

on a glass fiber with silicon grease. The sample was handled as above, and diffraction data were collected at -163 ± 4 °C. The structure was solved by direct methods, difference-Fourier, and full-matrix least-squares refinement techniques. No absorption correction ($\mu = 54.29$ cm⁻¹) was attempted. All atoms, with the exception of phenyl protons, were located and their positional and thermal parameters (anisotropic for W, C, O, and F) refined. Hydrogen atoms were included as fixed-atom contributors in the final stages of refinement. Two independent molecules were located, each with a crystallographic center of symmetry. A final difference Fourier was featureless, the largest peak being 1.2 e Å⁻³ located near W(1A). The final thermal parameters for atoms in the CF₃ groups were quite reasonable.

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Registry No. W₂(TFA)₄, 77479-85-7; W₂(TFA)₄·²/₃(diglyme), 77479-87-9; W₂(TFA)₄·2PPh₃, 77494-64-5; W₂Cl₆(THF)₄, 77479-88-0; W, 7440-33-7.

Supplementary Material Available: Tables of selected distances and angles, anisotropic thermal parameters, and observed and calculated structure factors for W₂(TFA)₄·²/₃digly (Tables III, VII, and VIII) and W₂(TFA)₄·2PPh₃ (Tables V, IX, and X) and derived hydrogen positional parameters for the latter complex (Table IV supplemental) (73 pages). Ordering information is given on any current masthead page. The complete structural reports (diglyme adduct, MSC-8046; PPh₃ adduct, MSC 82906) are available in microfiche form only from the Chemistry Library, Indiana University.

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Mononuclear Three-Coordinate Copper(I) Complexes: Synthesis, Structure, and Reaction with Carbon Monoxide¹

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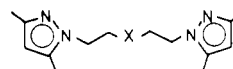
The new ligands bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (pza), bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl] ether (pze), and bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl] sulfide (pzs) form three-coordinate, T-shaped Cu(I) derivatives in the solid state, typified by the structure determined for Cu(pze)BF₄. Reaction of the copper complexes with carbon monoxide in nitromethane solution results in the formation of carbonyl adducts with $\nu(\text{CO}) = 2082, 2106, \text{ and } 2123$ cm⁻¹, respectively. Measured binding constants of CO for all three compounds reveal that Cu(pze)BF₄ reacts much more weakly with carbon monoxide than do the others, suggesting stabilization of the decarbonylated form because of the ligand. Crystal data for Cu(pze)BF₄: monoclinic, $a = 11.286$ (4) Å, $b = 13.456$ (5) Å, $c = 12.051$ (4) Å, $\beta = 99.269$ (25)°, $V = 1806.2$ (1.9) Å³, space group $P2_1/n$, $Z = 4$.

Investigation of the reaction chemistry of coordinatively unsaturated copper(I) complexes is prerequisite to understanding the reaction mechanisms by which dioxygen-activating copper proteins function. Two- or three-coordination for the cuprous form of those enzymes² would appear to be compulsory for interaction of the dioxygen molecule with the metal ion prior to oxidation of substrate.

The paucity of well-characterized Cu(I) complexes³ has deterred a detailed study of their chemistry. One reason for that is the spectroscopic "invisibility" of the d¹⁰ cuprous ion, which hinders structural characterization of the complex in solution. One way to circumvent this problem is to allow the copper center to interact with a spectroscopically observable ligand and to observe the effects of the complex on the spectral properties of that ligand. In our studies of Cu(I) complexes, we have chosen initially to use carbon monoxide as the spectral probe and the reasons for this are threefold: (1) carbonyl complexes of metal ions, including copper,⁴ are reasonably well understood, and unusual bonding modes are unlikely; (2)

spectroscopic analysis of the carbonyl adducts is straightforward and confined to a normally blank portion of the infrared region; (3) carbonyl derivatives have been characterized for several copper proteins including hemocyanin^{5,6} and cytochrome oxidase,⁷ and understanding the interaction of CO with simple complexes might give us clues to the structures of those systems.

This paper reports the synthesis of a new series of ligands, 1-3, having two pyrazolyl groups in addition to a third, neutral,



- 1, X = NH (pza)
2, X = O (pze)
3, X = S (pzs)

donor, as well as the preparation and characterization of their cuprous derivatives. These results thus add to our understanding of Cu(I) chemistry by expanding the range of stable, characterized cuprous complexes and by demonstrating one facet of their reactivity, namely their reaction with carbon monoxide.

(1) Presented in part at the 183rd National Meeting of the American Chemical Society, Las Vegas, NV, March 1982; see Abstract INOR 182.

