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X-ray Structures and Redox Properties of Copper(II) Bis(pyrazole) Complexes

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The copper complexes of bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (**1**) and its benzylated derivative (**2**) have been studied as single crystals by X-ray crystallography and as powders and solutions by a variety of techniques. [Cu(**1**)·2NO$_3$] ($C_{14}H_{25}CuN_7O_7$ including 1 H_2O, **3**) crystallized in the monoclinic space group *Pc* (No. 7) with $a = 8.1596(9)$ Å, $b = 31.164(2)$ Å, $c = 7.7966(9)$ Å, $\beta = 94.75(2)°$, $V = 1975.7(3)$ Å^3, and $Z = 4$ (structure refinement converged to $R_F = 0.066$ and $R_{wF^2} = 0.227$); [Cu(**1**)ClO$_4$·C$_2$H$_5$OH]ClO$_4$ ($C_{16}H_{29}Cl_2CuN_5O_9$, **4**) crystallized in the orthorhombic space group *Pna*2$_1$ (No. 33) with $a = 13.3463(7)$ Å, $b = 10.3925(9)$ Å, $c = 17.511(1)$ Å, $V = 2432.1(3)$ Å^3, and $Z = 4$ (refined to $R_F = 0.063$ and $R_{wF} = 0.052$); [Cu(**2**)·2NO$_3$] ($C_{21}H_{29}CuN_7O_6$, **5**) crystallized in the monoclinic space group *C*2/*c* (No.15) with $a = 28.719(2)$ Å, $b = 8.6043(6)$ Å, $c = 23.034(2)$ Å, $\beta = 124.767(7)°$, $V = 4675.7(7)$ Å^3, and $Z = 8$ (refined to $R_F = 0.042$ and $R_{wF} = 0.034$); [Cu·(**2**)·C$_2$H$_5$OH·Y](ClO$_4$)$_n$ ($C_{48}H_{78}Cl_4Cu_2N_{10}O_{20}$, **6**) (Y = H_2O, $n = 2$, or ClO_4^-, $n = 1$) crystallized in the monoclinic space group *P*2$_1$/*c* (No. 14) with $a = 10.9488(9)$ Å, $b = 17.030(2)$ Å, $c = 32.893(3)$ Å, $\beta = 92.185(7)°$, $V = 6129(1)$ Å^3, and $Z = 4$ (refined to $R_F = 0.104$ and $R_{wF} = 0.119$). In complexes **3**, **4**, and **6**, the ligand coordinated Cu(II) with a T-shaped arrangement of the nitrogen donor atoms. Ethanol coordinated in one of the apical positions in complexes **4** and **6**. The amine nitrogen moved from the basal plane in **3** to the apical position in **5**, where the copper had square pyramidal coordination geometry. The largest difference between **4** and **6** was a lengthening of 0.1 Å in the bond between the Cu(II) and the amine nitrogen. Conductivity measurements revealed that the nitrate complexes behave as 1:1 electrolytes in acetonitrile solution, whereas the perchlorate complexes behaved as 2:1 electrolytes. The half-wave potentials, measured in acetonitrile by cyclic voltammetry, were −0.01, +0.15, +0.10, and +0.28 V for **3**−**6**, respectively. The high redox potentials of the copper(II) bis(pyrazole) complexes, in particular for complex **6**, are explained by the fact that the Cu(II) complexes have the correct ligand geometry for the stabilization of Cu(I).

Introduction

The elucidation of the mechanisms[2−4] by which the dicopper metalloprotein hemocyanin[5] binds dioxygen continues to be a topic of great interest.[6−8] Model compounds mimicking the action of hemocyanin and related metalloproteins have been designed and synthesized by several groups.[9−11] Karlin and co-workers have shown that Cu(I) bis(pyridine) complexes are effective dioxygen binders.[12,13] Sorrell and co-workers on the other hand have presented evidence that the related copper(I) bis(pyrazole) complexes do not bind dioxygen.[14] More detailed insight in the factors regulating the properties of these types of complexes is therefore required.

Recently, we reported on the reduction of Cu(II) bis(pyrazole) crown ether complexes in alcoholic solutions.[15] The observed rapid reduction of the Cu(II) complexes, and the remarkable stability of the Cu(I) species, even in the presence of dioxygen, prompted us to investigate this system in detail. In particular we were interested to elucidate the factors that control the geometry, electrochemical behavior, and reactivity of our Cu(II) bis(pyrazole) complexes.

Central in this study are the ligands bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (**1**) and the benzylated derivative **2** (Chart 1). These two ligands are treated with Cu(NO$_3$)$_2$·3H$_2$O and Cu-

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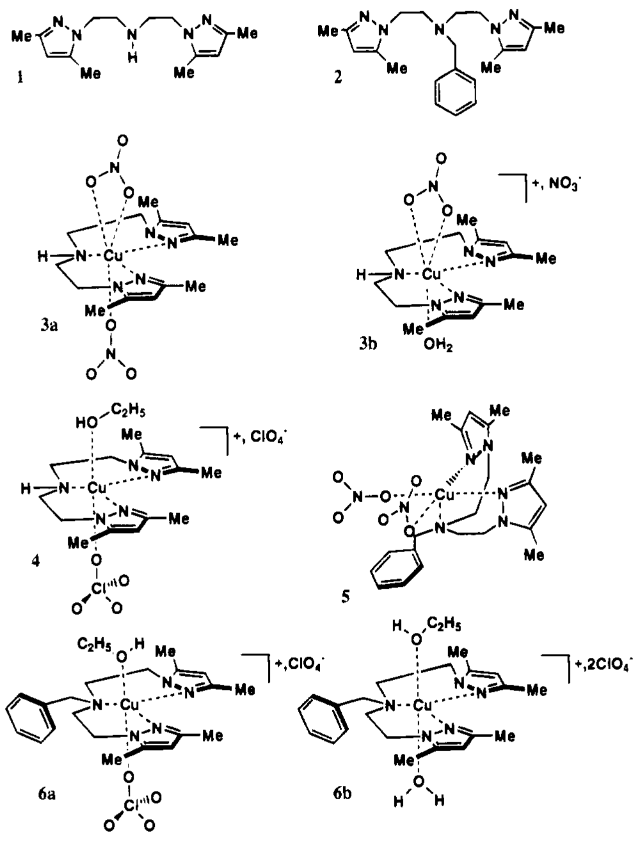
Chart 1



$(ClO_4)_2·6H_2O$ to yield 4 metal complexes (**3**–**6**; see Chart 1) that display different geometries around the copper ion and different redox behavior. The factors that regulate these effects are discussed.

Experimental Section

Warning! Although we have experienced no difficulties with the perchlorate salts described, these compounds should be regarded as potentially explosive and handled accordingly.[16]

Materials. All chemicals were obtained commercially. Solvents were dried and distilled prior to use. Diethyl ether was distilled from sodium; dichloromethane and acetonitrile were distilled from calcium hydride. Dimethylformamide (DMF) was stored over 4 Å molecular sieves and distilled at reduced pressure. Acetonitrile used in the electrochemical measurements was deoxygenated by three repetitive freeze–pump–thaw cycles. $Cu(ClO_4)_2·6H_2O$ was purchased from Janssen Chimica and $Cu(NO_3)_2·3H_2O$ was obtained from Merck. TLC analysis was performed on Merck precoated silica gel 60 F-254 plates.

Preparation of the Ligands. Bis[2-(3,5-dimethyl-1-pyrazolyl)-ethyl]amine (1). Under a dinitrogen atmosphere 7.36 g (73.6 mmol) of 3,5-dimethylpyrazole was slowly added to a suspension of 4.6 g (115 mmol) of 60% sodium hydride in 70 mL of dry DMF at room temperature. After hydrogen evolution had ceased, the mixture was warmed to 70 °C and stirred for 2 h. Subsequently, 6.84 g (38.2 mmol) of bis(2-chloroethyl)amine hydrochloride was added to the solution and the mixture was stirred overnight producing a cream white dispersion. After filtration of the precipitated NaCl, the solvent was evaporated *in vacuo*. The resulting oil was dissolved in 50 mL of $CHCl_3$, washed with saturated aqueous sodium chloride (3 × 50 mL), and dried over $MgSO_4$. Flash chromatography (silica 60H eluent 5% methanol in chloroform (v/v)) yielded 6.3 g (63%) of a yellow oil, which crystallized upon standing. Mp = 32 °C. R_f (TLC, eluent 10% MeOH in $CHCl_3$) = 0.33 *(note: this compound is not visible under a regular UV lamp; TLC plates were therefore treated with iodine vapor or sprayed with TDM ((4,4'-(tetramethyldiamino)diphenyl)methane)*[17] *after exposure to Cl_2 gas).* IR (KBr, cm^{-1}): 3301 (NH), 2925 (CH_2). ^1H NMR (90 MHz, $CDCl_3$, 298 K): δ 2.2 (s, 6H, CH_3), 2.3 (s, 6H, CH_3), 3.0 (t, 4H, NCH_2CH_2), 4.0 (t, 4H, NCH_2CH_2-pyrazole), 5.8 (s, 2H, pyrazole-*H*). MS (CI): m/z = 262 (M^+ + 1, 65%), 165 (55%), 152 (100%). Anal. Calcd for $C_{14}H_{23}N_5·0.44CHCl_3$: C, 55.25; H, 7.53; N, 22.31. Found: C, 55.79; H, 7.62; N, 21.89.

