# Structurally Diverse Copper(II)−Carboxylato Complexes: Neutral and Ionic Mononuclear Structures and a Novel Binuclear Structure

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The copper complexes with the commercial auxin herbicides MCPA, 2,4-D, and 2,4,5-T in the presence of a nitrogen donor heterocyclic ligand, phen or bipyam, were prepared and characterized. The available evidence supports a dimeric structure for the 2,4-D complex in the presence of bipyam while phen leads to monomeric forms. The EPR spectrum of $Cu_2(2,4\text{-}D)_4(bipyam)_2$ at 4 K in the solid state exhibits an axial signal which corresponds to almost isolated $S = {}^1/_2$ magnetic ions. Magnetic data for the dimer show a weak antiferromagnetic interaction between the two metal ions with $J = -0.8$ cm$^{-1}$. The crystal structures of tetrakis[(2,4-dichlorophenoxy)-acetato]bis(2,2′-bipyridylamine)dicopper(II), **1**, bis(1,10-phenanthroline)[(2,4,5-trichlorophenoxy)acetato]copper(II) chloride, **2**, and aqua(1,10-phenanthroline)bis[((2-methyl-4-chlorophenoxyacetato]copper(II), **3**, were determined and refined by least-squares methods using three-dimensional MoKα data. **1** crystallizes in space group $P\bar{1}$, in a cell of dimensions $a = 10.813(1)$ Å, $b = 12.138(1)$ Å, $c = 11.909(1)$ Å, $\alpha = 86.448(3)°$, $\beta = 80.127(3)°$, and $\gamma = 63.982(3)°$, and $V = 1383.7(2)$ Å$^3$, with $Z = 1$. **2** crystallizes in space group $I2/a$, in a cell of dimensions $a = 29.958(9)$ Å, $b = 11.342(3)$ Å, $c = 21.196(7)$ Å, $\beta = 107.94(1)°$, and $V = 6852.2(4)$ Å$^3$, with $Z = 8$. **3** crystallizes in space group $P\bar{1}$, in a cell of dimensions $a = 8.7419(8)$ Å, $b = 12.512(1)$ Å, $c = 14.598(1)$ Å, $\alpha = 110.737(1)°$, $\beta = 95.742(2)°$, $\gamma = 103.286(2)°$, $V = 1424.1(2)$ Å$^3$, with $Z = 2$.

## Introduction

Many binuclear Cu(II) carboxylato compounds have been isolated and their magnetostructural correlations studied.[1−3] In most cases, the formula of the complexes is $Cu_2(OOCR)_4L_2$ [L = $H_2O$, dmf (dimethylformamide), dmso (dimethyl sulfoxide), Py (pyridine)]. The presence of binuclear copper(II) carboxylates under catalytic reaction conditions has enhanced the interest in the coordination modes of this class of compounds. In general, binuclear copper(II) carboxylates exhibit a paddle-wheel cage structure, but due to the various coordination modes of the carboxylato ligand, additional interesting structures have been confirmed by X-ray crystallography (vide infra). The isolation of mononuclear carboxylato compounds has also confirmed the existence of unidentate and bidentate coordination modes of the ligands.[4−7] The electrochemical behavior of binuclear complexes as one means of determining reactivity differences between binuclear and mononuclear complexes has also attracted much interest.[8−14] Phenoxyalkanoic acids interact with Cu(II) ions to form complexes which have been shown to have diverse stereochemistries.[15−21]

We have initiated studies on the coordination of herbicide and/or antiinflammatory carboxylate agents with Cu(II) and d$^{10}$ ions in an attempt to examine their mode of binding and possible synergetic effects.[22−29] In this paper, we report the solid and solution behavior of mononuclear and binuclear Cu(II) com-

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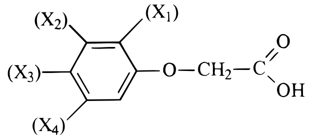
**Chart 1**



2,4-D: $X_1$ = Cl, $X_2$ = H, $X_3$ = Cl, $X_4$ = H

MCPA: $X_1$ = $CH_3$, $X_2$ = H, $X_3$ = Cl, $X_4$ = H

2,4,5-T: $X_1$ = Cl, $X_2$ = H, $X_3$ = Cl, $X_4$ = Cl

plexes with the commercial auxin herbicides MCPA, 2,4-D, and 2,4,5-T (Chart 1) in the presence of phen or bipyam. A biological study of a series of copper complexes with herbicide ligands will be presented in a following paper.[29b]

We also report the molecular and the crystal structures of tetrakis[(2,4-dichlorophenoxy)acetato]bis(2,2′-bipyridylamine)dicopper(II), **1** the first example of a binuclear structure with two bridging and two unidentate carboxylato ligands, [bis(1,10-phenanthroline)[(2,4,5-trichlorophenoxy)acetato]copper(II) chloride, **2**, and aqua(1,10-phenanthroline)bis[(2-methyl-4-chlorophenoxy)acetato]copper(II), **3**.

## Experimental Section

**Materials.** The chemicals for the syntheses of the compounds were used as purchased. Acetonitrile ($CH_3CN$) was distilled from calcium hydride ($CaH_2$) and $CH_3OH$ from magnesium (Mg), and both were stored over 3 Å molecular sieves. Diethyl ether, anhydrous grade, and absolute ethanol were used without any further purification. 2,4-D, 2,4,5-T, MCPA, phen, bipyam, and $CuCl_2 \cdot 2H_2O$ were purchased from Aldrich. All chemicals and solvents were of reagent grade.

**Physical Measurements.** Infrared spectra (200−4000 $cm^{-1}$) were recorded on a Perkin-Elmer FT-IR 1650 spectrometer with samples prepared as KBr pellets, and UV−vis spectra were recorded on a Shimadzu 160A dual-beam spectrophotometer. Room-temperature magnetic measurements were carried out by Faraday's method using mercury tetrathiocyanatocobaltate(II) as a calibrant. Variable-temperature magnetic susceptibility measurements were carried out on powdered samples in the 3−300 K temperature range using a Quantum Design SQUID susceptometer in a 6.0 kG applied magnetic field. Magnetization measurements were performed at 4 K and in the field range 0−5 T. EPR spectra were recorded on a Bruker ER 200D-SRC X-band spectrometer equipped with an Oxford ESR 9 cryostat. C, H, and N elemental analyses were performed on a Perkin-Elmer 240B elemental analyzer; Cu was determined by atomic absorption spectroscopy on a Perkin-Elmer 1100B spectrophotometer. Electric conductance measurements were carried out with a WTW model LF 530 conductivity outfit and a type C cell, which had a cell constant of 0.996. This represents a mean value calibrated at 25 °C with potassium chloride. All temperatures were controlled with an accuracy of ±0.1 °C using a Haake thermoelectric circulating system.