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(3) We limit this statement to those Cu(I) complexes that are well-defined, mono- or binuclear molecular entities, ligated by "innocent" N, O, or S ligands. See: Osterberg, R. *Coord. Chem. Rev.* 1974, 12, 309-347.

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Experimental Section

All reagents and solvents were purchased from commercial sources and used as received, unless noted otherwise. Methanol and 2-propanol were distilled under N_2 from the respective magnesium alkoxide; acetonitrile and dimethylformamide (DMF) were distilled from calcium hydride; and tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl. Melting points were obtained with use of a Fisher-Johns apparatus and are uncorrected. Microanalyses were performed by Integral Microanalytical Laboratories, Inc., Raleigh, NC.

1H NMR spectra were recorded on a Perkin-Elmer R-24B instrument at 60 MHz with $CDCl_3$ as the solvent. All chemical shifts are relative to an internal standard of Me_4Si . Infrared spectra were obtained by using a NaCl cell with a path length of 0.1 mm on a Beckman Model 4250 spectrometer. All manipulations involving the cuprous complexes were performed in a Vacuum Atmospheres glovebox, operating with less than 1 ppm of O_2 and H_2O .

Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (1). Under a dinitrogen atmosphere, 107.7 g (1.12 mol) of 3,5-dimethylpyrazole was slowly added to a suspension of 40.3 g (1.68 mol) of NaH in 1 L of dry DMF. The solution was stirred at 60 °C for 2 h. To the resulting solution was added 100.0 g (0.561 mol) of bis(2-chloroethyl)amine hydrochloride portionwise, with evolution of H_2 and precipitation of NaCl. The mixture was allowed to stir at 60 °C for 30 h, cooled, and filtered. The filtrate was evaporated to dryness under reduced pressure, the residue was extracted with 100 mL of methanol, and the solution was poured into 5 L of hot H_2O . Crystallization occurred upon cooling to give 63.5 g (43%) of white needles, mp 50–54 °C. 1H NMR: δ 2.13 (6 H, s), 2.17 (6 H, s), 2.90 (4 H, t, $J = 6$ Hz), 3.93 (4 H, t, $J = 6$ Hz), 5.64 (2 H, s).

Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl] Ether (2). Under a dinitrogen atmosphere, 9.1 g (0.094 mol) of 3,5-dimethylpyrazole was slowly added to a suspension of 3.4 g (0.141 mol) of NaH in 100 mL of dry DMF and 75 mL of dry THF. The solution was stirred at 60 °C for 2 h. To the resulting solution was added dropwise with stirring a solution of 6.74 g (0.047 mol) of bis(2-chloroethyl) ether in 25 mL of dry DMF. The mixture was allowed to stir for 18 h at 60 °C, cooled, and treated cautiously with 50 mL of H_2O to decompose excess NaH. The solvents were then evaporated under reduced pressure. The residue was extracted with four 150-mL portions of ethyl acetate, which were washed with two 100-mL portions of 10% NaOH, 100 mL of H_2O , and then dried over $MgSO_4$. The solvent was evaporated to give 12.2 g (98%) of a tan solid, which was crystallized from ethyl acetate as white needles, mp 87.5–88.0 °C. 1H NMR: δ 2.11 (6 H, s), 2.14 (6 H, s), 3.51 (4 H, t, $J = 6$ Hz), 3.96 (4 H, t, $J = 6$ Hz), 5.65 (2 H, s).

1-(2-Chloroethyl)-3,5-dimethylpyrazole Hydrochloride. A solution of 4.4 g (31.4 mmol) of 1-(2-hydroxyethyl)-3,5-dimethylpyrazole⁸ and 7.0 g (58.8 mmol) of thionyl chloride in 25 mL of chloroform was allowed to reflux for 4 h. The solution was evaporated under reduced pressure, and the oil was dissolved in 5 mL of methanol. After 50 mL of ether had been layered over the methanol solution, the mixture was allowed to stand for 3 days. The resulting white crystals were filtered, washed with ether, and dried in air: yield 4.7 g (77%); mp 126–127 °C. 1H NMR: δ 2.52 (3 H, s), 2.55 (3 H, s), 4.02 (2 H, t, $J = 6$ Hz), 4.59 (2 H, t, $J = 6$ Hz), 6.16 (1 H, s).

Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl] Sulfide (3). A solution of 1.95 g (10 mmol) of 1-(2-chloroethyl)-3,5-dimethylpyrazole and 0.4 g (10 mmol) of sodium hydroxide in 100 mL of 50% aqueous ethanol was treated with 1.5 g (6.25 mmol) of $Na_2S \cdot 9H_2O$. The solution was allowed to reflux for 2 h, cooled, and evaporated at reduced pressure. Water was added, the product was extracted with dichloromethane, and the organic extracts were dried over Na_2SO_4 . The pure product was obtained as an oil after purification by flash chromatography⁹ using 1:1 ethyl acetate–petroleum ether ($R_f = 0.35$); yield 0.92 g (66%). 1H NMR: δ 2.08 (6 H, s), 2.11 (6 H, s), 3.90 (8 H, m), 5.63 (2 H, s).

[Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine]copper(I) Tetrafluoroborate, [Cu(pza)]BF₄ (4). A solution of ligand 1 (2.0 g, 7.6 mmol) in 50 mL of THF was treated with a filtered solution of 2.4 g (7.6 mmol) of $[Cu(CN_3CN)_4]BF_4$ in 50 mL of CH_3CN . The

resulting solution was evaporated to dryness under vacuum, and the residue was dissolved in 10 mL of acetonitrile. 2-Propanol was added, and upon standing for several days, the solution deposited colorless crystals. Anal. ($C_{14}H_{22}BCuF_4N_5$): C, H, N.

[Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl] ether]copper(I) tetrafluoroborate, [Cu(pze)]BF₄ (5), was prepared as described above and crystallized from methanol–2-propanol.

[Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl] sulfide]copper(I) tetrafluoroborate, [Cu(pzs)]BF₄ (6), was prepared as described for 4. Anal. ($C_{14}H_{22}BCuF_4N_4S$): C, H, N.

X-ray Data Collection. An irregularly shaped prismatic crystal of $Cu(pze)BF_4$ of approximate dimensions $0.30 \times 0.36 \times 0.47$ mm was mounted on the end of a glass fiber, and a preliminary diffractometer search revealed monoclinic symmetry. Systematic absences were observed consistent with the space group $P2_1/n$. Diffraction data were collected at 293 K on an Enraf-Nonius CAD-4 computer-controlled diffractometer using $Mo K\alpha$ radiation (0.7107 \AA) from a graphite-crystal monochromator. The unit cell constants were derived from a least-squares refinement of the setting angles of 24 reflections. The ω - 2θ scan technique was used to record the intensities for a unique set of reflections, where $2^\circ \leq 2\theta \leq 55^\circ$, which covered the ranges $+h$, $+k$, and $\pm l$. Peak counts were corrected for background counts that were obtained by extending the final scan by 25% at each end to yield net intensities, I , which were assigned standard deviations calculated with a conventional ρ factor selected as 0.01. Intensities were corrected for Lorentz and polarization effects and showed no decay during the data collection. The data were further corrected for absorption effects by using an empirical correction based on ψ scans. The linear absorption coefficient, μ , was 13.096 cm^{-1} , and the transmission factors ranged from 0.872 to 1.00. A total of 1611 independent reflections had $I \geq 3\sigma(I)$ out of a total of 4139 reflections. Crystal data: space group $P2_1/n$, $a = 11.286(4) \text{ \AA}$, $b = 13.456(5) \text{ \AA}$, $c = 12.051(4) \text{ \AA}$, $\beta = 99.269(25)^\circ$, $V = 1806.2(1.9) \text{ \AA}^3$, $d(\text{obsd}) = 1.49$ (floatation in CCl_4 -toluene), $d(\text{calcd}) = 1.52$, $Z = 4$.

Structure Determination and Refinement. A three-dimensional Patterson synthesis was used to locate the copper atom position, and a series of difference Fourier maps revealed the remaining non-hydrogen atoms. The refinement was effected by full-matrix least-squares techniques. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and the weight, w , is $4F_o^2/\sigma^2(F_o^2)$. Hydrogen atom positions were calculated and included during the later stages of refinement in the structure factor calculations although they were not refined. Programs used for the structure solution and refinement were supplied as a package by Enraf-Nonius. Atomic scattering factors for the non-hydrogen atoms were taken from ref 10 and those for hydrogen atoms from Stewart et al.¹¹ The final weighted R factor (on F) was 0.072, and the unweighted R factor was 0.085. Although these factors are high by modern standards, they arise for the most part from high thermal motion in the BF_4 groups. This phenomenon has been documented recently by Meek.¹² A final difference Fourier map shows no significant electron density within 1.0–2.0 \AA of any of the atoms of the BF_4 group, so it is likely not disordered. Final parameters are given in Table I, and structure factors and thermal parameters are included as supplementary material.