Benzylbis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (2). To a solution containing 1.46 g (5.6 mmol) of **1** in 15 mL of acetone was added 958 mg (5.6 mmol) of benzyl bromide and 700 mg (5.15 mmol) of triethylamine. The reaction mixture was refluxed for 3 h. The solvent was evaporated *in vacuo*, and the resulting oil was dissolved in 40 mL of dichloromethane, washed 2 times with 30 mL of brine, and dried (Na_2SO_4). After filtration, the dichloromethane was evaporated and the resulting oil was purified by column chromatography (silica 60H, eluent 5% MeOH in $CHCl_3$ (v/v)). Yield: 1.93 g (98%) of **2** as an oil. R_f (TLC, eluent 5% MeOH in CH_2Cl_2 (v/v)) = 0.22. ^1H NMR (90 MHz, $CDCl_3$, 298 K): δ 2.2 (s, 6H, CH_3), 2.3 (s, 6H, CH_3), 3.0 (t, 4H, NCH_2CH_2), 3.45 (s, 2H, CH_2Ar), 4.0 (t, 4H, NCH_2CH_2-pyrazole), 5.8 (s, 2H, pyrazole-*H*), 7.2 (s, 5H, Ar*H*). ^{13}C NMR (400 MHz, $CDCl_3$, 298 K): δ 10.90 (CH_3), 13.38 (CH_3), 47.12 (pyrazole-CH_2CH_2), 54.39 (pyrazole-CH_2CH_2), 59.54 (CH_2-Ar), 104.77 (pyrazole-*C*), 127.07 (Ar*C*), 128.25 (Ar*C*), 128.60 (Ar*C*), 138.91 (Ar*C*), 147.24 (pyrazole-CCH_3). MS (EI): m/z = 351 (M^+). Anal. Calcd for $C_{21}H_{29}N_5·0.5CH_2Cl_2$: C, 62.80; H, 7.23; N, 17.03. Found: C, 62.70; H, 7.30; N, 16.90.

Preparation of the Complexes. $[Cu(1)·2NO_3]$ (3). To a solution of 0.75 g (2.8 mmol) of **1** in 50 mL of ethanol was added 0.52 g (2.8 mmol) of $Cu(NO_3)_2·3H_2O$. The solution turned green immediately. After the solution was refluxed for 1 h, the solvent was evaporated *in vacuo*. Complex **3** was recrystallized from ethanol/ether. Yield: 1.1 g (86%) of dark green crystals. Mp = 160 °C. Anal. Calcd for dried complex $C_{14}H_{23}CuN_7O_6$: C, 37.46; H, 5.16; N, 21.84. Found: C, 37.50; H, 5.15; N, 20.26. FAB-MS: m/z = 386 (**1** + Cu + NO_3). IR (acetonitrile, cm^{-1}): 1323 (free NO_3^-), 1288 (coord. NO_3^-). UV–vis (acetonitrile) [λ_{max}/nm ($\epsilon/M^{-1}·cm^{-1}$)]: 225.5 (15 100), 264.1 (2200), 708 (180).

$[Cu(1)ClO_4·C_2H_5OH]ClO_4$ (4). To a solution of 80 mg (0.306 mmol) of **1** in 2 mL of ethanol was added 11.4 mg (0.306 mmol) of $Cu(ClO_4)_2·6H_2O$. The solution turned green immediately and was refluxed for 1 h. The solvent was evaporated *in vacuo*, and the product was recrystallized from ethanol/ether to yield 70 mg (40%) of **4** as dark green crystals. Mp = 220 °C. Anal. Calcd for $C_{14}H_{23}CuN_5Cl_2O_8·C_2H_5OH$: C, 33.72; H, 5.13; N, 12.29. Found: C, 32.99; H, 5.16; N, 12.98. FAB-MS: m/z = 423 (**1** + Cu + ClO_4). IR (acetonitrile, cm^{-1}): 1102 (free ClO_4^-). UV–vis (acetonitrile) [λ_{max}/nm ($\epsilon/M^{-1}·cm^{-1}$)]: 226.5 (15 800), 272.0 (1960), 324.3 (shoulder, 620), 685.7 (60).

$[Cu(2)·2NO_3]$ (5). To a solution of 253 mg (0.72 mmol) of **2** dissolved in 2 mL of ethanol was added while stirring a solution of 2 mL of ethanol containing 174 mg (0.72 mmol) of $Cu(NO_3)_2·3H_2O$. The reaction mixture immediately developed a dark blue-green color. After 1.5 h the solvent was evaporated *in vacuo*. The resulting blue-green powder was recrystallized from hot ethanol. Mp = 160 °C. Anal. Calcd for $C_{21}H_{29}N_7O_6Cu$: C, 46.79; H, 5.42; N, 18.19. Found: C, 46.27; H, 5.64; N, 17.09. FAB-MS: m/z = 476 (**2** + Cu + NO_3). IR (acetonitrile, cm^{-1}): 1341 (free NO_3^-), 1291 (coord. NO_3^-). UV–vis (acetonitrile) [λ_{max}/nm ($\epsilon/M^{-1}·cm^{-1}$)]: 225.5 (13 700), 297.6 (2100), 688.7 (30).

$[Cu(2)·C_2H_5OH·Y](ClO_4)_n$ (6) (Y = H_2O, with $n = 2$, and ClO_4^-, with $n = 1$). Ligand **2** (241.5 mg, 0.69 mmol) was dissolved in 2 mL of ethanol. To this solution was added dropwise while stirring a solution of 254.9 mg (0.69 mmol) of $Cu(ClO_4)_2·6H_2O$ in 2 mL of ethanol. The reaction mixture turned dark green immediately. After the solution was stirred for 1.5 h, the solvent was evaporated *in vacuo*. Complex **6** was recrystallized from hot ethanol. Mp = 109 °C. Anal. Calcd for dried complex **6**, $C_{21}H_{29}N_5Cl_2O_8Cu·2H_2O$: C, 38.75; H, 5.26; N, 10.76. Found: C, 38.87; H, 5.21; N, 10.69. FAB-MS: m/z = 513 (**2** + Cu + ClO_4). IR (acetonitrile, cm^{-1}): 1102 (free ClO_4^-). UV–vis (acetonitrile) [λ_{max}/nm ($\epsilon/M^{-1}·cm^{-1}$)]: 217.6 (13 400), 224.6 (13 250), 293.7 (1800), 400 (shoulder, 520), 690 (80).

Physical Measurements. UV–vis spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker WH90 or a Bruker WM-400 instrument.

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Table 1. Crystallographic Data for Complexes **3**–**6**

complex	**3**	**4**	**5**	**6**
formula	$C_{14}H_{25}CuN_7O_7$ (1 H_2O included)	$C_{16}H_{29}Cl_2CuN_5O_9$	$C_{21}H_{29}CuN_7O_6$	$C_{48}H_{78}Cl_4Cu_2N_{10}O_{20}$
M_r	466.95	569.89	539.05	1384.10
space group	*Pc* (No. 7)	$Pna2_1$ (No. 33)	*C*2/*c* (No. 15)	$P2_1/c$ (No. 14)
cryst system	monoclinic	orthorhombic	monoclinic	monoclinic
Z	4	4	8	4
a, Å	8.1596(9)	13.3643(7)	28.719(2)	10.9488(9)
b, Å	31.164(2)	10.3925(9)	8.6043(6)	17.030(2)
c, Å	7.7966(9)	17.511(1)	23.034(2)	32.893(3)
β, deg	94.75(2)		124.767(7)	92.185(7)
V, Å^3	1975.7(3)	2432.1(3)	4675.7(7)	6129(1)
D_{calcd}, g·cm^{-3}	1.570	1.556	1.531	1.500
μ_{calcd}, cm^{-1}	11.6	11.7	9.9	9.5
radn (Mo Kα), Å	0.710 73 (graphite mon.)	0.710 73 (Zr-filtered)	0.710 73 (graphite mon.)	0.710 73 (graphite mon.)
T, K	293(2)	298	150	150
$R_F{}^a$	0.066	0.063	0.042	0.104
$R_{wF}{}^a$		0.052	0.034	0.119
$R_{wF^2}{}^a$	0.227			

[a] Definition of *R* factors: $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_{wF} = [\Sigma[w(||F_o| - |F_c||)^2]/\Sigma[w(F_o^2)]]^{1/2}$; $R_{wF^2} = [\Sigma[w(||F_o|^2 - |F_c|^2|)^2]/\Sigma[w(F_o^4)]]^{1/2}$.

Chemical shifts are denoted in ppm relative to the internal standard tetramethylsilane. FAB-MS spectra were recorded on a VG 7070E instrument using 3-nitrobenzyl alcohol as the matrix. IR spectra were measured on a Perkin-Elmer 1720X instrument. Melting points were measured on a Reichert-Jung hot stage mounted on a microscope and are reported uncorrected. Conductivity measurements were carried out in acetonitrile with a Schott Geräte CG 852 Konduktometer at various concentrations of the complexes (1×10^{-3} to 1×10^{-4} M). EPR spectra were recorded at X-band (9 GHz) on a Bruker ESP 300 equipped with an Oxford Instruments helium continuous flow cryostat. Cyclic voltammetry experiments were performed with a Par 173 potentiostat equipped with a PAR Model 176 I/E converter coupled to a PAR Model 175 universal programmer using a platinum auxilary as well as working electrode and a Ag^+/Ag (0.1 M $AgNO_3$) electrode as the reference electrode. All measurements were carried out in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte; the concentrations of metal complexes amounted to 5×10^{-4} M. The half-wave potential of a 10^{-3} M solution of ferrocene was measured under the same experimental conditions: $E_{1/2} = 0.045$ V. All potentials are quoted vs the potential of the Fc/Fc^+ redox couple, measured under the same experimental conditions.

Crystals. Crystals were grown by slow diffusion of diethyl ether into an ethanolic solution of the respective complexes. This procedure yielded dark green crystals of **3** ($0.45 \times 0.35 \times 0.18$ mm, plate-shaped) and **5** ($0.7 \times 0.2 \times 0.1$ mm, needle-shaped), blue-green crystals of **4** ($0.14 \times 0.30 \times 0.40$ mm, plate-shaped), and light green crystals of **6** ($0.4 \times 0.1 \times 0.1$ mm, needle-shaped).

Collection and Reduction of the X-ray Diffraction Data for Complex 3. Standard experimental and computational details for the procedure followed for the structure elucidation of complex **3** are given elsewhere.[18] Unit cell dimensions were determined from 25 reflections with $16° < \theta < 20°$. Intensity data were collected for 12 207 reflections (half a sphere up to $\theta = 30°$, 2θ range 2–60°). The instrumental drift correction factors were between 1.001 and 1.082. The empirical absorption correction factors (EMPABS)[19] were in the range 0.961–1.070. After preliminary refinement (to $R = 0.093$) an additional semi-empirical absorption correction (DIFABS)[20] was applied with factors ranging from 0.734 to 1.125. Averaging of symmetry equivalent reflections gives 6110 unique reflections ($R_{merge} = 0.043$ on F_o values). Systematic extinctions are $h0l$, $l = 2n + 1$, and possibly $0k0$, $k = 2n + 1$, although six of these reflections had intensities with $I = 4\sigma(I)$.

