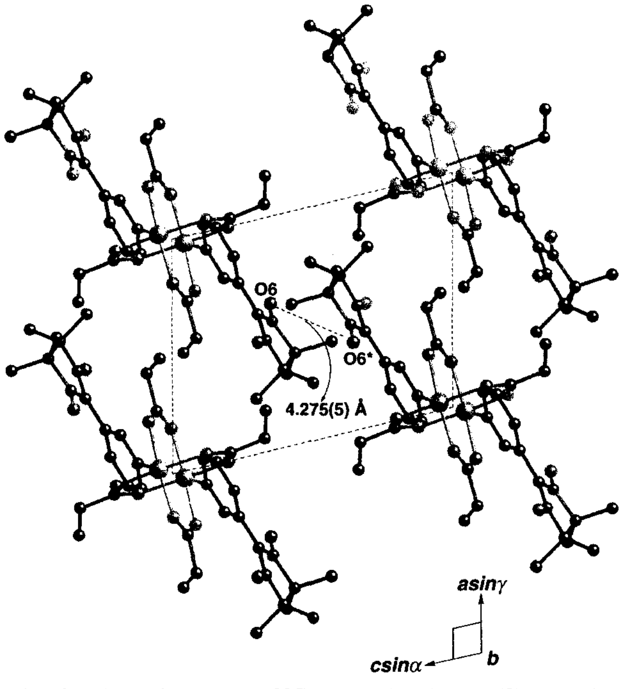

Fig. 6. Crystal structure of [$Cu_2(pro)_4$(*m*-nitpy)$_2$] (**2**) viewed along the *b* axis.

In contrast, a treatment of copper(II) propionate with 2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide (*o*-nitpy) led to the isolation of blue crystals (**3**·$2H_2O$). The X-ray crystallography of **3**·$2H_2O$ reveals that it is an unexpected compound, bis(picolinato)copper(II) dihydrate. As illustrated in Fig. 8, the copper atom takes a four-coordinated square with two picolinato ligands. The coordinating feature is very similar to the reported crystal structure of bis(picolinato)copper(II) dihydrate.[28] The picolinato ligands seem to come from the degradation of *o*-nitpy during a reaction with the copper(II) ion. The sterically crowded *o*-nitpy ligand could not be accomodated around the Cu_2 core, and possibly causes hydrolysis of the nitronyl nitroxide. Such a degradation of an organic ligand in the presence of metal ion was noted in the literature.[29,30] The magnetic moment of **3** is 1.96 B.M. at 300 K, and decreases slightly upon lowering the temperature (1.68 B.M. at 4.5 K), showing a monomeric property (Fig. 9).

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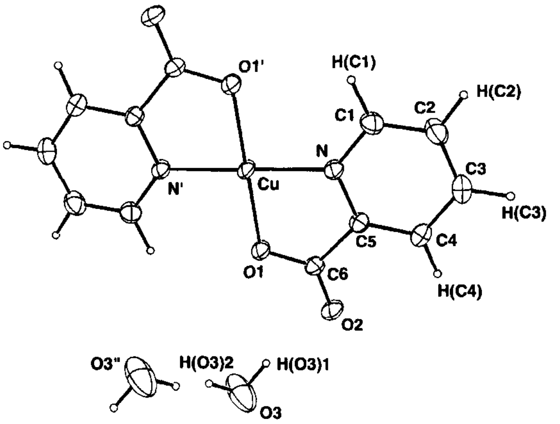

Fig. 8. ORTEP drawing of the structure of [Cu(pic)$_2$]·2H$_2$O (**3**·2H$_2$O) showing the 35% probability thermal ellipsoids and atom labeling scheme.

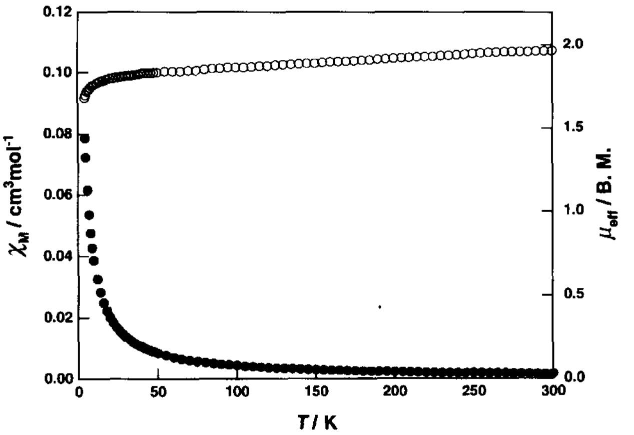

Fig. 9. Magnetic susceptibility data (●) and effective magnetic moments (○) of [Cu(pic)$_4$] (**3**).

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