Binding Constant Measurements. The binding constants for interaction of carbon monoxide with complexes 5–6 were determined by a manometric method using the apparatus shown in Figure 1. In the glovebox, a known amount of the compound was placed in pistol A and nitromethane (3.0 mL) was added to flask B. The entire apparatus was sealed against air and removed from the inert-atmosphere box. With nitrogen flowing through stopcock C, the apparatus was connected to the lower manometer section and the mercury level, E, was adjusted so that a known volume (calibrated beforehand) was contained by the apparatus. Carbon monoxide was added through septum D and the amount measured on the calibrated scale. A known partial pressure of CO was thus established.¹³ The pistol A was then

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(13) We also demonstrated that the compound does not react with CO in the solid state, so no uptake of CO occurred until the compound was dissolved.

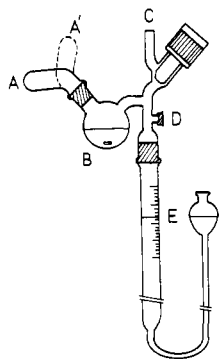

Figure 1. Apparatus for measurement of CO uptake.

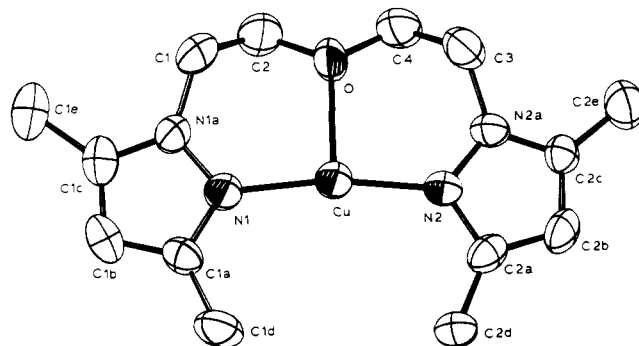
Table I. Final Positional Parameters for Cu(pze)(BF₄)

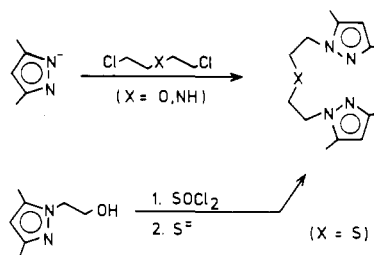
| atom | x | y | z |
|------|-------------|-------------|-------------|
| Cu | 0.0859 (1) | 0.20495 (9) | 0.1290 (1) |
| F1 | 0.0261 (6) | 0.3088 (5) | 0.6848 (5) |
| F2 | 0.0900 (9) | 0.2704 (9) | 0.5330 (7) |
| F3 | 0.2025 (8) | 0.2544 (9) | 0.6766 (8) |
| F4 | 0.1427 (10) | 0.3905 (8) | 0.6166 (10) |
| O | 0.2077 (6) | 0.1784 (4) | 0.0071 (5) |
| N1 | 0.0805 (6) | 0.0707 (5) | 0.1702 (6) |
| N2 | 0.0834 (6) | 0.3437 (5) | 0.1148 (5) |
| N1a | 0.1358 (6) | -0.0046 (5) | 0.1239 (6) |
| N2a | 0.1501 (6) | 0.3918 (5) | 0.0448 (6) |
| C1 | 0.1911 (10) | 0.0099 (8) | 0.0227 (9) |
| C2 | 0.2665 (9) | 0.0883 (8) | 0.0137 (9) |
| C3 | 0.1841 (9) | 0.3410 (7) | -0.0529 (8) |
| C4 | 0.2672 (9) | 0.2603 (8) | -0.0302 (8) |
| C1a | 0.0294 (8) | 0.0299 (7) | 0.2495 (7) |
| C1b | 0.0492 (8) | -0.0711 (7) | 0.2536 (8) |
| C1c | 0.1172 (8) | -0.0912 (7) | 0.1720 (8) |
| C1d | -0.0412 (9) | 0.0878 (8) | 0.3179 (8) |
| C1e | 0.1613 (10) | -0.1890 (7) | 0.1380 (9) |
| C2a | 0.0538 (8) | 0.4134 (7) | 0.1854 (7) |
| C2b | 0.0979 (9) | 0.5051 (7) | 0.1564 (8) |
| C2c | 0.1590 (8) | 0.4890 (7) | 0.0686 (7) |
| C2d | -0.0185 (9) | 0.3889 (7) | 0.2720 (8) |
| C2e | 0.2238 (9) | 0.5599 (7) | 0.0072 (8) |
| B | 0.125 (1) | 0.306 (1) | 0.638 (1) |

tilted to position A', dropping the compound into the solution in B, which was stirred with a magnetic stirring bar. The amount of gas absorbed by the complex, as determined by the calibrated scale, was taken to be equal to the amount of carbonyl derivative at that pressure.