The structure of **3** was originally solved in the centrosymmetric space group $P2_1/c$ using automated vector search methods: a fragment of one pyrazole ring plus a Cu atom bound to it was oriented by ORIENT[21] and positioned by TRACOR[22] and automatically expanded by DIRDIF.[23] Least squares refinement led to approximately $R = 0.07$ (based on *F*, with $F > 4\sigma$). All atoms of the complex were well determined except one nitrate which seemed to be disordered. Inspection of the disorder revealed the possibility of an ordered structure in the noncentrosymmetric space group *Pc*, with two molecules in the asymmetric unit (including two nitrates and two water molecules). This structure could be refined properly by SHELXL.[24a] The hydrogen atoms were fixed at calculated positions (for CH_3 groups C–H = 0.96 Å; for CH_2 groups C–H = 0.97 Å, for aromatic C C–H = 0.93 Å, N–H = 0.91 Å) except for the methyl hydrogen atoms. The hydrogen atoms of the methyl groups were obtained by rotation of an idealized methyl group to match maximum electron density in the difference map. The hydrogen atoms of the water molecules could not be found in a difference Fourier map and were not included in the least squares refinement. The other hydrogen atoms were refined riding on the parent atoms. The hydrogen bonds of the idealized methyl groups were refined by refinement of the torsion angle around the concerned C–C bonds. Isotropic temperature factors for the hydrogen atoms were set to 1.2 times or for methyl hydrogen atoms to 1.5 times the equivalent isotropic temperature factor of the parent atoms. The function minimized was $\Sigma w(F_o^2 - F_c^2)^2$ with $w = 1/[\sigma^2(F_o^2) + (0.1346P)^2]$ where $\sigma^2(F_o^2)$ is derived from counting statistics and $P = (F_o^2 + 2F_c^2)/3$ for $F_o^2 \geq 0$ and $P = 2F_c^2/3$ for $F_o^2 < 0$. The final agreement factor based upon F^2 was $R_w = 0.227$, $S = 1.13$, for 481 parameters, 194 restraints, and all 6110 reflections. The Flack acentricity parameter refined to −0.017(30) showing that the absolute structure is correct. The conventional agreement factor based upon *F* is $R = 0.066$, for 3637 reflections with $F > 4\sigma(F)$. Final difference Fourier peaks were less than 1.19 e Å^{-3} (occurring in the neighborhood of isotropically refined nitrate groups). Crystal data are collected in Table 1.

Crystal Structure Determination of Complexes 4–6. Crystals suitable for X-ray structure determination were mounted on a Lindemann glass capillary and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4-Turbo diffractometer on a rotating anode (**5** and **6**) or to an Enraf-Nonius CAD4-F sealed-tube diffractometer (**4**). Accurate unit-cell parameters and an orientation matrix were determined by least-squares refinement of 25, 25, and 18 well-centered reflections (SET4) in the ranges $6.0° < \theta < 14.1°$, $10.5° < \theta < 13.9°$, and $9.9° < \theta < 13.5°$ for **4**–**6**, respectively. Reduced-cell calculations did not indicate higher lattice symmetry.[25] Crystal data and details on data

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collection are given in Table 1. Data were collected at 150 K for **5** and **6** and at ambient temperature for **4**, in the $\omega/2\theta$ scan mode. The scan angle was $\Delta\omega = a + 0.35 \tan \theta°$ with $a = 0.75$, 0.54, and 0.50 for **4**−**6**, respectively. Intensity data were collected up to $\theta = 27.50°$ (2θ range 2−55°). Total data of 6346, 11 692, and 16 850 reflections were collected of which 2883, 5372, and 14032 were independent for **4**−**6**, respectively. Data were corrected for *Lp* effects and for the linear decay of the three periodically measured reference reflections during X-ray exposure time. Standard deviations of the intensities as obtained by counting statistics were increased according to an analysis of the excess variance of the reference reflections: $\sigma^2(I) = \sigma^2_{cs}(I) + (pI)^2$[26] with $p = 0.01$, 0.01, and 0.03 for **4**−**6**, respectively. An empirical absorption/extinction correction was applied (DIFABS,[20] correction ranges 0.66−1.32, 0.86−1.10, and 0.73−1.18 for **4**−**6**, respectively). The structure of **4** was solved by automated direct methods (SIR-92[27]); the structures of **5** and **6** were solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92[28]). Refinement on F was carried out by full-matrix least-squares techniques (SHELX76[24b]). Hydrogen atoms were included in the refinement on calculated positions (C−H = 0.98 Å) riding on their carrier atoms. The data set of **6** did not allow anisotropic refinement of all non-hydrogen atoms; therefore only Cu and Cl were refined anisotropically. For the other structures all non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with overall isotropic thermal parameters. Weights were introduced in the final refinement cycles. For **4** convergence was reached at $R = 0.063$, $R_w = 0.052$, $w = 1/[\sigma^2(F) + 0.000271F^2]$, $S = 2.11$, for 315 parameters and 1281 reflections with $I > 2.5\sigma(I)$. A final difference Fourier map showed no residual density outside −0.54 and 0.75 e Å^{-3}. Refinement of the alternative chirality did not yield significantly different results. For **5** convergence was reached at $R = 0.042$, $R_w = 0.034$, $w = 1/[\sigma^2(F) + 0.000053F^2]$, $S = 2.90$, for 329 parameters and 3731 reflections with $I > 2.5\sigma(I)$. No residual density was found outside −0.48 and 0.40 e Å^{-3}. For **6** convergence was reached at $R = 0.104$, $R_w = 0.119$, $w = 1/[\sigma^2(F) + 0.00181F^2]$, $S = 10.1$, for 382 parameters and 3052 reflections with $I > 2.5\sigma(I)$. A final difference Fourier map showed no residual density outside −0.82 and 1.81 e Å^{-3}. The high residual density was located near a ClO_4^- ion and is indicative of a slight disorder in this counterion. Neutral atom scattering factors were taken from Cromer and Mann,[29] and anomalous dispersion corrections from Cromer and Liberman.[30] Geometrical calculations and illustrations were performed with PLATON.[31] All calculations were preformed on a DECstation 5000/125.

Results

X-ray Structures. Dinitrato{bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine}copper(II) (3). Crystallographic data are given in Table 1, selected bond lengths and angles are presented in Table 2, and the positional parameters are in Table 3. The crystal structure contains two symmetrically independent complexes (denoted **3a,b**), which are very similar. The most important difference between the two complexes is the coordination of a nitrate group in **3a**, whereas a water molecule occupies this position in **3b**. The two complexes **3a** without the nitrate and **3b** without the water are related by a pseudo center of symmetry (largest deviation between corresponding atoms, 0.27 Å; root-mean-square deviation of the 24 non-hydrogen atoms, 0.11 Å). Both complexes (see Figure 1a,b) contain a copper(II) ion surrounded by three nitrogen atoms and three oxygen atoms in a geometry intermediate between that of a distorted trigonal bipyramid and an octahedron. The basal plane is formed by the nitrogen atoms of the two pyrazole units and the amine nitrogen. These atoms make a T-shaped arrangement around the metal ion, a situation more often encountered with pyrazole[32] and the related pyridine[33,34] ligands when the metal is in the 1+ oxidation state. The copper to pyrazole (N) distances (Å) are Cu(1)−N(1) 1.971(6) and Cu(1)−N(5) 1.953(6) in **3a** and Cu(1A)−N(1A) 1.981(7) and Cu(1A)−N(5A) 1.972(8) in **3b**; the copper to amine distances are 2.075(8) to N(3) in **3a** and 2.001(10) to N(3A) in **3b**. The N(1)−Cu−N(5) angle in **3a** (165.6(3)°) and the N(1A)−Cu(1A)−N(5A) angle in **3b** (165.9(3)°) slightly deviate from linearity. The copper centers are displaced out of the planes formed by the three nitrogens of the bispyrazole ligands in the direction of coordinating nitrate groups. These nitrate groups coordinate anisobidentately with one short (Cu(1)−O(1), 2.102(8) Å in **3a**, and Cu(1A)−O(1A), 2.072(3) Å in **3b**) and one long distance (Cu(1)−O(2), 2.540(8) Å in **3a**, and Cu(1A)−O(2A), 2.683(10) Å in **3b**). In **3a**, there is another nitrate in the trans position, which coordinates monodentately with Cu(1)−O(4), 2.487(7) Å (Figure 1a). In **3b**, this position is taken up by a water molecule (Cu(1A)−O(1W), 2.395(10) Å), which is at hydrogen bonding distance from a noncoordinating nitrate (Figure 1b).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes **3a,b**

	Distances for **3a**		
Cu(1)−N(1)	1.971(6)	Cu(1)−O(1)	2.102(8)
Cu(1)−N(5)	1.953(6)	Cu(1)−O(2)	2.540(8)
Cu(1)−N(3)	2.075(8)	Cu(1)−O(4)	2.487(7)
	Angles for **3a**		
N(1)−Cu(1)−N(5)	165.6(3)	N(3)−Cu(1)−O(4)	88.6(3)
N(1)−Cu(1)−N(3)	94.3(3)	N(5)−Cu(1)−O(1)	93.1(3)
N(5)−Cu(1)−N(3)	93.6(3)	N(1)−Cu(1)−O(1)	89.2(3)
N(1)−Cu(1)−O(2)	91.7(3)	N(3)−Cu(1)−O(1)	137.1(3)
N(5)−Cu(1)−O(2)	101.1(3)	O(2)−Cu(1)−O(4)	167.5(3)
N(3)−Cu(1)−O(2)	83.5(3)	O(1)−Cu(1)−O(4)	133.8(3)
N(5)−Cu(1)−O(4)	89.0(3)	O(1)−Cu(1)−O(2)	53.7(3)
N(1)−Cu(1)−O(4)	79.2(3)		
	Distances for **3b**		
Cu(1A)−N(1A)	1.981(7)	Cu(1A)−O(1A)	2.072(8)
Cu(1A)−N(5A)	1.972(8)	Cu(1A)−O(2A)	2.683(10)
Cu(1A)−N(3A)	2.001(10)	Cu(1A)−O(1W)	2.395(10)
	Angles for **3b**		
N(1A)−Cu(1A)−N(5A)	165.9(3)	N(3A)−Cu(1A)−O(1w)	100.8(4)
N(1A)−Cu(1A)−N(3A)	95.2(3)	N(5A)−Cu(1A)−O(1A)	87.3(4)
N(5A)−Cu(1A)−N(3A)	96.9(3)	N(1A)−Cu(1A)−O(1A)	89.0(4)
N(1A)−Cu(1A)−O(2A)	90.4(3)	N(3A)−Cu(1A)−O(1w)	135.7(4)
N(5A)−Cu(1A)−O(2A)	98.3(4)	O(2A)−Cu(1A)−O(1w)	174.4(3)
N(3A)−Cu(1A)−O(2A)	82.7(4)	O(1A)−Cu(1A)−O(1w)	123.5(3)
N(5A)−Cu(1A)−O(1w)	85.7(4)	O(1A)−Cu(1A)−O(2A)	53.1(2)
N(2A)−Cu(1A)−O(1w)	84.9(3)		

{Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine}copper(II) Diperchlorate (4). The structure of complex **4** is given in Figure 2. Crystal data and details of the structure determination are given in Table 1, selected bond lengths and angles are presented in Table 4, and positional parameters are in Table 5. As can be seen from Figure 2, the copper ion in complex **4** is four coordinated by three nitrogen atoms (N(1), N(3), and N(5)) from ligand **1** and an ethanol oxygen atom (O(1)). The pyrazole

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Table 3. Atomic Positional and Vibrational Parameters (with Esd's) for Complex **3**

atom	*x*	*y*	*z*	U_{eq}, Å^2
Cu(1)	0.1684(1)	0.3841(1)	0.3546(1)	0.038(1)
N(3)	0.3916(10)	0.3581(3)	0.4500(12)	0.052(3)
N(1)	0.2510(8)	0.4436(2)	0.3563(11)	0.031(2)
N(2)	0.3965(10)	0.4578(2)	0.4348(10)	0.040(2)
C(1)	0.1720(11)	0.4784(3)	0.2925(15)	0.047(3)
C(2)	0.2682(13)	0.5151(2)	0.3275(16)	0.056(4)
C(3)	0.4093(12)	0.5008(3)	0.4181(13)	0.040(3)
C(4)	0.0069(13)	0.4758(4)	0.1920(19)	0.069(5)
C(5)	0.5561(14)	0.5263(3)	0.4848(15)	0.053(3)
C(11)	0.5169(12)	0.4283(3)	0.5209(13)	0.045(3)
C(12)	0.5320(10)	0.3874(2)	0.4260(14)	0.039(3)
N(5)	0.0724(9)	0.3283(2)	0.2921(10)	0.031(2)
N(4)	0.1406(9)	0.2905(2)	0.3365(11)	0.039(2)
C(6)	−0.0624(10)	0.3202(2)	0.1913(12)	0.030(2)
C(7)	−0.0822(14)	0.2761(2)	0.1679(16)	0.047(3)
C(8)	0.0445(11)	0.2577(2)	0.2688(14)	0.043(3)
C(9)	−0.1632(18)	0.3550(3)	0.1006(17)	0.067(5)
C(10)	0.0852(15)	0.2121(3)	0.2930(17)	0.058(3)
C(13)	0.2907(15)	0.2865(3)	0.4511(18)	0.072(5)
C(14)	0.4271(11)	0.3130(3)	0.3931(18)	0.059(4)
N(6)	−0.0236(11)	0.4027(3)	0.6205(3)	0.041(2)
O(1)	−0.0476(10)	0.4063(2)	0.4548(8)	0.043(2)
O(2)	0.1158(10)	0.3883(2)	0.6708(10)	0.047(2)
O(3)	−0.1247(9)	0.4169(3)	0.7078(10)	0.051(2)
Cu(1A)	−0.1710(1)	0.1162(1)	−0.3538(1)	0.041(1)
N(3A)	−0.3855(11)	0.1398(2)	−0.4554(15)	0.047(3)
N(1A)	0.2434(10)	0.0555(2)	−0.3607(11)	0.043(3)
N(2A)	0.3944(8)	0.0418(2)	−0.4266(12)	0.040(2)
C(1A)	−0.1659(9)	0.0210(2)	−0.2915(12)	0.036(3)
C(2A)	−0.2648(10)	−0.0148(2)	−0.3264(12)	0.039(3)
C(3A)	−0.4065(11)	−0.0019(2)	−0.4127(15)	0.042(3)
C(4A)	−0.0044(12)	0.0233(3)	−0.1889(14)	0.047(3)
C(5A)	−0.5524(14)	−0.0264(4)	−0.04867(21)	0.068(5)
C(11A)	−0.5107(14)	0.0708(3)	−0.5177(16)	0.058(4)
C(12A)	−0.5292(16)	0.1128(3)	−0.4267(24)	0.071(5)
N(5A)	−0.0648(11)	0.1718(2)	−0.2969(12)	0.050(3)
N(4A)	−0.1299(10)	0.2119(2)	−0.3407(13)	0.047(3)
C(6A)	0.0718(14)	0.1789(3)	−0.1949(16)	0.065(4)
C(7A)	0.0960(12)	0.2237(3)	−0.1820(15)	0.048(3)
C(8A)	−0.0347(15)	0.2436(3)	−0.2670(15)	0.056(4)
C(9A)	0.1685(12)	0.1433(3)	−0.1073(14)	0.048(3)
C(13A)	−0.2819(11)	0.2157(3)	−0.4493(18)	0.061(4)
C(14A)	−0.4111(13)	0.1845(3)	−0.4067(21)	0.064(4)
C(10A)	−0.0762(22)	0.2902(2)	−0.2941(20)	0.081(6)
N(6A)	0.0219(10)	0.0975(3)	−0.6109(10)	0.047(3)
O(1A)	0.0479(10)	0.0974(3)	−0.4481(9)	0.050(2)
O(2A)	−0.1064(11)	0.1118(3)	−0.6852(13)	0.065(3)
O(3A)	0.1388(14)	0.0887(4)	−0.7002(12)	0.103(5)
O(1W)	−0.2206(13)	0.1129(3)	−0.0556(13)	0.068(2)
N(7)	0.3204(10)	0.3607(2)	−0.0418(10)	0.053(2)
O(4)	0.2770(10)	0.3880(2)	0.0662(10)	0.053(2)
O(5)	0.4265(10)	0.3698(3)	−0.1410(10)	0.068(2)
O(6)	0.2662(12)	0.3226(2)	−0.0457(12)	0.082(2)
O(2W)	0.5195(14)	0.2745(3)	−0.1863(15)	0.082(3)
N(8)	−0.4553(14)	0.1884(3)	0.1304(14)	0.078(3)
O(9)	−0.5210(20)	0.2239(4)	0.1720(21)	0.128(6)
O(7)	−0.4804(16)	0.1530(3)	0.1948(15)	0.111(4)
O(8)	−0.3617(20)	0.1886(4)	0.0067(18)	0.158(6)

N to copper distances are 1.964(12) and 1.922(14) Å for N(1) and N(5), respectively. The amine nitrogen N(3) to copper distance is 2.006(9) Å. In addition to these short contacts, an additional long-range interaction between the perchlorate oxygen O(14) and copper is observed (distance 2.607(12) Å, not shown in Figure 2). An interesting feature is the presence of a hydrogen bond between the hydroxyl group of the coordinating ethanol molecule and the perchlorate oxygen O(22′) (related through the symmetry operation $\frac{1}{2} - x$, $y - \frac{1}{2}$, $z - \frac{1}{2}$) with an O- - -O distance of 2.715(16) Å and an O−H- - -O angle of 179.2(1.3)°. Furthermore a borderline hydrogen bond exists between the secondary amine nitrogen N(3)−H(3) and the perchlorate oxygen O(11″) (related through symmetry operation x, $y - 1$, z) with an O- - -O distance of 3.180(20) Å and an O−H- - -O angle of 154.9(1.2)°. The hydrogen bonds are not represented in the drawing in Figure 2 for clarity.

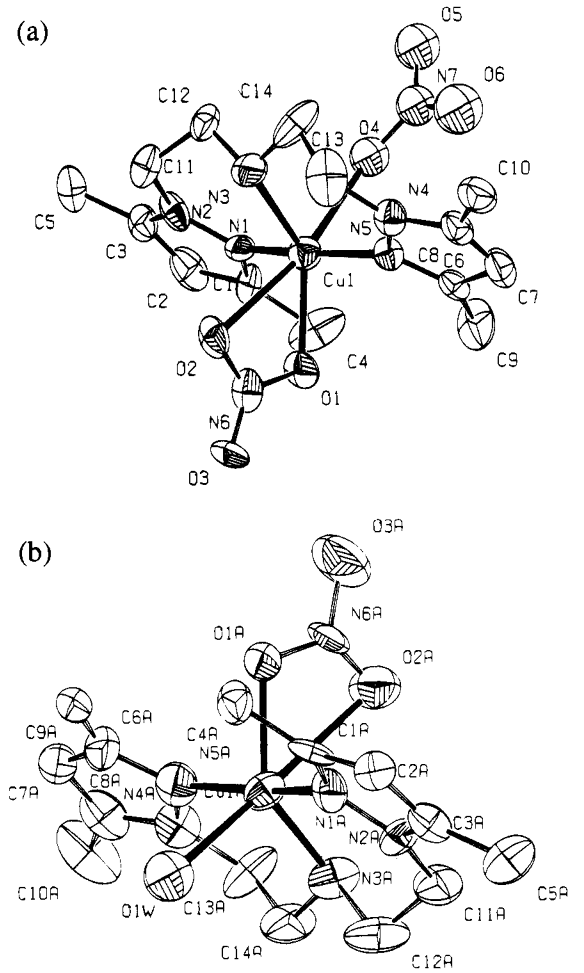

Figure 1. (a) X-ray structure of complex **3a**. The ORTEP plot is at the 50% probability level. (b) X-ray structure of complex **3b**. The ORTEP plot is at the 50% probability level.