**Preparation of the Ligands.** The sodium salts of the ligands were prepared by the reaction of the protonated ligand with NaOH or $CH_3ONa$ in methanol. The white solids were recrystallized from methanol and dried in the air.

**Synthesis of Tetrakis[(2,4-dichlorophenoxy)acetato]bis(2,2′-bipyridylamine)dicopper(II), 1.** 2,4-D (2.21 g, 10 mmol) was dissolved in $CH_3OH$ (50 $cm^3$), and $CH_3ONa$ (0.54 g, 10 mmol) was added. After 30 min of stirring, $CuCl_2 \cdot 2H_2O$ (0.85 g, 5 mmol) and bipyam (1.71 g, 10 mmol) in $CH_3OH$ (25 $cm^3$) were added dropwise. The reaction mixture was refluxed for 1 h. The blue solution was reduced in volume and left for slow evaporation. Crystals of $Cu_2(C_6H_3Cl_2{-}OCH_2COO)_4(bipyam)_2$, **1**, suitable for X-ray structure determination deposited over 1 week. Yield: 70%. Anal. Calcd for $C_{52}H_{38}Cl_8N_6O_{12}Cu_2$ (fw = 1349.62): C, 46.28; H, 2.84; N, 6.23; Cu, 9.42. Found: C, 46.50; H, 3.00; N, 6.10; Cu, 9.50. IR, (KBr pellet), $\nu_{max}/cm^{-1}$; $\nu$(N−H) 3275 (m), 3230 (m); $\nu_{as}(CO_2)$ 1635, 1585 (vs); $\nu$(C=N) 1470 (vs), 1435 (vs); $\nu_{sym}(CO_2)$ 1395 (vs). UV−vis (dmf solution), $\lambda$/nm ($\epsilon/dm^3\ mol^{-1}\ cm^{-1}$); 735 (111), 400 (162), 314 (16 600).

**Synthesis of Bis(1,10-phenanthroline)[(2,4,5-trichlorophenoxy)acetato]copper(II) Chloride, 2.** 2,4,5-T (2.555 g, 10 mmol) was dissolved in $CH_3OH$ (50 $cm^3$), and $CH_3ONa$ (0.54 g, 10 mmol) was added. After 30 min of stirring, $CuCl_2 \cdot 2H_2O$ (0.85 g, 5 mmol) and phen (1.80 g, 10 mmol) in $CH_3OH$ (25 $cm^3$) were added dropwise. The reaction mixture was refluxed for 1 h. The blue solution was reduced in volume and left for slow evaporation. Crystals of $[Cu(C_6H_2Cl_3OCH_2COO)(phen)_2]Cl$, **2**, suitable for X-ray structure determination were deposited over 1 week. Yield: 65%. Anal. Calcd for $C_{31}H_{37}Cl_4N_4O_8Cu$ (fw = 799.01): C, 46.60; H, 4.67; N, 7.01; Cu, 7.95). Found: C, 46.90; H, 4.25; N, 7.35; Cu, 8.10. IR (KBr, pellet), $\nu_{max}/cm^{-1}$: $\nu_{as}(CO_2)$ 1620, 1585 (vs); $\nu$(C=N) 1465(vs), 1430(vs); $\nu_{sym}(CO_2)$ 1395 (vs). UV−vis (dmf solution), $\lambda$/nm ($\epsilon/dm^3\ mol^{-1}\ cm^{-1}$): 957 (63), 723 (100), 328 (2450), 293 (20 240).

**Synthesis of Aqua(1,10-phenanthroline)bis[(2-methyl-4-chlorophenoxy)acetato]copper(II), 3.** MCPA (2.00 g, 10 mmol) was dissolved in $CH_3OH$ (50 $cm^3$) and $CH_3ONa$ (0.54 g, 10 mmol) was added. After 30 min of stirring, $CuCl_2 \cdot 2H_2O$ (0.85 g, 5 mmol) in $CH_3OH$ (25 $cm^3$) was added dropwise. The reaction mixture was stirred for 1 h and reduced in volume under vacuum. Microcrystalline $Cu[C_6H_3(CH_3)ClOCH_2COO]_2(H_2O)_2$ deposited and was collected by filtration. $Cu[C_6H_3(CH_3)ClOCH_2COO]_2(H_2O)_2$ (3 mmol) was dissolved in $CH_3CN$ (50 $cm^3$), phen (0.54 g, 3 mmol) in $CH_3CN$ (25 $cm^3$) was added, and the mixture was stirred for 1 h and left for slow evaporation. Crystals of $Cu[C_6H_3(CH_3)ClOCH_2COO]_2(phen)(H_2O)$, **3**, suitable for X-ray structure determination deposited over 1 week. Yield: 60%. Anal. Calcd for $C_{30}H_{26}Cl_2N_2O_7Cu$ (fw = 660.97): C, 54.51; H, 3.97; N, 4.24; Cu, 9.61. Found: C, 54.40; H, 3.90; N, 4.45; Cu, 9.50. IR (KBr pellet), $\nu_{max}/cm^{-1}$: $\nu_{as}(CO_2)$ 1630 (vs), 1605 (vs); $\nu$(C=N) 1490 (vs), 1430 (vs); $\nu_{sym}(CO_2)$ 1408 (vs). UV−vis (dmf solution), $\lambda$/nm ($\epsilon/dm^3\ mol^{-1}\ cm^{-1}$): 675 (94).