Table II. Bond Distances and Angles for Cu(pze)BF₄

| Distances, Å | | | | | |
|--------------|-------------|-------------|-------------|-------------|--------------|
| Cu-N1 | 1.877 (5) | N1a-C1 | 1.469 (7) | C1c-C1e | 1.487 (7) |
| Cu-N2 | 1.874 (5) | N1a-C1c | 1.333 (6) | C2a-C2b | 1.395 (7) |
| Cu-O | 2.197 (4) | N2a-C3 | 1.464 (6) | C2a-C2d | 1.463 (7) |
| N1-N1a | 1.356 (5) | N2a-C2c | 1.339 (6) | C2b-C2c | 1.370 (7) |
| N1-C1a | 1.314 (6) | C1-C2 | 1.370 (8) | C2c-C2e | 1.473 (7) |
| N2-N2a | 1.379 (5) | C3-C4 | 1.432 (7) | B-F1 | 1.328 (10) |
| N2-C2a | 1.344 (6) | C1a-C1b | 1.377 (7) | B-F2 | 1.356 (21) |
| O-C2 | 1.378 (7) | C1a-C1d | 1.460 (7) | B-F3 | 1.153 (9) |
| O-C4 | 1.401 (6) | C1b-C1c | 1.368 (7) | B-F4 | 1.190 (21) |
| Angles, deg | | | | | |
| N1-Cu-N2 | 169.12 (22) | C1-N1a-C1c | 126.51 (56) | N1a-C1c-C1e | 124.78 (59) |
| N1-Cu-O | 94.05 (17) | N2-N2a-C2c | 110.87 (48) | N2-C2a-C2b | 108.91 (52) |
| N2-Cu-O | 95.91 (18) | N2-N2a-C3 | 120.84 (48) | N2-C2a-C2d | 121.23 (60) |
| Cu-N1-N1a | 125.03 (37) | C3-N2a-C2c | 127.39 (53) | C2b-C2a-C2d | 129.79 (58) |
| Cu-N1-C1a | 129.14 (45) | N1a-C1-C2 | 121.39 (65) | C2a-C2b-C2c | 107.29 (52) |
| Cu-N2-N2a | 121.42 (37) | C1-C2-O | 112.49 (62) | C2b-C2c-N2a | 106.89 (53) |
| Cu-N2-C2a | 129.74 (44) | N2a-C3-C4 | 116.62 (54) | C2b-C2c-C2e | 129.63 (63) |
| Cu-O-C2 | 116.85 (35) | C3-C4-O | 108.98 (51) | N2a-C2c-C2e | 123.48 (58) |
| Cu-O-C4 | 118.02 (34) | N1-C1a-C1b | 110.54 (55) | F1-B-F2 | 105.41 (166) |
| N1a-N1-C1a | 105.78 (49) | N1-C1a-C1d | 122.10 (61) | F1-B-F3 | 118.91 (92) |
| N2a-N2-C2a | 105.99 (49) | C1b-C1a-C1d | 127.32 (59) | F1-B-F4 | 104.32 (131) |
| C2-O-C4 | 117.35 (52) | C1a-C1b-C1c | 106.02 (51) | F2-B-F3 | 104.43 (174) |
| N1-N1a-C1c | 111.06 (46) | C1b-C1c-C1e | 128.62 (65) | F2-B-F4 | 99.56 (89) |
| N1-N1a-C1 | 121.76 (50) | N1a-C1c-C1b | 106.58 (54) | F3-B-F4 | 121.41 (228) |


Figure 2. Structure of the Cu(pze)⁺ cation showing 40% probability thermal ellipsoids. Bond distances and angles are compiled in Table II.

Scheme I


A plot of mole percent vs. partial pressure of CO gave a straight line from which $P_{1/2}$ could be readily determined.

Results and Discussion

(A) Synthesis. Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (1) and bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl] ether (2) are readily prepared by nucleophilic substitution on the corresponding chloride with the pyrazolate ion as depicted in Scheme I. The analogous sulfide 3 could not be made from bis(2-chloroethyl) sulfide because of the competing elimination pathway, but displacement of chloride ion in 1-(2-chloroethyl)-3,5-dimethylpyrazole by S²⁻ gave the desired ligand. The compounds were shown to be pure by thin-layer chromatography and were characterized unambiguously by NMR spectroscopy. The most significant features of the NMR spectrum for each ligand are the two singlets at ~2 ppm due to the inequivalent pyrazolyl methyl groups.