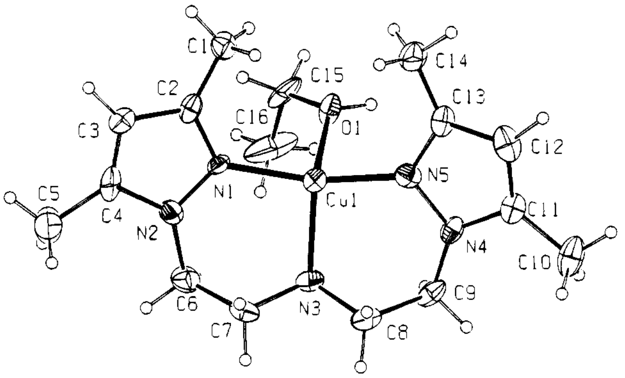

Figure 2. ORTEP[31] plot of the X-ray structure of complex **4** at the 30% probability level.

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

	Distances		
Cu−N(1)	1.964(12)	Cu−N(5)	1.922(14)
Cu−N(3)	2.006(9)	Cu−O(1)	2.044(10)
	Angles		
N(1)−Cu−N(3)	96.8(6)	N(1)−Cu−O(1)	93.6(4)
N(1)−Cu−N(5)	160.5(5)	N(3)−Cu−O(1)	126.5(4)
N(3)−Cu−N(5)	97.0(6)	N(5)−Cu−O(1)	89.2(5)

Table 5. Final Coordinates and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms for Complex **4**

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Cu(1)	0.31825(13)	0.96637(15)	0.17100	0.0436(6)
O(1)	0.2011(8)	1.0870(8)	0.1486(5)	0.051(4)
N(1)	0.3199(9)	1.0072(11)	0.2805(7)	0.035(4)
N(2)	0.3153(10)	0.9194(12)	0.3374(8)	0.046(5)
N(3)	0.3115(8)	0.7745(8)	0.1824(9)	0.043(4)
N(4)	0.3509(10)	0.8610(13)	0.0168(8)	0.042(5)
N(5)	0.3523(10)	0.9693(14)	0.0644(8)	0.042(5)
C(1)	0.3614(12)	1.2374(16)	0.2677(9)	0.048(6)
C(2)	0.3420(11)	1.1192(17)	0.3094(9)	0.042(6)
C(3)	0.3520(11)	1.1040(15)	0.3890(9)	0.040(6)
C(4)	0.3323(12)	0.9825(19)	0.4058(8)	0.050(6)
C(5)	0.3256(16)	0.9083(18)	0.4795(10)	0.082(8)
C(6)	0.2880(12)	0.7868(15)	0.3248(10)	0.053(7)
C(7)	0.3480(13)	0.7268(16)	0.2593(10)	0.049(7)
C(8)	0.3624(13)	0.7018(15)	0.1206(10)	0.054(7)
C(9)	0.3157(12)	0.7392(17)	0.0437(10)	0.048(7)
C(10)	0.3876(12)	0.8028(19)	−0.1178(10)	0.074(8)
C(11)	0.3789(12)	0.8992(17)	−0.0538(10)	0.046(6)
C(12)	0.4032(12)	1.026(2)	−0.0505(10)	0.060(7)
C(13)	0.3830(12)	1.0735(17)	0.0219(10)	0.045(7)
C(14)	0.3973(15)	1.2011(18)	0.0519(11)	0.063(18)
C(15)	0.1178(12)	1.1150(16)	0.1985(10)	0.071(8)
C(16)	0.0581(15)	1.0050(18)	0.2168(18)	0.122(12)
Cl(1)	0.0948(3)	0.5525(4)	0.1925(3)	0.0547(17)
O(11)	0.1023(12)	0.6488(17)	0.1377(11)	0.148(9)
O(12)	0.0824(17)	0.615(2)	0.2604(12)	0.190(11)
O(13)	0.1799(10)	0.4788(13)	0.1918(13)	0.130(8)
O(14)	0.0079(9)	0.4803(11)	0.1856(12)	0.105(6)
Cl(2)	0.4339(4)	0.4987(4)	0.4661(3)	0.0653(19)
O(21)	0.404(2)	0.494(3)	0.3966(13)	0.28(2)
O(22)	0.3820(12)	0.5920(12)	0.5072(7)	0.101(6)
O(23)	0.5290(15)	0.515(3)	0.472(2)	0.228(16)
O(24)	0.4126(16)	0.3846(17)	0.4999(13)	0.193(13)

[a] U_{eq} = $^1/_3$ of the trace of the orthoginalized **U**.

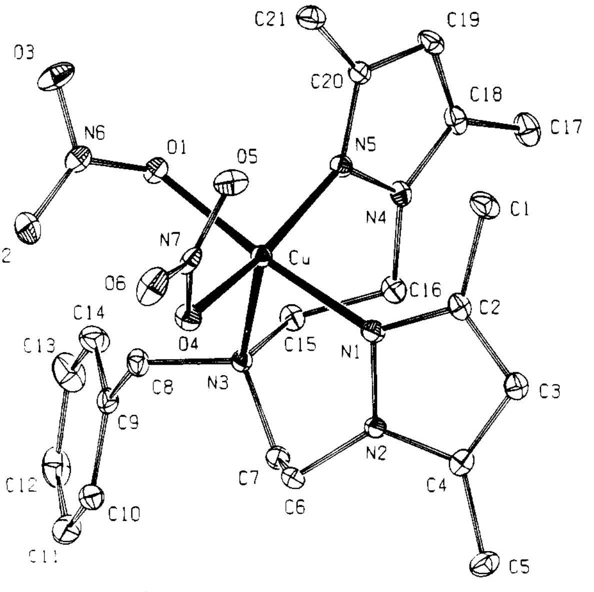

Figure 3. ORTEP[31] plot of the X-ray structure of complex **5** at the 30% probability level.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for Complex **5**

	Distances		
Cu−O(1)	1.999(2)	Cu−N(3)	2.330(3)
Cu−O(4)	1.991(2)	Cu−N(5)	1.984(3)
Cu−N(1)	2.007(3)	Cu−O(5)	2.6213(18)
	Angles		
O(1)−Cu−O(4)	93.95(9)	O(4)−Cu−N(5)	162.42(10)
O(1)−Cu−N(1)	174.62(11)	N(1)−Cu−N(3)	89.91(10)
O(1)−Cu−N(3)	94.69(8)	N(1)−Cu−N(5)	92.47(12)
O(1)−Cu−N(5)	84.44(10)	N(3)−Cu−N(5)	93.96(11)
O(4)−Cu−N(1)	87.67(11)	N(5)−Cu−O(5)	108.26(10)
O(4)−Cu−N(3)	103.62(10)	O(4)−Cu−O(5)	54.22(9)

Table 7. Final Coordinates and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of Complex **5**

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Cu	0.15324(1)	−0.12318(4)	0.29487(2)	0.0156(1)
O(1)	0.08360(8)	−0.2280(2)	0.21520(10)	0.0211(6)
O(2)	0.11089(10)	−0.3801(3)	0.16351(12)	0.419(9)
O(3)	0.05126(9)	−0.4620(3)	0.18502(12)	0.0347(8)
O(4)	0.20595(8)	−0.2711(2)	0.29352(11)	0.0240(7)
O(5)	0.17855(9)	−0.4031(2)	0.34954(11)	0.0297(7)
O(6)	0.24094(9)	−0.5006(3)	0.33485(12)	0.0350(8)
N(1)	0.22136(10)	−0.0263(3)	0.38091(12)	0.0196(8)
N(2)	0.25957(10)	0.0567(3)	0.37554(12)	0.0177(8)
N(3)	0.14815(10)	0.0846(3)	0.22660(12)	0.0167(7)
N(4)	0.09652(9)	0.1297(3)	0.31999(11)	0.0183(7)
N(5)	0.10064(9)	−0.0270(3)	0.31425(12)	0.0170(8)
N(6)	0.08254(10)	−0.3599(3)	0.18754(12)	0.0211(8)
N(7)	0.20861(10)	−0.3957(3)	0.32680(13)	0.0226(8)
C(1)	0.20520(13)	−0.0779(4)	0.47432(16)	0.0282(10)
C(2)	0.23655(12)	−0.0039(3)	0.44726(15)	0.0203(9)
C(3)	0.28348(12)	0.0934(3)	0.48338(16)	0.0222(9)
C(4)	0.29725(11)	0.1314(4)	0.43665(14)	0.0203(8)
C(5)	0.34281(13)	0.2326(4)	0.44543(17)	0.0283(10)
C(6)	0.25376(12)	0.0637(4)	0.30280(15)	0.0219(9)
C(7)	0.20344(12)	0.1620(3)	0.25448(15)	0.0208(9)
C(8)	0.12432(13)	0.0173(3)	0.15492(14)	0.0224(9)
C(9)	0.10019(12)	0.1332(4)	0.09435(14)	0.0209(8)
C(10)	0.13366(13)	0.2038(4)	0.07603(15)	0.0260(10)
C(11)	0.11033(15)	0.3125(4)	0.02199(17)	0.0338(11)
C(12)	0.05396(16)	0.3497(4)	−0.01505(17)	0.0380(11)
C(13)	0.01999(15)	0.2774(5)	0.00080(18)	0.0419(13)
C(14)	0.04279(13)	0.1699(4)	0.05486(16)	0.0320(11)
C(15)	0.10782(12)	0.1972(3)	0.22356(15)	0.0213(9)
C(16)	0.12154(13)	0.2395(3)	0.29621(15)	0.0225(9)
C(17)	0.05126(14)	0.3237(4)	0.35369(18)	0.0301(11)
C(18)	0.06337(12)	0.1616(4)	0.34299(15)	0.0225(10)
C(19)	0.04596(12)	0.0209(4)	0.35248(15)	0.0236(10)
C(20)	0.06942(11)	−0.0938(3)	0.33419(14)	0.0185(9)
C(21)	0.06515(13)	−0.2648(4)	0.33722(17)	0.0254(10)

[a] U_{eq} = $^1/_3$ of the trace of the orthogonalized **U**.

Dinitrato{benzylbis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine}copper(II) (5). The structure of this complex is shown in Figure 3. The crystallographic details are given in Table 1, the selected bond lengths and angles in Table 6, and the positional parameters in Table 7. In complex **5** the copper ion is five coordinated by three nitrogen donors from the ligand and two oxygen atoms from the nitrate counterions. The geometry is best described as a square pyramid with a trigonal bipyramidal distortion. The distortion from an idealized trigonal bipyramid toward a square pyramid was calculated to be 83.1%.