**X-ray Crystal Structure Determinations.** A green prismatic crystal of tetrakis[(2,4-dichlorophenoxy)acetato]bis(2,2′-bipyridylamine)dicopper(II), **1**, with approximate dimensions 0.15 × 0.30 × 0.60 mm, and a blue crystal of bis(1,10-phenanthroline)[(2,4,5-trichlorophenoxy)acetato]copper(II) chloride, **2**, with approximate dimensions 0.10 × 0.25 × 0.55 mm, were mounted in air. Diffraction measurements were made on a Nicolet $P2_1$ diffractometer upgraded by Crystal Logic using Ni-filtered Cu radiation for **1** and on a Crystal Logic dual-goniometer diffractometer using graphite-monochromated Mo radiation for **2**. A pale blue prismatic crystal of aqua(1,10-phenanthroline)bis[2-methyl-4-chlorophenoxy)acetato]copper(II), **3** with dimensions 0.77 × 0.16 × 0.16 mm, was mounted on the top of a glass fiber, and data were collected at room temperature with a Bruker SMART Platform CCD diffractometer. A full sphere of data (2082 frames) were collected. Final cell constants were calculated from a set of 6770 strong reflections ($I > 10\sigma(I)$) obtained from the data collection. Crystal data and parameters for the data collections of **1**−**3** are reported in Table 1. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the ranges $24° < 2\theta < 54°$ for **1** and $11° < 2\theta < 23°$ for **2**. Intensity data were recorded using $\theta{-}2\theta$ scans. Three standard reflections, monitored every 97 reflections, showed <3.0% intensity fluctuation and no decay. Lorentz, polarization,

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**Table 1.** Crystallographic Data for Complexes **1**−**3**

| | **1** | **2** | **3** |
|---|---|---|---|
| formula | $C_{52}H_{38}Cl_8Cu_2N_6O_{12}$ | $C_{31}H_{37}Cl_4CuN_4O_8$ | $C_{30}H_{26}Cl_2CuN_2O_7$ |
| space group | *P*1 | *I*2/*a* | P1 |
| crystal system | triclinic | triclinic | triclinic |
| fw | 1349.62 | 799.01 | 660.97 |
| *a*/Å | 10.813(1) | 29.958(9) | 8.7419(8) |
| *b*/Å | 12.138(1) | 11.342(3) | 12.512(1) |
| *c*/Å | 11.909(1) | 21.196(7) | 14.598(1) |
| α/deg | 86.448(3) | | 110.737(1) |
| *β*/deg | 80.127(3) | 107.94(1) | 95.742(2) |
| *γ*/deg | 63.982(3) | | 103.286(2) |
| *V*/Å$^3$ | 1383.7(2) | 6852.2(4) | 1424.1(2) |
| *Z* | 1 | 8 | 2 |
| $D_{calcd}$, $D_{measd}$/g cm$^{-3}$ | 1.620, 1.59 | 1.508, 1.48 | 1.541, 1.51 |
| $\mu$/cm$^{-1}$ | 5.077 | 9.97 | 10.06 |
| *a*, *b* for $w^a$ | 0.0406, 1.0929 | 0.0375, 19.0622 | |
| R1, wR2$^b$ | 0.0369, 0.0976 | 0.0542, 0.1513 | 0.0464, 0.0839 |
| R1, wR2$^b$ (all data) | 0.0405, 0.1016 | 0.0769, 0.1818 | 0.0878, 0.0971 |

[a] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P\ [\max(P_o^2\ 0) - 2F_c^2]/3$. [b] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$; $wR^2 = [\Sigma w(|F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

and $\psi$-scan absorption corrections were applied using Crystal Logic software. Scattering factors were taken from ref 30. The structures of **1** and **2** were solved by direct methods using the program SHELXS-86[31] and refined by full-matrix least-squares techniques on $F^2$ with SHELXL-93.[32] For the structure of **3** four different sets of frames were collected using 0.30° steps in $\omega$. The exposure time was 15 s per frame, and the detector-to-crystal distance was ∼5 cm. The resolution of the data set was 0.78 Å. SMART[33] software was used for data acquisition and SAINT[34] for data extraction. The absorption correction was applied using SADABS[35] and all refinements were done using the SHELXTL[36] or SHELX97[37] package of crystallographic programs. The structure was solved with direct methods. Initially attempts to solve the structure in $P\bar{1}$ were unsuccessful, so the symmetry was dropped and the structure was solved in *P*1. Later, using a missing-center utility in teXsan,[38] a center of symmetry was found, and the space group was changed to $P\bar{1}$. All nonhydrogen atoms were refined anisotropically. The water hydrogen atoms were found from a difference map and were refined using a riding model. The rest of hydrogen atoms were placed in idealized positions and also refined using a riding model. The final R1, wR2, and GOF values for all data were 0.0878, 0.0971, and 0.552, the maximum and minimum residual peaks in the final difference map were 0.353 and −0.532 e/Å$^3$, and the largest shift/esd on the final cycle was 0.012. Further crystallographic details for **1**: $2\theta = 130°$; scan speed 4.5°/min; scan range 2.45° + $\alpha_1-\alpha_2$ separation; numbers of collected/unique/used reflections = 4943/4675 ($R_{int}$ = 0.0093)/4675; 437 parameters refined; R1/wR2 (for all data) = 0.0405/0.1016; $(\Delta\rho)_{max}$ and $(\Delta\rho)_{min}$ = 0.392 and −0.652 e/Å$^3$: $(\Delta/\sigma)_{max}$ = 0.003. All hydrogen atoms were located by difference maps and refined isotropically. All non-hydrogen atoms were refined anisotropically. Further crystallographic details for **2**: $2\theta = 50°$; scan speed 3.0°/min; scan range 2.15 + $\alpha_1-\alpha_2$ separation; numbers of collected/unique/used reflections = 6154/6018 ($R_{int}$ = 0.0164)/6018; 521 parameters refined; R1/wR2 (for all data) = 0.0899/0.1427; $(\Delta\rho)_{max}/(\Delta\rho)_{min}$ = 0.569 and −0.580 e/Å$^3$; $(\Delta/\sigma)_{max}$ = 2.507 for the torsion parameter of HCM2. All hydrogen atoms (except those of the methanol solvents which were introduced at calculated positions as riding on bonded atoms) were located by difference maps and refined isotropically. All non-hydrogen atoms were refined anisotropically.