Table III. Spectral and Physical Properties of Cu(pzx)(CO)⁺ Complexes

| complex | $\nu(\text{CO}), \text{cm}^{-1}$ | $P_{1/2}, \text{torr}$ |
|--------------------------|----------------------------------|------------------------|
| Cu(pza)(CO) ⁺ | 2082 | 120 |
| Cu(pze)(CO) ⁺ | 2106 | >1600 |
| Cu(pzs)(CO) ⁺ | 2123 | 730 |

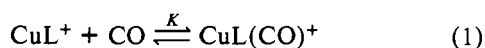
A methanolic solution of **1**, **2**, or **3** reacts with Cu(CH₃CN)BF₄ to give the highly crystalline, colorless cuprous derivatives **4–6**.

(B) Solid-State Structures. The complexes Cu(pza)⁺, and Cu(pze)⁺, and Cu(pzs)⁺ appear to be structurally similar, having a T-shaped geometry that is dictated by the steric constraints of the ligand. Although we have not determined the structures for Cu(pza)⁺ and Cu(pzs)⁺ per se, there is ample precedent provided by the structures of the [α, α' -bis[[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amino]xylyl]dicopper(I) dication [Cu₂(*m*-XyN₆)]²⁺,¹⁴ and the [bis[2-(3-ethyl-2-benzimidazolyl)ethyl] sulfide]copper(I) cation¹⁵ to be entirely confident in assigning the T-shaped coordination environment. However, because there are no precedents for oxygen ligation in three-coordinate Cu(I) complexes, we determined the structure of Cu(pze)BF₄, shown in Figure 2.

As in its amine¹⁴ and sulfide¹⁵ analogues, Cu(pze)⁺ has a T-shaped structure in which the Cu atom sits 0.067 (1) Å out of the plane described by N1, N2, and O. The Cu–N distances of 1.877 (5) and 1.874 (5) Å are shorter than those in the previously reported structures^{14,15} but are close to the distances found for two-coordinate copper(I) complexes.¹⁶ In fact, the shortness of the copper–pyrazole bonds suggests that the interaction of the ether oxygen with copper may be very weak, barely perturbing what is essentially a two-coordinate copper(I) species. On the other hand, the Cu–O distance of 2.197 (4) Å is the same as the Cu–N distance of 2.195 Å in Cu₂(*m*-XyN₆)²⁺¹⁴ and that fact would advocate proposal of a bonding interaction in the solid state. Thus, according to this interpretation, the Cu–N distances may not provide a significant criterion for distinguishing between two- and three-coordinate Cu(I) complexes.

(C) Reaction with Carbon Monoxide. All three complexes react with CO in CH₃NO₂ to form carbonyl derivatives as indicated by infrared spectroscopy (Table III). Attempts to isolate the carbonyl adducts were unsuccessful, resulting in crystallization of the three-coordinate species. On the assumption that all three carbonyl adducts have the same tetrahedral⁴ structure in solution, $\nu(\text{CO})$ can be rationalized on the basis of the effects of electronegativity and back-bonding. The greater electronegativity of oxygen vs. nitrogen means that the electron density at Cu will be lower for Cu(pze)(CO)⁺ than for Cu(pza)(CO)⁺; hence, there should be less back-bonding into the carbonyl ligand, and $\nu(\text{CO})$ will be higher. For Cu(pzs)(CO)⁺, back-bonding into the sulfur d orbitals will compete with back-bonding into the coordinated CO, and $\nu(\text{CO})$ for that complex should be higher than for Cu(pza)(CO)⁺. Both of those relationships are observed.

Binding of carbon monoxide was also evaluated in a more quantitative fashion by measurement of the equilibrium constant for the reaction between the Cu(I) complex and CO according to eq 1. These measurements were made by ob-



serving the amount of CO absorbed by each complex as a function of the partial pressure of CO in N₂. For a particular pressure at which the complex absorbs 0.5 equiv of CO, [CuL(CO)⁺] = [CuL⁺] and the equilibrium expression shown in eq 2 simplifies to that of eq 3. The equilibrium constant

$$K = [\text{CuL}(\text{CO})^+]/([\text{CuL}^+][\text{CO}]) \quad (2)$$

$$K = 1/[\text{CO}] \quad (3)$$

is thus inversely proportional to the concentration of carbon monoxide (i.e., its partial pressure), and we can compare these pressures ($P_{1/2}$) at which half of the complex is carbonylated. The $P_{1/2}$ values are included in Table III.