The basal plane is formed by the pyrazole nitrogen atoms N(1) and N(5) and the oxygen atoms O(1) and O(4). The distances of these atoms to the copper center are 2.007(3), 1.984(3), 1.999(2), and 1.991(2) Å, respectively. The apical position is occupied by the amine nitrogen N(3); its distance to the copper center is 2.330(3) Å. The copper ion is displaced 0.194(10) Å out of the plane defined by O(1), O(4), N(1), and N(5) in the direction of N(3). Oxygen atom O(5) shows a long-range interaction with the copper atom, the distance being 2.6213(18) Å.

{Benzylbis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine}copper(II) Diperchlorate (6). The X-ray analysis revealed two different structures (**6a**,**b**), which are present in the unit cell in a 1 to 1 ratio, and are presented in Figure 4. The crystallographic data are given in Table 1. The selected bond lengths and angles are presented in Table 8, and the positional parameters in Table 9; the coordinates for noncoordinating perchlorate ions and ethanol molecules are given in the

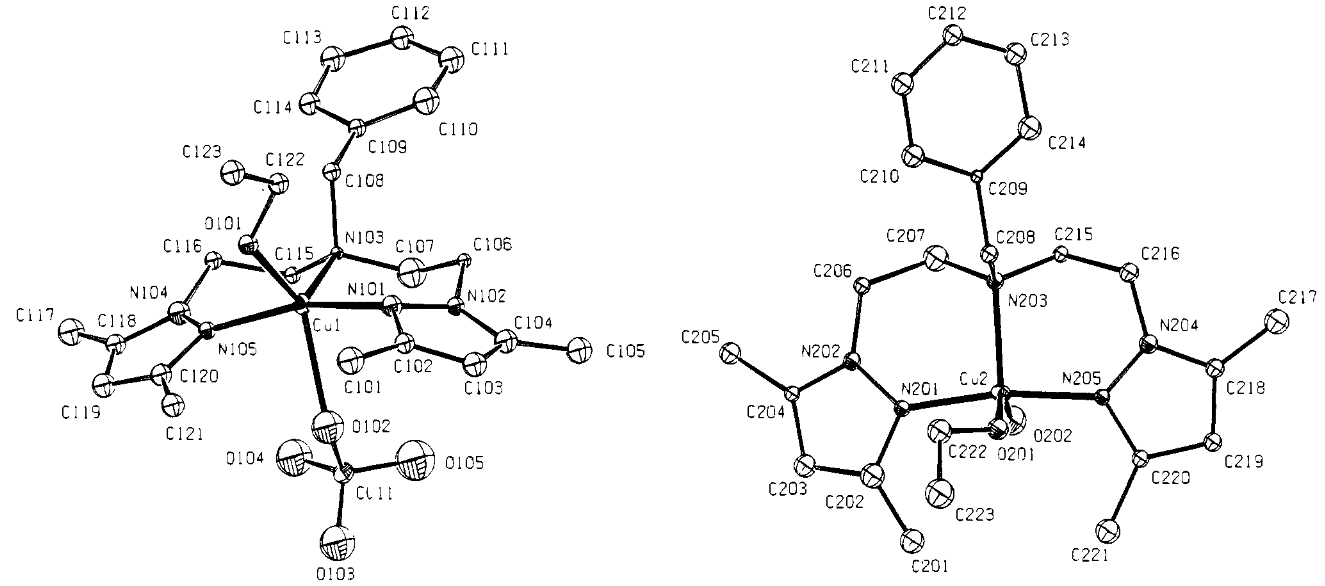

Figure 4. ORTEP[31] plots of the X-ray structures of complex **6a** (left) and **6b** (right) at the 30% probability level.

Table 8. Selected Bond Lengths (Å) and Angles (deg) for Complexes **6a,b**

	Distances for **6a**		
Cu(1)−N(101)	1.94(2)	Cu(1)−O(101)	2.07(2)
Cu(1)−N(103)	2.09(2)	Cu(1)−O(102)	2.34(2)
Cu(1)−N(105)	1.96(2)		
	Angles for **6a**		
N(101)−Cu(1)−N(103)	97.9(8)	N(103)−Cu(1)−O(101)	118.9(7)
N(101)−Cu(1)−N(105)	162.4(8)	N(103)−Cu(1)−O(102)	110.6(7)
N(103)−Cu(1)−N(105)	96.7(8)	N(105)−Cu(1)−O(101)	85.3(7)
N(101)−Cu(1)−O(101)	96.1(8)	N(105)−Cu(1)−O(102)	86.4(7)
N(101)−Cu(1)−O(102)	79.3(8)	O(101)−Cu(1)−O(102)	130.4(7)
	Distances for **6b**		
Cu(2)−N(201)	1.94(2)	Cu(2)−O(201)	2.08(2)
Cu(2)−N(203)	2.12(2)	Cu(2)−O(202)	2.09(2)
Cu(2)−N(205)	1.94(2)		
	Angles for **6b**		
N(201)−Cu(2)−N(203)	95.4(7)	N(203)−Cu(2)−O(201)	108.6(7)
N(201)−Cu(2)−N(205)	169.1(7)	N(203)−Cu(2)−O(202)	104.5(8)
N(203)−Cu(2)−N(205)	95.2(7)	N(205)−Cu(2)−O(201)	87.2(7)
N(201)−Cu(2)−O(201)	92.1(7)	N(205)−Cu(2)−O(202)	88.1(8)
N(201)−Cu(2)−O(202)	86.6(8)	O(201)−Cu(2)−O(202)	146.9(8)

supporting information. The two structures **6a,b** are very similar and are best described as five-coordinated Cu(II) complexes with a trigonal bipyramidal distortion around copper. In both **6a,b** a molecule of ethanol coordinates to the copper center. The most important difference between the two compounds is the coordination of a perchlorate molecule in **6a**, whereas a water molecule occupies this position in **6b**. In complex **6a** the pyrazole nitrogen atoms coordinate to the copper center at distances of 1.94(2) Å (N(101)) and 1.96(2) Å (N(105)). The central amine N(103) to copper distance is 2.09(2) Å. The ethanol oxygen atom O(101) to copper bond is 2.07(2) Å. The interaction of the perchlorate molecule with the copper center is rather weak as can be concluded from the relatively long bond length of 2.34(2) Å. The angles found for **6a** are slightly different from those found for **6b** (see below). The N(101)−Cu(1)−N(103) angle is 162.4(8)°, and the N(101)−Cu(1)−N(105) and N(105)−Cu(1)−N(103) angles are 97.9(8) and 96.7(7)°, respectively. The angles made by the axial oxygen atoms O(101) and O(102) with the the central amine N(103) (with Cu(1) as the vertex) are 118.9(7) and 110.6(7)°, respectively. The distortion from an idealized trigonal bipyramid toward a square pyramid was calculated to be 37.8%.

In structure **6b** the pyrazole N to copper distances are 1.94(2) and 1.94(2) Å for N(201) and N(205), respectively. The central amine nitrogen atom is positioned at 2.12(2) Å from the copper center. The ethanol oxygen atom O(201) is found at 2.08(2) Å from the copper center and the water oxygen atom O(202) at 2.09(2) Å. The T-shaped structure found in **6a** is preserved in **6b**. The N(201)−Cu(2)−N(205) angle is 169.1(7)°, and the N(201)−Cu(2)−N(203) and N(205)−Cu(2)−N(203) angles are 95.4(7) and 96.7(7)°, respectively. The difference in the angles made by the axial oxygen atoms with the nitrogen atom N(203) (copper is the vertex) is less than in **6a**: the O(201)−Cu(2)−N(203) angle is 108.6(7)°, and the O(202)−Cu(2)−N(203) angle is 104.5(8)°. The distortion from an idealized trigonal bipyramid toward a square pyramid was calculated to be 63.2%.

Comparison of the Structures. When complexes **3** and **5** are compared, the most striking difference is the change in arrangement of the ligands around the metal center that has occurred upon benzylation of the central amine nitrogen.[35] In **3** the basal plane is composed of three N-donors, whereas in **5** this plane is formed by two N-donors and two oxygen atoms. The amino nitrogen N(3) in **5** has moved out of the basal plane to occupy an apical position. Its place is taken over by a nitrato group that occupied one of the apical sites before benzylation. The relative positions of the pyrazole units with respect to the metal center have also changed. In **3** they are almost in a trans configuration, whereas in **5** they are cis positioned. Apart from the different spatial arrangement of the ligands and anions around the copper center, changes have also taken place in the coordination distances. When the amine nitrogen N(3) moves out of the basal plane to occupy an apical position the N(3) to Cu distance changes from 2.032(3) Å in **3** to 2.330(3) Å in **5**. Each of the two pyrazole to copper distances lengthen by approximately 0.03 Å upon benzylation.

The changes that occur within the perchlorate series upon benzylation of the central amino nitrogen are less dramatic than within the nitrate series. When the overall geometries are

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(35) While this manuscript was in preparation, crystal structures of the Cu(II) complexes of bis{2-(3,5-dimethyl-1-pyrazolyl)ethyl}ethylamine or "ddae" were reported, viz. $[Cu(ddae)Cl_2]C_2H_5OH$, $[Cu(ddae)(NO_3)H_2O](NO_3)$, and $[Cu(ddae)(NO_3)_2]$, which show distorted square-pyramidal, not so much distorted square-pyramidal, and distorted octahedral coordination geometries, respectively; Driessen, W.L.; de Graaff, R. A. G.; Parlevliet, F. J.; Reedijk, J.; de Vos, R. M. *Inorg. Chim. Acta* **1994**, *216*, 43.