## Results and Discussion

The synthesis of the binuclear complex was achieved via the reaction of $CuCl_2 \cdot 2H_2O$ with the sodium salt of the ligand in the presence of bipyam. The reaction involves deprotonation of the ligand using NaOH or $CH_3ONa$ as the base, e.g.

$$C_6H_3Cl_2OCH_2COOH + CH_3ONa \rightarrow C_6H_3Cl_2{-}OCH_2COONa$$

$$4C_6H_3Cl_2OCH_2COONa + 2CuCl_2 + 2\text{bipyam} \rightarrow Cu_2(C_6H_3Cl_2{-}OCH_2COO)_4(\text{bipyam})_2$$

The complex is a green crystalline solid soluble in dmf, dmso, and Py.

The synthesis of the mononuclear complexes was achieved in two ways:

(i) A one-step reaction of $CuCl_2 \cdot 2H_2O$, NaOH, phen, and 2,4,5-T resulted in the formation of the cationic complex:

$$C_6H_2Cl_3OCH_2COOH + NaOH + 2CuCl_2 + 2\text{phen} \rightarrow \{Cu[C_6H_2Cl_3OCH_2COO](\text{phen})_2\}Cl$$

The compound is a 1:1 electrolyte in dmf and dmso solutions.

(ii) The synthesis of the mononuclear neutral complex was carried out via the addition of phen to the copper complex without any nitrogen donor heterocyclic ligands, e.g.

$$C_6H_3(CH_3)ClOCH_2COOH + NaOCH_3 \rightarrow C_6H_3(CH_3)ClOCH_2COONa$$

$$2C_6H_3(CH_3)ClOCH_2COONa + CuCl_2 \rightarrow \{Cu[C_6H_3(CH_3)ClOCH_2COO]_2\}_2(H_2O)_2$$

$$Cu[C_6H_3(CH_3)ClOCH_2COO]_2(H_2O)_2 + \text{phen} \rightarrow Cu[C_6H_3(CH_3)ClOCH_2COO]_2(\text{phen})(H_2O)$$

The complex is blue crystalline solid and nonelectrolyte in dmf and dmso solution.

**Description of the Structure $Cu_2(C_6H_3Cl_2OCH_2COO)_4$(bipyam)$_2$ (1).** The crystal structure of **1** is composed of centrosymmetric dimers. An ORTEP diagram of the complex

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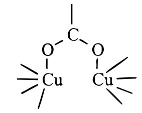
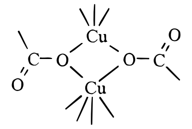
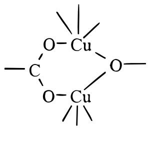
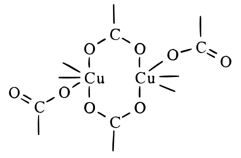
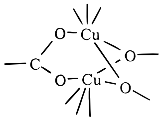
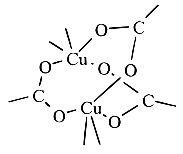
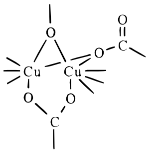
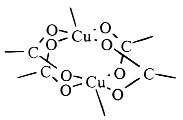
**Table 2.** Coordination Modes, Cu···Cu Separations, and *J* Values for Carboxylato-Bridged Complexes

| Coordination mode | | $Cu^{II}\cdots Cu^{II}$(Å) | *J* (cm$^{-1}$) | Coordination mode | | $Cu^{II}\cdots Cu^{II}$ (Å) | *J* (cm$^{-1}$) |
|---|---|---|---|---|---|---|---|
| 1 |  | 5.254[a] | - | 2 |  | 3.299[b], 3.339[c]<br>3.245[d], 3.537[e] | +17.7[b], +0.95[b]<br>-1.05[c], -8.5[e] |
| 3 |  | 3.017[f], 3.156[g]<br>3.185[h], 3.288[i]<br>3.41-3.496[j], 3.55[k] | +111[f], +1.3[g] | 4 |  | 4.50[l] | -0,8[l] |
| 5 |  | 3.035[m], 3.071[n]<br>3.149[o] | +19.3[m] | 6 |  | 2.85[p], 2.92[q]<br>3.39[r] | +3.6[r] |
| 7 |  | 3.029[s] | -1.5[s] | 8 |  | 2.583-2594[t]<br>2.601-2.689[u]<br>2700-2766[v] | (-400) - (-200)<br>Depends of the<br>ligand |