The equilibrium constant for the reaction shown in eq 1 may be indicative of the structure and/or stability of the starting cuprous complexes in solution, since K depends on the nature of the starting material as well as on that of the product. For example, some previously reported copper carbonyls¹⁷ bind CO tenaciously (under vacuum at elevated temperatures) because the decarbonylated form is unstable due to disproportionation. For the compounds reported here, the three-coordinate form is apparently quite stable, so binding of CO is much weaker.

If we were to assume that all three complexes have the same stability in the absence of CO, then we would predict that $P_{1/2}$ should relate directly with $\nu(\text{CO})$; that is, more back-bonding to carbon monoxide (lower $\nu(\text{CO})$) will result in stronger Cu–C bonding and a lower value for $P_{1/2}$. The fact that Cu(pze)⁺ reacts very weakly with CO suggests that the stabilities of the three-coordinate forms **4–6** are *not* comparable and that Cu(pze)⁺ is more stable without CO than are Cu(pza)⁺ and Cu(pzs)⁺.

The explanation for the greater stability of Cu(pze)⁺ assumes that the oxygen donor in **5** will bind only weakly to copper(I). This assumption is plausible because ethers are usually poor ligands, and one would expect binding of a "hard" ether donor by the "soft" Cu(I) center to be unfavorable. Stabilization of the *nominally* three-coordinate Cu(I) ion therefore will require greater overlap between the bonding orbitals on copper and those of the pyrazole nitrogens in much the same way as is found for two-coordinate Cu(I) species.¹⁸ This enhanced orbital mixing, which manifests itself in the short Cu–N(pyrazole) bonds, consequently results in stabilization of the decarbonylated form.

Summary and Conclusions. We have prepared and characterized a new series of stable three-coordinate Cu(I) complexes and examined their reactions with carbon monoxide. These results provide additional evidence that three-coordinate Cu(I) species react readily with CO, in contrast to most two-¹⁸ and four-coordinate¹⁹ complexes, and that their detailed structures will influence the strength of CO binding. The reaction of Cu(I) complexes with carbon monoxide may prove to be an important one because it provides a way to assess the structure of a Cu(I) species in solution or at the active site of a protein by generating a derivative that can be studied by spectroscopic and physical methods.

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Registry No. 1, 85650-01-7; 2, 85650-02-8; 3, 85650-03-9; 4, 85662-15-3; 5, 85662-17-5; 6, 85662-19-7; Cu(pza)(CO)⁺, 85662-20-0;

Cu(pze)(CO)⁺, 85662-21-1; Cu(pzs)(CO)⁺, 85662-22-2; [Cu(CN₃)₄]BF₄, 15418-29-8; 3,5-dimethylpyrazole, 67-51-6; bis(2-chloroethyl)amine hydrochloride, 821-48-7; bis(2-chloroethyl) ether, 111-44-4; 1-(2-chloroethyl)-3,5-dimethylpyrazole hydrochloride, 85650-04-0.

Supplementary Material Available: Listings of final hydrogen atom positions, final thermal parameters, and observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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Dinuclear, Metal-Metal-Bonded Platinum(III) Compounds. 2. Synthesis and Properties of Complexes Containing the [Pt₂(HPO₄)₄(B)₂]²⁻ Anions (B = a Heterocyclic Tertiary Amine) or the [Pt₂(H₂PO₄)(HPO₄)₃(py)₂]⁻ Ion