Table 9. Final Coordinates and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of Complexes **6a,b**

atom	x	y	z	U_{eq} (Å^2)	atom	x	y	z	U_{eq} (Å^2)
Compound **6a**									
Cu(1)	0.2706(3)	0.33630(19)	0.07654(9)	0.0215(11)	C(107)	0.216(3)	0.1666(18)	0.0856(9)	0.052(9)
Cl(11)	0.1476(7)	0.2910(4)	−0.0172(2)	0.035(3)	C(108)	0.240(2)	0.2426(13)	0.1497(6)	0.020(6)
O(101)	0.3622(15)	0.4200(9)	0.1117(5)	0.024(4)	C(109)	0.191(2)	0.1769(13)	0.1741(7)	0.019(6)
O(102)	0.2334(19)	0.3298(13)	0.0062(6)	0.064(6)	C(110)	0.253(3)	0.1057(16)	0.1793(8)	0.042(8)
O(103)	0.150(2)	0.3231(13)	−0.0563(7)	0.076(7)	C(111)	0.212(3)	0.0446(16)	0.2011(8)	0.040(8)
O(104)	0.034(2)	0.3031(13)	0.0012(7)	0.080(8)	C(112)	0.102(2)	0.0557(15)	0.2231(8)	0.032(7)
O(105)	0.181(2)	0.2102(16)	−0.0189(8)	0.096(8)	C(113)	0.044(3)	0.1265(15)	0.2210(8)	0.037(7)
N(101)	0.4153(18)	0.2812(12)	0.0601(6)	0.027(5)	C(114)	0.085(2)	0.1863(14)	0.1968(7)	0.027(7)
N(102)	0.4161(17)	0.2020(11)	0.0535(6)	0.019(5)	C(115)	0.052(2)	0.2524(13)	0.1035(7)	0.016(6)
N(103)	0.1862(16)	0.2426(10)	0.1055(5)	0.010(4)	C(116)	0.006(2)	0.3281(13)	0.1218(6)	0.019(6)
N(104)	0.022(2)	0.3948(12)	0.0948(6)	0.032(6)	C(117)	−0.174(2)	0.4591(16)	0.1037(8)	0.044(8)
N(105)	0.1315(17)	0.4089(11)	0.0774(5)	0.018(5)	C(118)	−0.056(2)	0.4543(14)	0.0869(7)	0.025(6)
C(101)	0.525(3)	0.3944(15)	0.0287(8)	0.045(8)	C(119)	0.005(2)	0.5063(15)	0.0623(7)	0.034(7)
C(102)	0.496(2)	0.3097(14)	0.0342(7)	0.025(6)	C(120)	0.121(2)	0.4770(15)	0.0573(7)	0.028(6)
C(103)	0.546(3)	0.2487(15)	0.0130(8)	0.035(7)	C(121)	0.221(2)	0.5116(15)	0.0347(7)	0.032(7)
C(104)	0.495(2)	0.1816(15)	0.0252(8)	0.033(7)	C(122)	0.471(2)	0.4045(14)	0.1385(7)	0.026(6)
C(105)	0.505(3)	0.0968(14)	0.0122(8)	0.040(8)	C(123)	0.533(2)	0.4825(14)	0.1465(7)	0.037(7)
C(106)	0.3486(18)	0.1494(12)	0.0814(6)	0.012(5)					
Compound **6b**									
Cu(2)	0.2428(3)	0.33912(18)	0.32843(9)	0.0213(10)	C(218)	0.458(2)	0.4934(14)	0.2672(7)	0.022(6)
O(201)	0.3905(15)	0.2929(10)	0.3622(5)	0.027(4)	C(219)	0.504(2)	0.4239(13)	0.2515(7)	0.021(6)
O(202)	0.1328(18)	0.3324(13)	0.2751(6)	0.053(6)	C(220)	0.438(2)	0.3641(13)	0.2708(7)	0.018(6)
N(201)	0.1305(17)	0.2652(10)	0.3516(5)	0.016(5)	C(221)	0.439(3)	0.2777(14)	0.2617(8)	0.037(7)
N(202)	0.0292(18)	0.2798(11)	0.3726(6)	0.020(5)	C(222)	0.395(2)	0.2492(15)	0.4009(7)	0.037(7)
N(203)	0.1761(17)	0.4386(11)	0.3596(5)	0.018(5)	C(223)	0.488(3)	0.1873(16)	0.4038(9)	0.053(9)
N(204)	0.3701(17)	0.4753(11)	0.2935(6)	0.022(5)	O(601)	0.903(2)	0.3245(14)	0.2580(7)	0.078(7)
N(205)	0.3605(16)	0.3973(10)	0.2979(5)	0.015(4)	C(601)	0.807(3)	0.3174(17)	0.2860(9)	0.054(9)
C(201)	0.217(2)	0.1496(15)	0.3155(8)	0.037(7)	C(602)	0.759(3)	0.2328(17)	0.2869(9)	0.068(10)
C(202)	0.126(3)	0.1865(15)	0.3405(8)	0.036(7)	Cl(31)	0.6432(7)	0.4223(5)	0.3897(3)	0.047(3)
C(203)	0.019(2)	0.1564(16)	0.3553(8)	0.031(7)	O(301)	0.761(2)	0.4530(13)	0.3897(6)	0.072(7)
C(204)	−0.037(2)	0.2144(13)	0.3768(6)	0.015(5)	O(302)	0.561(4)	0.476(2)	0.3935(11)	0.179(15)
C(205)	−0.146(2)	0.2152(14)	0.4007(7)	0.029(6)	O(303)	0.637(3)	0.368(2)	0.4230(10)	0.155(13)
C(206)	0.016(2)	0.3539(12)	0.3944(6)	0.017(6)	O(304)	0.614(2)	0.3705(13)	0.3568(7)	0.072(7)
C(207)	0.047(2)	0.4273(16)	0.3675(8)	0.042(8)	Cl(41)	0.1567(6)	0.4829(4)	0.19429(17)	0.025(2)
C(208)	0.254(2)	0.4511(13)	0.4000(7)	0.020(6)	O(401)	0.2094(17)	0.4053(11)	0.2038(5)	0.045(5)
C(209)	0.2135(19)	0.5138(12)	0.4288(6)	0.010(5)	O(402)	0.0309(17)	0.4753(10)	0.1858(5)	0.039(5)
C(210)	0.173(2)	0.4899(16)	0.4669(7)	0.032(7)	O(403)	0.1778(16)	0.5350(10)	0.2282(5)	0.034(5)
C(211)	0.140(2)	0.5467(14)	0.4938(8)	0.030(7)	O(404)	0.2133(15)	0.5145(10)	0.1590(5)	0.032(5)
C(212)	0.149(2)	0.6237(14)	0.4842(7)	0.026(6)	Cl(51)	0.6943(6)	0.2565(4)	0.1621(2)	0.031(2)
C(213)	0.194(2)	0.6478(15)	0.4493(7)	0.030(7)	O(501)	0.7052(18)	0.3258(12)	0.1872(6)	0.057(6)
C(214)	0.229(2)	0.5916(14)	0.4202(8)	0.034(7)	O(502)	0.6995(16)	0.2778(10)	0.1194(5)	0.033(5)
C(215)	0.187(2)	0.5072(12)	0.3317(6)	0.016(6)	O(503)	0.7956(16)	0.2051(10)	0.1725(5)	0.036(5)
C(216)	0.313(2)	0.5288(14)	0.3189(7)	0.023(6)	O(504)	0.5826(18)	0.2155(11)	0.1682(6)	0.050(6)
C(217)	0.483(3)	0.5758(14)	0.2549(8)	0.039(7)					

[a] U_{eq} = $^1/_3$ of the trace of the orthogonalized **U**.

compared, an increase in coordination number from 4 in **4** to 5 in both **6a,b** is observed. It should be noted, however, that in **4** the perchlorate oxygen atom O(14) interacts weakly with the copper center. An interesting observation is also the *ca.* 0.1 Å lengthening of the central amine N(3) to copper Cu(1) bond when a benzyl group is present on N(3). Although slight differences are noted for the pyrazole nitrogen to copper bond lengths and angles, the overall geometries of complexes **4** and **6a,b** are rather similar.

Conductivity Measurements. Important differences in geometry in the series of complexes **3**–**6** are clearly reflected by the X-ray measurements. Since the structure of the complexes in solution is likely to be different from that in the solid state, conductivity measurements were carried out at various concentrations in acetonitrile solution. The molar conductivity of all complexes varied linearly with the square root of the concentration. These measurements revealed that the nitrate complexes behave as 1:1 electrolytes in acetonitrile solution ($\Lambda_{0(\mathrm{mol})}$ = 137 and 178 cm^2·Ω^{-1}·mol^{-1} for **3** and **5**, respectively). This indicates that one of the nitrato groups which is coordinated to the copper center in the solid state dissociates in solution. For the perchlorate complexes **4** and **6** the conductivity values lie in the range of 2:1 electrolytes ($\Lambda_{0(\mathrm{mol})}$ = 418 and 384 cm^2·Ω^{-1}·mol^{-1} for **4** and **6**, respectively), indicating that these complexes are completely dissociated in acetonitrile solution. Likely, the free coordination sites are occupied by solvent molecules.[36]

Solution IR Measurements. IR spectra of complexes **3**–**6** were recorded in acetonitrile solution. These spectra showed two nitrate vibrations for complexes **3** and **5** corresponding with a free and a coordinated nitrate group (at 1323 and 1288 cm^{-1} for **3** and at 1341 and 1291 cm^{-1} for **5**). For complexes **4** and **6** one single ClO_4^- vibration was observed at 1102 cm^{-1}, indicating that the perchlorate ion is noncoordinating in solution. These results are in line with the conductivity measurements above.

Electrochemistry. The redox properties of the complexes were examined by cyclic voltammetry in acetonitrile solutions at a platinum electrode. The results are summarized in Table 10. All complexes, except **5**, are reduced in a reversible (i_b/i_f = 1, $\Delta E_p \approx$ 60–65 mV) charge transfer process to produce the Cu(I) species. The complexes with the benzylated ligand display the highest redox potentials for the Cu(II)/Cu(I) couple. A half-wave potential of +0.15 V is observed for **5**, and a value of +0.28 V, for **6**. For complexes **3** and **4** the half-wave potentials are −0.01 and +0.10 V, respectively. Thus, the

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(36) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

Table 10. Cyclic Voltammetry Data for the Metal Complexes **3**–**6**[a]

complex	$E_{1/2}$ (V)[b]	ΔE_p (mV)[c]	i_b/i_f
3	−0.01	64	1.0
4	+0.10	62	1.0
5	+0.15	72	1.0
6	+0.28	59	1.0

[a] Measured at *ca.* 25 °C in acetonitrile using a Pt working electrode, a Pt auxiliary electrode, an Ag/Ag$^+$ reference electrode, and 0.1 mol·dm^{-3} tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. Scan rate: 100 mV·s^{-1}. Potentials are reported *vs* Fc/Fc$^+$ in acetonitrile. [b] Determined with differential pulse polarography. [c] Cathodic to anodic peak-potential separation.