[a] $[Cu(idae)Cl(H_2O)]_n$ idae = *O*-ethyliminodiacetato.[39] [b] $Cu^{II}{}_4[(2\text{-}Py)_2CO(OH)_2](O_2CCH_3)_6(H_2O)_2$.[40] [c] $[\{Cu(tzq)_2(HCO_2)\}(\mu\text{-}HCOO)_2]\cdot 4H_2O$, tzq = [1,2,3]triazolo[1,5-*a*]quinoline.[41] [d] *catena*-Poly((bis($\mu$-Diphenylacetato-*O,O′*)dicopper)($\mu_3$-Diphenylacetato-*1-O,2-O′*,1′-*O′*)($\mu_3$-diphenylacetato-*1-O*,2-*O′*,2′-*O′*)).[42] [e] $[\{Cu_4(bdmap)_2(O_2CCH_3)_6(H_2O)_6\}_n]$, Hbdmap = 1,3-bis(dimethylamino)propan-2-ol.[43] [f] $[Cu_2(\mu\text{-}OH)(\mu\text{-}CH_3COO)(phen)_2](NO_3)_2\cdot 2H_2O$, phen = 1,10-phenanthroline.[44] [g] $[Cu_2L(\mu\text{-}OH)(\mu\text{-}CH_3COO)](ClO_4)_2\cdot 2H_2O$, L = a hexaimidazole dinucleating ligand.[45] [h] $[Cu_2(SalDpl)(Phenac)(4\text{-}ethylphenol)]$, PhenacH = phenylacetic acid, SalDpl = a dinucleating ligand formed by the condensation of a substituted salicylaldehyde and 1,3-diamino-2-propanol.[46] [i] $[Cu_2(\mu_2\text{-}OH)(\mu_2\text{-}CH_3COO)(tacd)_2](ClO_4)_2$, tacd = 1,4,7-triazacyclododecane.[47] [j] $\{[Cu_2(BMDP)(OAc)_2]N_3\}(ClO_4)_2\cdot 8.5H_2O$, HBMDP = *N,N,N′*-tris[(*N*-methyl-2-benzimidazolyl)methyl]-*N′*-methyl-1,3-diamino-2-propanol.[48] $[Cu_2(L\text{-}1)(CH_3COO)](ClO_4)\cdot H_2O\cdot 0.5NaClO_4$, $H_2L$-1 = racemic 1-[bis(2-pyridylmethyl)amino]-3-(salicylideneamino)propan-2-ol.[49] $[Cu_2L_2(\mu\text{-}OH)(\mu\text{-}C_6H_5COO)](ClO_4)_2$, L = 1,4,7-trimethyl-1,4,7-triazacyclononane.[50] $[\{Cu_4(bdmap)_2(O_2CCH_3)_6(H_2O)_6\}_n]$, Hbdmap = 1,3-bis(dimethylamino)propan-2-ol.[43] [k] $[Cu_2(BMDP)(OAc)](ClO_4)_2\cdot 2H_2O$, HBMDP = *N,N,N′*-tris[(*N*-methyl-2-benzimidazolyl)methyl-*N′*-methyl-1,3-diamino-2-propanol.[48] [l] Present work. [m] $[Cu_2(\mu\text{-}OH)(\mu\text{-}H_2O)(\mu\text{-}CH_3COO)(bipy)](ClO_4)_2$, bipy = 2,2′-bipyridine.[51] [n] $[Cu_3(OH)_2(H_2O)_2(Me_3NCH_2COO)_4](ClO_4)_4\cdot 2H_2O$.[52] [o] $[Cu_2(\mu\text{-}H_2O)_2(\mu\text{-}\mathrm{L}\text{-}AlaH^+)]_n = [Cu_2(alanine)_2(H_2O)_4](SO_4)_2\cdot 2H_2O$.[53] [p] $[Cu_5(PIBA)_{10}(H_2O)_4] = [Cu(H_2O)_4]^{2+}\{[Cu_2(PIBA)_5]^-\}_2$, HPIBA = 2-methyl-2-phenoxypropanoic acid.[54] [q] $[Cu_5(PIBA)_{10}(H_2O)_9] = [Cu(H_2O)_5]^{2+}\{[Cu_2(PIBA)_5]^-\}_2\cdot 4H_2O$, HPIBA = 2-methyl-2-phenoxypropanoic acid.[54] [r] $[Cu_2(O_2CMe)_3(bipy)_2](ClO_4)$.[51] [s] $[Cu_2L(OAc)_2]^+$.[55] [t] More than 200 examples are available in the literature. Some representative compounds are given here: *catena*-tetrakis[$\mu$-(2-chlorophenoxy)ethanoato-*O,O′*]dicopper(II), $[\{Cu_2(O_2CCH_2OC_6H_4Cl\text{-}2)_4\}_n]$;[56] $[Cu_2(O_2CCPh_3)_4(H_2O)_2]\cdot 2H_2O$;[57] $[Cu_2(O_2CCPh_2Me)_4(H_2O)_4]\cdot H_2O$.[57] [u] Tetrakis($\mu$-1-phenylcyclopropane-1-carboxylato-*O,O′*)bis(ethanol-*O*)dicopper(II);[42] $[Cu_2(PCIBA)_4(2\text{-}aminopyrimidine)_2]_2$, HPCIBA = 2-methyl-2-(4-chlorophenoxy)propanoic acid.[54] [v] *catena*-(2-Aminopyrimidine-*N,N′*)-tetrakis[$\mu$-(2-chlorophenoxy)ethanoato-*O,O′*]dicopper(II);[56] $Cu_2(CF_3COO)_4\cdot 2CH_3CN$.[58]

appears in Figure 1. Selected bond distances and angles are given in Table 3. Two bidentate carboxylato ligands form *syn*−*syn* bridges between isolated pairs of copper atoms separated by 4.50 Å. The other two carboxylato ligands are bound to the Cu(II) atoms in a unidentate mode, while the two bipyam neutral ligands are coordinated to the copper atoms in a bidentate fashion. The present mode of coordination is unique (Table 2),[39−58] and the Cu···Cu distance of 4.50 Å falls in the range between 4.0 and 5.0 Å, for which no other examples have been reported. Thus, the present compound provides an opportunity to study the magnetic behavior and the EPR spectra of a Cu···Cu system separated by 4.50 Å and having only carboxylato

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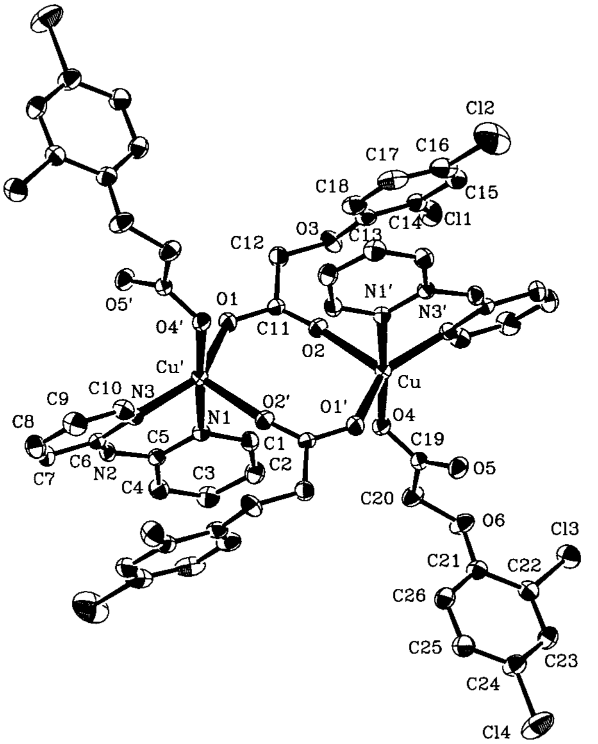

**Figure 1.** ORTEP view of complex **1** with 50% thermal ellipsoids showing the atom-labeling scheme around the Cu atoms.