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The reactions of phosphoric acid solutions containing the diplatinum(III) anion [Pt₂(HPO₄)₄]²⁻ with heterocyclic tertiary amines afford yellow complexes of stoichiometry (BH)₂[Pt₂(HPO₄)₄(B)₂], where B = pyridine, 4-methylpyridine, or 3,4-dimethylpyridine. These products are probably contaminated with small amounts of the mixed salts (BH)[Pt₂(H₂PO₄)(HPO₄)₃(B)₂]₂·H₂O, a complex of this type apparently being the principal product when 4-phenylpyridine is used as the nitrogen base. During attempts to grow suitable crystals of the pyridine (py)-containing complex (pyH)₂[Pt₂(HPO₄)₄(py)₂], we instead isolated (pyH)[Pt₂(H₂PO₄)(HPO₄)₃(py)₂]₂·H₂O, the identity of which was determined by an X-ray structure analysis. The crystals are orthorhombic, and the structure was solved and refined in space group *Pc2₁n* (a nonstandard setting of *Pna2₁*). The unit cell dimensions are as follows: *a* = 8.460 (2) Å; *b* = 16.476 (6) Å; *c* = 19.466 (6) Å; *V* = 2713 (2) Å³; *Z* = 4. The structure was refined to *R* = 0.031 and *R_w* = 0.039. The Pt-Pt distance is 2.494 (1) Å, the mean Pt-O(coord) distance is 2.004 [4] Å, and the mean P-O(coord) distance is 1.528 [4] Å. The Pt-N distances are 2.11 (2) and 2.18 (1) Å, with the py planes being almost perpendicular to each other and staggered with respect to the Pt-O bonds. The water molecule is loosely hydrogen bonded to the [Pt₂(H₂PO₄)(HPO₄)₃(py)₂]⁻ ion. The pattern of P-O distances, the occurrence of hydrogen-bonded O...O contacts, and the chemical analysis are all consistent with the formulation of this compound. Preliminary studies of the reaction of (pyH)₂[Pt₂(HPO₄)₄(py)₂] with triphenylphosphine and *tert*-butyl isocyanide have been carried out. Mononuclear products such as Pt(PPh₃)₂(O₂CCH₃)₂ (formed in glacial acetic acid) and Pt(CN-*t*-Bu)₂(CN)₂ attest to the relative ease with which reductive cleavage of the Pt-Pt bond occurs.

Introduction

Dimetal species having metal-metal single bonds based upon the electron-rich $\sigma^2\pi^4\delta^2\delta^*2\pi^*4$ or $\sigma^2\pi^4\delta^2\pi^*4\delta^*2$ configuration are especially prevalent in rhodium(II) chemistry, the dirhodium(II) acetate complex Rh₂(O₂CCH₃)₄(H₂O)₂ being the best known example.² Recent evidence attests to the existence of isoelectronic singly bonded species in the chemistry of diplatinum(III), of which the α -pyridone-bridged species [X-(NH₃)₂Pt(C₅H₄NO)₂Pt(NH₃)₂X]²⁺ (X = NO₂ or NO₃),^{3,4} the trifluoroacetate-bridged complex (*p*-CH₃C₅H₄N)₂Pt₂(CH₃)₄(O₂CCF₃)₂,⁵ and the sulfate-bridged complex K₂[Pt₂(SO₄)₄(H₂O)₂]⁶ and its dimethyl sulfoxide adduct K₂[Pt₂(SO₄)₄(Me₂SO)₂]₂·4H₂O⁷ constitute the majority of the structurally characterized examples.

A recent report describing the synthesis of a complex purported to be "(NH₄)₂(H)₄[Pt₂(PO₄)₄(H₂O)₂]", and several derivatives thereof,⁸ prompted further investigations of this and related materials in both of these laboratories with a view

to using them as starting materials for the synthesis of other diplatinum(III) species. As already reported, it has been possible to obtain an accurate structure determination of the sodium salt Na₂[Pt₂(HPO₄)₄(H₂O)₂]⁹, thereby establishing the true identity of the [Pt₂(HPO₄)₄(H₂O)₂]²⁻ unit. In a continuation of our efforts to develop and expand the useful chemistry of diplatinum(III) species, we have carried out a collaborative study into further aspects of the chemistry of salts containing the [Pt₂(HPO₄)₄]²⁻ anion. Details of this work are reported herein and include the isolation and structural characterization of the novel complex (pyH)[Pt₂(H₂PO₄)(HPO₄)₃(py)₂]₂·H₂O.

Experimental Section

Materials. All solvents and reagents were reagent grade unless specified otherwise. *cis*- and *trans*-Pt(NH₃)₂(NO₂)₂,¹⁰ *tert*-butyl isocyanide,¹¹ (NH₄)₂[Pt₂(HPO₄)₄(H₂O)₂]⁸ and (NH₄)₂[Pt₂(SO₄)₄(H₂O)₂]⁶ were prepared by standard literature methods.

Reaction Procedures. Unless otherwise stated, all reactions were carried out with use of a mineral oil bubbler vented in an efficient fume hood. Reactions involving phosphines and *tert*-butyl isocyanide were carried out under an inert nitrogen atmosphere.

Preparation of (NH₄)₂[Pt₂(SO₄)₄(H₂O)₂] from (NH₄)₂[Pt₂(HPO₄)₄(H₂O)₂]. A suspension of 0.10 g of (NH₄)₂[Pt₂(HPO₄)₄(H₂O)₂] in 10 mL of a 1:1 concentrated sulfuric acid-water mixture was heated to 100-110 °C for 2 h, during which time a deep red solution formed.

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