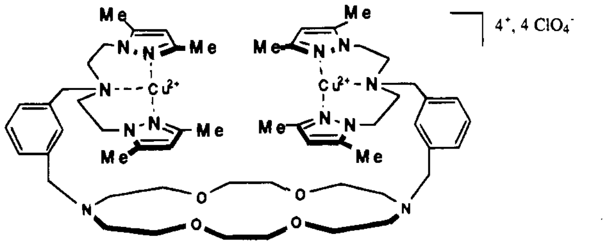
Table 11. Apparent *g* Values Derived from Powder EPR Spectra at 7 K

complex	spectrum	*g* values
3	rhombic compressed	2.03, 2.13, 2.28
4	isotropic	2.14
5	near isotropic	2.06, 2.19
6	rhombic compressed	2.02, 2.17, 2.28

introduction of a benzyl group shifts the reduction potential for the Cu(II)/Cu(I) couple by approximately 0.17 V in positive direction (0.16 V for the nitrate series and 0.18 V for the perchlorate series). These numbers reflect the different electron-donating abilities of the ligand systems. Ligand system **1** is expected to be the most electron donating, and its copper complexes are consequently the most difficult to reduce. The half-wave potentials also clearly reveal the influence of the coordinating nitrato group: the $E_{1/2}$ shifts 0.11 V when nitrate is substituted by perchlorate in the nonbenzylated series and 0.13 V when this anion is substituted in the benzylated series. Complexes **3**, **4**, and **6** behave as chemically and electrochemically reversible systems. A slight deviation of the electrochemical reversibility is noted for complex **5** where a value for the peak to peak separation of 72 mV is observed. A possible explanation for this behavior may be that the reduction of Cu(II) to Cu(I) in this complex is accompanied by a relatively slow structural rearrangement of the ligands around the metal center. As was shown by Sorrell,[32] Cu(I) prefers a planar arrangement of the nitrogen donor atoms. In **5** this planar arrangement is absent. The larger peak separation observed for **5** (72 mV) is in line with this structural rearrangement. Our observation that the peak separation depends on the scan rate further supports this idea. Such a scan rate dependency was not observed for **3**, **4**, and **6**. In the latter complexes, the pyrazole ligands are occupying the basal positions, a situation preferred by the Cu(I) state. A rearrangement is thus not expected to take place.

EPR. The powder EPR spectra of complexes **3**–**6** were recorded at 7 K. Compounds **3** and **6** displayed rhombic spectra from which three distinct *g* values could be derived (Table 11), as expected on the basis of the low symmetry observed in the crystal structures. The fact that the lowest g-value for **3** and **6** is ≤2.03 indicates that these complexes have a compressed rhombic site (cf. Cu–ligand distances, Tables 2 and 8) with a d_{z^2} ground state.[37] From the EPR spectrum of **4** no distinct *g* values could be calculated. The spectrum is isotropic due to exchange broadening probably caused by misalignment of the molecules in the crystal packing.[38] The spectrum of **6** is nearly isotropic. The long-range order in the crystals of this compounds is such that the axes of the molecules are aligned in an antiparallel fashion.

Chart 2



7

Discussion

The data presented under Results indicate that the introduction of a substituent on the amino nitrogen of the pyrazole ligand system and a change in the counterion can influence the geometry and half-wave potential of the copper complexes. The most pronounced transformation takes place in the nitrate series, where the amino nitrogen moves to an apical position when a benzyl group is introduced. In this case, various bond lengths increase, the most important one being the 0.3 Å lengthening of the Cu(II)–amine bond. It is known from the literature[39] that the introduction of bulky groups in the ligand stabilizes Cu(I) over Cu(II). It results in a more hydrophobic environment, raising the half-wave potential and stabilizing Cu(I). Furthermore, the electrochemical trend observed parallels the generally accepted notion that the incorporation of an electron-withdrawing group (e.g. benzyl) on the amine nitrogen reduces the electron density on this atom.[34] This is reflected in the higher reduction potential measured for complex **5** as compared to complex **3**. A similar increase in bond lengths on the introduction of a substituent is observed in the perchlorate series albeit to a lesser extent. With both anions, the introduction of the benzyl substituents leads to a lengthening of the Cu(II) amine bond and an increase in reduction potential (compare **4** and **6**, Table 10).

Conductivity measurements and IR data indicate that in acetonitrile solution one of the nitrato groups of **3** and **5** dissociates, rendering 1:1 electrolytes. The perchlorate complexes **4** and **6** on the other hand form 2:1 electrolytes in this solvent. The nitrate group that remains coordinated to the copper center in complexes **3** and **5** modifies the redox potential resulting in a 0.12 V less positive half-wave potential for the Cu(II)/Cu(I) couple in the nitrate series as compared to the perchlorate series.

In a previous publication we reported that certain crown ether–pyrazole copper(II) complexes (*e.g.* **7**, Chart 2) undergo reduction in alcoholic solvents even in the presence of oxygen.[15] More recently, we have shown that the bis(pyrazole)copper complexes can be incorporated in a diphenylglycoluril cavitand, resulting in a selective rate enhancement of the reduction for alcoholic substrates that are bound in the cavitand.[40] These complexes have a xylene group attached to the amino nitrogen atom of the ligand set instead of the benzyl group reported here. The electronic effect of the two groups is expected to be the

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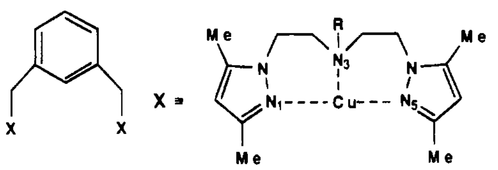
Table 12. Comparison of the Bond Lengths (Å) and Angles (deg) in **6a,b** with Those in Sorrell's Dinuclear Cu(I) Complex[32]



atoms	dist	atoms	angle
	Data for Sorrell's Complex		
Cu(1)−N(1)	1.895(4)	N(1)−Cu(1)−N(3)	100.0(2)
Cu(1)−N(3)	2.195(3)	N(1)−Cu(1)−N(5)	156.0(2)
Cu(1)−N(5)	1.916(4)	N(3)−Cu(1)−N(5)	99.2(2)
	Data for Complex **6a**		
Cu−N(1)	1.94(2)	N(1)−Cu−N(3)	97.9(8)
Cu−N(3)	2.09(2)	N(1)−Cu−N(5)	162.4(8)
Cu−N(5)	1.96(2)	N(3)−Cu−N(5)	96.7(8)
	Data for Complex **6b**		
Cu−N(1)	1.94(2)	N(1)−Cu−N(3)	95.4(7)
Cu−N(3)	2.12(2)	N(1)−Cu−N(5)	169.1(7)
Cu−N(5)	1.94(2)	N(3)−Cu−N(5)	95.2(7)

same. This is confirmed by cyclic voltammetry measurements which indicate that the half-wave potential of complex **6** is similar to those of the dinuclear bis(pyrazole) crown ether complex **7** ($E_{1/2}(1) = 0.29$ V and $E_{1/2}(2) = 0.32$ V) and to that of a mononuclear congener of **7** ($E_{1/2} = 0.29$ V).[15] A mechanism for the chemical reduction reaction was proposed,[15] involving the coordination of a solvent molecule, *viz.* methanol, to one of the Cu(II) centers. In a subsequent fast reaction this solvent molecule bridges between the two coppers. Finally, transfer of electrons to the Cu(II) centers is proposed to occur and the methanol molecule is oxidized to formaldehyde. This mechanism is supported by conclusions that can be drawn from the results presented here. First of all, coordination of an alcohol molecule to the Cu(II) centers is very likely in view of the X-ray structures of complexes **4** and **6a,b**. Second, our results show that the introduction of a substituent on the amino nitrogen of the ligand changes the redox properties of the complex. Third, Sorrell has reported the X-ray structure of a dinuclear Cu(I) complex of a ligand system related to **2** (see Table 12).[32] This ligand system adopts a configuration around the Cu(I) centers that is similar to the one present in Cu(II) complex **6**. Comparison of the bond lengths and angles in **6a,b** with those in Sorrell's dinuclear Cu(I) complex[32] (see Table 12) reveals that the pyrazole nitrogen to copper distances in the former complexes are only slightly longer than the corresponding distances in the latter complexes. The central amine to copper distance is comparable for all three complexes. Furthermore, **6a,b** and Sorrell's complex have the same planar configuration of the coordinating nitrogen atoms around copper. We may therefore conclude that our Cu(II) complexes have the correct geometry required for the stabilization of a Cu(I) center. This feature in combination with the highly positive $E_{1/2}$ for **6** may be the origin of the observed easy reduction of the copper(II) centers in **7**. Complexes of type **6** and **7** can be regarded as models for the entatic state[41] of metalloproteins. In this state, the metal ion is poised for electron transfer or for catalytic action in the absence of a substrate. For **7** this action is the acceptance of electrons with the concomitant oxidation of a methanol molecule.

It has been reported in the literature that certain Cu(I) complexes of unsubstituted pyrazole-based ligand systems show a relatively high stability toward dioxygen in aprotic solvents.[14] Our study provides an explanation for this. In view of the type of anion (PF_6^-, BF_4^-) for copper and the substituent on the central amine nitrogen (xylene) used in these studies,[14] the situation is comparable with that for complex **6** (ClO_4^- counterion, benzyl substituent). The reaction of a dinuclear Cu(I) complex with dioxygen can be seen as an one-electron oxidation of each of the copper ions. The positive redox potential of the Cu(II)/Cu(I) couple found for complex **6** indicates that a reaction of the Cu(I) complex with dioxygen will be difficult or even prohibited. In other reported pyrazole ligand systems an extra phenolic oxygen atom is present.[42] Copper(I) complexes of these ligands do have a high affinity for dioxygen. This behavior can also be explained with the results presented here. Oxygen atoms coordinating to the copper center lower the $E_{1/2}$ of the Cu(II)/Cu(I) couple (see Table 6, complexes with coordinating NO_3^- groups). In this way the Cu(I) state will be destabilized and electron transfer to dioxygen will be favored.

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Supporting Information Available: Tables of hydrogen atom positions and isotropic thermal parameters, anisotropic thermal parameters, and bond lengths and angles of the structures of **3a,b**, **4**, **5**, and **6a,b** (22 pages). Ordering information is given on any current masthead page.

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