**Table 3.** Selected Bond Distances (Å) and Angles (deg) for Complex **1**

| | | | |
|---|---|---|---|
| Distances | | | |
| Cu−O(4) | 1.951(2) | Cu−N(3)′ | 2.027(2) |
| Cu−N(1)′ | 1.984(2) | | |
| Cu−O(2) | 2.209(2) | Cu···Cu′ | 4.502(2) |
| Cu−O(1)′ | 1.963(2) | Cu···O(5) | 3.100(2) |
| Angles | | | |
| O(4)−Cu−O(1) | 89.19(8) | O(4)−Cu−N(1)′ | 177.54(8) |
| O(1)−Cu−N(1) | 89.60(8) | O(4)−Cu−N(3)′ | 93.55(8) |
| O(1)−Cu−N(3) | 148.61(8) | N(1)′−Cu−N(3)′ | 88.60(8) |
| O(4)−Cu−O(2) | 87.13(7) | O(1)′−Cu−O(2) | 113.23(7) |
| N(1)′−Cu−O(2) | 91.38(8) | N(3)′−Cu−O(2) | 98.14(7) |

bridges. An analogous distance of 4.96 Å has been observed for the helix-like-chain copper(II) complex $[\mathrm{CuL(H_2O)}]_n$ ($\mathrm{H_3L}$ = 1,3-dimethyl-5-[(2-carboxyphenyl)azo]barbituric acid).[59] In binuclear structures, the Cu···Cu distance generally increases as the number of bridging ligands decreases, with that of four bridging ligands falling in the range 2.58−2.76 Å for more than 200 paddle-wheel structures, that of three bridging ligands falling in the range 2.85−3.39 Å (coordination modes 5, 6, 7 in Table 2) for about 10 examples, and that of two bridging ligands falling in the range 3.01−4.50 Å (coordination modes 2, 3, 4, in Table 2) for more than 15 examples but only one example, the present compound, with a Cu···Cu separation above 4.0 Å. For one bridging ligand, only one example has been reported, with a distance of 5.25 Å.

The bridging ligands are bound to two Cu(II) metal ions in an asymmetric fashion [Cu−O(1) = 1.963(2) Å, Cu−O(2) = 2.209(2) Å]. Each unidentate carboxylato ligand is bound to a Cu(II) ion through O(4) at a distance of 1.951(2) Å, while the uncoordinated carboxylato oxygen O(5) is H-bonded to the bipyam ligand of a neighboring molecule, through the NH group, [N(2)H′···O(5) = 2.045 Å and N(2)′···O(5) = 2.797 Å] giving a polymeric arrangement with interdimer Cu···Cu separations of 6.46 Å.

Each copper atom is five-coordinate with the two nitrogen atoms N(1) and N(3) (1.984(2) and 2.027(2) Å) of the bipyam molecule occupying the remaining two positions. The polyhedron cannot be described as having a regular square pyramidal or trigonal bipyramidal geometry. The tetragonality[60a] $T^5$ = 0.897 based on the changes in bond lengths, along with the trigonality index[60b] ($\tau = (\rho_1 - \rho_2)/60°$, where $\rho_1$ and $\rho_2$ are the largest angles in the coordination sphere; $\tau = 0$ for a perfect square pyramid, and $\tau = 1$ for a perfect trigonal bipyramid), $\tau = (177.54 - 148.61)/60 = 0.48$, show a distortion from the regular square-based pyramidal geometry.[61−64]

**Description of the Structure of $[\mathrm{Cu(C_6H_2Cl_3OCH_2COO)_2(phen)_2}]\mathrm{Cl}\cdot 2\mathrm{CH_3OH}$, (2).** In **2** the carboxylate group of 2,4,5-T behaves as a unidentate ligand. An ORTEP diagram of **2** is shown in Figure 2, and selected bond distances and angles are listed in Table 4. In this complex, the copper atom is five-coordinate and could be described as having a distorted square pyramidal geometry. The tetragonality[60a] $T^5 = 0.914$, based on the changes in bond lengths, along with the trigonality index,[60b] $\tau = (175.7 - 160.01)/60 = 0.2615$, show distortion from the regular square-based pyramidal geometry. N(1) and N(2) [2.006(4) and 2.059(4) Å] of one phen molecule, N(4) [2.010(4) Å] of the second phen molecule, and the carboxylate oxygen atom O(1) [1.987(4) Å] occupy the four positions in the basal plane, while N(3) of the second phen molecule is 2.205(4) Å away in the apical position. An arrangement similar to that of the two phen ligands has been observed in a series of $[\mathrm{Cu(bipy)_2X}]^+$ complexes.[61−64] The uncoordinated carboxylato oxygen atom O(2) [Cu···O(2) = 2.728(4) Å] lies below the basal plane of the pyramid. The trans atom system of the basal plane gives angles of O(1)−Cu−N(2) = 160.0(1)° and N(1)−Cu−N(4) = 175.7(2)°. The ionic unit $[\mathrm{Cu(C_6H_3Cl_3OCH_2COO)(phen)_2}]^+$ is neutralized by a chloride ion 5.038 Å away from the metal atom.

**Description of the Structure $\mathrm{Cu[C_6H_3(CH_3)(Cl)OCH_2COO]_2(phen)(H_2O)}$ (3).** In **3**, the carboxylate group of MCPA behaves as a unidentate ligand. An ORTEP diagram of **3** is shown in Figure 3, and selected bond distances and angles are given in Table 5. In this complex, the copper atom is five-coordinate and could be described as having a distorted square pyramidal geometry. The tetragonality[60a] $T^5 = 0.872$, based on the changes in bond lengths, along with the trigonality index,[60b] $\tau = (174.1 - 161.4)/60 = 0.2117$, show a small

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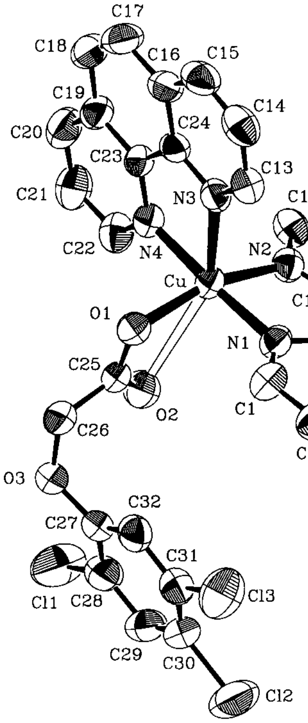


**Figure 2.** ORTEP view of complex **2** with 50% thermal ellipsoids showing the atom-labeling scheme around the Cu atom.

**Table 4.** Selected Bond Distances (Å) and Angles (deg) for Complex **2**

| | | | |
|---|---|---|---|
| | Distances | | |
| Cu−O(1) | 1.987(3) | Cu−N(1) | 2.006(4) |
| Cu−N(4) | 2.010(4) | Cu−N(2) | 2.059(4) |
| Cu−N(3) | 2.205(4) | Cu···O(2) | 2.727(3) |
| | Angles | | |
| O(1)−Cu−N(1) | 92.4(2) | O(1)−Cu−N(4) | 91.8(1) |
| N(1)−Cu−N(4) | 175.7(2) | O(1)−Cu−N(2) | 160.0(1) |
| N(1)−Cu−N(2) | 81.4(2) | N(4)−Cu−N(2) | 94.3(2) |
| O(1)−Cu−N(3) | 98.8(1) | N(1)−Cu−N(3) | 100.5(1) |
| N(4)−Cu−N(3) | 79.5(2) | N(2)−Cu−N(3) | 101.0(1) |

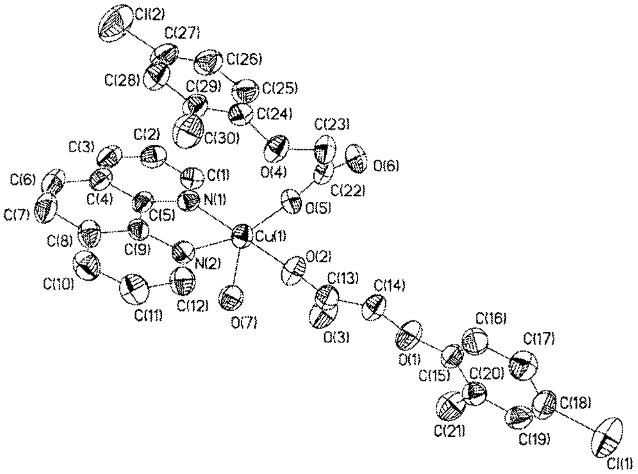
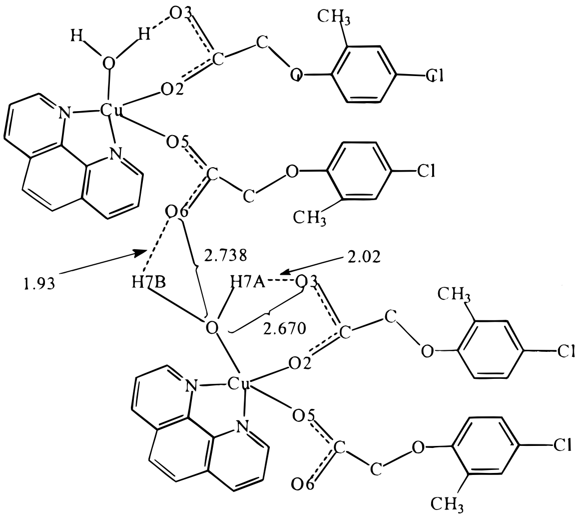


**Figure 3.** ORTEP view of complex **3** with 50% thermal ellipsoids showing the atom-labeling scheme around the Cu atom.

**Table 5.** Selected Bond Distances (Å) and Angles (deg) for Complex **3**

| | | | |
|---|---|---|---|
| | Distances | | |
| Cu(1)−O(5) | 1.937(2) | Cu(1)−O(2) | 1.944(2) |
| Cu(1)−N(1) | 2.012(3) | Cu(1)−N(2) | 2.023(3) |
| Cu(1)−O(7) | 2.269(2) | | |
| | Angles | | |
| O(5)−Cu(1)−O(2) | 93.3(1) | O(5)−Cu(1)−N(1) | 90.8(1) |
| O(2)−Cu(1)−N(1) | 174.2(1) | O(5)−Cu(1)−N(2) | 161.5(1) |
| O(2)−Cu(1)−N(2) | 93.3(1) | N(1)−Cu(1)−N(2) | 81.6(1) |
| O(5)−Cu(1)−O(7) | 99.5(1) | O(2)−Cu(1)−O(7) | 94.1(1) |
| N(1)−Cu(1)−O(7) | 89.3(1) | N(2)−Cu(1)−O(7) | 97.4(1) |

**Chart 2**



distortion from the regular square-based pyramidal geometry. N(1) and N(2) (2.012(3) and 2.023(3) Å) of the phen molecule and the carboxylate oxygen atoms O(2) and O(5) (1.937(2) and 1.944(2) Å) occupy cis positions in the basal plane, while the water oxygen is 2.269(2) Å away. The uncoordinated carboxylato oxygen atoms O(3) and O(6) [Cu···O(3) = 3.127(3) Å, Cu···O(6) = 4.059(3) Å] lie below and above the basal plane of the pyramid, respectively. The ligand atoms that form this basal plane of the pyramid are not strictly coplanar. The Cu−O(W) distance of 2.269(2) Å is comparable to those observed for the methoxyacetato (2.24 Å)[7] and maleato (2.26 Å) analogues.[53]

There are intra- and intermolecular hydrogen-bonded interactions. The intramolecular interaction is between the water molecule and the uncoordinated O(3) atom at a distance H(W)···O(3) = 2.02 Å, while the intermolecular interaction is between the water molecule and the uncoordinated carboxylato oxygen atom, O(6), of a neighboring molecule at a distance H(W)···O(6)′ = 1.93 Å, giving a polymer chain. The oxygen atom O(W) lies 2.670 and 2.738 Å away from O(3) and O(6)′, respectively (Chart 2). The copper atom is displaced 0.23 Å toward the water ligand. The trans N−Cu−O system of the basal plane gives angles of O(5)−Cu−N(2) = 161.4(1)° and O(2)−Cu−N(1) = 174.1(1)°.

**Magnetic Susceptibility and EPR Studies of Complex 1.** Variable-temperature solid-state magnetic susceptibility data were collected on powdered samples of complex **1** in a 6.0 kG applied magnetic field and in the temperature range 3.0−300 K. Magnetization measurements were carried out at 4 K and in a field range from 0 to 5 T.

The temperature dependence of the $\chi_M T$ for the **1** reveals a plateau from room temperature to 50 K having a value of 0.82 cm$^3$ mol$^{-1}$ K, which is expected for two uncoupled $S = {}^1/_2$ spins ($g = 2.09$), and then decreases with decreasing temperature to the value of 0.67 cm$^3$ mol$^{-1}$ K at 3 K. This behavior is consistent with a small antiferromagnetic interaction between the two metal ions.

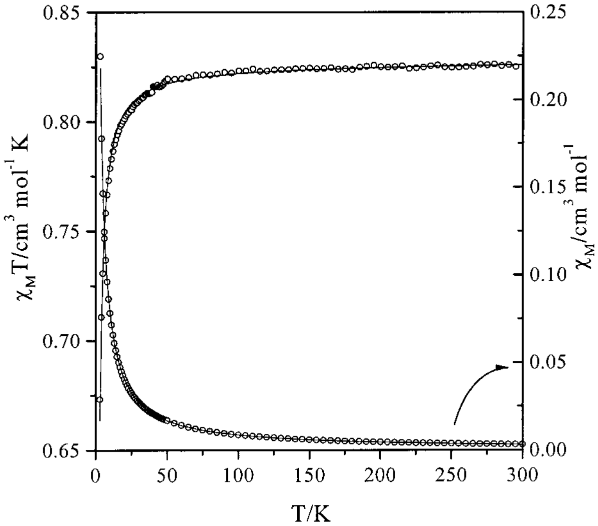


**Figure 4.** Magnetic susceptibility of **1** plotted as $\chi_M T$ versus $T$ (left axis) and $\chi_M$ versus $T$ (right axis) with the fit to eq 1 (solid line).

The $\chi_M T$ vs $T$ and the $\chi_M$ vs $T$ plots for complex **1** are shown in Figure 4. The data were fit to the Bleaney−Bowers equation[65] based on the zero-field spin Hamiltonian $H = -2JS_1S_2$,

$$\chi_M = \frac{2Ng^2\mu_B{}^2}{kT}\left[\frac{1}{3 + \exp(2x)}\right] \qquad (1)$$

where $x = -J/kT$, $N$ is Avogadro's number, and the other symbols have their usual meanings. Data were satisfactorily fit into eq 1 with $J = -0.8$ cm$^{-1}$, $g = 2.098(2)$, and $R = 5.4 \times 10^{-6}$ for

$$R = \frac{\sum[(\chi T)_{\mathrm{exp}} - (\chi T)_{\mathrm{calc}}]^2}{\sum(\chi T)_{\mathrm{exp}}{}^2}$$

The magnetization measurements, at 4 K, along with the Brillouin (dotted line, $g = 2.0$; solid line $g = 2.09$) function for a system with two $S = 1/2$ magnetic ions, are shown in Figure 5. The discrepancy between the solid curve and the magnetization data is due to the small antiferromagnetic interaction between the metal ions in accordance with the fitting results.

The EPR spectrum of **1** at 4 K in the solid state exhibits an axial signal ($g_{x,y} = 2.067$, $g_z = 2.24$) which corresponds to almost isolated $S = {}^1/_2$ magnetic ions (Figure 6). The value of $g = (g_{x,y} + g_z)/3 = 2.12$ is close to the value obtained from the susceptibility data. The EPR spectra of **2** and **3** are given as Supporting Information. The ESR spectrum of **2** in frozen solution is a typical axial spectrum with $g_{x,y} = 2.042$, $g_z = 2.252$, and $A = 165$ G, while the polycrystalline ESR spectrum of **3** is rhombic with $g_x = 2.017$, $g_y = 2.103$ and $g_z = 2.243$.

**Conclusions.** The coordination chemistry of copper(II) has been extensively studied and well understood. Especially for binuclear complexes with carboxylate ligands, the coordination modes show a rich variety of structure motifs, giving the opportunity for a better understanding of Cu(II) behavior. However, it seems that the copper chemistry can be extended even more. In this paper, for the first time, a novel motif of a binuclear tetracarboxylato copper(II) complex with two bridging and two unidentate ligands is reported. This structure shows a Cu(II)···Cu(II) distance of 4.5 Å, which is also unique and provides an opportunity to study the interaction of two copper atoms separated by this length. These results are quite surprising, considering the strong Cu···Cu interactions of the dinuclear tetracarboxylate compounds with a paddle-wheel motif. The structure of this compound can be considered as an intermediate in the transition from the paddle-wheel structure to mononuclear structure achieved adding N-donor ligands.

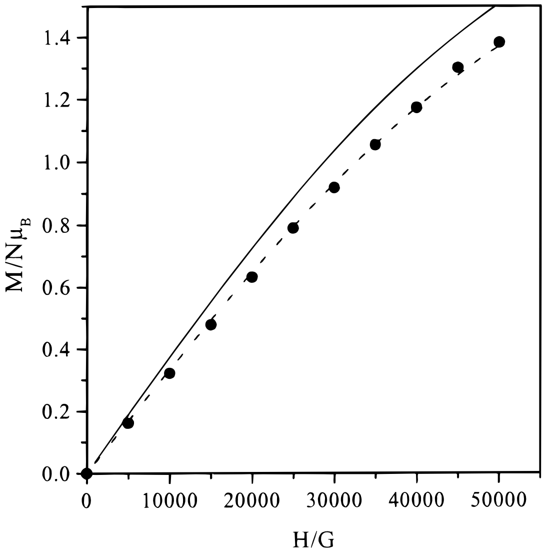


**Figure 5.** Magnetization measurements, at 4 K, along with the Brillouin (dotted line, $g = 2.0$; solid line, $g = 2.09$) function for a system with two $S = {}^1/_2$ magnetic ions.

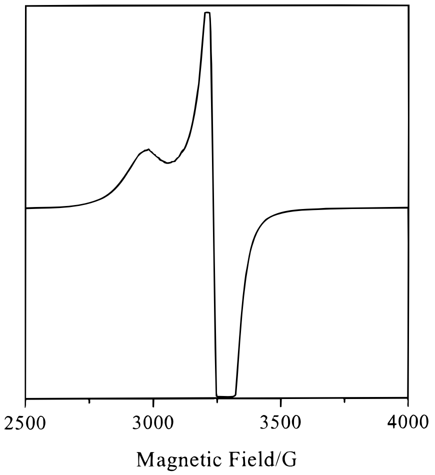


**Figure 6.** X-Band powder ESR spectrum of **1** at 4 K.

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**Supporting Information Available:** EPR spectra of **2** and **3** and X-ray crystallographic files, in CIF format, for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(65) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451.